Recent Developments in the Application of In- and Ex-situ NMR Spectroscopy to Batteries and Supercapacitors

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This talk will focus on our work on the development of methods that allow devices to be probed while they are operating (i.e., *in-situ*). This allows, for example, the transformations of the various cell components to be followed under realistic conditions without having to disassemble and take apart the cell. To this end, the application of new *in* and *ex-situ* Nuclear Magnetic Resonance (NMR), magnetic resonance imaging (MRI) and X-ray diffraction approaches to correlate structure and dynamics with function in lithium- and sodium-ion batteries and supercapacitors will be described. The *in-situ* approach allows processes to be captured, which are very difficult to detect directly by ex-situ methods. For example, we can detect side reactions involving the electrolyte and the electrode materials, sorption processes at the electrolyte-electrode interface, and processes that occur during extremely fast charging and discharging. Complementary Ex-situ investigations, and parallel diffraction studies, allow more detailed structural studies to be performed, to correlate local and long-range structure with performance.

As an illustration of the approach I will describe our recent work on sodium anode materials, these materials exhibiting considerable structural disorder, either as synthesized, or during cycling. Our work has used two probes of local structure, ^{23}Na MAS NMR and pair distribution function (PDF) analysis of X-ray total scattering data to monitor structural (and electronic) changes during cycling. For example, PDF studies of hard carbons show that these materials comprise graphene sheets with considerable curvature.[1] The extent of curvature can be determined by analysing the PDF real and reciprocal space data. The electrochemical data observed on reaction with Na comprises two regions, a higher voltage sloping region, and a longer, flatter low voltage region. ^{23}Na NMR data acquired *operando* show that the Na^+ ions occupy sites within the hard carbons that do not interact significantly with the carbon layers in the high voltage region, the ^{23}Na NMR shifts being consistent with ionic environments that are affected by the local fields from the aromatic graphene-like layers. The ^{23}Na shifts change dramatically during the low voltage region, shifting to higher frequencies. These Knight shifts are indicative of metallic behaviour and are a measure of the density of states at the Fermi Level, as probed by the Na nuclei. Analogous behaviour is seen during the lithiation of hard carbons with ^{6,7}Li NMR spectroscopy.[2] Extensions of the approach to examine other anodes such as tin will be presented, where we have determined the structures of the various phases that form on cycling.

In a second application, I will review our recent work on the development of NMR and MRI methods to determine how porous carbons store charge. Quantitative NMR spectroscopy as a function of state of charge can be used to determine whether mechanisms involving ion expulsion, sorption or exchange are operative.[3] Sorption increases the total number of ions within the pores, which we show with pulse field gradient (PFG) NMR methods reduces the mobility of ions within the pores. By contrast, ion-exchange results in negligible changes in mobility.[4] The results have implications for the design of high rate supercapacitors.

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Photoelectrochemistry, Solid-State Chemistry, and Solar Fuels: A Nexus?

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Solid-state chemistry languished as an esoteric discipline till interest exploded on the so-called high-Tc superconductor materials; oxides were discovered to have unique properties in this regard. Paralleling this was the gradual realization that solid-state chemistry principles underpinned many technologically-important areas such as batteries, supercapacitors, and even solar cells. The culmination of this trend was in the application of solid-state chemistry to the preparation and characterization of electrode materials in photoelectrochemical (PEC) cells.

This perspective talk will examine how solid-state chemistry principles have contributed both to the design and synthesis of photoelectrode materials for PEC applications related to water splitting, CO_2 reduction, and environmental remediation. The design of new-generation oxide semiconductors with the correct optoelectronic and bulk/interfacial chemistry characteristics needed to efficiently drive the above reactions will be addressed. The list of material pre-requisites for efficient solar fuels generation or photocatalytic degradation is daunting and it is hardly surprising that a "magic bullet" material has not emerged even after 4 decades of R&D effort. However, these same challenges have attracted researchers drawn from diverse communities including solid-state/device physics, photophysics/photochemistry, colloid chemistry, ultra-fast spectroscopy, classical inorganic chemistry, environmental chemistry and organometallics.

To keep the discussion coherent, only a very limited subset of topics will be addressed in this plenary talk. The progression from binary to ternary, and even quaternary oxides will be examined from the perspective of "band-gap engineering" (a much-maligned word!) and tuning of the interfacial semiconductor surface/fluid energetics. Examples will be drawn from recent research in the speaker's laboratory and with collaborators.

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Reactivity Descriptors of MN_x catalysts for the Oxygen Reduction Reaction

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Transition metal macrocyclic complexes like metal-phthalocyanines and metal porphyrins have been studied for many years as alternative materials to platinum group metal (PGM) catalysts for the oxygen reduction reaction (ORR). However, they lack the long-term stability required for fuel cell operation. More stable PGM-free catalysts, containing MN_4 or MN_x structural motifs have been developed, which are produced by pyrolysis of up to 1000°C of different N-containing ingredients and metal salts. These pyrolyzed catalysts are more stable and also more active. In this work the most important reactivity descriptors for the activity of MN_4 molecular catalysts for ORR will be discussed and compared with the reactivity descriptors of metals and metal alloys. The pH dependent $M^{+n}OH^-/M^{+(n-1)}$ redox potential of the MN_4 catalyst is a very predictive reactivity descriptor for ORR for metal phthalocyanines, metallo-porphyrins and other macrocyclic complexes in general [1] and also for pyrolyzed MN_x catalysts [3]. In general a more positive M^{ox}/M^{red} redox potential increases the ORR activity of intact MN_4 catalysts and pyrolysis of some intact MN_4 complexes dramatically shifts the M^{ox}/M^{red} transition to more positive values favouring ORR catalysis [1]. Fe(III)OH is catalytically inactive as the active Fe site is occupied by strongly adsorbed OH^- so the desorption energy of OH^- has been proposed to be also a reactivity descriptor for ORR in such systems [4]. Recently, it has been shown that a direct linear correlation does exists between the $M^{ox}OH^-/M^{red}$ redox potential of the catalysts and the M-O_2 binding energy[4],which is a classical activity predictor for pure metals and metal alloys. Low activity Fe porphyrins have relatively high Fe-O_2 binding energies where as more active Fe phthalocyanines have lower Fe-O_2 binding energies and are located closer to the apex of an activity volcano correlation. For intact MN_4 metal complexes the redox potential can be shifted to positive values by placing electron-withdrawing groups on the ligand or by the action of an electron-withdrawing axial ligand that can also serve to anchor the MN_4 catalysts to an electrode surface. The axial ligands mimics the action of cytochrome *c* in the ORR in living systems.

For Cu phenanthrolines, the active species is tetrahedric Cu(I). The reactivity index for these complexes is the Cu(II)/Cu(I) redox potential. It can be shifted by electron-withdrawing groups on the ligand and also by bulky groups that hinder the Cu(II)(planar) → Cu(I)(tetrahedral) transition shifting the redox potential positively and again increasing the ORR activity. The interplay of all these factors plus other electronic parameters will be discussed and also the similarities between the activity volcano correlations for MNx systems with those of metals. These reactivity descriptors apply to many other electrochemical reactions catalyzed by MN4 complexes where activity volcano correlations with the formal potential of the catalyst are observed [5].

Ackowledgements

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Operando Methods for The Study of Energy Materials

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This presentation will deal with the development of operando methods for the study and characterization of fuel cell and battery materials. The presentation will begin with a brief overview of the methods employed. Particular emphasis will be placed on the use of X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) X-ray microscopy and tomography and transmission electron microscopy (TEM) under active potential control. The utility of these methods will be illustrated by selected examples including electrocatalysts for the oxygen reduction reaction and spectroscopic studies of Li/S batteries. The use of operando TEM will be illustrated by studies of fuel cell catalyst degradation and coalescence and lithiation/de-lithiation dynamics of $LiFePO_4$ via energy-filtered TEM. Finally the concept of symmetrical redox flow batteries will be demonstrated. The presentation will conclude with an assessment of future directions.

Electrochemical Glucose Monitoring for Diabetes Management: Making the Monitoring Painless and Bloodless

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Diabetes devastates lives and burdens society. Low glucose episodes cause blackouts, and severe ones are life-threatening. Periods of high glucose cause circulatory disease, stroke, amputations, blindness, kidney failure and nerve degeneration. Consequently, humanity performs more glucose assays than all other assays combined and uses more electrochemical cells in diabetes management than in all other applications.

TheraSense, a venture founded by my son Ephraim Heller and myself, now a major part of Abbott Diabetes Care, developed two products that have improved the lives of people with diabetes. The first is a microcoulometer (300 nL volume), the FreeStyle blood glucose monitoring system.[1] It was introduced in 2000 and made the monitoring of blood glucose virtually painless. The second, the FreeStyle Libre continuous monitoring system has been available in Europe since 2014. It made the monitoring of glucose bloodless, simple and innocuous. The system is based on our electrical wiring of redox enzymes at the University of Texas at Austin, i.e. on the electrical connection of their redox centers to electrodes without using a diffusing and therefore leached redox mediator. The turnover of the wired enzyme, e.g. of wired glucose oxidase, produces the monitored current. [1b, c]

The system's miniature subcutaneously implanted wired enzyme amperometric sensor is connected to an external disposable amplifier/short-range transmitter, transmitting the stored readings to a mobile phone-like device when it is swiped over the clothing near the sensor. The wearer does not feel the presence of the implanted sensor under the skin. The sensor is self-replaced with minimal pain by the patient after two weeks.[2] The system is factory-calibrated, [3]i.e. it refutes the long held notion of physiological variability in between skins of people causing clinically significant glucose-sensitivity differences.

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Bifunctional Nanophotonic-Nanoelectrochemical Arrays for Luminescence Studies of Single Molecule Electron Transfer Events

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Abstract. Single electron transfer events in both immobilized and freely diffusing redox-active molecules can now be studied with some facility using bimodal nanoelectrochemical-nanophotonic nanopore arrays. High density recessed dual-ring electrode nanopores have been fabricated, which can moderate the interaction between single electron-transfer events and fluorescence emission, in the zeptoliter optical confinement volume of a zero-mode waveguide. The dual optical-electrochemical functionality makes it possible to perform single molecule spectroelectrochemical measurements under redox cycling conditions – both when the upper electrode is potential-controlled and using self-induced redox cycling. These have been performed with flavin mononucleotide, FMN, which contains an isoalloxazine chromophore which is fluorescent in the oxidized state, while the reduced state, $FMNH_2$, exhibits a substantially lower quantum efficiency, thus permitting the redox state of single FMN molecules to be followed by observing their fluorescence behavior. Single molecule cycling behavior is evidenced by the distribution of on- and off-times. Capture efficiencies are characterized as a function of the potential applied to the upper ring electrode, and single molecule electrochemical-spectroscopic cross-correlation measurements are performed as a function of nanopore occupancy down to $\langle n \rangle \sim 0.001$.

Recent Advances in Electrochemical C-H Functionalization

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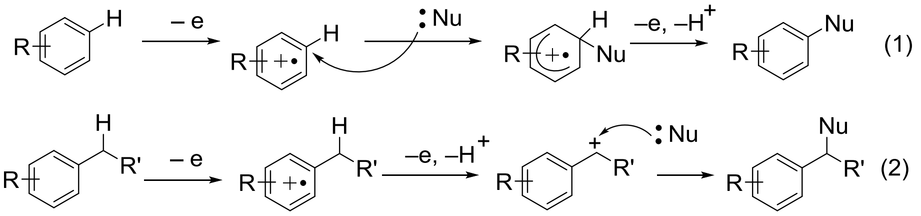
C-H functionalization serves as an atom- and step-economical way for streamlined organic synthesis. Although transition-metal catalyzed and photoredox-mediated methods[1] have been extensively studied, the electrochemical method also serves as a powerful tool. This presentation focuses on the following transformations based on the electrochemical method that have been recently developed in our research group.

1. aromatic C-H amination[2]
2. aromatic C-H/aromatic C-H crosscoupling[3]
3. benzylic C-H amination[4]
4. benzylic C-H/aromatic C-H crosscoupling[5]



The electrooxidative fuctionalization of aromatic C-H is generally proceeds according to the mechanism shown in eq 1, whereas that of benzylic C-H is generally proceeds according to the mechanism shown in eq 2. As nucleophiles nitrogen-containing compounds are used for amination and aromatic compounds are used for crosscoupling, although use of some tricks is necessary to avoid undesired processes such as overoxidation. These methods have been successfully applied to synthesis of some biologically interesting molecules demonstrating their usefulness in organic synthesis.

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Electrochemical, Spectroscopic and Surface Imaging Studies of Antimicrobial Peptides Incorporated into Biomimetic Membranes Supported at a Au Electrode

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Antimicrobial peptides (AMPs) are important components of the innate immunity which is the first line of defense of all organisms, including plants and humans. AMPs have typically 12-50 amino acids and about 50 % of them are hydrophobic. They are involved in antiseptic, immune modulatory and chemotactic processes. They aggregate in the cellular membrane of pathogens and form pores leading to the cell death caused by the osmotic shock and leakage of intracellular content. In this lecture I will review our recent studies of antimicrobial peptides such as gramicidin, alamethicin, trichogin and valinomycin incorporated into phospholipid membranes supported at a gold electrode surface. In this architecture, we were able to apply scanning probes such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), photon polarization infrared reflection absorption spectroscopy (PM IRRAS) and electrochemical techniques to determine the nature of peptide aggregation, orientation and conformation in phospholipid monolayers and bilayers. We will present molecular resolution STM and AFM images of pores formed by antimicrobial peptides in phospholipid membranes. We will also show a correlation between the conductivity of ion channels formed by antimicrobial peptides in gold supported bilayers to their orientation and conformation in such membranes.

Counting Molecules, Dodging Blood Cells: Real-time Molecular Measurements Directly In the Living Body

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The development of technology capable of continuously tracking the levels of drugs, metabolites, and biomarkers in situ in the body would revolutionize our understanding of health and our ability to detect and treat disease. It would, for example, provide clinicians with a real-time window into organ function and would enable therapies guided by patient-specific, real-time pharmacokinetics, opening a new dimension in personalized medicine. In response my group has pioneered the development of a "biology-inspired" electrochemical approach to monitoring specific molecules that supports real-time measurements of arbitrary molecular targets (irrespective of their chemical reactivity) directly in awake, fully ambulatory subjects.

New views on the electrochemistry of platinum

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Platinum is the most used electrocatalyst in electrochemical energy conversion devices such as fuel cells and electrolysers. In my talk I will highlight recent work of my group on understanding the surface chemistry of platinum in an aqueous electrolyte, by combining single-crystal electrochemistry, density functional theory calculations, ultra-high-vacuum modeling, in situ spectroscopy and in situ electrochemical scanning tunneling microscopy. I will challenge some existing explanations and interpretations of platinum electrochemistry, and will show the sometimes surprising surface disordering of platinum that happens at both positive (anodic) and negative (cathodic) conditions.

Modeling and experimental validation of Li-ion (LFP) degradation

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Aging is one of the most important battery characteristics in the development of economically viable (Hybrid) Electric Vehicle and Smart Grid applications. Cyclable Li losses, due to Li^+ immobilization, and electrode materials decay are considered to be the most important factors leading to battery degradation. $C_6/LiFePO_4$ (LFP) batteries are excellent candidates to study the graphite anode aging since the cathode has outstanding (electro)chemical stability and voltage characteristics at moderate temperatures. However, at higher temperatures the cathode also turned to be chemically unstable, giving rise to additional capacity losses. The various degradation mechanisms [1-4] will be discussed based on simple analyses of measured battery voltage characteristics. Particularly the development of the thermodynamically determined Electro Motive Force (EMF) curves upon ageing will be highlighted. It will be shown that by properly analyzing the EMF curves a nice distinction can be made between calendar ageing (Fig. 1a) and cycling-induced ageing (Fig. 1b). Advanced models has been set up to describe the degradation of LFP batteries properly at both low (Fig. 2a) and high temperatures (Fig. 2b). The simulations results (lines in Fig. 3) will be validated with experimental results (symbols in Fig. 3).

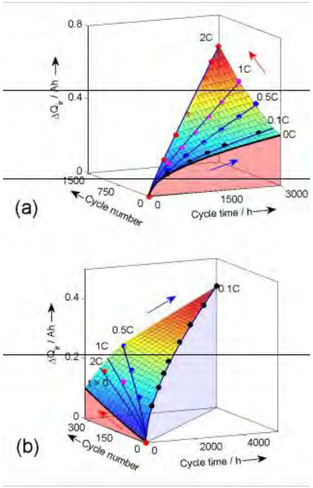

Fig. 1. Experimental ageing results.

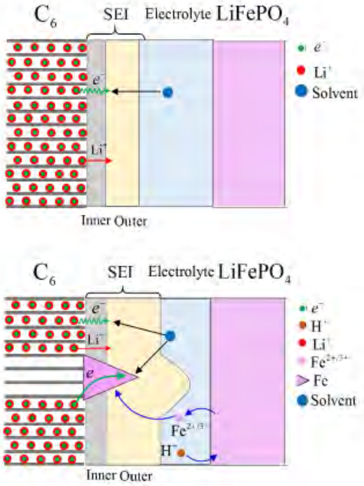

Fig. 2. SEI formation mechanisms.

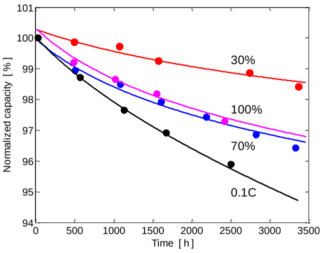

Fig. 3. Validation SEI models.

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New Materials, Detection Strategies and Devices for Electrochemiluminescent Analysis

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Electrochemiluminescence (ECL), or electrogenerated chemiluminescence, has been extensively used in immunoassays, DNA probe assays, aptasensors, enzymatic biosensors, coreactant detection, light-emitting devices, drug screening, and so on. It is one of most successful electrochemical in vitro diagnostic techniques with huge sale. ECL reactions frequently involve in electrodes, luminophores, coreactants, electrocatalysts, additives, quenchers, electrochemical devices, and so on. The performance of these materials and electrochemical devices together with detection strategies have significant effects on ECL detection [1].

In this talk, we reported our recent progress on the development of wireless ECL multiplex device (Fig.1) , new detection strategies and some new materials, such as coreactants, luminophores, noble metal nanocrystal electrocatalyst with high-index facets, single-walled carbon nanohorn ECL quencher, reactive materials, and magnetic microbead. These materials extend ECL applications, improve ECL sensitivity or selectivity, or simplify detection.[1-10] The wireless ECL multiplex device holds great promise for high throughput analysis and point-of-care testing (POCT) by coupling with low cost detectors, such as digital cameras and smart phones.

Acknowledgements

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Li_2TiSiO_5: A Low Potential and Large Capacity Ti-Based Anode Material for Li-Ion Batteries

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Today's anode for lithium ion batteries is dominated by graphite, with a low operate voltage at 0.1 V *vs.* Li^+/Li, easy to format lithium dendrite and cause to safety risk. As an alternative anode material, the "zero-strain" spinel structure $Li4Ti_5O_{12}$ could avoid Li plating with a relative high intercalation potential (1.55 V *vs.* Li^+/Li) and exhibits an excellent cycling stability. However, the slightly low capacity and high voltage of $Li_4Ti_5O_{12}$ result in low energy density. Therefore, it is very important, but nevertheless a challenge, to develop a negative electrode material with a large capacity and an intercalation potential below 1 V, but not close to the Li plating potential, to ensure the safety of batteries. Herein, we report a new anode material of Li_2TiSiO_5 as anode material for LIBs. The electrochemical profile, structure and Li storage mechanism were extensively studied.

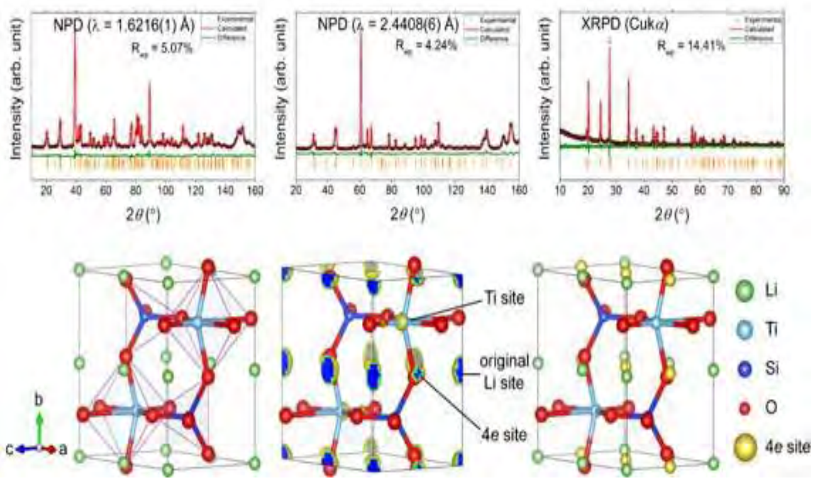
The crystal structure of Li_2TiSiO_5 is illustrated as a layered structure with infinite sheets of distorted TiO_6 octahedra and SiO_4 tetrahedra, linked by Li atoms. The distorted TiO_6 octahedral and SiO_4 tetrahedral networks are thought to be the origin of the structural stability of this material. The crystal structure is depicted in Fig. 1b (left) and the details are summarized in Table 1. Along with the refined structure of Li_2TiSiO_5, the nuclear-density difference (Fourier) map in Fig. 1b (middle) reveals negative nuclear density only at the 4*d*, 4*e*, and Ti (2*c*) sites, implying that lithium can only reside at these sites. The 4*e* sites are indicated by the yellow balls in Fig. 1b (right). Figure 2 give the typical charge/discharge curve of Li_2TiSiO_5 at between 0 and 3 V (*vs.* Li^+/Li), delivers a reversible charge capacity (Li-ion extraction) of 308 mAh/g, with a voltage plateau below 1.0 V.

The neutron powder diffraction (NPD) data indicate that the 4*d* site is fully occupied by lithium, leaving only the 4*e* and Ti (2*c*) sites (Table 1) free for further lithium inclusion. We performed density functional theory (DFT)-based calculations, which demonstrated that the 4*e* site cannot accommodate 2 lithium ions. NPD data reveal, however, the possibility of lithium-ions replacing titanium at the 2*c* site, indicating a possible conversion mechanism. Nevertheless, taken together, our results support the proposition that the Li_2TiSiO_5 discharge process can be divided into three parts: from 3 V to 0.28 V, delivering a sloped voltage curve without obvious structural change as lithium occupies 4*e* sites to form $Li_{2+x}TiSiO_5$ (see Table S1, simulated structure of $Li_{2.5}TiSiO_5$ has only 2.3% expand along *a* and *b* axis, 0.2% expand along c axis), from 0.28 V to 0.1 V, delivering a flat voltage plateau and undergoing a conversion reaction from $Li_{2+x}TiSiO_5$ to Li_4SiO_4 and TiO, and below 0.1 V, delivering a sloped voltage curve resulting from lithiation of TiO and possible Li plating.

$$Li_2^{4d}TiSiO_5 + xLi \leftrightarrow Li_2^{4d}Li_x^{4e}TiSiO_5\ (x \leq 0.5,\ 3\ \text{to}\ 0.28\ \text{V}) \quad (1)$$

$$Li_2^{4d}Li_x^{4e}TiSiO_5 + (2-x)\ Li \leftrightarrow Li_4SiO_4 + TiO;\ (\text{from}\ 0.28\ \text{to} > 0.1\ \text{V}) \quad (2)$$

$$TiO + yLi \leftrightarrow Li_yTiO;\ (< 0.1\ \text{V}) \quad (3)$$



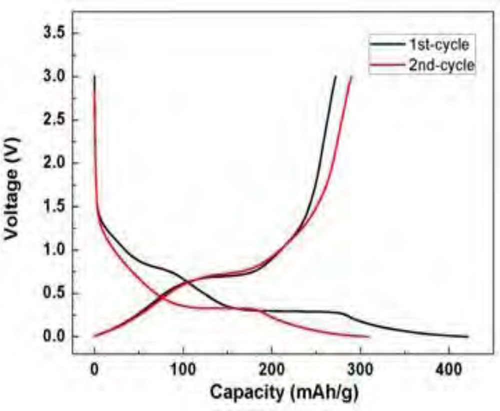


Fig. 1 Crystal structure characterization of Li_2TiSiO_5 Fig. 2 Typical charge/discharge curve of Li_2TiSiO_5

Tuning the Surface and Interface of Metal-based Nanocrystals for Energy Electrocatalysis

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Abstract: Engineering nanocrystals with size, shape, composition, structure and strain control is the key to enhance the performance of energy conversion devices. In this award lecture, I will focus on my recent advances in making/tuning high-quality metal-based nanocrystals for boosting the electrocatalysis of fuel cells and solar fuels. I will start with several examples on how to tune the surface and interface of multimetallic nanocrystals for achieving more efficient oxygen reduction electrocatalysis. Then, I will move to tune the defects and high-index facets of multimetallic nanocrystals for boosting the liquid fuels oxidation catalysis. Finally, I will discuss how to introduce the interface of metal-based materials for highly efficient hydrogen evolution reaction.

Slurry Electrodes for Flow Batteries and Other Electrochemical Technologies

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Slurry electrodes have many advantages in electrochemical devices and systems. They can be used to de-couple power and energy in energy storage, such as with flow capacitors and flow batteries involving deposition reactions. Slurry electrodes also have desirable features making them applicable for recovering metals from dilute streams, for chemical synthesis, sacrificial electrodes, for mechanical regeneration of electrodes, as well as other electrochemical processes.

In this presentation, we will address some of the challenges of this approach, specifically related to overpotential and current distribution within the slurry electrode, electrode materials utilization, and electrode performance. Simple models will be presented that relate physical and electrical properties of a slurry electrode to performance. These models are discussed with application towards an iron flow battery (see Figure 1) and a flow capacitor, and demonstrate the role of surface area and effective electronic conductivity of the slurry. We will then discuss some of our more recent work on understanding the effective electronic conductivity in slurries of carbon particles.

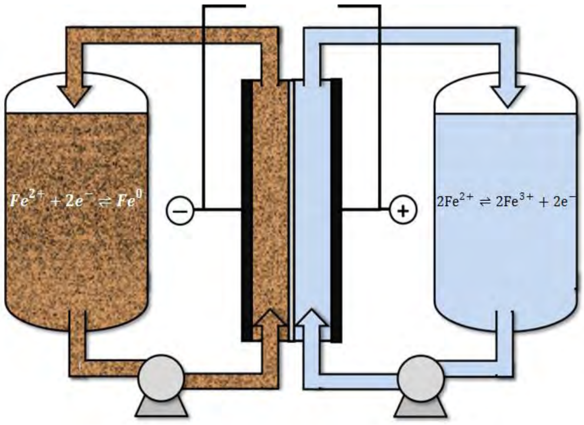

Figure 1: Iron flow battery with a slurry negative electrode.

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Morphology Evolution During Dealloying At High and Low Homologous Temperature

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Nanoporous gold (NPG) and its congeners spontaneously form at ambient temperature during dealloying of noble metal single-phase alloys such as Ag-Au and Cu-Pt by a process termed percolation dissolution. In order for this to occur the mole fraction of the less-noble component in the alloy has to be greater than a compositional threshold historically called the parting limit. Another prerequisite for percolation dissolution is that the applied electrochemical potential has to be large enough to dissolve the less-noble component from terrace sites, which necessarily results in the creation of new surface. This potential is called the critical potential. Since at low homologous temperature, T_H, the solid-state mobility of the components is of order 10^{-30} cm^2s^{-1} or less, percolation dissolution is the only mechanism available to support dealloying over technologically relevant time scales. Percolation dissolution operates without the necessity of solid-state mass transport since it involves the dissolution of the less-noble component along pre-existing atomic-scale pathways throughout the volume of the solid allowing the electrolyte to invade the evolving porous structure along the vacant atomic-scale channels produced by this process. Accordingly, the composition of the un-dealloyed parent phase/electrolyte interface remains at the original alloy composition. At low T_H and for alloy compositions below the parting limit, dealloying results in passivation owing to noble-metal surface enrichment by several potential-dependent mechanisms yielding either a planar surface or a surface characterized by monolayer deep vacancy clusters.

Dealloying under conditions of high T_H (or high intrinsic diffusivity of the more electrochemically reactive component) is considerably more complicated than at low T_H. In this case solid-state mass transport is available to support dealloying which results in a rich set of morphologies including negative dendrites, Kirkendall voids and bi-continuous porous structures. Owing to diffusive transport, there is no parting limit for dealloying, however, there is a compositional threshold, p_{PD}, as well as a critical potential for the operation of percolation dissolution and the formation of bi-continuous structures. Negative or void dendrite morphologies evolve at compositions below p_{PD} and at large values of the applied electrochemical potential when the rate of dealloying is limited by solid-state mass transport. This process is isomorphic to dendrite formation in electrodeposition. Kirkendall voiding morphologies evolve below the critical potential over the entire range of alloy compositions. In order to study dealloying at high T_H we have examined the behavior of Mg-Cd and Li-Sn alloys. Li-Sn alloys present an additional complication since the equilibrium phase diagram for this system shows a multitude of intermetallic phases and corresponding regions of two-phase coexistence. The intrinsic diffusivities of Cd and Li were measured in these alloys using electrochemical techniques and the resultant dealloying morphologies were characterized as a function of composition under fixed potential and fixed current density conditions. In the case of Li-Sn alloys, we determined p_{PD} and connected this composition to the Li_7Sn_3 phase. We used a model for the critical potential similar to that previously developed for noble-metal alloy systems that explains the measured values to within experimental uncertainty.

We summarize our results by introducing dealloying morphology diagrams to graphically illustrate the electrochemical conditions resulting in the various morphologies that form under conditions of low and high T_H.

Electron-Transfer Chemistry of Functional Nanoparticles: An Interfacial Perspective

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Transition-metal nanoparticles represent a unique class of functional nanomaterials where the physical and chemical properties deviate markedly from those of their atomic and bulk forms. In order to stabilize the nanoparticles and further manipulate the materials properties, surface functionalization with organic molecules has been utilized as a powerful tool. Among those, mercapto derivatives have been used extensively as the ligands of choice for nanoparticle surface functionalization by taking advantage of the strong affinity of thiol moieties to transition metal surfaces forming (polar) metal–thiolate linkages. Yet, the nanoparticle material properties are generally discussed within the context of the two structural components, the metal cores and the organic capping layers, whereas the impacts of the metal-sulfur interfacial bonds are largely ignored because of the lack of interesting chemistry. In recent years, it has been found that metal nanoparticles may also be functionalized by stable metal–carbon (or even –nitrogen) covalent bonds. Because of the formation of dπ–pπ interactions between the transition-metal nanoparticles and terminal carbon moieties, the interfacial resistance at the metal–ligand interface is markedly reduced, leading to the emergence of unprecedented optical and electronic properties.

In this presentation, we will summarize recent progress in the studies of metal nanoparticles functionalized by conjugated metal–ligand interfacial bonds that include metal–carbene (M=C) and metal–acetylide (M–C≡)/metal–vinylidene (M=C=C) bonds. Such interfacial bonds are readily formed by ligand self-assembly onto nanoparticle metal cores. The resulting nanoparticles exhibit apparent intraparticle charge delocalization between the particle-bound functional moieties, leading to the emergence of optical and electronic properties that are analogous to those of their dimeric counterparts, as manifested in spectroscopic and electrochemical measurements. This is first highlighted by ferrocene-functionalized nanoparticles that exhibit nanoparticle-mediated intervalence charge transfer (IVCT) among the particle-bound ferrocenyl moieties, as manifested in electrochemical and spectroscopic measurements. Such intraparticle charge delocalization has also been observed with other functional moieties such as pyrene and anthracene, where the photoluminescence emissions are consistent with those of their dimeric derivatives. Importantly, as such electronic communication occurs via a through-bond pathway, it may be readily manipulated by the valence states of the nanoparticle cores as well as specific binding of selective molecules/ions to the organic capping shells. These fundamental insights may be exploited for diverse applications, ranging from chemical sensing to (nano)electronics and fuel cell electrochemistry. These results demonstrate that metal-ligand interface is a unique platform for ready manipulation of nanoparticle properties and applications.

Superconcentrated aqueous electrolytes

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A new class of aqueous electrolytes has been recently reported and used in rechargeable lithium batteries (1). It is based on superconcentrated aqueous solutions of salt such as lithium bis(trifluoromethylsulphonyl)imide (LiTFSI). A representative example consists of a 5 M LiTFSI solution, which contains 21 moles of LiTFSI in 1 kg of water (21 m). This solution is characterized by a H_2O/ Li^+ molar ratio of 2.6 that is insufficient for full solvation of all Li^+ cations. These solutions have been arbitrarily termed “water-in-salt” electrolytes because of their low number of free water molecules and the solvation shell of Li^+ cations is incomplete in comparison to less concentrated (eg. 1 M) solution.

Superconcentrated aqueous solutions have been used in rechargeable batteries (1) and electrochemical capacitors (2). In these electrolytes, a significant increase of the cell voltage has been reported and attributed to a shift to more negative and positive potential of the onset of hydrogen and oxygen evolution, respectively. These observations are mainly limited to the active electrode materials and the current collector. In addition to energy storage systems, “water-in-salt” use can be envisioned in other electrochemical technologies. Therefore, since the electrochemical behavior of superconcentrated aqueous electrolytes has not been investigated in details, it would be useful to get more insight in their electrochemical behavior in presence of various metal and carbon electrodes (3).

In this talk, the properties of superconcentrated aqueous solutions will be presented. In addition, their behavior in various electrochemical systems will be also presented and discussed.

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The Essential Physics of Direct and Reverse Electroactuation: from Energy Storage to Energy Harvesting and Robotics

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Sister systems to supercapacitors are electroactuators, that transform the AC voltage into mechanical motion and reverse electroactuators that do the opposite. The former are considered promising for microrobotics, whereas the latter – for converting the energy of mechanical motion into AC current, e.g. for current generation from walking.

The principle of operation of electroactuators is usually based on the directed motion of large ions between two parallel bendable electrodes of a capacitor in a polymer matrix that fill the capacitor: rearrangement of ions induced by applied voltage causes stress and strain. The reverse actuators can be the same systems but in which the strain is applied mechanically, generating voltage. Alternatively, the reverse electroactuators may be based on the principle of reverse electrowetting: pressing a nonwetting electrolytic solution into a pore. The latter increases the area of electrode-electrolyte interface and leads to increase of capacitance. Under an applied voltage, this change of capacitance will generate a transient or an AC current (if the pressure that pushes the liquid into a pore oscillates).

All classes of these systems will be described in my talk. I will highlight the operation principles of such gadgets based on the originally proposed theories, which helped to rationalize some of such systems as well as propose new scenarios for their functioning. The whole research area can be classified as "*ionics*". Progress in this kind of systems is tightly related with understanding the interplay between elasticity, electrostatics, and kinetics of ion transport at micro- as well as nano-scale.

First publications of my group with co-authors from Rice University (A.B.Kolomeisky) and PennState (R.Colby) are listed below, but more results and model developments are currently on the way in a wider consortium of researchers, which would be disclosed in my lecture.

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Electrochemical Reduction of Atrazine at Carbon and Silver Cathodes

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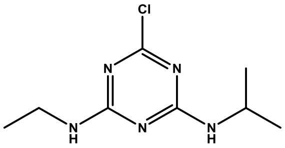
Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, **1**) has been one of the most widely used pesticides in the world. Though banned by the European Union since 2004, it is still employed widely in the United States, and it can be detected in water sources, soil, and even air.[1] Environmental persistence of atrazine and its metabolites has caused contamination to spread far away from regions of its application. Studies have revealed evidence of endocrine disruption in amphibians exposed to these compounds.[1] Consequently, the degradation of atrazine to less environmentally harmful compounds is of interest.



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In this study, electroreduction at different cathodes has been probed as a way to degrade atrazine. Previous electrochemical studies of atrazine with mercury cathodes were successful for its detection with the aid of square-wave voltammetry and for its degradation by means of controlled-potential (bulk) electrolysis.[2–4] At mercury cathodes, electrolyses resulted both in cleavage of the carbon–chlorine bond and in reduction of the triazine ring.[4] Our laboratory has been exploring the use of carbon and silver cathodes for the degradation of atrazine; glassy carbon offers a simple, environmentally friendly alternative to mercury, and silver is catalytic for the reductive cleavage of carbon–halogen bonds. Cyclic voltammograms (Fig. 1) for reduction of 5.0 mM atrazine at carbon and silver cathodes, respectively, in dimethylformamide (DMF) containing 0.050 M tetramethylammonium tetrafluoroborate ($TMABF_4$), reveal one irreversible cathodic peak at –1.77 or –1.62 V vs. a Cd(Hg) reference electrode. Gas chromatographic examination of products arising from bulk electrolyses of atrazine at both glassy carbon and silver cathodes indicate the presence of dechlorinated atrazine.

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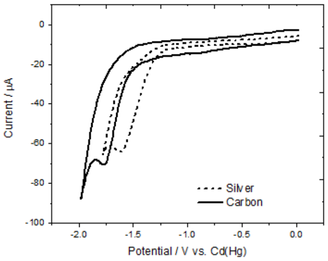

Figure 1. Cyclic voltammograms recorded at 100 mV s^{-1} for reduction of 5.0 mM atrazine at carbon and silver cathodes (each electrode was 0.071 cm^2) in oxygen-free DMF containing 0.050 M $TMABF_4$. Potentials are with respect to a cadmium-saturated mercury amalgam reference electrode in contact with DMF saturated with both cadmium chloride and sodium chloride; this reference electrode has a potential of –0.76 V versus an aqueous saturated calomel electrode (SCE) at 25 °C. Scans begin and end at 0 V vs. the reference electrode.

Transport and Activity in Dealloyed Nanoporous Electrocatalysts

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Dealloying has emerged as a central phenomenon in many electrochemical systems. Intercalation electrodes in batteries undergo alloying/dealloying cycles during charging and discharging, and the materials degradation upon dealloying remains one of the critical problems in corrosion. Here we will discuss the utility of dealloying to make high surface area nanoporous electrocatalysts, such as for oxygen reduction in fuel cells or other small molecule reduction. We ask the basic question – why bother? If nanoparticles can yield the same surface area to volume ratio as dealloying, what is the advantage of porosity? We address the answer to this from a number of different angles. First, dealloying is a relatively easy processing method. In certain cases it even leads spontaneously to highly active core-shell structures such as with dealloyed Ni-Pt for the oxygen reduction reaction; in other cases the high fraction of saddle point features in the porous structure yields interesting and unusual structural features. Second, you can fill the pores with secondary materials that can bias reactions of interest to completion. For instance, filling nanoporous dealloyed Ni-Pt with hydrophobic and oxophilic ionic liquids has led to a new class of highly active oxygen reduction electrocatalysts. These catalysts work because nanoporosity is allowing control over reactant and product flux to the active surface, enhancing aggregate activity by increasing reactant concentration, and decreasing product concentration. The observation that we can control such fluxes has led to a third useful feature of nanoporous electrocatalysts, namely, that by engineering solution concentrations appropriately, nanoporous electrocatalysts can mediate multiple reactant fluxes, suppressing certain reactions (e.g., hydrogen evolution) in favor of more desired ones (small molecule reduction), including nearly independent control of both reaction activity and selectivity.

Strategies for accelerating electrochemical reactions

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Electrochemical analysis measures the electrochemical signals including Faradaic current, charge, voltage, capacitance and resistance of electrodes as functions of target concentrations. If one correlates the Faradaic current with the concentration of targets in electroanalysis, electron transfer between the targets and electrodes should be considered. The electron transfer kinetics is significantly determined by the surface properties of the electrode surfaces, *i.e.*, the orientation of the target molecules, surface structures of the electrodes, activity of the electrocatalysts. This talk will present strategies to accelerate the electron transfer rate of targets with electrodes, increasing the electrochemical currents for analyis.

The control of target orientation at electrode surface will be considered. We found that the surface properties, i.e., charges and wettability, can manipulate the orientation of cytochrome c. On a hydrophilic electrode surface, cytochrome c is assembled on electrode surface with the hemin plan parallel to the electrode surface, thus direct electron transfer between cytochrome c and the electrode can occur; while the electron transfer of cytochrome c cannot occur on a hydrophobic surface due to the vertical orientation of hemin plane of cytochrome c. For electrochemical reactions, the Faradaic current is proportional to the reaction turnover of targets at functional electrodes which is certainly determined by the active sites of the electrocatalysts. If we can properly turn the electron density of the active sites in electrocatalysts to the level where the adsorption of substrate and desorption of electrochemical reaction product are both favorable, high reaction turnover might be achieved. This strategy can be realized by turning the liable ligands of the active sites and/or injecting hot electrons or holes generated by localized surface plasmon resonance into the active sites.

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Effect of Impurities on Product Distribution at Li-O_2 Battery Cathode

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Li-air or Li-O_2 battery has attracted much attention as one of the promising energy storage devices for electric vehicles due to its high theoretical capacity. There are, however, many issues to be solved before it will become a practical device. One of the most important issues is the high overpotential for charging process, in which insulating Li_2O_2 formed during discharge process must be anodically decomposed. The overpotential seems to be dependent on the morphology of Li_2O_2, which in turn depends on the conditions of discharge, i.e., cathodic, process. Thus, many investigations have been carried out to understand the reaction mechanism of the discharge process but results do not agree with each other.

Here we show that impurities in electrolyte solution such as water strongly influence the amount, composition, and morphology of discharge products including O_2^-, Li_2O_2, H_2O_2, $LiHO_2$, and LiOH based on the results of electrochemical quartz crystal microbalance (EQCM), rotating ring-disk electrode (RRDE) and in situ surface enhanced Raman scattering (SERS). Some of the products induce the decomposition of the solvent. Detailed reaction mechanism will be discussed.

Recent Development on Electrochemical Application on Boron-doped Diamond Electrodes

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Boron-doped diamond (BDD) electrodes are very attractive material, because of their wide potential window, low background current, chemical inertness, and mechanical durability[1]. In these years, we have reported several examples for electrochemical sensor applications[2]. Here, we report some recent examples of electrochemical sensor application of BDD such as influenza virus [3], oxytocin, which is known as a simple cuddle chemical [4] using BDD microelectrodes.

As other applications such as organic synthesis [5], ozone generation, and CO2 reduction [6] are also shown. Furthermore, one of the main problems for waste water treatment application is a electrolytic corrosion of BDD electrodes. Here, we have studied on the mechanisms of the corrosion, and then, proposed conditions required to prevent them during the electrolysis of organic compounds in aqueous solutions [7].

Highly sensitive detection of influenza virus [3]

Several dozen plaque-forming units (pfu) of influenza virus (IFV) could be detected using a boron-doped diamond (BDD) electrode terminated with a sialic acid-mimic peptide. The peptide was used instead of the sialyloligosaccharide receptor—the common receptor of influenza A and B viruses required during the early phase of infection—to capture IFV particles. The peptide, which was previously identified by phage-display technology, was immobilized by click chemistry on the BDD electrode. Electrochemical impedance spectroscopy revealed that H1N1 and H3N2 IFVs were detectable in the range of 20–500 pfu by using the peptide-terminated BDD electrode..

Continuous and selective measurement of oxytocin [4]

Oxytocin, which is known as a simple cuddle chemical, is a nonapeptide with many important biological functions. In addition to its functions as a hormone in facilitating uterine contractions and mammalian milk ejection, it was also discovered that oxytocin works as a neurotransmitter and is considered to mediate social behavior, such as pair bonding and instinctive maternal aggression. Cyclic voltammetry of oxytocin in a phosphate buffer solution exhibits an oxidation peak at +0.7 V (vs. Ag/AgCl), which is attributable to oxidation of the phenolic group in the tyrosyl moiety. The linearity of the current peaks obtained in flow injection analysis (FIA) using BDD microelectrodes over the oxytocin concentration range from 0.1 to 10.0 μM with a detection limit of 50 nM (S/N = 3) was high ($R^2 = 0.995$). Furthermore, a clear distinction between oxytocin and vasopressin was observed with anodically-oxidized BDD electrodes due to the attractive interaction between vasopressin and the oxidized BDD surface.

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The Structure of Aluminum Alloys Electrodeposited from Chloroaluminate Ionic Liquids

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The electrodeposition of aluminum alloys from chloroaluminate electrolytes has a rich history, beginning with the high temperature alkali halide-based melts, such as $AlCl_3$-NaCl, and transitioning into the ambient temperature analogs, such as $AlCl_3$-1-ethyl-3-methylimidazolium chloride ([EMIM]Cl). Although still very much moisture sensitive, these organic halide systems became widely accepted due to their extremely low vapor pressure, which made them experimentally less challenging. More recently with the introduction of the air- and water-stable systems that do not necessarily require handling in an inert atmosphere, a significant portion of the current electrodeposition research is being conducted at or near ambient temperature.

Electrodeposited alloys are rarely in thermodynamic equilibrium, and several unique microstructural features such as extended solid solubility, metastable crystalline phases, and metallic glasses are generally observed. While exact correlations between electrodeposition and vapor deposition have not been developed, the excess free energy possible in alloys produced by these two techniques is similar and on the order of 50 kJ mol^{-1}. Because the excess free energy of the deposit is inversely proportional to the atomic mobility, phase constitution depends strongly on deposition temperature. This talk will focus on the influence of deposition temperature on the crystal structure of electrodeposited aluminum-transition metal alloys from chloroaluminate ionic liquids.

Electrochemical Atomic Layer Deposition: Self-terminated Electrodeposition Reactions and Pulse Plating

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Development of a sustainable hydrogen economy based on water electrolysis and fuel cells is constrained by the performance, longevity and high cost of Pt group electrocatalysts. Important strategies for improving catalytic reactivity include alloying, forming bimetallic or alloyed surfaces, and engineering substrate–catalyst interactions. At the same time, significant effort is underway to minimize the loading of Pt group metals by examining new synthesis methods and electrode geometries. Of specific interest is atomic layer deposition (ALD) that can be used for growing ultrathin films to maximize utilization of rare, expensive metals and facilitate the exploration of bimetallic effects in electrocatalysis.

Recently, an inexpensive "wet form" of ALD based on self-terminated electrodeposition reactions was uncovered that enables controlled formation of ultrathin films of Pt, Ir and iron group metals and alloys thereof. The mechanism of self-terminated deposition reactions will be discussed and the utility of these films as bimetallic electrocatalysts will be demonstrated. For example, monolayer equivalent Pt and Ir films were found to match or exceed the best known specific HER/HOR activity for bulk polycrystalline Pt or Ir electrodes and thereby offer the promise of increasing the scalability of these important precious metals in energy conversion devices. The effectiveness of such reaction on a variety of different substrates will also be examined.

Exploring the Reactive Modulation of Soluble Redox Active Polymers via Versatile Electrochemical Interrogation

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Redox active polymers (RAPs)[1] and colloids (RACs)[2] are a new class of materials for energy storage in fluid dispersion format.[3] Despite RAPs displaying excellent charge storage properties, such as high solubility, competitive redox potentials, quantitative accessibility, and stable cyclability, their complex electrochemical reactive pathways are just becoming elucidated. Unlike small redox molecules, RAPs and RACs rely on intra-particle electron transfer, in addition to direct reactivity on the electrode, for achieving full electrolysis. Charge mobility via inter-pendant electron hopping combines with the polyelectrolyte nature of these materials to exhibit a rich electrochemical behavior that is strongly modulated by specific and non-specific interactions with the electrolyte, and modified through versatile architectural design.[4] In this talk, we will highlight the impact of several key factors on the reactivity of RAPs and RACs, **Figure 1**, including the role of adsorption on the electrode, charge transfer mediation, electrolyte interactions, particle size and backbone structure.

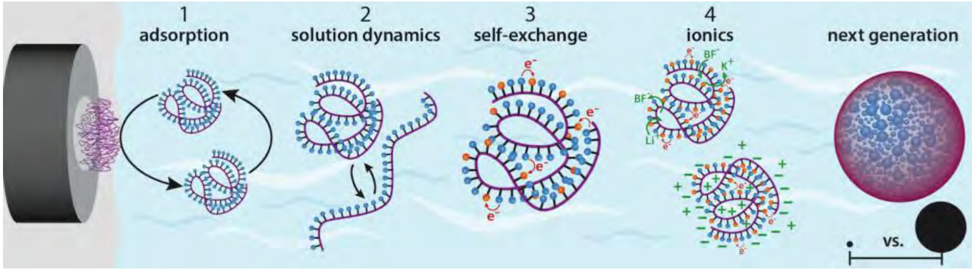

Figure 1. Several electrode and solution-phase effects modulate RAP and RAC reactivity.[3]

The mechanistic characterization of RAPs and RACs requires a spectrum of powerful electrochemical techniques that range from the bulk of the flow battery to single particle experiments.[3] We will describe new insight provided by nano-resolved scanning electrochemical microscopy to understand charging mechanisms in single colloidal particles and in well-ordered monolayers made with RACs. These experiments enable the exploration of intra-particle and inter-particle interactions, the identification of kinetic or transport bottlenecks such as charge trapping, and the detection of the maximum current densities attainable in individual particles. Advanced *in-situ* spectroelectrochemical analysis promise to provide clarity on the charge propagation mechanisms. Altogether, the combination of novel structural motifs, the identification of structure-reactivity relationships, and their exploration using advanced electrochemical techniques, result in new directions for modified electrodes and electrolytes using RAPs and RACs for applications in sensing, catalysis, surface engineering, and energy storage.

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Control of Selectivity in the Electrochemical Synthesis of Biaryls by a Solvent Effect

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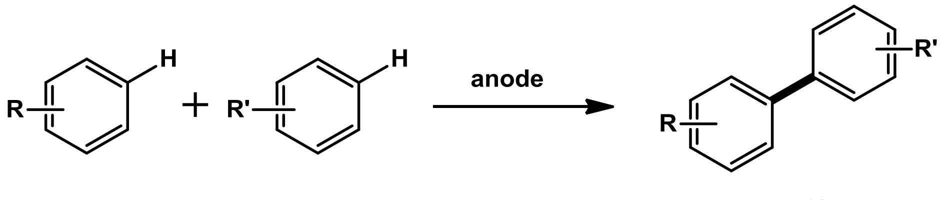
The use of electricity as reagent has several benefits for the generation of value added chemicals since no reagent waste formed and alternative reaction pathways can be exploited. In general, the electrochemical oxidation potential and nucleophilicity are in most cases coupled. Therefore, the intermolecular cross-coupling is usually less preferred and homo-coupling products are predominantly obtained.

The talk will deal with a novel concept to tackle the desired electro-conversion by using innovative electrolytes.[1] The dehydrogenative C,C bond formation of aryls is anodically accomplished. The direct electrolysis represents a reagent- and metal-free cross-coupling reaction. From relatively simple starting materials phenol-arene, phenol-phenol, phenol-aniline, and aniline-aniline cross-coupling reactions were achieved.[2-6] It turns out that this electro-organic method is scalable and superior to peroxide based conversions.[7] Moreover, the electrolyte system based on 1,1,1,3,3,3-isopropanol seems to be the key for very robust electrosyntheses.



up to 92%
selectivity >100:1

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Challenges in the accurate measurement of oxygen reduction electrocatalyst activity by RDE and in CCMs

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A key to achieving efficient, cost-effective hydrogen fuel cells is having a highly efficient, durable cathode electrocatalyst for the oxygen reduction reaction, while minimizing the amount of platinum and other expensive precious metals. Accordingly, the identification of new low-Pt electrocatalysts has been a productive research area. At the Naval Research Laboratory, we attempted to reduce the platinum content of cathode electrocatalysts by supporting the Pt on a range of oxides and oxyphosphates and take advantage of metal support interactions. The challenge then became, how good was our electrocatalyst vs. a platinum standard? We started with measurements of platinum on carbon standards (Pt/C) by rotating disk electrode (RDE) voltammetry. We discovered that uniform film thickness of the electrocatalyst film on the RDE was one of the most important factors in reproducibility. After developing a standard RDE method for characterizing Pt/C, we then were able to confirm that our platinum tantalum phosphate (Pt-TaOPO/C) electrocatalyst had 2x higher activity than Pt/C.

However, once integrated into the catalyst-coated membrane (CCM) of a hydrogen fuel cell, the Pt-TaOPO/C performed poorly compared to commercial Pt/C ones. We have since tried to resolve this puzzle by embarking on a path to make reproducible CCMs in house, first starting with the optimization of Pt/C CCMs. We opted to use ultrasonic spray deposition of the fuel cell electrocatalysts because it can deposit uniform layers of electrocatalysts and only requires small amounts of materials. The catalyst layer thickness was optimized along with the hot pressing conditions and pressure used during the assembly of the CCM into a membrane electrode assembly (MEA) in a fuel cell. We found that a key parameter was the normal stress on the cell, set in our laboratory-scale systems by the gasket thickness in the fuel cell. The resulting compression impacts the microporous layer structure of the gas diffusion media, and thus the mass transport of O_2 and H_2O to and from the Pt in the catalyst layer. With such mechanical issues resolved, we could tackle the problems of make an oxide and/or phosphate based electrocatalyst active in CCMs, for which the hydrophilicity of the electrocatalyst, and thus flooding, plays a significant role. We also see that low equivalent weight ionomers can be useful in improving the performance of Pt/C and PtCo/C electrocatalysts. Understanding such issues are critical as researchers move to oxygen- and nitrogen-containing non-precious metal electrocatalysts.

Electro-Catalysis for Electro-Chemicals

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The chemical industry should in the future be based on renewable energy. Therefore material development for environmentally friendly, electrocatalytic production of valuable chemicals is needed.

In general the electrochemical synthesis of chemicals holds several advantages:

- The reaction energy is directly tunable by controlling the bias in the electrochemical cell.
- One can use more benign reaction conditions and less costly reactants.
- It is very scalable.
- It is decentralized; it just requires access to the feedstock molecules and electricity.

Chemicals could therefore be produced using safe, cheap, more environmentally friendly and more abundant reactants than today. The products could be provided on demand at the place where they are needed, reducing expensive and hazardous transport of chemicals. However, stable, efficient and selective catalysts have to be discovered. This requires insight into the surface chemistry at the atomic scale. Surface chemistry can be revealed based on density functional simulations. I will give examples where the insight from simulations might pave the way for rational discovery of new catalyst materials and new electrocatalytic processes for sustainable production of fuels and chemicals. Some examples are: oxygen reduction to H_2O_2 and carbonylation of methanol.

Synthesis and Electrochemical Performance of Two-dimensional Transition Metal Nitrides

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Two-dimensional (2D) transition metal nitrides are recently a very highly sought family of materials that is expected to exhibit plasmonic and other promising properties. However, 2D metal nitrides are limited to only a handful of synthesized materials so far (MoN, Ti_4N_3 and GaN), although we anticipate that this field of 2D materials is of growing significance right now in terms of their superior conductivity and stability compared to their respective 2D transition metal carbide analogues. The bottleneck in the synthesis of these materials is a lack of known synthesis routes. Many 2D transition metal carbides, such as $Ti_3C_2T_x$ and other carbide MXenes, can be formed by selective etching and exfoliation of their ternary layered precursors (MAX phases). However, there are fewer bulk layered transition metal ternary nitrides known and so far only Ti_4AlN_3 has been successfully exfoliated to form 2D Ti_4N_3 (nitride MXene) by our group. Other synthesis procedures include our recently developed salt-templating method, which has successfully produced 2D MoN, V_2N and W_2N. In this procedure, a metal-containing precursor is mixed with a salt and then treated at high temperatures. A 2D metal oxide is obtained due to the lattice match between the surface of the salt and target oxide. The transition metal oxide is then treated in ammonia gas at high temperature and transformed into the 2D nitride. When the restacked 2D MoN film was used as a supercapacitor electrode, a remarkable volumetric capacitance of ~ 928 F cm^{-3} was achieved at 2 mV s^{-1} in H_2SO_4 electrolyte, and a very high capacitance of 200 F cm^{-3} was measured at an ultrahigh sweep rate of 20 V s^{-1}.

Probing the Electrocatalysis and Internal “Wiring” of the Hydrogen Dependent CO_2 Reductase

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The Hydrogen Dependent Carbon dioxide Reductase (HDCR) from *Acetobacterium woodii* provides a remarkable solution to the problem of H_2 storage, by reversibly coupling H_2 oxidation to CO_2 reduction through the coupling of two distinct active sites, with a “wire” of iron-sulfur clusters.[1] Recently, we have reported on the electrocatalytic properties of the Fe-Fe hydrogenase (Hase) module in the intact complex, including (an)aerobic oxidation, CO inhibition and the first systematic analysis of the catalytic bias (CB) of a Hase.[2] CB depends on pH, regardless of the H_2 concentration, despite a higher affinity for H_2 than other FeFe-Hases, and we describe this in terms of a phenomenological parameter (β) which allows for the direct comparison with other Hase electrocatalysts. Chronoamperometry studies enable the direct assessment for the action of CO as an inhibitor of Hase catalysis. We find that CO inhibition is fully reversible under all oxidation states of the active site, which is interpreted in terms of a current mechanistic model Together, these data render HDCR the first ‘‘syngas-friendly’’ FeFe-Hase. Here, we further report on the challenges of examining direct CO_2 reduction in the face of a highly reactive Hase subunit, which demonstrates fast rates of H^+ reduction, under all conditions. Examination of transient electrocatalytic behavior, however, does reveal a signature of electronic communication between the two active sites. A model for such communication will be presented.

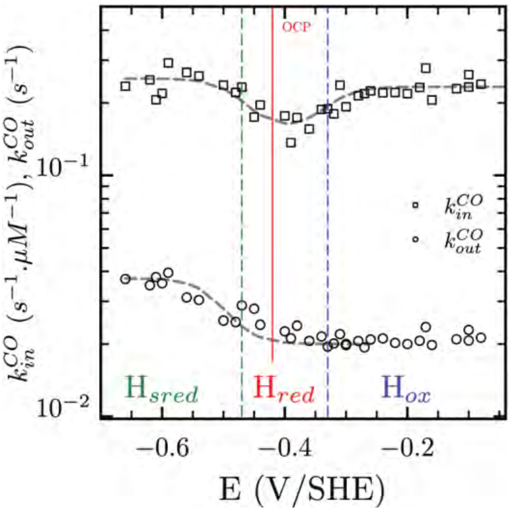

Figure 1. Electrochemically determined rates of CO inhibition (in terms of binding and release) of HDCR, as a function of potential. Figure taken from Reference 2.

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Low Temperature Electrolysis:
Pathways to Large Scale Renewable Hydrogen

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Global decarbonization goals require renewable sources of hydrogen, both to replace hydrogen generated from steam methane reforming of natural gas, and for conversion of existing carbon dioxide emissions to useful fuels. According to an energy analysis performed by Lawrence Livermore National Laboratory, 2% of energy in the U.S. goes through hydrogen as an intermediate from feedstock to end use. Much of this hydrogen is used in industrial processes such as ammonia production, metal heat treating, semiconductor processing, and oil refining. At the same time, as renewable sources of energy become a larger fraction of the electrical grid, energy storage solutions are required to load shift from periods of high renewable generation to periods when demand exceeds generation. Finally, fuel cell vehicles are finally beginning to roll out as commercial vehicles, and will require hydrogen infrastructure. Hydrogen generated via water splitting using excess renewable energy provides a carbon-free bridge across these different sectors. However, more cost effective and efficient solutions are required to enable displacement of fossil fuels in these applications.

Proton exchange membrane (PEM) electrolysis is has shown the potential for deployment at scale, and is an ideal near term technology to set the stage for other advanced technologies to follow (Figure 1). PEM electrolysis has been scaled to multi-megawatt systems, and at smaller scale, Proton OnSite systems have been demonstrated to be stable over 10 years of operation. There is also still significant opportunity in PEM electrolysis for manufacturing and material improvements. While thinner membranes, reduced platinum group metal usage, and improved cell components have been demonstrated, manufacturing development is still needed. This talk will discuss the current status in PEM electrolysis and the long term projected impact on cost, as well as how the different material and manufacturing platforms can help drive multiple hydrogen generation technologies.

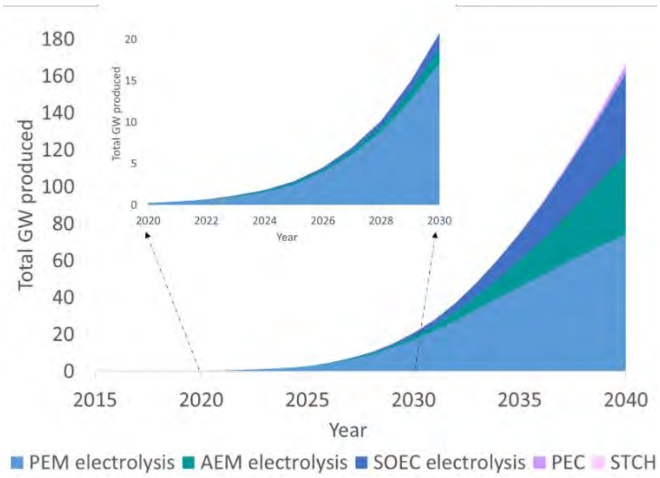

Figure 1: Estimate of cumulative GW of H_2 produced by various technologies based on current and projected TRL levels. AEM = alkaline exchange membrane; SOEC = solid oxide electrolysis cell; PEC = photoelectrochemistry; STCH = solar thermochemical hydrogen

The impedance response of a passive film revisited by a double modulation technique

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Passive film formed at the surface of metals provides a protection against corrosion. The impedance response of such a system shows mainly a capacitive behavior, even if in some cases, the impedance response may reveal different time-constants. For instance, the electrochemical impedance diagram of an iron electrode in a 1 M phosphoric acid solution is presented in Fig. 1 and shows 3 domains: the high frequency domain corresponding to the coupling of the interfacial capacitance and the charge-transfer resistance, an inductive loop in the medium frequency domain ascribed to the relaxation of charged species inside the passive film, and low frequency capacitive behavior corresponding to the faradaic accumulation of charge due to the modulation of the passive-film thickness.[1]

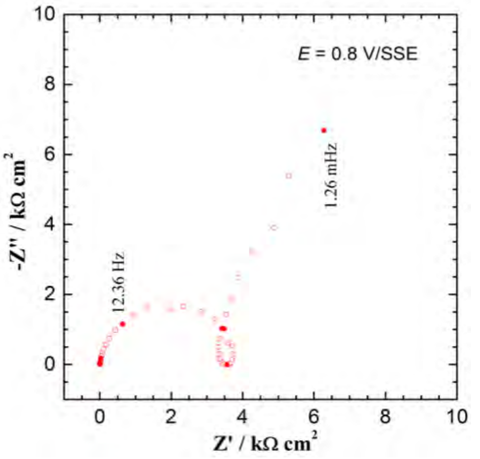

Figure 1: Impedance diagram of a pure iron electrode in 1 M H_3PO_4 solution in the passive domain.

The aim of this work is to revisit the relaxation associated with the formation and the 3D-growth of the passive film in the passive domain using the modulation of the interfacial capacitance (MICTF). The MICTF technique proposed few years ago by Antaño-Lopez *et al.*[2,3] consisted in a double excitation technique for determining simultaneously two spectra: the traditional electrochemical impedance and the frequency response of the interfacial capacitance modulated by the same EIS signal. The MICTF measurement takes advantage of the frequency domain for improving the signal-to-noise ratio especially in the low and very low frequency ranges. This measurement can be performed by the simultaneous application of two sinewave-potential perturbations: the first one in high frequency domain and the other one by scanning the low frequency domain at which traditional EIS can be performed.[2,4]

After a brief presentation of the technique, the results obtained on Fe will be presented. A specific attention will be paid to separate the contribution of the response ascribable to the relaxation of the thickness of the passive film to that of the charge reorganization in the thin film. It will also be shown that the MICTF technique provides a unique way of extracting the semi-conducting properties of the passive film.

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Novel Architectures for Future Hybrid Supercapacitors

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Hybrids of batteries and electrochemical capacitors represent an important future direction for supercapacitor energy storage devices. The attractive feature here is the prospect of achieving higher energy and power densities than what is potentially achievable with, respectively, lithium-ion battery materials or carbon-based electrical double layer capacitors (EDLC). To realize this objective, there is a critical need for novel materials and architectures which facilitate ion transport and electron transfer. Our research has focused on electrode materials that store charge by means of faradaic reactions which occur upon the insertion/de-insertion of lithium ions. In particular, we have been interested in pseudocapacitive materials in which reversible redox reactions occur at or near the surface of an electrode. These reactions are sufficiently rapid so that the device's electrochemical features are similar to those of an EDLC, but with significantly higher levels of energy storage because of the redox reactions. In recent years we have established several criteria for identifying materials that exhibit pseudocapacitor-like properties and retain high energy density at high rates of charge/discharge. One criterion is directly related to kinetics as the rate of charge storage should be dominated by surface-like kinetics rather than semi-infinite diffusion as occurs with battery materials. Another consideration is that the material should not undergo a phase transformation upon lithium-ion insertion as such processes generally involve nucleation and growth processes which are diffusion-limited. Both criteria are satisfied in Nb_2O_5 which retains a lithium capacity of 120 mAh/g at a charge/discharge rate of 60C.

Novel architectures also influence the energy storage properties of pseudocapacitive materials. Mesoporous architectures are especially attractive as the electrolyte penetrates the pores and has access to the redox-active walls of the material. By keeping the wall thickness below 10 nm, we achieve a condition where the diffusion distance for the lithium ions is less than $(Dt)^{1/2}$ and surface-like charge storage kinetics are observed. Another popular approach for creating materials with high energy density at high charge/discharge rates has involved the synthesis of nanoscale materials. There is growing evidence that the electrochemical properties of materials tend to become capacitor-like when dimensions are less than 20 nm. One reason for this behavior is that there are a larger number of surface sites for charge storage with nanoscale materials so that the material exhibits the electrochemical properties of the surface rather than the bulk. Another consideration with nanoscale materials is that the small particle size leads to a decrease in diffusion distance and a higher power density. Oxides are not the only systems of interest for high energy density redox materials. A rapidly emerging area in the materials community is that of two-dimensional materials, such as transition metal dichalcogenides. The large van der Waals gaps which characterize these materials are ideal for 2D lithium-ion diffusion. To date, studies with TiS_2 and MoS_2 materials have shown that these materials exhibit high energy density at high charge/discharge rates. The ensemble of these results suggests that over the next few years the combination of both novel materials and architectures will lead to a growing number of high-rate redox materials that can achieve improved properties for hybrid supercapacitor devices.

Carbon Nanomaterial Electrodes for Neuroscience Applications

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Carbon fibers have been used for the direct detection of neurotransmitters for some time. However, new materials are needed to increase the sensitivity, selectivity, and reversibility of detection while maintaining a size small enough to measure near a synapse. Our lab has examined several new materials, including aligned CNT yarns, carbon nanospikes, and carbon nanopipette electrodes to address the challenges of neurotransmitter detection. Carbon nanospikes can be grown on any material and thus are useful for coating a variety of substrates and providing good electrochemistry. The carbon nanopipette electrodes allow a high sensitivity measurement with submicron spatial resolution, small enough for possible single synapse measurements. CNT yarns microelectrodes are highly desirable for tissue applications because of their small size and superior electrical and mechanical properties. In addition, we have explored surface treatments of CNT yarn microelectrodes, including laser treatment, oxygen plasma treatment, and antistatic gun treatment. These treatments increase the sensitivity and change the selectivity of the sensors, allowing the properties to be tuned. Thus, different materials and different treatments can be used tune the electrochemical properties for real-time, *in vivo* neurotransmitter detection.

Biochar Activated Carbon Materials and their Applications in Solid Supercapacitors

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Biochar activated carbon (AC), produced from the pyrolysis of inexpensive biomass feedstock (wood, agricultural residues, etc.) has been studied extensively as low cost EDLC electrode materials. Their parent biomass materials also impart biochar ACs with a different natural porous templates which can be further tuned or modified via chemical activation techniques. This approach enables the design and engineering of ultra-high surface area biochar AC materials with pore structures and surface chemistries that can be tailored for different energy storage applications. We have investigated several inexpensive waste biomass ACs ranging from corn-cobs, pine cones, to chitosan and found that, while all inherited porous structures from nature, their displayed quite different surface chemical compositions and pore structures.

Solid-state supercapacitors, enabled by polymer electrolytes, are ideal solutions for future energy storage applications that require high performance, safe operation, light-weight, thin and flexible form factors. Ideal polymer electrolytes should be highly conductive, have wide operating voltage window and possess good chemical and environmental stability in ambient conditions to facilitate high throughput and low cost processes. We have developed a series of aqueous-based polymer electrolytes that are proton-conducting, hydroxide ion-conducting or neutral salt ion-conducting to match various cell chemistries. Many of these electrolytes exhibited ionic conductivities $>10^{-2}$mS/cm and maintained stable performance under ambient conditions (room temperature and 45% relative humidity).

In this talk, we will present the development of solid EDLC devices leveraging biomass ACs and aqueous based polymer electrolytes. Starting with the electrochemical behavior of several biomass AC electrodes, we will first demonstrate their performance in both liquid and solid-polymer proton-conducting electrolytes and compare with commercial baselines. We will also illustrate and compare these AC electrodes in hydroxide ion-conducting or neutral salt ion-conducting polymer electrolytes and provide an overview of the strengths and issues of each device chemistry and their viability as solid supercapacitor devices.

Microfluidic Electrochemical Nitric Oxide Sensors for Sepsis Risk Assessment

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Nitric oxide has been implicated in a number of physiological processes, including vasodilation, neurotransmission, immune response, and wound healing. Despite several hurdles related to measuring nitric oxide in physiological fluids, the quantification of nitric oxide and its analogs may lead to improved diagnosis and treatment for a number of disease states. This talk will introduce the development of a microfluidic nitric oxide sensor platform capable of nitric oxide detection in blood as a function of sepsis progression. Several device requirements that impact clinical utility will be addressed including sample volume, sensitivity and selectivity, response time, and concentration range. Data collected in pre-clinical models of sepsis infection (rodent and swine) suggest that the use of this platform may be suitable for point-of-care risk assessment.

Electro- Chemi- Luminescence of Au NanoClusters: EDTA Enhancement, Metal Ions Modulation and Mechanistic Improvements

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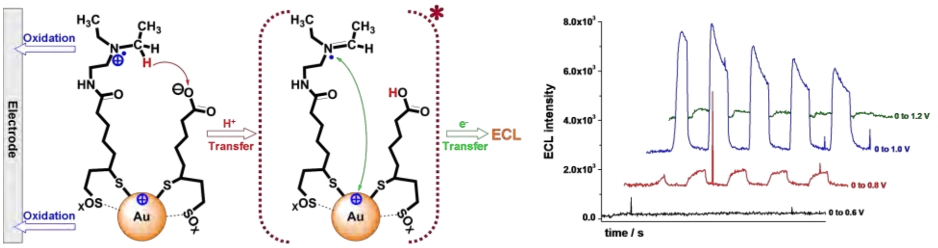
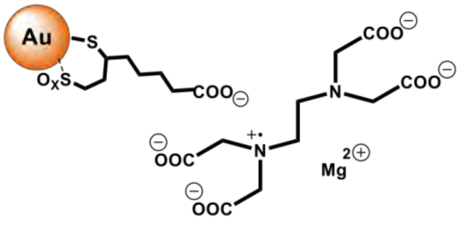
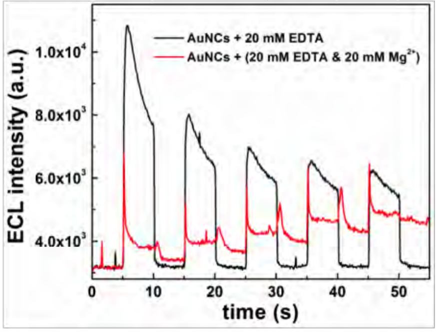
Electrochemiluminescence (ECL) refers to the photoemission activated by electrode driven electron transfer (ET) reactions. Chemiluminescence is not limited by the heterogeneous ET but also results from homogenous ET processes. Redox activity of reagents is essential in the generation of ECL or CL that finds wide applications in sensing, assay among many other applications. Gold nanoclusters stabilized by a monolayer of ligands are well-known to exhibit rich electrochemical and optical properties. This talk will discuss the basics and exciting potentials of Au nanocluster ECL/CL/PL in representative bioimaging and metal ion sensing applications. ECL in the near infrared spectrum window, highly advantageous in bioimaging and sensing with reduced interferences, is generated under ambient atmosphere conditions and physiological pH ranges. Favorable factors in electronic structures will be discussed in relevance to the widely-studied near infrared photoluminescence. Two routes will be introduced to drastically enhance the ECL through the interplay between the electronic structures of Au nanoclusters and the employed molecules/orbitals. The first is adopting common chelators such as EDTA in a conventional free diffusion enhancement pathway for generalizable and broader applications. The second is to covalently attached molecules with accessible and matching redox properties as part of ligand monolayers. The corresponding ECL generation pathway is greatly simplified by such intra-nanocluster charge transfer mechanism. Impacts of metal ions and pH reveal interesting charge and/or energy transfer associated with the highly reactive intermediate species that is under further investigation.

The diagram below shows the simplified ECL generation pathway via covalent assembly of Au nanoclusters and tertiary amines (Ref.: J. Am. Chem. Soc., 2016, 138 (20), 6380–6383).



The next diagram illustrates EDTA as free diffusing coreactant that greatly enhances the near IR ECL from Au nanoclusters. Presence of Magnesium ions has profound effects: the ECL decreases at oxidative potentials but accumulates and sustains over time when the electrode potential is cyclically stepped to zero or non-oxidative (Ref.: ChemElectroChem, DOI: 10.1002/celc.201700125).





Microstructure Evolution during and after Dealloying – Highlighting the Link to Materials Behavior

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Size- and interface effects on the behavior of nanoscale objects are of interest both from a fundamental science point of view and with an eye on exploiting new handles for materials design towards functionality or mechanical behavior for possible technological application. While isolated nanoscale objects are readily synthesized, it remains challenging to assemble them into nano *materials*, that is, aggregates of nano objects that can be upscaled to macroscopic dimensions and that support shaping into engineering parts. 3D lithographic techniques are under consideration, yet the number of microstructural elements that can be assembled (in the order of 1000) fall well short of the 10^{15} objects per mm^3 that are required for a nanomaterial with 10 nm structure size. This emphasizes the power of dealloying, which provides uniform network of struts or "ligaments" with a well-defined size in the low nanoscale regime in the form of monolithic, mm- or cm sized bodies. Making nanomaterials by dealloying thus underlines once more the versatility of a key strategy of materials science, namely exploiting the thermodynamics and kinetics of metallurgical microstructure evolution for shaping materials properties in essentially scalable processes. It is believed that the elementary processes of dealloying are identified – dissolution of the less noble element, vacancy island nucleation, and curvature-driven growth by surface diffusion. Yet, even with this simple set of processes, highly complex microstructures are found to evolve in a way that remains to be explored in full detail. The content in and distribution of residual less noble element are among these issues, as are the various stages in which the corrosion proceeds either in isolation or along with a coarsening of the network structure. Not all microstructural characteristics of the network have been explored in depth, as is exemplified by the ongoing search for suitable measures of the connectivity – and for the way in which the affect the material's behavior – in the context of the strength and stiffness of nanoporous gold. The talk will address selected aspects of the state-of-the-art in microstructure evolution during dealloying and during ageing of dealloying-derived microstructures, with an eye on their impact for the effective materials properties.

Related publications by the author

T. Krekeler, A.V. Straßer, M. Graf, K. Wang, C. Hartig, M. Ritter, J. Weissmüller, *Silver-Rich Clusters in Nanoporous Gold*, Mater. Res. Lett. (2017), DOI 10.1080/21663831.2016.1276485

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The Analysis of Single and Bimetallic Nanoparticle Electrode Assemblies by Stripping Voltammetry

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In this presentation, I will describe recent experiments involving the use of linear sweep stripping voltammetry (LSSV) for the analysis of the size, aggregation state, composition, and atomic arrangement of single metal and bimetallic alloy citrate-stabilized nanoparticles (NPs) deposited by electrostatic attraction to chemically-modified electrodes or by electrophoretic deposition (EPD) onto unmodified electrodes. The peak potential in the LSSV decreases by about 200 mV as the NP size decreases from bulk values (~50 nm or larger) down to 4 nm in diameter. The decrease is 800 mV to 1.0 V for NPs with diameters of 1-2 nm. This acts as a method to analyze the size of the NPs and fundamentally understand their size-dependent electrochemical reactivity. The peak potential in the LSSV shifts positive by about 200 mV and 300 mV upon aggregation of 15 nm and 4 nm diameter citrate-coated Au NPs, respectively, which is caused by decreasing the solution pH. 50 nm diameter bulk Au NPs show no change in the LSSV peak potential upon aggregation because it already oxidizes at the highest potential observed for the bulk metal. Large changes in the LSSV peak potential upon aggregation of small metal NPs could replace optical aggregation-based detection assays, especially for small NPs that do not exhibit a localized surface plasmon resonance (LSPR) band. The LSSV of Cu/Au core/shell NPs depends dramatically on the thickness of the Au shell and the presence of halide ions during stripping. In the presence of chloride, distinct peaks appear for Cu and Au stripping that correspond well to the metal composition, while in the presence of bromide, a significant amount of Cu oxidizes at the same potential as the Au. This reveals interesting details about the atomic arrangement of the Cu and Au atoms in the core/shell structure, which the LSSV is sensitive to. LSSV is very useful for monitoring citrate-coated metal NPs deposited onto electrodes by EPD because it provides the total coverage as well as the size of the deposited NPs. Our EPD deposition strategy involves the addition of molecules in the deposition solution that release protons upon oxidation (H_2O_2, hydroquinone, catechol). The release of protons at the appropriate potential at the electrode surface leads to local reduction of pH and neutralization of the citrate stabilizer around the NPs, causing them to deposit onto the electrode surface. The size of the deposited NPs depends on the potential since different size particles catalyze the oxidation of the proton releasing molecules to different extents. Those that reduce the overpotential the most deposit onto the electrode surface at the lowest potential. This makes it possible to fish out smaller, more catalytic NPs from a solution containing many different-sized NPs by using EPD. I will describe the details of the deposition mechanism, the LSSV analysis of the deposited NPs, and the use of EPD for capturing highly electrocatalytic NPs onto porous, high surface area electrode supports. In summary, LSSV is a simple, but highly useful analytical tool for studying metal and alloy NP assembly on electrode surfaces, providing important information on their size, composition, atomic arrangement, and assembly structure (individual NPs or aggregates).

Probing Concepts in Single-Molecule Wires: Diodes, Electromechanics, FETs, Spinterface, Photo-switches and… Single-molecule Chemistry?

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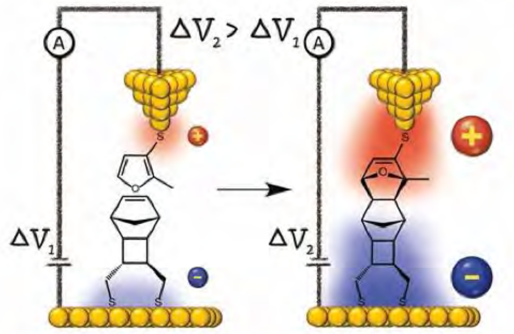
Inspired by the vision that single molecules could ever be functional elements in future nano-optoelectronic devices, there has been considerable interest in understanding charge transport in individual molecular backbones [1]. The birth of the Single-molecule Electronics field occurred with the first experimental realization of single-molecule wires [2]. Today, this field is powered by the combined efforts from very different disciplines; engineering, physics, chemistry and, lately, molecular biology. Our contributions to this field come from the Chemistry branch, with a vision based on developing new molecular moieties to provide new electrical capabilities into the single-molecule device. Along this adventure, it is also our goal to deepen into the understanding of chemistry-related charge transport in order to ultimately transfer all this knowledge into the biological electron transport, undoubtedly one of the key fundamental processes in life. As the title suggests, this seminar will show you a list of recent examples reporting newly designed molecules with very specific electronic targets when they are placed in a single-molecule wire [3-7]. We hope to convince you of the pivotal paper of molecular design in this field and of the vision that the Single-molecule Electronics field can directly profit from well-described chemistry supra-molecular chemistry processes. In this vein, the last example will show you our first attempt of using Single-molecule Electronics tools to analyze new catalytic aspects of a textbook chemical reaction employing external oriented electrical fields [8].



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Electrode/electrolyte interfaces in lithium and sodium batteries

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Lithium-ion batteries (LIB) and sodium-ion batteries (SIB) and their materials is today a large research area due to the practical need for efficient energy storage. SIBs show, compared to LIBs, unique electrochemical reactions that mechanistically need to be understood. The kind of materials that can host sodium ions are, for instance, structurally different from the negative and positive electrode materials for LIBs. Also interfacial reactions occurring between the electrode and the electrolyte are different from LIBs.

To understand the chemical properties of electrolyte/electrode interfaces in LIBs and SIBs is one of the core research activities at the Ångström Advanced Battery Centre (ÅABC), Uppsala University. It is at these interfaces, the solid-electrolyte interphase (SEI) on the anode and the cathode electrolyte interface (CEI) on the cathode, charge transfer reactions take place, unwanted side reactions might start and the stability of the interface also influence the thermal stability of the battery. Careful characterization is therefore needed as a base for creating new and more stable interfaces for prolonged battery life. In this presentation we will make a review of several studies we have performed combining electrochemical characterization with in-house and synchrotron-based photoelectron spectroscopy (such as hard X-ray Photoelectron Spectroscopy, HAXPES). We will primarily dwell on the difference in chemical composition of the SEI of anodes used in LIBs and SIBs, respectively. We will also give some examples of ways to improve cycle life: the role of the electrolyte salt, electrolyte additives, but also of ways to protect electrode particle surfaces.

We have investigated materials from three different categories of anodes: *i.e.* conversion, alloying, and insertion anodes. Our HAXPES results on Fe_2O_3 as a conversion anode material indicated that the SEI on Fe_2O_3 anode is thicker and more homogeneous in a SIB compared to that in an analogue Li-ion battery.[1] We will discuss our work of silicon anodes for LIBs and we will discuss the dissolution of the SEI components in a SIB which is larger than for a LIB[2]. We will discuss the results which show that the SEI on a carbonacous anode in a SIB is inferior to that of the LIB counterpart.

The interfaces of positive electrodes are also important. Often corrosion products will form during battery cycling leading to metal dissolution and poisoning of the negative electrode. We will also here compare the interfaces of Ni- and Mn-based oxide cathodes for LIBs and SIBs[3].

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The Electrochemistry & Corrosion of Zn-Al-Mg alloys: Quantifying the contribution of elemental components and individual phases

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In this work, we address the question of how various elements and various phases interact with each other during short term corrosion of complex alloys? For multi-phase alloys such as Zn-Al-Mg used here, predicting the corrosion behavior over a range of conditions is difficult because the solubility and of the corrosion products of each element and the electrochemical activity of the alloy components differ markedly with one another as a function of pH. The electrochemistry of the Zn-Al-Mg system is further complicated by the distribution of the elements into a complex multiphase structure[1].

To answer this question, we have applied the *atomic emission spectroelectrochemistry* (AESEC) which allows us to measure directly the dissolution rate of each element during either a spontaneous, open circuit corrosion experiment (*dissolution-corrosion profile*), or to decompose the polarization curve into elemental currents (*elemental polarization curve*). Examples of the later are shown in the Figure below. We also use AC polarization so as to measure charge transfer resistance for each element around the open circuit potential.

The approach is to compare the dissolution-corrosion profile with the elemental polarization curve and the AC elemental polarization to see to what extent the corrosion rate of each element may be predicted from the polarization techniques. The question of microstructure is addressed directly by analyzing the role of phase structure on the dissolution of the coating. This is done by performing experiments on pure phases, intermetallic compounds, and a multiphase Zn-Al-Mg alloy galvanized steel coating (nominally pure materials include: Zn, Al, and Mg; synthetic η-phase (Zn 0.7-Al), β–phase Al (Zn-22Al), and α-Al phase (Zn-68Al); and synthetic Zn_2Mg intermetallic compound). The results are interpreted in terms of the mixed potential theory which allows prediction of the corrosion behavior of a system a system over a wide range of experimental conditions. The necessity of applying the theory to the individual elements will be clearly demonstrated.

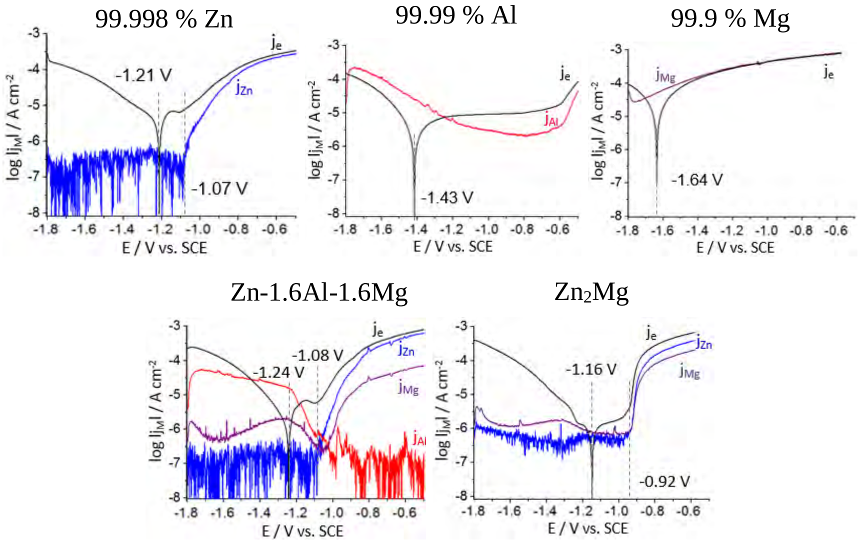

Fig.1. Elemental AESEC polarization curves of pure metals, Zn_2Mg, and alloy coating in deaerated 10 mM NaCl solution at pH=10.1 at 25 °C.

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Electrochemical Detection Strategies for Microchip Electrophoresis

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Separation and detection of biologically important molecules, such as reactive nitrogen species, antioxidants and catecholamine neurotransmitters, using microchip electrophoresis coupled with amperometric detection (ME-EC) is becoming increasingly popular. ME-EC is compatible with small sample volumes, offers fast analysis times, generates high separation efficiencies, and can easily be miniaturized. The coupling of microdialysis to ME-EC yields a separation-based sensor that can be used to continuously monitor the concentration of electroactive biomolecules in the extracellular space of the brain and other tissues in awake freely moving animals. A current drawback of the use of ME-EC is that the limits of detection (LODs) for most analytes are in the low micromolar range. This makes it difficult to monitor analytes that are present at submicromolar concentrations in biological samples. In this presentation, strategies to improve the LODs of ME-EC will be presented along with applications to *in vivo* monitoring and cellular analysis.

The first approach to improve the LOD for ME-EC involves the use of bipolar electrochemistry to generate a fluorescence signal from an electrochemical response. Using fluorescence detection in conjunction with microchip electrophoresis, picomolar LODs can be achieved. However, fluorescence detection usually normally requires the derivatization of the compound prior to analysis. This can diminish selectivity and sensitivity of the method, as well as introduce interferants. An alternative approach to chemical derivatization is to use a bipolar electrode, where two redox reactions coupled at two opposite poles can be used to convert amperometric current to an optical measurement, such as fluorescence. In these studies, a PDMS channel was used for the separation and detection of analytes at the sensor end (ME-EC), while a second flow channel was used for fluorescence reporting. Dichlorodihydrofluorescein was used as the fluorescence reporter in these studies. The system was successfully demonstrated with benzoquinone and resazurin as model analytes in the reductive mode.

A second approach for improving LODs involves the use of a decoupler. For normal polarity separations, a palladium decoupler can be used since it will adsorb the hydrogen gas that is produced at the separation cathode. However, in the case of reverse polarity separations, oxygen is generated instead of hydrogen. This makes it necessary to develop an alternative decoupler design. A decoupler for reverse polarity separations was developed by producing a micrometer dimension hole in the glass substrate that covers the separation channel. The hole is filled with a conductive polymer that is connected externally via a platinum electrode to the separation ground immersed in the background electrolyte. This design has been shown to significantly reduce the effect of the separation voltage on the noise and background at the working electrode used for amperometric detection.

The application of these two approaches to the analysis of biological samples will be described. Specifically, the application of ME-EC for the determination of nitric oxide and related substances in macrophage cell lysates will be discussed. The on-line monitoring of catecholamines and adenosine using microdialysis sampling coupled to ME-EV will also be presented.

The support of NSF and NIH is gratefully acknowledged.

Mass Transport in Electrochemical Nanofluidic Devices

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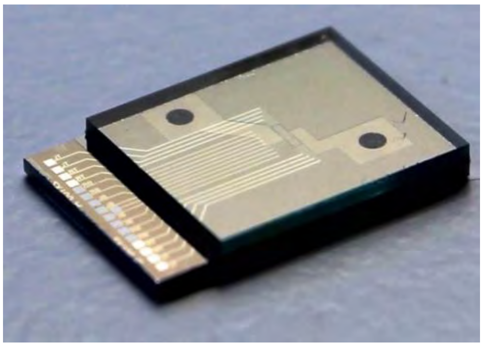
We have implemented methods for interfacing nanogap fluidic devices with microfluidics based on polydimethylsiloxane (PDMS) as well as wafer-scale glass wafer binding (illustrated in the image below). Nanogaps consist of a pair of separately addressable electrodes defining the floor and the roof of a <100 nm high channel and provide amplification of faradaic signals via efficient redox cycling. Mass transport in these devices exhibits several properties which are not encountered in conventional configurations. First, even weak molecule-surface interactions can have significant impact due to the high surface-to-volume ratio inherent to the nanochannel geometry. This leads to hindered diffusion and can adversely affect the response time for detection at low flow rates, but can also in principle be exploited for separating species advected along the channel. Second, the ability to locally control the ratio of reduced-to-oxidized species via electrode potentials, coupled with the differences in diffusion coefficients exhibited by the majority of redox couples, can cause spatially varying analyte concentrations along a channel. This in turn leads to counter-intuitive behavior such as the potential at a downstream electrode influencing the response of an upstream detector. While nanogaps provide an ideal tool for studying these effects which are otherwise difficult to observe directly, we expect that the behavior is general and also occurs in other systems where electrochemical conversion takes place in confined fluidic geometries.



Modeling of Localized Corrosion under Atmospheric Conditions: Cathodic Limitations

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The vast majority of electrochemical studies of pitting corrosion have focused on processes related to the anodic reaction as it is the dissolution reaction at the heart of localized corrosion. Under atmospheric exposure conditions, the thin film of electrolyte that forms can lead to limitations on the ability of the surface surrounding the pit to provide the required cathodic current to allow the pit to grow. This cathodic limitation is the basis for a model that predicts the maximum pit size that can occur under thin film conditions. [1] The cathodic kinetics used in the model are critical to the prediction of the maximum pit size. Cathodic kinetics under thin film conditions have typically been assessed using forced convection methods (e.g., rotating disk electrodes) to impose a hydrodynamic boundary layer that is then equated to the thin electrolyte layer on the surface and is used in a Fick's First Law relation for the diffusion limited current density for the oxygen reduction reaction. In this work, we assess the utility and limitations of that approach with particular emphasis on the means to determine the conditions under which either passive oxide films on the surface or natural convection in the electrolyte become important. The presence of an oxide can impose substantial limitations on the cathodic kinetics, with aluminum alloys serving as an example for which the apparent diffusion limited current density is almost independent of the hydrodynamic boundary layer thickness. Even stainless steels have oxides that form and grow under open circuit conditions that restrict the maximum cathodic current density available at low water layer thickness. At large water layers, there is a thickness at which the current density no longer continues to fall with increasing water layer thickness due to the existence of natural convection. This water layer thickness essentially defines a transition from "thin film" conditions to "full immersion". The other transition from thin film to full immersion is connected to the ohmic drop between anode and cathode. Several systems are used to illustrate these limitations: aluminum alloys with different oxidants and oxide film thicknesses as well as stainless steel surfaces with very thin oxides.

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Conversion-Type Cathodes for Rechargeable Lithium and Lithium-Ion Batteries

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Commercial lithium-ion (Li-ion) batteries using the Ni- and Co-based intercalation-type cathodes suffer from low specific energy, high toxicity and high cost. Further increase in the energy storage characteristics of such cells is challenging because capacities of such intercalation compounds approach their theoretical values and further increase in their maximum voltage induces serious safety concerns.[1] Conversion-type cathode materials are some of the key candidates for the next-generation of Li-ion batteries.[2, 3] However, conversion-type cathode materials typically suffer from high resistance, small capacity utilization at room temperature, dissolution of active material (or active material components) during cycling, irreversible structural changes and overall relatively fast capacity fading with cycling. Here I will report on the successful application of multiple complimentary approaches by our laboratory and our collaborators to engineer nanocomposite materials to overcome such limitations and dramatically enhance electrochemical performance of sulfur/lithium sulfide (S/Li_2S)-Li, selenium (Se)-Li and metal fluoride (MF)-Li cells.[4-15] We demonstrated S-Li and MF-Li cells capable of achieving near-theoretical capacity utilization, remarkable stability and excellent rate performance exceeding state-of-the art. In addition, we demonstrated the ability of certain electrolytes to successfully prevent the cathode dissolution and leaching via in-situ formation of a Li ion permeable protective surface layer.[16, 17] This layer forms during electrolyte reduction/oxidation reactions during the first cycle of the conversion reaction, thus minimizing the capacity losses during cycling. Published, recently accepted and latest unpublished studies will be presented.

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Sodium-Ion Batteries Using FSA-Based Ionic Liquids

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Recent years, we have been conducting R&D of sodium-ion batteries using amide ionic liquids as electrolytes. The new batteries intrinsically have high safety due to the nonflammability and nonvolatility of ionic liquids. Moreover, they can be operated in a wide temperature range of 273-363 K. We found that several types of FSA-based (FSA: bis(fluorosulfonyl)amide) ionic liquids exhibit superior properties for the application to sodium secondary batteries.

In the present paper, we first investigated the fundamental electrolyte properties for the binary Na[FSA]-[C_3C_1pyrr][FSA] (C_3C_1pyrr: *N*-methyl-*N*-propylpyrrolidinium) ionic liquid system [1,2]. We found that $Na_{0.2}[C_3C_1pyrr]_{0.8}[FSA]$ has a wide operable temperature range of 253-393 K and a high ionic conductivity of 19.8 mS cm^{-1} at 363 K.

Then, $NaCrO_2$ [1,3] and hard carbon (HC) [4] were selected as positive electrode and negative electrode active materials, respectively, and their fundamental charge–discharge characteristics were examined with coin-type half-cells. On the basis of these results, a 1.5 mAh coin-type full cell composed of HC/$NaCrO_2$ was fabricated and its performance was examined [5]. It exhibited excellent cycle properties, maintaining 90% of its initial capacity after 1000 cycles at 333 and 363 K. It also showed a high charge–discharge energy efficiency of 97.5% at C/5 rate at 363 K. Finally, we constructed a large-sized prismatic HC/$NaCrO_2$ full cell with a capacity of 27 Ah by a mass production process [5]. We confirmed that its performance is comparable with that of the 1.5 mAh coin-type cell.

Acknowledgements
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New Strategies for the Development of Aqueous Electrochemical Capacitors

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Electrochemical capacitor is an attractive energy storage system with a high power and long-term cyclability. However, still a lot of studies are devoted to increase its moderate specific energy.

Assessment of new approaches to enhance capacitance values and to extend capacitor voltage will be shown. Redox active species present in electrolyte and/or incorporated at electrode/electrolyte interface is a good strategy to involve faradaic reactions as additional source of pseudocapacitance. Electrosorption of hydrogen into microporous carbon plays a dual role: an increase of capacitance values and a shift of operating potential to more negative values. Such redox species as halides (iodides I^{-1}/I_2, bromides Br^{-1}/Br_2), pseudohalides (thiocyanates SCN^{-1}) will be considered and they are extremely beneficial for the positive electrode. Combination of various redox couples on both electrodes is another strategy. Additional modification can be realized by selection of different pH of anolyte and catholyte solution. In this case a separation of both electrolytes is indispensable.

The influence of salt concentration and current collectors on the capacitance value and carbon electrode stability will be discussed. The effect of carbon porosity on charge accumulation, reversible energy storage and power delivery is crucial; pore size should match with the ion dimensions especially if they are bulky. Carbons with a suitable micro/meso ratio allow the redox active species to be transported to the interface and efficiently used preserving a high energy and short response time of device.

The stability of the carbon electrode against oxidation in the presence of redox species has been confirmed by Raman in-situ technique. Interestingly the limit of optimal potential and reversibility of redox reactions were precisely evaluated. An example of operando Raman study under polarization in 1M iodide solution is shown in Fig. 1.

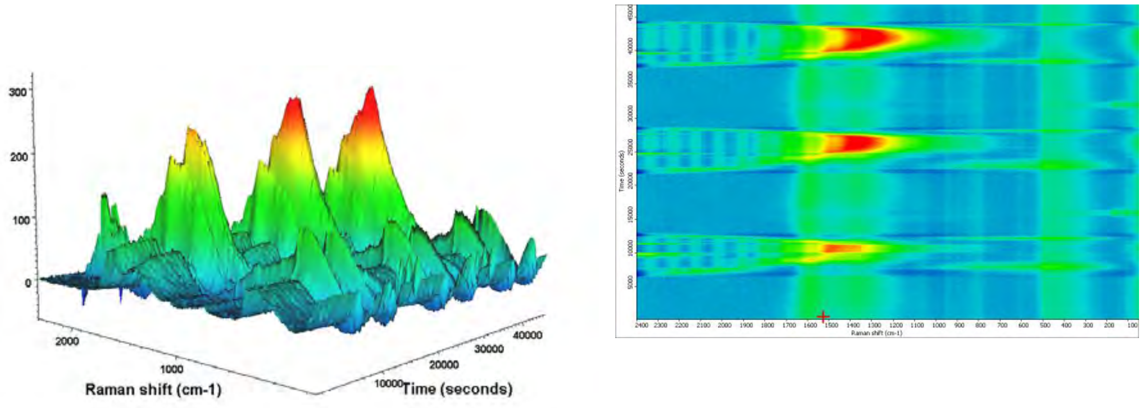

Fig. 1 Raman spectra of carbon electrode in 1M KI during voltammetry cycling

The detailed electrical examination of such capacitors (by galvanostatic charge/discharge, cyclic voltammetry, electrochemical impedance spectroscopy, floating etc.) confirmed a good cycling, perfect charge dynamics as well as beneficial energy and power values. Long-term stability of capacitor system operating in various redox active electrolytes was proved.

Energy values of aqueous ecofriendly capacitors with a high capacitance exceeding 200 F/g and voltage > 1.6 V were comparable to electrochemical capacitors operating in organic medium.

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3D Electrodes for Wireless, Multiplexed Detection in ECL

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Porous electrodes can significantly enhance the performance of a wide range of electrochemical processes from highly sensitive electrochemical and electrochemiluminescent detection to redox flow batteries for energy storage. Their advantages over planar electrodes include enhanced mass transport and high surface areas within a small volume. Moreover, in bipolar electrochemistry they open up the possibility of tuning the local electric field strength so as to control the type and rates of electrochemiluminescent reactions. However, there are relatively few well-defined studies on size effects of the three-dimensional (3D) electrode architecture, due to the lack of suitable material platforms where the critical length scales (such as pore size and thickness of the active material) can be freely and deterministically adjusted over a wide range without affecting the overall 3D morphology of the electrode.

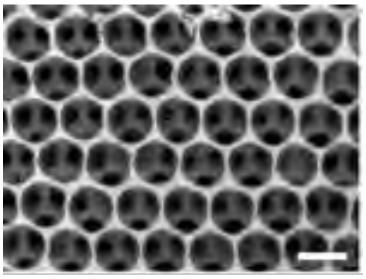

Figure 1. Porous electrode containing interconnected spherical voids with a diameter of 600nm.

In this work, we report on the electrochemiluminescent properties of electrodes with spherical or cubic pores produced using nanosphere lithography or 3D-printing. Using these strategies, robust porous electrodes with tailored surface areas, volumetric porosity and flow properties have been developed. Significantly, enhanced electrochemiluminescence is observed for polymeric, monolayer and solution phase reactants. COMSOL modelling of the electric field, and direct imaging of the ECL intensity within the cavities using confocal and super resolution (STED) microscopy, reveals the distribution of the electric field within the porous electrode. Moreover, we show that in bipolar or "wireless" electrochemiluminescence, the electric field distribution can be influenced by tailoring the geometry of the porous electrodes. By decorating the porous electrodes with metal nanoparticles, plasmonic enhancement of both the ECL and Raman responses can be achieved. Finally, the application of these novel structures for the electrochemical incineration of water pollutants and the detection of disease biomarkers is discussed.

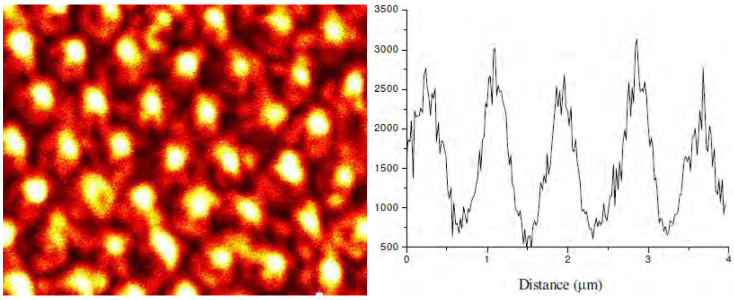

Figure 2. Electrochemiluminescence from a 1 mM solution of Ru(2,2'-bipyridyl)2(2,2':4,4'':4'4''-quarterpyridyl)]2+ dye within a porous electrode containing interconnected spherical voids with a diameter of 1 μm.

From Complex Molecules to Controlling Molecular Surfaces: Electrochemistry as a Tool for Synthesis

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Electrochemistry has long held potential as a tool for constructing a wide variety of organic molecules. For many years, this idea was kept alive by a dedicated cadre' of scientists around the world who probed the scope of electrochemical reactions and illustrated their utility. Now, with a growing need for sustainable methods, the larger synthetic community is rediscovering electrochemistry and in so doing are both adopting existing electrochemical methods and inventing new ones. Against this backdrop, it is imperative for those with experience to help new colleagues think about electrochemical reactions in a manner that best allows them to take full advantage of the methods for their needs. In that light, the talk to be presented will focus on three distinct challenges.

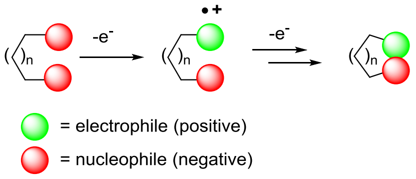

Figure 1: Umpolung chemistry

In the first of these stories, a view of chemistry that is exploring the use of electrochemistry for generating reactive intermediates and triggering new “umpolung” reactions (Figure 1) will be discussed. The goal will be to examine the mechanistic considerations necessary to invent new reactions that in turn provide new ways to put together the complex molecules.[1]

In the second, the same principles used to guide the formation of new bonds will be used to guide the construction of complex molecular surfaces on microelectrode arrays. The functionalized arrays are being prepared so that electroanalytical methods can be brought to bear on problems requiring the “real-time” monitoring of interactions between small molecules and biological targets (Figure 2).[2]

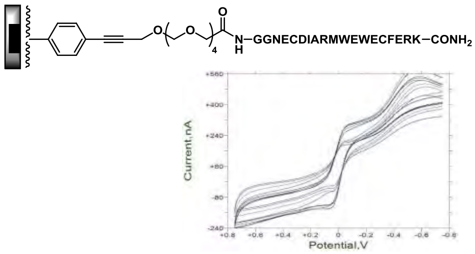

Figure 2: Drop off in the current of ferrocene on a v107 functionalized array when treated with the human VEGF receptor.

Finally, lessons learned on the arrays will be used to develop new methods for the valorization of molecules that are derived from lignin (Figure 3).[3] This portion of the talk will emphasize the key concepts needed for synthetic chemists to capitalize on the full capability that electrochemistry offers for developing more sustainable syntheses.

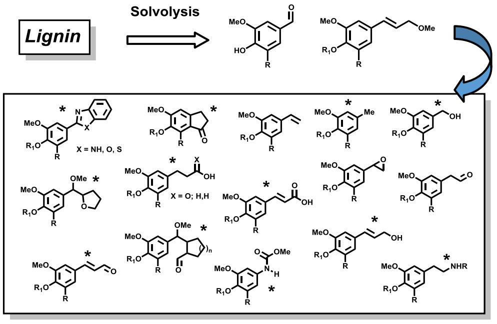

Figure 3. New molecules from sawdust

In combination, the discussion of these three seemingly diverse problems will dramatically highlight the power of electrochemistry as one of the most versatile tools that a chemist can (and should) have in their synthetic aresenal.

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Silver Nanoparticles In Electrochemical Biosensors

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Nanomaterials are widely used in the field of biosensors to develop new platforms with an increased specific surface, enhanced electron transfer or improved sensitivity and/or sensibility [1, 2]. Among them silver nanoparticles, Ag-NPs, are less used than gold nanoparticles, Au-NPs, and carbon nanotubes, CNTs, although they exhibit conductive and electroactive properties that can be advantageously exploited to develop original electrochemical biosensors. Some of these aspects will be presented here based on an overview of our recent works on the use of Ag-NPs in electrochemical biosensors.

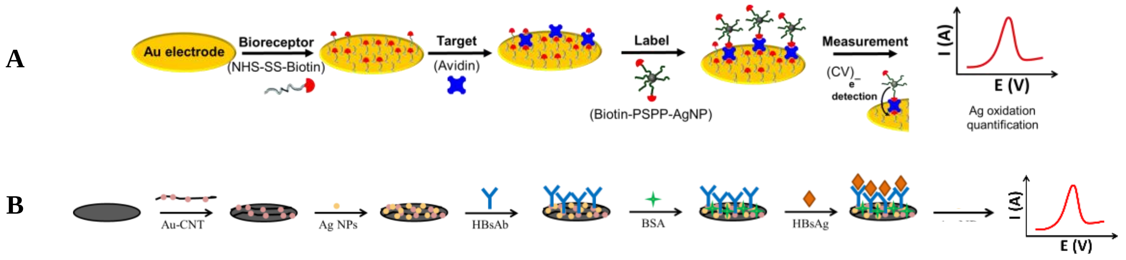
Recently, we used Ag-NPs functionalized with biotin (or avidin) to anchor them on self-assembled monolayer of avidin (or biotin respectively) to enhance electron transfer through the layer constituted by the biotin and the avidin [3]. In such case Ag-NPS act as a relay on electron transfer.

However, we focused more on the ability of Ag-NPs to be electrochemically oxidized [4] and therefore, to be used as electroactive labels to enhance sensitivity of electrochemical biosensors. Indeed, the oxidation of each nanoparticle (each label) will release several ten thousand of electrons.

With this goal, we have synthesized zwitterionic polymer-grafted Ag-NPs that were functionalized with biotin [5]. The addition of poly(N,N'-dimethyl(methacrylamidopropyl)ammonium propanesulfonate), PSSP, as the zwitterionic polymer grafted onto AgNPs surface, induces an excellent colloidal stability in high ionic strength medium like physiological ones and the functionalization with biotin ensures biorecognition. These properties open the way to prepare sandwich type biosensors with Ag-NPs labels in physiological media. We prepared such sensor using avidin as a model target (**Scheme A**). The sensing tests proved the direct electrochemical oxidation of Ag-NPs enhances the detection signal and that the oxidation of Ag-NPs is quantitative and proportional to the concentration of avidin in the medium. A limit detection of 1,5 nM was obtained.

In one of our latest work that deal with an electrochemical immunosensor for hepatithis B surface antigen, HBsAg, Ag-NPs were used as redox probes immobilized on modified screen printed electrode, SPE, before biofunctionnalization to avoid a labelling step after the biorecognition of the target. This configuration allows an easier handling of biosensor by end user (**Scheme B**). We will show the synergetic effect of the combination of Ag-NPs with other nanomaterials on the intensity of the electrochemical oxidation of Ag-NPs. The best results were obtained from SPE modified with CNT/Au-NPs/Ag-NPs. We will present their use for the sensing and quantification of HBsAg at levels down-to 40 ng/mL.

Finally, a last example concerning the addition of Ag-NPs in polymer to promote electron transfer between electrode and enzyme will be given.



Schemes of electrochemical biosensors using Ag-NPs: A) Sandwich type biosensor using zwitterionic grafted Ag-NPs - B) Ag-NPs modified electrode for HBsAg sensing.

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Developing a Sensitive and Fast Method for CO_2 Electroreduction Product Detection

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It is well known that the product distribution of electrochemical reduction of CO_2 depends greatly on the type of metal catalysts. Typically, they can be categorized into four groups. Group one contains Pb, Hg, In, Sn, Cd and Tl and their main reduction product is $HCOO^-$. Group two contains Au, Ag and Zn and they mainly reduce CO_2 to CO. The third group contains Cu and its alloys, and it can give us various reduction products, like methane, ethylene, ethanol, propanol, etc. While group four (Ni, Fe, Pt and Ti) prefers to reduce H_2O to H_2. In order to enhance the catalytic activity, great efforts have been put into designing different new catalysts (e.g., metal alloys, different nanostructures). With lots of catalyst candidates synthesized, a fast and sensitive product detection method is highly needed to do a quick catalyst screening. Normally, the reduction products are detected by GC (takes about 20-30 mins) and NMR (takes about several hours), which is very time consuming for a large amount of catalyst candidates screening.

Thus, here we propose a fast and sensitive detection method based on the Rotating Ring Disk Electrode (RRDE) that can greatly shorten the detection period and enhance the detection sensitivity. The RRDE in this work uses a changeable metal disk electrode with a polycrystalline Pt ring electrode as the two working electrodes, a Pt mesh counter electrode and a reversible hydrogen electrode serves as the reference electrode. Under rotating conditions, the Pt ring electrode can be used to detect the in-situ formation of products during the CO_2 reduction on the disk electrode. Both the peak current and peak potential collected on the Pt ring CV can be used to compare with the calibration curves from different standards and quickly identify and quantify the products. It only takes about 1 minute to finish one Pt ring CV cycle scan, which greatly shortened the product detection time. This feature enables it to do a fast screening on the catalyst candidates and quickly report the product distribution for each candidate. Here we are focusing on applying this detection method to catalyst system with less than two products, like Au (product is mainly CO), Sn (product is mainly $HCOO^-$) and Pt (product is mainly H_2). In the future, we will move on to catalyst system with more complicated product distribution, like Cu (product contains different hydrocarbons).

Diffusion Profiles and Analyte Signal Amplification at Gold Interdigitated Nanowire Electrode Arrays

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Recent advances in micro and nanofabrication techniques [1] have enabled the routine fabrication of electrodes with controllable dimensions on technology relevant substrates, thereby opening the door to novel electrochemical devices used as integrated sensing elements in a wide range of applications, e.g., environmental analysis, healthcare and security applications [2, 3]. For example, gold nanoelectrodes, nanoelectrode arrays and interdigitated nanoelectrode arrays with critical dimensions on the order of 100 nm (or less) have been fabricated on silicon-based substrates. Interdigitated nanoelectrode arrays are particularly interesting as they may be built such that N electrodes (generator, WE1) are surrounded by N+1 electrodes (collector, WE2) with micro to nanoscale inter-electrode distances, thus enabling highly efficient analyte mass transport.

In this work, we report on the fabrication of fully functional gold interdigitated nanowire electrode arrays on Si/SiO$_2$ chip substrates. Electrochemical characterisation was performed in non-Generator-Collector (GC) mode (either WE1 or WE2 connected) and in GC mode (WE1 was swept while WE2 was held at a constant potential). In non-GC mode, arrays behaved as microelectrodes with planar diffusion to the closely spaced electrode array. By contrast, in GC-mode arrays displayed significantly enhanced electrochemical behavior such as fast establishment (within a hundred milliseconds at 5000 mV.s^{-1}) of steady-state conditions arising from redox cycling. Simulations of analyte diffusion were in excellent agreement with experimental results, see Figure 1. Metal ion content in tap water as an application will be discussed.

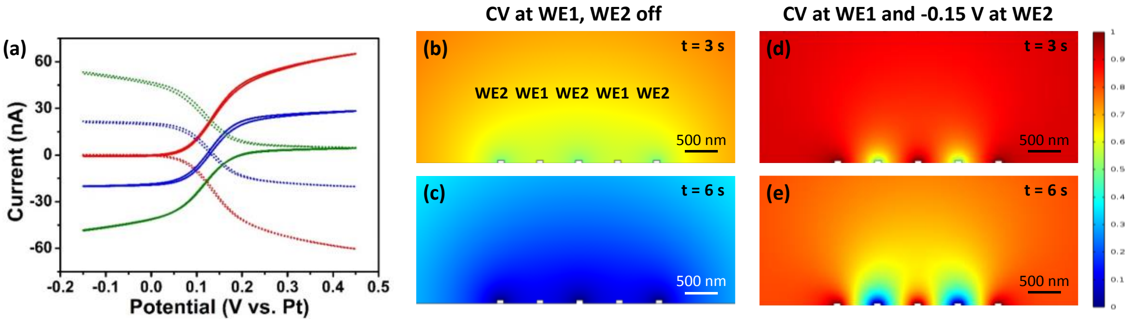

Figure 1. (a) CVs in 1 mM FcCOOH in 10 mM PBS for arrays in GC mode: the potential of WE1 was swept while the potential of WE2 was held at -0.15 V (red lines), 0.15 V (blue lines) or 0.45 V (green lines). The current was measured at both WE1 (solid lines) and WE2 (dashed lines). Cross-sectional view of 2D simulations of FcCOOH concentration profiles at arrays of interdigitated nanowire electrodes separated by 500 nm at 100 mV.s^{-1} at t = 3 s and 6 s in (b)-(c) non-GC and in (d)-(e) GC modes (WE2 was held at -0.15 V).

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Biofouling of Ionophore-Doped Ion-Selective Electrode Membranes Revisited

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The primary focus of this research is the investigation of the mechanism of biofouling in current fluorous phase ion-selective electrode (ISE) systems. With prolonged exposure to biological samples, potentiometric measurements using conventional polymeric-membrane ISEs exhibit a breakdown of selectivity and response. Therefore, extensive washing procedures and frequent recalibrations are needed for many clinical and biological applications. Initial work with fluorous phase ISEs has shown significant improvements in selectivity and limits of detection over conventional polymeric-membrane ISEs.[1] Moreover, experiments with fluorous pH electrodes have shown that long term serum exposure does not affect the electrode selectivity but stirred serum solutions appeared to cause a transient EMF drift. To explore this effect more systematically, a potentiometric stir tests was developed. Both conventional polymeric membrane and fluorous membrane electrodes were exposed to solutions stirred intermittently. Both types of membranes exhibited an EMF response to stirring when exposed to of 10% v/v solutions equine blood serum but not when exposed to simple electrolyte solutions. The transient potentiometric response depends on the hydrophobicity of the ionic sites incorporated into the ISE membranes; specifically, a lower hydrophobicity results in a larger effect of stirring on the EMF. For the fluorous electrodes, synthesis of a more hydrophobic ionic site and its use along with fluorophilic H^+ ionophores successfully mitigated the effect of sample stirring on the emf. The use of a fairly simple phase boundary model confirms that the effect of stirring is caused by loss of ionic sites into the serum containing sample. While it has been known for a long time that the lifetime of ISEs in biological samples depends on the hydrophobicity of the ionophore and ionic sites, this is to the best of our knowledge the first report that shows that the leaching of ionic sites into serum samples can be directly observed by potentiometric monitoring of the effect of sample stirring on the EMF.

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New Electrochemical Sensing Strategies for Bisphenol A

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Bisphenol A (BPA) is an important raw material widely used in the production of epoxy resins and polycarbonate plastics for metal food cans, food and water containers, sports equipment, tableware and microwave ovenware. Thus, it will inevitably migrate into food and drinking water from product packaging, and thence humans may routinely ingest trace amounts of BPA, which is regarded as a health hazard compound. There is currently much interest in developing rapid and accurate methods for the determination of BPA [1], and electrochemical sensing is one of the most promising.

We have examined two strategies for the determination of BPA. The first of these comprises a multiwalled carbon nanotube and gold nanoparticle modified glassy carbon electrode. Voltammetric and electrochemical impedance characterisation of the sensor platform were carried out. Different loadings of these two nanomaterial components have been assessed and other experimental parameters optimized. Under optimized conditions, the sensor exhibited a linear response to BPA from 0.01 μM to 0.7 μM by differential pulse voltammetry, with a limit of detection of 4.3 nM, the lowest achieved until now at similar BPA sensor architectures, the selectivity and stability of the sensor being superior to those reported. The possibility of an impedimetric sensor was also successfully assessed and augurs well for future application.

The second approach is a new enzyme inhibition biosensor based on xanthine oxidase enzymatic inhibition by BPA. The biosensor was prepared from xanthine oxidase immobilised by crosslinking with glutaraldehyde on glassy carbon electrode substrates and was applied to the determination of BPA using fixed potential amperometry. Biosensor performance was optimized with respect to enzyme loading and enzyme substrate concentration as well as applied potential and pH. Xanthine oxidase enzyme inhibition was found to follow a competitive mechanism. The determination of BPA had a linear range between 1.0 and 41 nM with a detection limit of 1.0 nM and with excellent selectivity against interferents.

Both sensors were successfully tested for the determination of trace concentrations of BPA in waters.

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Nanogap Voltammetry of Clean Surface of Electron-Beam-Deposited Carbon

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Clean surfaces of conducting carbon materials are highly demanded for fundamental and applied electrochemistry to mechanistically understand and practically utilize their intrinsic reactivity. In this presentation, we will discuss about the nanoelectrochemical characterization of clean carbon surfaces to gain novel insights into heterogeneous electron-transfer (ET) mechanism with broad implications beyond carbon electrochemistry. Electron-beam deposited carbon (eC) is formed in high vacuum (<6 µtorr) and protected from adventitious contamination by a washable KCl layer deposited without breaking vacuum. Fast ET kinetics of exceedingly flat, clean eC surfaces is reliably measured in ultrapure water using nanogap voltammetry based on scanning electrochemical microscopy and compared quantitatively with Marcus and Frumkin theories. An outer-sphere ET mechanism, which is typically only presumed, is evidenced experimentally for (ferrocenylmethyl)trimethylammonium and tris(1,10-phenanthroline)cobalt(II) ($Co(phen)_3^{2+}$) by excluding an inner-sphere mechanism. Indeed, the oxidation of $Co(phen)_3^{2+}$ agrees unprecedentedly well with Marcus theory of adiabatic outer-sphere kinetics in comparison to any redox couple on carbon or metal electrodes reported previously. The coupled reduction of $Co(phen)_3^{3+}$ deviates from Marcus theory to reveal a unique double-layer effect caused by the adsorption of a redox molecule itself, i.e. $Co(phen)_3^{2+}$, which contrasts to the Frumkin effect based on the adsorption of inert electrolytes. Remarkably, the $Ru(NH_3)_6^{3+/2+}$ couple exceeds adiabatic limits not only at eC, but also at other carbons and metals, which we attribute to faster inner-sphere ET of adsorbed forms of this couple. In contrast, an inner-sphere pathway is not mediated by the adsorbed $Fe(CN)_6^{3-/4-}$ couple, which dramatically self-decelerates the outer-sphere pathway through a double-layer effect.

Miniaturised Solid State Sensors Containing Ionic Liquids for Environmental Analysis

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Diclofenac is a non-steroidal anti-inflammatory drug (NSAID), frequently prescribed globally as an analgesic and antipyretic. Prophylactic use of diclofenac in cattle herds in South Asia has led to the drug's biomagnification in scavenging bird populations across the region, resulting in significant population declines for these animals and other species. Diclofenac features on the EPA's recent lists of Contaminants of Emerging Concern, and has been banned for veterinary use in India, Pakistan and Nepal.

Our group proposes solid state potentiometric sensors for diclofenac quantification in water. These sensors are prepared from screen printed carbon electrodes (SPCEs), which are cost effective and facile to prepare. The sensors feature a dropcasted ion-selective sensing membrane and intermediate transducer layer. An imidazolium based ionic liquid is immobilised within the membrane, inducing a significant degree of selectivity. The sensors exhibit a near Nernstian response to diclofenac, with a high degree of reversibility between analyte activities and minimal response to interferent anions, such as chloride. The solid state, "dry" format negates the requirement for an inner reference solution, yielding a compact and flexible electrode. This, coupled with the passive (potentiometric) mode of measurement, infers electrode suitability for field analysis and continuous monitoring applications.

Electrochemical Pressure Impedance Spectroscopy (EPIS): A Promising Diagnostic Tool for Metal-air Batteries and Fuel Cells

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Electrochemical impedance spectroscopy (EIS) is a widely-used diagnostic technique to characterize electrochemical processes. It is based on the dynamic analysis of two electrical observables, that is, current and voltage. Electrochemical cells with gaseous reactants or products (e.g., fuel cells, metal/air cells, electrolyzers) offer an additional observable, that is, the gas pressure. The dynamic coupling of current and/or voltage with gas pressure gives rise to a number of additional impedance definitions, for which we have introduced the term electrochemical pressure impedance spectroscopy (EPIS) [1,2]. EPIS shows a particular sensitivity towards transport processes of gas-phase or dissolved species, in particular, diffusion coefficients and transport pathway lengths. It is as such complementary to standard EIS, which is mainly sensitive towards electrochemical processes. This sensitivity can be exploited for model parameterization and validation.

A general analysis of EPIS is presented, which shows the necessity of model-based interpretation of the complex EPIS shapes in the Nyquist plot (cf. Figure). We then present EPIS simulations for two different electrochemical cells: (1) a sodium/oxygen battery cell and (2) a hydrogen/air fuel cell. We use 1D or 2D electrochemical and transport models to simulate current excitation/pressure detection or pressure excitation/voltage detection. The results are compared to first EPIS experimental data available in literature [2,3].

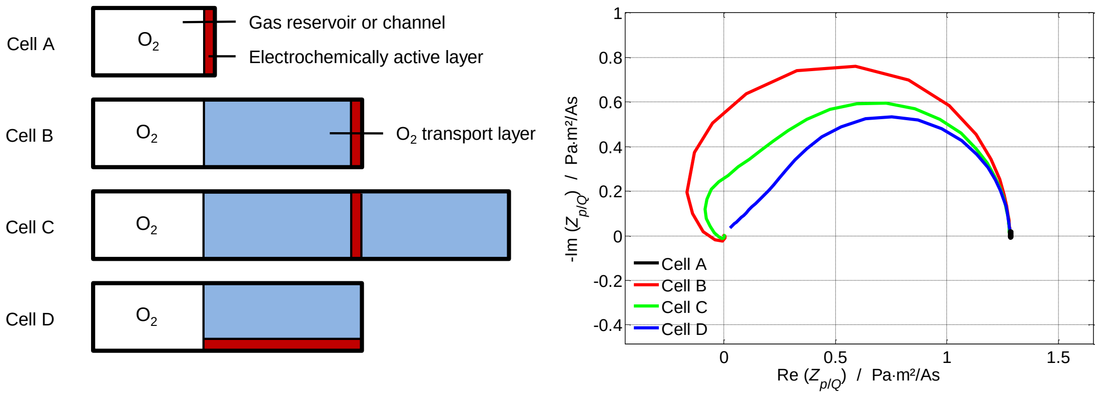

Figure: Typical transport situations in metal/air battery or fuel cell cathodes and their corresponding EPIS response in the Nyquist plot.

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Using Scanning Electrochemical Microscopy and Optical Microscopy to Study Diffusion Layer Chemistry during Metal Electrodeposition

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Our group has been investigating growth of thin metal films through self-terminated deposition reactions, *i.e.*, wet atomic layer deposition, producing films with precise thickness through potential modulation [1]. Self-termination behavior has been recently uncovered for iron-group metals [2] albeit through a different mechanism than that reported for Pt. Ni growth stops upon the onset of H_2O reduction whereas formation of a saturated H_{upd} monolayer is responsible for termination of Pt deposition. Possible explanations for Ni growth termination include formation of a passivating surface-bound OH^- species formed upon H_2O reduction or reactions between the egress of OH^- and the incoming Ni^{2+} species to form $Ni(OH)_2$ and related products. Here, we employed ultramicroelectrodes (UME's) and scanning electrochemical microscopy (SECM) to further probe electrodeposition of thin metal films of Ni on Au [3]. Advantages of UME's include minimized solution resistance and well-controlled mass transport. The dimensions of UME's and their diffusion layers are also amenable to optical microscopy. Thus, we took advantage of the contrast between Ni and Au to image the electrodepositon of Ni as a function of potential. Cyclic voltammetry of Au UME's in 5.0 mmol/L $NiCl_2$-NaCl, pH 3.0, electrolytes showed that at modest potentials between –0.6 V and –1.4 V vs. Ag/AgCl, the current was distributed between steady-state $[Ni(H_2O)_6]^{2+}$ and H_3O^+ reduction. However, an unusual sharp current spike appeared at the onset of H_2O reduction, demonstrating a unique and reproducible electrochemical signal corresponding to a metal self-termination process. The sharpness of this feature is reminiscent of a phase change or the initiation of a catalytic process. The generation/collection mode of SECM, where a second Pt UME was used as the collector electrode, indicated that H_2 is generated during the process giving rise to this cathodic spike. One explanation is that a highly-active species for the hydrogen evolution reation (HER) is generated upon H_2O reduction in the presence of Ni^{2+} [4], such as the heterogeneous nucleation of $Ni(OH)_2$ in the presence of increasing pH in the diffusion layer. Using pH probes in the SECM, we determined that the pH of the diffusion layer increased to least 10, thus exceeding the solubility product constant, K_{sp}, of $Ni(OH)_2$. In a separate phenomenon, as the rate of H_2O reduction was accelerated at potentials below –1.5 V vs. Ag/AgCl, homogeneous precipitation of a $[Ni(OH)_a(Cl)_b]^{2-a-b}\cdot xH_2O$ gel occurred within the nearly hemispherical diffusion layer of the UME. In some cases, hydrogen bubbles formed, destroying the Ni films.

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In Situ Electrochemical Surface-Enhanced Raman Spectroscopy (EC-SERS) at Screen-Printed Electrodes as Sensitive Analytical Platform

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Substrates for surface-enhanced Raman spectroscopy (SERS)[1] are typically fabricated with complex (micro/nano)structures of noble metals to obtain high surface-area plasmonic surfaces, which are capable to enhance this effect and, therefore, the detection of chemical species at very low concentrations. These substrates are frequently high-priced, difficult to reuse and, because their high reactivity, they often have a limited shelf life. Development of new SERS substrates that minimize these issues but preserving a good analytical performance is a constant concern. Screen-printed electrodes can be easily fabricated with different designs and with a myriad of materials turning them in versatile tools for numerous applications. They are fabricated with a well-established method (screen-printing) leading to mass production of low-cost and disposable devices. Therefore, screen-printed electrodes could be a promising platform as SERS substrates.

In this work, the feasibility of using readily available screen-printed electrodes of different materials (especially silver and gold-based) as low-cost and disposable substrates for the detection of different species by *in situ* electrochemical SERS (EC-SERS) is evaluated. Several electrochemical activation methods are considered to enhance the *in situ* Raman signal, allowing the sensitive detection at very low concentrations in comparison to the single electrochemical detection. In addition, a new compact and portable instrument for Raman spectroelectrochemistry, SPELEC-RAMAN, is used. This instrument integrates a laser source, a bipotentiostat/galvanostat and a high-resolution Raman spectrometer in a single box. All the components are controlled simultaneously by the same software. It can be coupled with a reflection Raman probe, which is easily placed on a specific cell for screen-printed electrodes. This system ensures a proper and reproducible position of the probe at the focal distance from the electrode surface, which simplifies the Raman spectroelectrochemical measurements.

Compact SPELEC-RAMAN instrument for Raman spectroelectrochemistry using screen-printed electrodes.

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Carbon-based ion-selective electrodes: microsensors for scanning electrochemical microscopy (SECM)

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Solid state potentiometric sensors have an inherent advantage of miniaturization. We developed a carbon-based solid state μ-Ion Selective Electrode (ISE) sensors. This unique low PVC content sensor is capable of performing amperometric measurements and then could be switched to potentiometric measurements. The 35-40 μm diameter Ca^{2+}-ISE showed fast response time (~1 sec or less), low limit of detection (~1 μM) and broad linear range (5 μM to 200 mM). In addition, the Ca^{2+}-μ-ISE was proven to demonstrate excellent selectivity towards major interfering ions (such as Na^+, K^+, and Mg^{2+}, with $\log K_{Ca^{2+},A} = -5.5$ to -6.0). Similarly, carbon-based μ-pH and μ-NH_4^+ sensors have also been developed which showed near Nernstian slope and been used in the chemical mapping of microbial biofilms (*S. gordonii* and *S. mutans*) using scanning electrochemical microscopy (SECM). New findings of how the bacterial metabolites produced by these biofilms is affecting the immediate microenvironment including the biomaterials and vice versa would be presented at the meeting.

This work was supported by National Institute of Dental and Craniofacial Research (NIDCR), NIH (Grant # R21DE025370).

Electrochemical Behavior of a Diode-Like Material in a Zn-rich Epoxy with Carbon Nanotubes Coating System

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In spite of impressive progresses in a zinc-rich coating system including the control of electrochemical degradation for a metal structure by offering cathodic protection within polymeric matrix, there are physical properties influencing the electrochemical system response that have not yet been explored. The study of anti-corrosion processes of zinc-rich primers (ZRP) has been performed using electrochemistry methods such as linear polarization, cyclic potentiodynamic polarization, open circuit potential (OCP), and electrochemical impedance spectroscopy (EIS) [1]. EIS is widely used to analysis protection mechanisms of ZRPs due to their steady state and non-destructive nature [2, 3]. However, continuous cyclic electrochemical testing was performed to examine the sensitivity response of a zinc-rich coating system from an electroanalytical experiment. The impedance responses from the continuous testing revealed an opposite trend from the classical macroscopic degradation mechanism of the ZRP film (Figs. 1(a) and (b)). The impedance of zinc-rich epoxy behaves like that of a diode-like interface forming on the presence of ZnO layer as a corrosion product, which is susceptible to a bias potential due to the presence of dielectric ZnO material. The electrochemical responses of ZRP coatings in the conditions of dry and immersion are considered when the presence of the semiconductor within the coating produces unexpected trend. In addition, the short-term and long-term effects of the anti-corrosion properties on electrochemical tests are characterized.

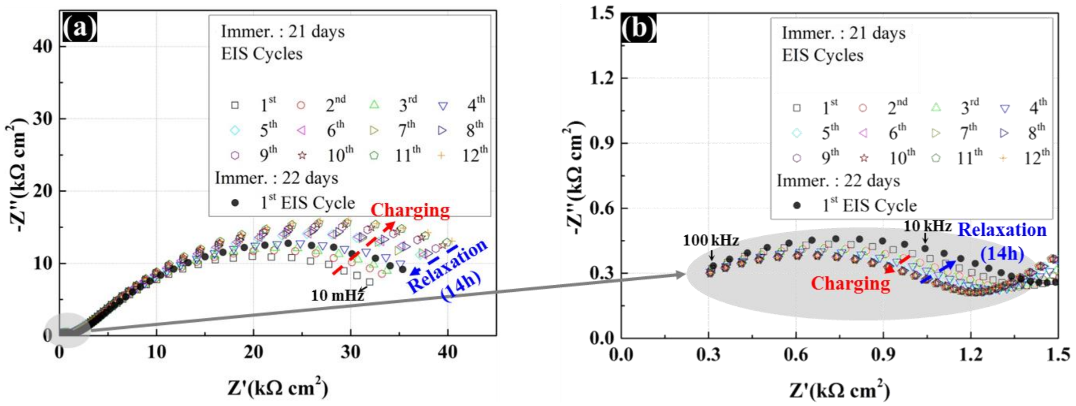

Fig. 1. Degradation process on the impedance response of zinc-rich coating/carbon steel system immersed in 3.5 wt% NaCl solution; b) Magnified view of Nyquist image a) close to high frequency region at 21st and 22nd immersion day in the condition of continuous cyclic tests.

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Electrochemically Silent Films on Electrodes - Means and Methods in Electroanalysis

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Electrochemically inert films on electrodes alter properties of transport, selectivity, and kinetics to enable new devices and measurement methods through enhance sensitivity and controlled transport. A brief survey of unusually engineered, electrochemically silent, polymer films on electrodes that enables analysis is presented. The three systems are developed from fundamental ideas and experimental studies.

- *Density gradient polymers* (e.g., Ficoll®, a sucrose polymer) establish near steady state transport to the electrode surface. Sigmoidal voltammograms of permeant redox probes characterize the gradient film properties. The unusual transport properties can be used for steady state supply of reagents to an interface such as an electrode.

- *Voltammetry of lanthanide species* is enabled at Nafion® (a cation exchange polymer) modified electrodes with triflate ligands in common organic solvents. Commonly, voltammetry of lanthanides is restricted to solvents with wide potential windows such as ionic liquids and molten salts. Novel catalysis of the oxygen reduction reaction (ORR) by lanthanides is noted.

- A *thermodynamic sketch of Nafion* allows design of properties. From numerous studies reported in the literature, Nafion water content dictates properties. The thermodynamic sketch based on electrochemical potentials characterizes diverse properties of Nafion that include conductivity, glass transition temperature, thermal decomposition, Young's modulus, gas solubility, swelling, and selectivity.

Electrochemically silent films may be exploited for novel analytical methods through control and design of transport and selectivity of permeant analytes.

Confocal Raman Microscope Measurements in the Study of Catalytic Membranes and Thin Film Materials

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Confocal Raman microscopy is being adapted for quantitation and structural characterization in the development of membrane and thin film materials for applications in electrochemistry. The presentation will discuss approaches to (i) quantifying component loadings and (ii) probing active site structure within biocatalytic membranes and (iii) spatially profiling within the AEM-CEM (anion exchange membrane - cation exchange membrane) junction region of bipolar membranes.

The aperture of a confocal Raman microscope defines a fixed volume within a sample, usually not more than a few femtoliters (fL), from which the detected Raman scattering originates. Analyte within the well-defined probe volume can be quantified from confocal Raman spectra. Furthermore, scanning capabilities can enable quantitative spatial mapping of materials composition with resolution approaching the diffraction limit.

In the study of catalytic membranes, steps in the processing of laccase air-breathing biocathodes were investigated. Membranes were prepared from dispersions of short side chain fluorinated ionomers (Aquivion). The ionomers were fully exchanged by tetra-*n*-butylammonium ions (TBA^+) to promote enzyme incorporation through enhanced size of the ionic domains and hydrophobic interactions.[1] Confocal Raman microscope measurements confirmed the presence of entrapped laccase within dispersion cast membranes and the ability to quantify TBA^+ ions and protein. Features associated with the catalytically active, enzyme coordinated copper center in laccase were evident between 400 cm^{-1} - 500 cm^{-1} (Figure 1), providing a possible route to interrogate mechanistic chemistry at the enzyme active site of biocathodes under fuel cell reaction conditions.

Using a similar experimental approach, the ability to probe spatially across the AEM-CEM junction of a bipolar membrane was investigated. Strong Raman scattering from perchlorate enabled its use as a probe for mobile anions. In preliminary work, ~5 μm depth resolution was attained in mapping the transition region.

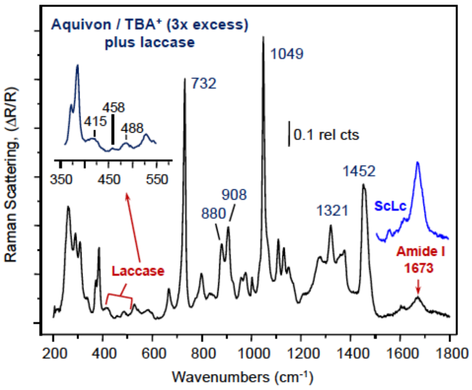

Figure 1. Raman spectrum of Aquivion ionomer membrane exchanged by TBA^+ after casting from aqueous solution in the presence of 1.8 mg/mL laccase. The left inset enlarges the spectral region containing features associated with vibrations of functional groups near the enzyme active site. The right inset (bright blue) labeled "ScLc" shows the amide I region recorded from a membrane prepared as described above except using a highly purified His-tagged laccase (ScLc) sample present at 4 mg/mL in the casting solution.

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In Operando monitoring of unique Cobalt Oxide nanoparticles: Electrodeposition and Electrocatalysis

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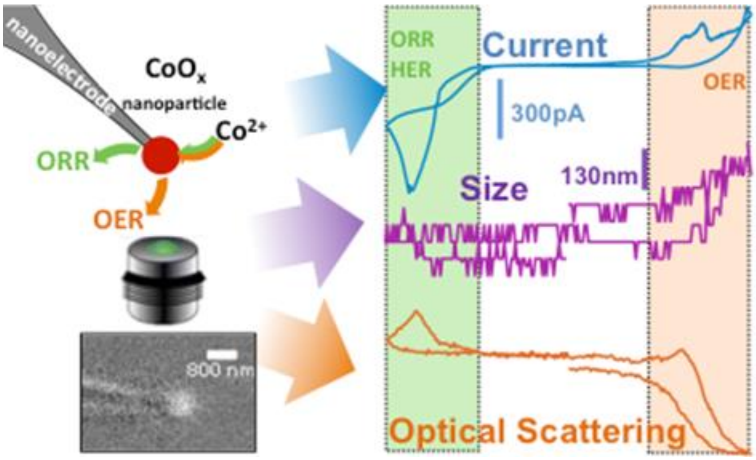
As the world's demands for renewable and sustainable sources of energy continue to increase, it becomes urgent to find clean alternative power sources. Having the photosynthetic process as inspiration, Man has insistently tried to use water splitting to respond to this demand. Man-made catalysts, still however fall short from the efficiency needed to meet mankind's actual demands. It is therefore crucial to develop new strategies to understand the catalytic mechanism in order to improve water splitting catalysts. Among available catalysts, transition metal oxides, and Cobalt Oxides nanoparticles (CoOx NPs) in particular, are extremely attractive candidates, due to their high efficiency, together with abundancy.

Building on previous works in single nanoparticle electrodeposition[1] and optical single particle monitoring of electrochemical reactions[2,3], we now develop a coupled opto-electrochemcial strategy to investigate *in operando* the reactivity of single CoOx NP. While the exchange of electrons can be monitored electrochemically, the optical setup allows quantification of particle size and of changes in chemical properties (electrochromism). Starting by their in situ electrodeposition, we investigate the chemical reactivity of a single particle in a complex chemical situation: electrodeposition, chemical reactivity and catalysis, all taking place simultaneously.



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Fuel cell operando IR/Raman spectroscopy

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A complex-molecule vibrational normal mode comprises small molecule pure modes whose internal coordinates are mechanically coupled. A functional-group pure mode is a descriptor of oscillatory motions (stretching, wagging, etc.). A subset of generalized coordinate eigenvectors, corresponding to selected groups of coupled atoms ("functional groups"), are used to quantify normal mode displacement contributions, of a functional group, to a group mode. Decomposition of group modes into color coded pure modes are exemplified by spectra of Nafion, its side chain fragments, and an exchange site model structure. Three dimensional spectra (i.e., intensity vs. wavenumber vs. pure mode) elucidate, with unprecedented clarity, the make-up of broad IR bands in terms of pure mode contributions. Color coded spectra show how synthetic modifications and/or changes in the environment affect the entire infrared spectrum.

Resonance Enhanced Impedance Spectroscopy for real –time monitoring of nanoparticles in lipid layers

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Resonance Enhanced Surface Impedance Spectroscopy (RESI) measures surface capacitance and resistance changes. RESI is shown as a complementary technique to Electrochemical Impedance spectroscopy for monitoring the interactions of modified gold nanoparticles and solid-lipid nanoparticles with tethered lipid mono and bilayers in real time. Charge, size and modification of nanoparticles have a significant effect on interactions with both lipid mono and bilayers. RESI, performed in a flow cell, is shown to be very sensitive to surface capacitance and interfacial resistance changes as shown in Figure 1. A series of modified AuNps was studied. Interactions profiles of cationic, anionic, zwitterionic and non-ionic AuNPs will be compared. Additionally interactions of solid lipid nanoparticles, which are commonly used for drug delivery, are shown to interact with lipidic membranes (Figure 2).[1]

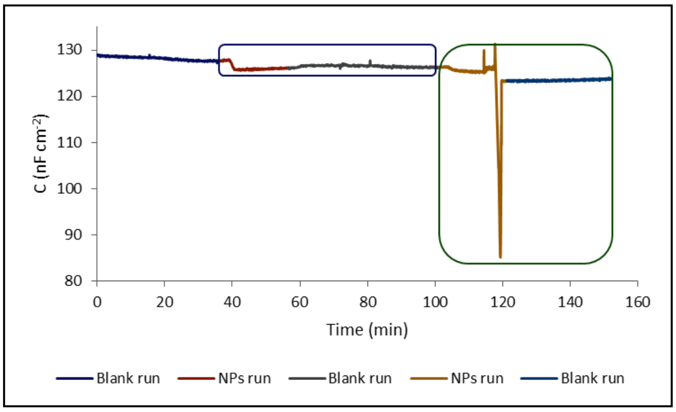
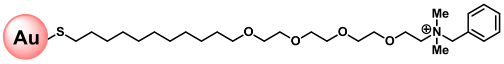


Figure 1



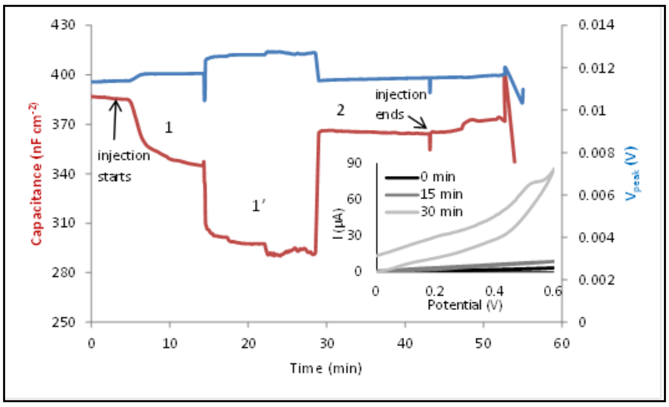


Figure 2

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Correlated Electrochemical and Optical Detection in Zero-Dimensional Nanophotonic Structures

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Arrays of nanoscale-recessed dual ring electrodes fabricated using layer-by-layer deposition coupled with focused ion beam etching can function both as working generator-collector electrode pairs and also as zero-mode waveguide (ZMW) arrays. The dual functionality makes it possible to perform single molecule spectroelectrochemical measurements under redox cycling conditions – both when the upper electrode is potential-controlled and self-induced redox cycling. Flavin mononucleotide, FMN, contains an isoalloxazine chromophore which is fluorescent in the oxidized state, while the reduced state, $FMNH_2$, exhibits a substantially lower quantum efficiency, thus permitting the redox state of single FMN molecules to be followed by observing their fluorescence behavior. Because the ~100 zeptoliter volumes of these nanopores dictate very short residence times, evidence for single molecule redox cycling is obtained from the fluorescence dynamics. Freely diffusing species exhibit characteristic behavior in which the probability of observing single reduced molecules increases as the potential is scanned to more negative values. Conversely, single molecule cycling behavior is evidenced by the distribution of on- and off-times, which are altered relative to freely diffusing $FMN/FMNH_2$. Comparisons are made between capture efficiencies with the upper ring electrode floating *vs.* potential controlled as well as the propensity for the dual ring structure to stabilize the intermediate redox species which are assigned tentatively to semiquinones.

Electrokinetic Manipulation of Ag and Pt Nanoparticles and Their Stochastic Electrochemical Detection

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Application of a high frequency (~100 MHz) ac waveform to a microelectrode leads to the appearance of electrokinetic phenomena such as dielectrophoresis and electrothermal fluid flow.[1,2] Here we are presenting the results of our investigations, in which we employed these phenomena for preconcentration of Ag and Pt nanoparticles (NPs). At the same time, the NPs were detected using the methods of stochastic electrochemistry.[3]

The objective of this research is to demonstrate the feasibility and advantages of ac electrokinetic phenomena compared to other methods of analyte preconcentration. It is expected that the developed technology will be particularly useful for the analysis of ultra-low concentrations of various biological analytes.

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Determination of the Soret Coefficient of a Trace Ion with Impedance Spectroscopy

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The migration of a solute due to a temperature gradient is known as thermodiffusion or the Soret effect [1]. The Soret effect builds up a concentration difference in the system until the resulting concentration gradient cancels out the migration due to thermodiffusion, and a steady-state is reached. The steady-state concentration difference is proportional to the Soret coefficient: a large and positive Soret coefficient relates to a strong tendency for the particle to be transported in the temperature field from hot to cold [1]. The phenomenon has great significance in non-isothermal systems with a plethora of applications, ranging from separation and purification of macromolecules [2] and thermoelectricity [3] even to the study of origin of life [4].

Here, we show how Electrochemical Impedance Spectrometry (EIS) can be used to study thermodiffusion in a thin-layer cell, and determine the Soret coefficient of a trace-ion in a supporting electrolyte. By applying a temperature gradient as a driving force in an electrochemical cell, the flux of the trace ion to the working electrode can either be increased or decreased depending on the direction of the gradient and the sign of the Soret coefficient. The change in flux decreases or increases the low frequency impedance from the isothermal case [5] (Figure 1a), and also has a minor effect on the charge transfer resistance. With the proposed method, we are able to study thermodiffusion of a trace ion electrochemically with good precision. Moreover, the cell geometry effectively eliminates natural convection, major source of error in thermodiffusion measurements.

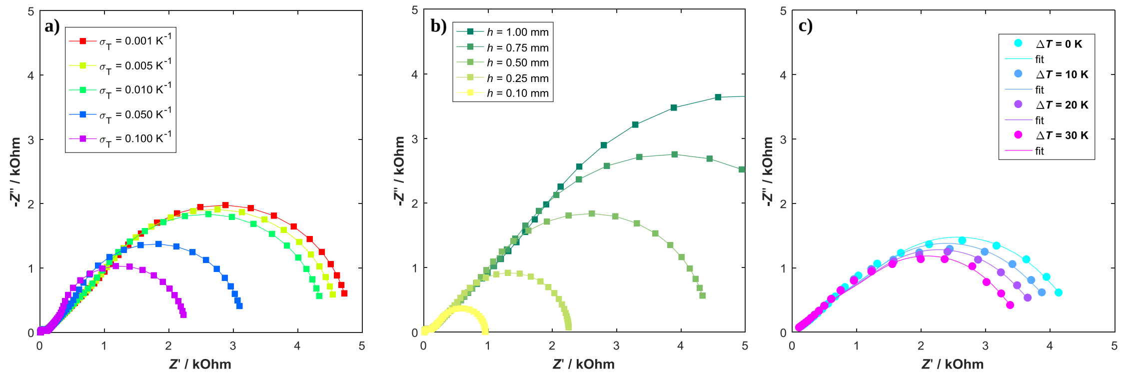

Figure 1. a) Simulation of the effect of changing the Soret coefficient σ_T at temperature difference between the working and counter electrode ΔT = 30 K and cell thickness h = 500 µm. b) Simulation of the effect of changing h with σ_T = 0.01 K^{-1} and ΔT = 30 K: the larger the gradient $\Delta T/h$ the more the impedance spectrum bends. c) Measured impedance spectra of 5 mM $K_4Fe(CN)_6$ / 5 mM $K_3Fe(CN)_6$ / 500 mM KCl in a thin-layer cell ($h \approx 300$ µm) with different temperature differences between the WE and CE; the mean temperature is kept constant. Simulations and experimental data are taken from 100 kHz to 1 mHz.

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Electrochemical Characterization of Darbufelone and electro-oxidation pathway

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Inflammatory diseases represent a serious ailment, and so, dual COX/5-LOX inhibitors, such as darbufelone, have been used and studied as potential novel treatment options for inflammation and related illnesses. Moreover, reactive oxygen species are linked to inflammation and gastric damage, thus, NSAIDs antioxidant activity is related to their overall anti-inflammatory effect. In this scope electroanalytical techniques are an excellent alternative to traditional approaches, in the assay of drugs and their antioxidant capacity. Moreover, unlike the excipients of pharmaceutical formulations, the drugs present one or more electroactive sites, thus offering good selectivity and broad applicability, especially on the quality control and medicinal chemistry contexts. In regards to such pharmaceutical sciences, the main electrochemical parameters, E_p and I_p, can be explored for qualitative and quantitative approaches. For instance, E_p can be useful in identification assays, whereas many I_p have widely explored in quantitative assays of medicines. On the other hand, E_p and I_p are thermodynamic and kinetics, parameters respectively, that can be used to estimate the reduction power of molecules. Also, they can be correlated to molecular electrostatic potential (MEP), which provides good insights into the redox reaction mechanisms and antioxidant capacity. In this scope, computational chemistry simulations using molecular modeling methods are very useful to ascertain this data. Voltammetric experiments were carried out with a potentiostat/galvanostat µAutolab III® integrated to the GPES 4.9® software, Eco-Chemie, Utrecht, The Netherlands. The measurements were performed in a 5.0 mL one-compartment electrochemical cell, with a three-electrode system consisting of a glassy carbon electrode (GCE), a Pt wire and the Ag/AgCl/KCl 3M(both purchased from Lab solutions, São Paulo, Brazil), representing the working electrode, the counter electrode and the reference electrode, respectively. Moreover, in order to evaluate the overall electronic structure of the darbufelone, semi-empiric PM6, density functional theory (DFT), and ab-initio Møller–Plesset (MP2) calculations for lowest energy enantiomorphs were performed. The 6-311+G** basis set was employed in both DFT and MP2. The well-known B3LYP exchange correlation functional was used in the DFT calculations. In order to illustrate and facilitate the analyses of the charge distributions, MEP were calculated for the the darbufelone lowest energy enantiomorphs. Sequential CV assays, were performed, and it was possible to observe two anodic peaks, 1a and 2a, at E_p1a ~ 0.2 V and E_p2a ~ 0.5 V, and a minor cathodic peak, 1c, at E_p1c ~ 0.2 V. Cyclic voltammetry assays in different scan rates plot, performed separately within the first ($0 \text{ V} < E_\mathrm{p} < 0.4 \text{ V}$) and second peak ($0.375 \text{ V} < E_p < 0.725 \text{ V}$), allowed the observance of the linearity in the plot of peak current vs. $\nu^{1/2}$, thus, it could be inferred, in accordance with Randles-Sevick equation, that the electron transference is mainly limited by the diffusional process. Then, DPV was performed in order to clarify such results and also to study the pH effect on redox processes. As expected for phenol/quinone redox systems, the E_p decrease according to deprotonation, being the slope close to the theoretical value of 59 mV / pH unite till the pKa value. Furthermore, SWV were performed to confirm the reversibility of redox process 1a and the irreversibility of anodic process 2a. In the calculated darbufelone MEP it was possible to infer the most likely oxidation sites, being the hydroxyl in the di-tert-butylphenol, followed by a sequential oxidation of the sulfur in the thioether group into a sulfoxide, corresponding to the two oxidation signals found in E_p1a ~ 0.2 V and E_p2a ~ 0.5 V in the DPV, respectively. The darbufelone molecule electrochemical performance and overall voltametric signal profile was successfully investigated. Theoretical electronic calculations and rendered MEP topology corroborated to the inference in the drug electrochemical oxidation pathway.

A polyamidoamine dendrimer – streptavidin supramolecular architecture platform for DNA biosensing

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One of the underlying philosophies of biosensor development is biomimicry. This necessitates the use of biocompatible materials and immobilisation chemistries that will not hamper the biomolecular integrity and functionality of the bioreceptor. In line with this philosophy, we have developed a novel polyamidoamine dendrimer-streptavidin supramolecular architecture suitable as a versatile platform for biosensors. The dendrimer was electrodeposited on a glassy carbon electrode by cyclic voltammetry at a potential window of -200 mV to 1200 mV at 50 mVs^{-1} scan rate[1]. Exploiting the isoelectric points, streptavidin was deposited on the dendrimer modified electrode by supramolecular chemistry[2]. The platform (i.e. the dendrimer-streptavidin nano-architecture) was electrochemically interrogated in phosphate buffer, ferrocyanide and H_2O_2. Based on this platform, a DNA biosensor and an aptasensor were developed. The electrochemical DNA biosensor was prepared using a biotinylated 15 base oligonucleotides and a thrombin aptamer was used for the aptasensor. Voltammetric and electrochemical impedance spectroscopy (EIS) studies were carried out to characterise the biosensors and its hybridisation/binding responses in phosphate buffer saline solution (PBS) and $[Fe(CN)_6]^{3-/4-}$ redox probe at pH 7.2 The electroactive response of the dendrimer was observed at around 400 mV. From the EIS circuit fitting results, the biosensor responded to the target DNA by exhibiting a decrease in charge transfer resistance (R_{ct}) in PBS and increase in R_{ct} in $[Fe(CN)_6]^{3-/4-}$ redox probe while in voltammetry, increase in anodic peak current is observed in PBS after hybridisation using square wave voltammetry (SWV). The platform was electroactive and stable. A detection limit of the biosensors were in the sub ng mL^{-1} levels. In principle, this supramolecular architecture approach lends itself to a wide biosensor application if the bioreceptor can be biotinylated.

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Revealing Li-Ion Battery Processes Using Operando Neutron Depth Profiling and NMR Methods

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Rechargeable Li-ion batteries (LIBs) have been the predominant energy storage for a wide range of portable devices like cell phones, laptops and digital electronics. Non-destructive methods such as neutron depth profiling (NDP) and solid state NMR are ideal for probing Li complex formation, accumulation and transport within the battery material during charge/discharge. Currently, our work is focused on understanding the effect of an electrochemical event to the materials' storage properties using NDP and NMR techniques *in operando*. Specifically we report our recent work on the preferential Li nucleation, Li trapping, Li transport in intermetallic materials like Li_xSn_y, Li_xSi_y and Li_xAl_y and evidence of formation and accumulation of a LiSn metastable phase that is correlated to capacity fade.

Measuring Single Nanoparticle Reaction Kinetics by Time-Resolved Nano Impact Electrochemistry

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In recent years, nano impact electrochemistry has been successfully introduced as a new tool to characterize size, agglomeration state, composition and catalytic activity of individual nanoparticles [1,2]. The method employs the stochastic impacts of solution-phase nanoparticles at a potentiostated electrode, for instance to electrochemically oxidize individual particles one by one. Each of these destructive impacts results in a spike in the current transient and the charge transferred in each impact provides the individual particle size. Here we present that due to the well-defined mass transport at individual particles, not only the charge, but also the duration and shape of individual current spikes contain valuable analytical information that can readily be extracted from nano impact experiments. Using conventional nano impact measurements but at high bandwidth, we unravel this information and obtain hitherto inaccessible quantitative insights into nanoparticle reactivity at a single particle scale. This is shown using the oxidation of individual 29 nm diameter silver nanoparticles in four different electrolytes as a proof-of-concept.

Firstly, it is demonstrated that for low overpotentials the peak duration decreases exponentially, that is the time needed to fully oxidize a single nanoparticle decreases with increasing potential applied at the electrode [3]. Since the charge transferred per impact remains constant, the peak height increases accordingly, as shown in Figure 1. Secondly, an analytical expression is established that uses the well-defined mass transport at a single dissolving nanoparticle to determine the reaction rate constant from the measured peak duration at a given overpotential. The reaction rate constants for electrochemical oxidation of single silver nanoparticles in four different electrolytes are thus calculated. Thirdly, the peak duration at high overpotentials is found to scale with the concentration of chloride in the electrolyte. Hence, the reaction mechanism of Ag oxidation to form AgCl(s) with chloride diffusion being the mass transport limiting step is identified. Last but not least, it is observed that in the absence of chloride, the peak shape at high overpotentials changes significantly, indicating that the oxidation occurs by formation of Ag^+(aq) and in a step-wise manner.

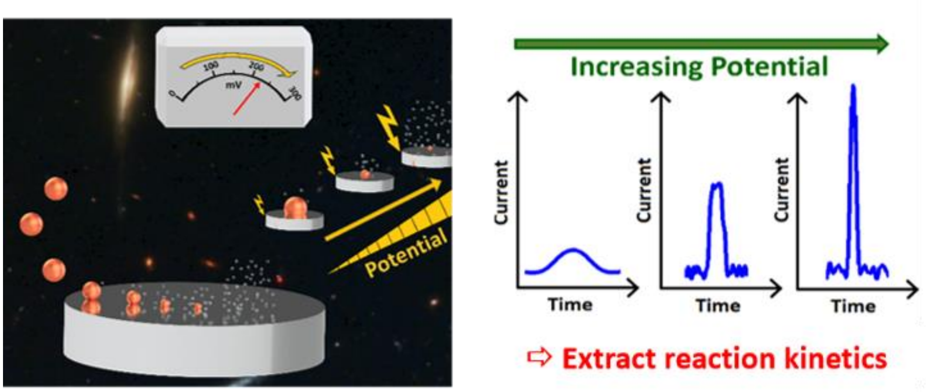

Figure 1 (a) Oxidative nano-impacts of Ag nanoparticles at an electrode potentiostated at different potentials, (b) decrease of the peak duration with increasing overpotential allows determination of reaction rate constant for individual nanoparticles.

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Disposable amperometric biosensing platforms for food safety

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Allergen control and detection of food adulteration are particularly important nowadays in the field of food safety to ensure maximum satisfaction and protection of consumers. Although there are available several analytical methods for food allergens and adulterants detection, there is still an urgent need to develop alternative methods able to perform rapid and multiplexed determinations with high sensitivity and selectivity with low-cost instrumentation and adaptable to miniaturization, ideal to perform decentralized and routine analysis. Within this context, novel amperometric immunosensing platforms for the sensitive, selective and rapid biosensing of the main protein allergens associated with milk (β-lactoglobulin [1] and α-lactalbumin [2]) and peanuts (Ara h 1 and Ara h 2 [3-5]) and genosensing scaffolds, coupled or not with novel reduced time PCR amplification strategies, for the specific determination of fragments characteristics of the halzenut *Cor a 9* coding sequence (Figure 1) [6] and horse meat will be summarized and discussed in this presentation. The developed methodologies, based on the appropriate use and coupling of specific bioreceptors, functionalized magnetic microbeads, novel PCR amplification strategies and disposable screen-printed electrodes, have demonstrated applicability for the selective and accurate determination of the endogenous content of the target analytes in scarcely pretreated complex matrices (milks, food extracts and saliva samples). These electrochemical bioplatforms, advantageously compared with other commonly used methodologies in terms of simplicity, cost, assay time and portability of the required instrumentation, constitute particularly attractive analytical tools for the implementation of affordable cost and user-friendly devices for routine determinations to ensure food quality and consumer protection. Moreover, the implemented bioscaffolds could be easily multiplexed, even for simultaneous determination of different molecular levels analytes, and extended to the determination of other relevant targets.

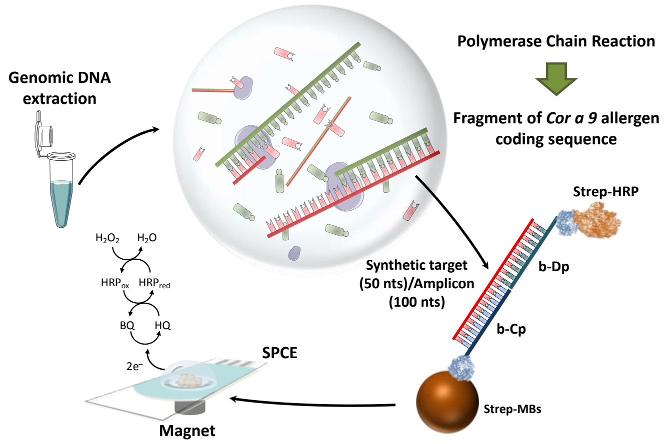

Figure 1. Schematic display of the electrochemical genosensing platform developed for the determination of the *Cor a 9* allergen coding sequence.

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Imaging electrochemical current, reaction and surface stress optically

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The beauty of electrochemistry is the direct interrogation and control of a chemical process electrically. Indeed electrical measurement (current, voltage, charge etc.) has been the primary approach in the study of electrochemistry to date. While this approach powerful, it has limited spatial and temporal resolutions. The former is needed for studying heterogeneous reactions, and the latter is critical for monitoring fast electrochemical processes. We report on several optical methods for studying electrochemical processes, including faradic and non-faradic processes, and surface stress and strain, with high spatial and temporal resolutions. We discuss the basic principles of the methods, and demonstrate their applications using selected examples, including imaging of single cells (neurons and bacterial cells) and viruses, detection of fast conformal fluctuations in redox proteins associated with electron transfer, and tracking of electrochemical reaction and surface stress in single nanowires and graphene sheets.

Analysis of MDMA by Square Wave Voltammetry with carbon paste electrode

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It is known the benefits in voltammetric analysis when some factors such as quickness, sensitivity, specificity and simple sample preparation are required. Inside forensic scenario, these characteristics are valuable in seized drug analysis. Among the variety of illicit drugs, it has been increasing the consumption of MDMA (N-Methyl-3,4-methylenedioxyamphetamine), a synthetic psychoative drug found commonly as ecstasy pills.

This work explores the possibility in analyzing and quantifying MDMA by Square Wave Voltammetry in aqueous medium, using a simple methodology and carbon paste as the working electrode.

The conditions for the voltammetric measurements required aqueous $LiClO_4$ as the supporting electrolyte and carbon paste (in proportion 90:10 with paraffin). A pre concentration step of 10 seconds at -0.1 V was necessary for the best definition of the oxidative peak got in a step potential of 0.004 V and frequency at 25 Hz.

In Figure 01, it is presented the anodic response at 1.21 V for successive additions of standard solution of MDMA, whose relation to peak current resulted in the linear response (R=0.9937) of the analytical curve. The Limit of Detection and Limit of Quantification calculated were equal to 2.79 10^{-6} and 8.87 10^{-6} mol L^{-1}, respectively for a voltammetric sensitivity of 0.27 A L mol^{-1}.

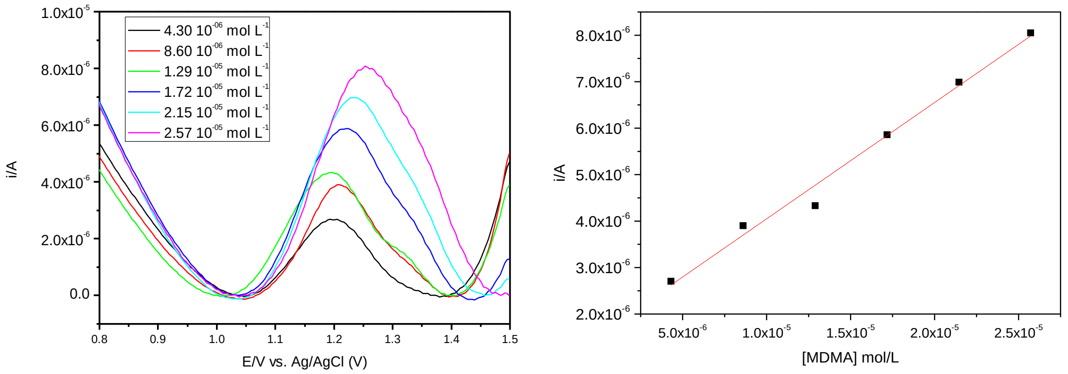

Figure 01: Square Wave Voltammograms for MDMA and the analytical curve obtained.

The present methodology allows quantifying MDMA in a concentration level equivalent to 5.15µg of MDMA in solution, in a fast measurement of less than 2 minutes and a low cost working electrode, what make this result of great value for forensic laboratories.

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Combination of Voltammetry of Immobilized Microparticles and Nanostructured Carbon Black Films for the Determination of Organic Compounds

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Voltammetry of Immobilized Microparticles (VIM), initially referred to as Abrasive Stripping Voltammetry (AbrSV) by Scholz et al. [1], is an electroanalytical technique in which the analyte is immobilized on the electrode surface by an abrasive process. In the “conventional” voltammetric analysis, the analyte is dissolved in an electrolytic solution and, consequently, small amounts of this material are measured (low current values) because the redox process that occurs in the double layer involves part of the material, influencing the limits of detection (LOD) and quantification (LOQ). In the case of VIM, the analytical signal obtained is due to all the material immobilized on the electrode surface, thus presenting a higher response with a very small amount of analyte [2]. In this work we will present two electrodes for the quantitative determination of (a) hydroquinone and (b) eugenol (4-allyl-2-methoxyphenol). The designed electrodes were based on (a) a glassy carbon electrode modified with a crosslinked chitosan film containing carbon black nanoparticles and an immobilized hydroquinone standard or a dermatologic cream sample and (b) a glassy carbon electrode modified with a dihexadecyl hydrogen phosphate (DHP) film containing immobilized carbon black nanoparticles and an eugenol standard or a clove oil sample. Electrochemical experiments were performed using an Autolab PGSTAT204 (Metrohm-Autolab, Utrecht, Netherlands) potentiostat/galvanostat controlled by the NOVA 2.0 software (Eco Chemie) fitted with an three-electrode electrochemical cell (15 mL): an Ag/AgCl (3.0 mol L^{-1} KCl) reference electrode, a Pt foil as the counter electrode, and the modified GCE (a or b) as the working electrode. Using Differential Pulse Voltammetry (DPV), the obtained analytical curve was linear in the hydroquinone concentration range of 2.7 to 43 ng/film, with LOD and LOQ values of 0.045 ng/film and 0.15 ng/film, respectively. Two commercial dermatologic cream samples (A1 and A2) were successfully immobilized and analyzed using the proposed VIM procedure; the hydroquinone mass fractions were 3.8 and 4.2%, respectively. Using Square-Wave Voltammetry (SWV), the analytical curve for eugenol was linear in the concentration range of 29 ng/film to 26000 ng/film, with LOD and LOQ values of 8.7 ng/film and 29 ng/film, respectively. Three commercial clove oil samples were successfully immobilized and analyzed; the eugenol mass fractions ranged from 14 to 68.3%. The advantages of using the analyte immobilized within a very thin film in comparison to the solid analyte immobilized in a paraffin-impregnated graphite electrode (PIGE) will be discussed.

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Integrated electrochemical devices based on micro/nano-chemistry for bioassays

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Micro/nanochemistry focuses on the unique chemical reactions occurring in micrometer or nanometer spaces and/or involving micrometer or nanometer structures. I has developed novel electrochemical devices incorporating micro/nano structures for sophisticated analytical electrochemical measurements applicable to bioassays. These devices allow highly sensitive and high throughput assays, in addition to high resolution electrochemical imaging using features unique to small-scale environments. The outline of the research is shown in Fig. 1.

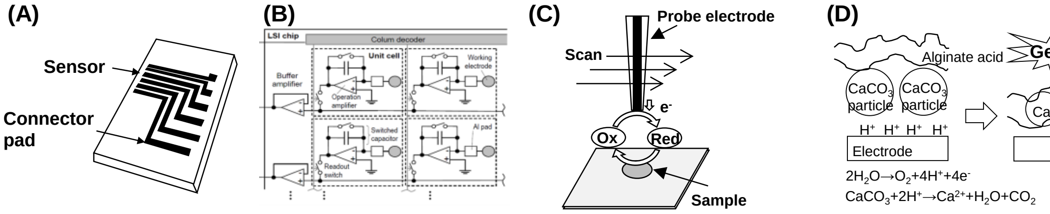
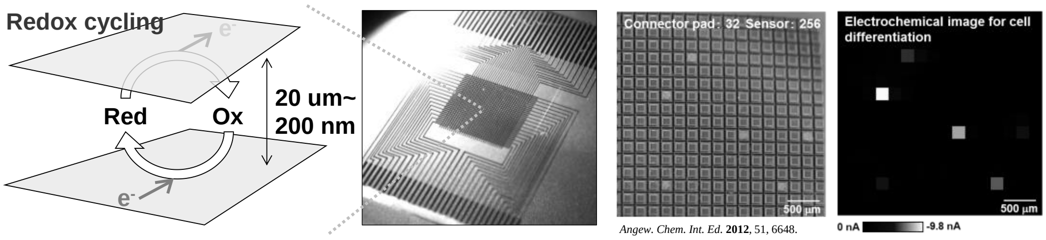


Figure 1. Research outline. (A) Chip device. (B) LSI device. (C) Probe device. (D) Device/system for electrodeposition of hydrogels.

Electrochemical chip devices based on the micro/nanochemistry were developed for bioassays (Fig. 1A). For example, integrated electrode array devices, which can induce locally redox cycling, were developed, so that n^2 sensors can be incorporated using only $2n$ connection pads into a small chip device (Fig. 2). The amperometric devices were applied for DNA detection, cell analysis for cell differentiation. The device where nanocavities are incorporated can perform highly sensitive assays.



Angew. Chem. Int. Ed. **2012**, 51, 6648.

Figure 2. Redox cycling-based electrochemical imaging device. Cell differentiation of cell aggregates were electrochemically imaged.

A large-scale integration (LSI) device was developed for bioassays (Fig. 1B). The CMOS-based device consists of 400 electrochemical sensors with a 250-µm pitch. An operational amplifier with a switched-capacitor type *I*-*V* converter is incorporated into each sensor to amplify the in-pixel signal for amperometric detection. The device was successfully applied for analysis in cell arrays for evaluation of cell differentiation of stem cells and dopamine release from neuron-like cells. Furthermore, the device was applied for evaluation of enzyme activity, topography and conductivity.

A detection system using scanning electrochemical microscopy (SECM) and several probes for electrochemical detection was developed (Fig. 1C). For example, a probe consisting of a carbon nanoelectrode and an Ag/AgCl reference electrode (carbon-Ag/AgCl probe) was developed for the electrochemical analysis of microenvironments. I has also proposed an electrochemical assay for proteins secreted from cells using a microwell array and SECM in which secreted proteins from single cells were concentrated in the microenvironment and detected. The system was utilized for single cell analysis.

An electrodeposition method was developed for forming designated gel structures (Fig. 1D). Microwells, tubular structures of hydrogels were successfully fabricated. This simple method is a useful approach for the construction of hydrogel structures for bioanalysis and tissue engineering.

Thus, the integrated electrochemical devices based on micro/nano-chemistry were developed for analytical electrochemistry and biotechnology.

Electrochemical Paper-Based Analytical Devices for Clinical and Environmental Diagnostics

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Abstract

One major push in the field of sensor development is production of very cheap and easy to use sensors that require minimal external equipment. Microfluidic Paper-based Analytical Devices (mPADs) have received significant attention in this field because they are cheap (costing pennies per device), easy to use, and can carry out a wide range of chemical assays. A range of applications has been demonstrated for mPADs from clinical diagnostics to environmental monitoring. While significant progress has been made with these systems, sensitive, selective detection remains a challenge. Detection with mPADs is normally done with colorimetry but this method can have limited sensitivity and selectivity. Electrochemistry can provide an excellent option for improving detection sensitivity and selectivity while maintaining the low cost of the devices. This talk will focus on recent developments from the Henry laboratory using electrochemical paper-based analytical devices (ePADs) with applications in both environmental and clinical diagnostics. ePADs are attractive in this application space because they are made from low cost materials and utilize simple, low cost instrumentation for analysis. While significant developments have been made in this field, key issues of electrode fabrication and characterization as well as field based applications have been limited. Here, analysis of heavy metals using chemically-modified electrodes to assess environmental and occupational exposure will be discussed first as an example of environmental diagnostics. Detection of metals (Zn, Pb, Cd, Ni, etc) from aerosol samples collected with a new wearable aerosol sampler will be discussed first. A simple combination of paper-microfluidics with electrodes modified with either silver nanoparticles or boron-doped diamond has allowed generation of a new device capable of performing electrochemistry at multiple conditions simultaneously to extend the range of test that can be done from a single sample. Next, new ePAD systems for detecting bacteria and viruses will be presented as an example of clinical diagnostics. A new composite carbon electrode material than be readily patterned into a variety of geometries will be discussed. The electrodes can be combined with simple microfluidic devices to enable sensitive, selective detection of pathogenic bacteria.

Platforms for Chemical Analysis Interfaced with Redox Magnetohydrodynamic Microfluidics

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The miniaturization of methods for chemical analysis is enabled by automating ways to manipulate small volumes of fluid. Microfluidics propelled by redox-magnetohydrodynamics (RMHD) has capabilities that are different from traditional fluid-pumping approaches. It offers opportunities for the development of unique devices for chemical analysis. Fluid flow is directed without requiring valves or channel sidewalls by tuning ionic current density, **j**, and magnetic flux density, **B**, whose cross product generates the MHD force, $\mathbf{F_B}$ (the magnetic component of the Lorentz force). In our laboratory, microelectrodes patterned in different, individually-addressable geometries on chips produce **j** by converting electronic to ionic current at their interface with a liquid. Therefore, in the presence of a magnet, selective activation of these "pumping" electrodes in a chamber containing the liquid (aqueous or non-aqueous solutions) can "program" the start, stop, reversal, speed, and profiles of the fluid flow. Improvement of the sensitivity of anodic stripping analysis of heavy metals in 150-µL samples has been possible using the stirring capabilities of RMHD during the accumulation step, without the need for mechanical agitation [1]. The uniform, flat flow profile generated by RMHD has been implemented to demonstrate a proof-of-concept for multiple, parallel, electroanalytical assays involving superparamagnetic microbeads [2]. In these two applications, redox species were added to the solution to facilitate the electronic-to-ionic conversion without bubble formation or corrosion at the pumping electrodes. By modifying the electrodes with a conducting polymer, essentially immobilizing and concentrating "redox centers" instead of adding them to the solution, interferences can be eliminated and compatibility can be improved with biological samples [3]. We will discuss our newest applications of RMHD microfluidics to chemical analysis that utilize conducting polymer-modified pumping electrodes. One involves coupling RMHD, to control the speed and uniform fluid flow of a sample of white blood cells in a self-contained cartridge, with an epitaxial light sheet confocal microscope for image cytometry [4] that can count and differentiate granulocytes, monocytes, and lymphocytes. We will also describe our latest results on loop-based pumping by RMHD for the separation of chemical mixtures. In addition, we will report strategies that extend the pumping time of conducting polymer-modified RMHD for such applications that include polymerizing different monomers, optimizing the polymer-forming conditions, and reconfiguring the spatial and temporal relationships between **j** and **B**.

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Electrocatalyic flow systems combined with advanced EPR techniques to unravel reaction mechanisms and determine rate constants at different nano-structured electrodes

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Electrocatalytic processes are defined by the transfer of an electron at the surface of the electrode by an electrocatalyst to a molecule that was adsorbed from the bulk of the solution. To improve the catalytic properties of electrocatalysts, a profound understanding of the underlying mechanism is necessary. To this end, electrochemical techniques are often combined with analytical techniques. The most frequently used detection systems analyze the stable products resulting from the reaction. What actually happens during the reaction is often ambiguous. Electron Paramagnetic Resonance spectroscopy (EPR) provides a window to lift this ambiguity by detecting radicals formed at the electrode. The measured spectrum is dependent of the molecule's surroundings. This implies that nearby atoms have an influence on the spectrum e.g.; the adsorbed radicals at the surface, the solvent, impurities and the electrodes. This information combined with that obtained by the in-situ electrochemical synthesis yield an in-depth understanding of the electrocatalytic properties of nanostructured electrode materials and their influence on the reaction mechanism and the products that are formed. This allows tuning the electrocatalytic materials which will finally gap the bridge between the actual and desired energy consumption in these processes.

In the last quarter of the twentieth century, the combination of EPR and electrochemistry was investigated and mostly static cells (and some flow cells) for use in an X-band continuous-wave EPR spectrometer were developed. Since then, the field of EPR has undergone rapid changes, whereby many advanced pulsed and high-field EPR methods have been introduced, enormously increasing the performance of EPR. Similarly, the field of electrocatalysis has known a strong progress in the last decade with much focus now being given to nanoparticles to reduce material costs and improve catalytic activity. To fully benefit from the advancements in both fields, and to further optimize electrocatalyst development, new and improved spectroelectrochemical flow cells for combined EPR and electrochemistry impose themselves.

In this work, a new and improved flow cell based on a channel cell design is developed. Utilizing a flow cell instead of a static cell allows the derivation of kinetic and mechanistic data in addition to the identification of reaction intermediates. A well-defined hydrodynamic flow which can be correlated to the current response and the EPR-signal is essential to discriminate between reaction mechanisms. A modular design of the cell provides the possibility to incorporate and in-situ study nano-structured electrocatalysts such as (hemispherical) nanoparticles, core-shells, bimetallic or dendritic particles prepared by electrodeposition and galvanic displacement.

As a case study to evaluate the cell and demonstrate the applicability to in-depth electrocatalyst research, the reductive cyclisation of halogenated allyl benzyl ethers is studied. The influence of the catalyst morphology and composition on the reaction mechanism is investigated.

Integrated Electrochemical Analysis of Circulating Tumor Cells Isolated by Dielectrophoresis

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We demonstrate continuous high-throughput selective cell capture by dielectrophoresis (DEP) at arrays of up to 1,400 wireless electrodes (bipolar electrodes, BPEs). The use of wireless electrodes removes the requirement of ohmic contact to the individual array elements, thus enabling otherwise unattainable device formats. Here, we evaluate the performance of a device containing branched microchannels interconnected by BPEs for the isolation of circulating tumor cells (CTCs) from blood cells. In this format, capacitive charging of the electrical double layer (EDL) at opposing ends of each BPE allows an AC electric field applied by only two driving electrodes to be transmitted across the entire device. Additionally, pockets extruding from either side of the microchannels volumetrically control the number of cells captured at each BPE tip and enhance trapping. We show that the electric field distribution is readily tuned by the dimensionality of the BPEs. High-fidelity single-cell capture was achieved in the parallel-channel design when the pocket dimensions were matched to those of the cells. Additionally, we describe the integration of *in situ* electrochemical analysis at the BPE array.

Portable Low-Cost Instrumentation for Trace Electrochemical Analysis of Heavy Metals in the Field

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Developments in microcontroller and consumer battery technologies have facilitated the development of several advanced portable instruments. We have developed a hand held portable potentiostat operating on the Arduino microcontroller platform. This instrument has several key features making it ideal for in-the-field measurement and analysis. The final assembled instrument is highly portable, with a footprint of just a few inches and a battery life of over 15 days, assuming several hours of daily use. It has a sweep rate range of 0-400 mV/s, and is currently programmed to perform several electrochemical experiments. The instrument is capable of autonomous on-the-fly gain control and self-calibration, and has a linear range spanning six orders of magnitude. This feature allows the user to conduct electrochemical experiments on unknown systems without prior knowledge of the expected current output. The instrument is capable of detecting and storing background subtracted peak currents, allowing autonomous analysis of unknown analytes when coupled to the appropriate experimental controls. Finally, the instrument is capable of storing thousands of experiments in internal memory, and costs just $100 to produce.

These features allow the device to make measurements of several metals in ground water, including copper, lead, arsenic, and cadmium, in the low parts per billion range using anodic stripping voltammetry. This analysis lends itself well to simplified instrumentation for field-analysis. We quantified these metals directly and autonomously using our device, independent of user input, and without the need for a laptop or personal computer. This analysis was done “in the field” by novices with no prior electrochemical experience. This device enables the testing of water for environmental pollutants.

Development of a portable, microfluidic, multi-analyte electoanalytical device for monitoring dynamic changes in human tissue.

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We have been developing a range of electroanalytical sensors and biosensors for monitoring the injured human brain (1), kidney and during free-flap surgery and exercise (2). Our approach has been to use the tissue sampling technique of microdialysis, where a probe is placed into the tissue to be monitored and perfused at low microliter / min flow rates. The dialysate that emerges from the probe is then fed along a extra fine bore tubing to a bedside analysis instrument of our design. This currently contains a PDMS microfluidic manifold with two amperometric biosensors (glucose and lactate typically). The 1m tubing required for patient safety has a profound effect on the temporal resolution of the contuinuous analysis due to Taylor dispersion along the tube. It also introduces a significant delay, typically 20 min, between then liquid emerging from the tissue and subsequent analysis. To address both issues we have developed a robust wireless microfluidic manifold with changeable sensors and integrated electronics.

At the core of this new device is a 3D printed microfluidic manifold, optimized for fast response time and leak free connections.. It can contain upto four independent detectors - either amperometric biosensors (glucose, lactate, pyruvate, glutamate) or potentiometric ion selective electrodes (K^+, Na^+, $Ca^{2+,}$ Mg^{2+}) or a mixture of the two types of sensor. Individual sensors and biosensors can be replaced when required. The amperometric biosensors are based on a 400 µm diameter electrochemical cell coated with electropolymerised polyphenylenediamine to provide selectivity, an enzyme containing hydrogel to give both sensitivity and specificity, and a polyurethane outer layer to limit the diffsusional flux to the hydrogel improving both linear range for enzymes with a low Km, and reducing sensitivity to dissolved oxygen. Potentiometric sensors are also 400µm diameter using carefully optimized ionophore containing PVC membranes, with either liquid or solid junction conducting polymer contacts. Electrochemical instrumentation are based on high-performance low power circuits developed with the group (3). The systems are full portable and wireless using either Zigbee (better noise performance) or Bluetooth (ease of implementation on tablets). Optimization of the electrochemical performance of the system will be described. The talk will close with results from our monitoring of severely injured traumatic brain injury (TBI) patents while in the intensive care unit, and monitoring of freshly removed porcine kidneys and subsequent machine perfusion as a model for human kidney transplant monitoring.

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Electrochemical Detection of Droplet Contents in Microfluidic Devices: Chronoamperometric Analysis of Plugs

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Over the last few years, droplet-based microfluidic systems have attracted great interest in a wide range of chemical and biological processes. These systems offer capabilities to compartmentalize very small volumes with a flexible control of composition.[1] They allow the enhancement of reaction speed and process efficiency by rapid mixing. Therefore, droplet-based microfluidic systems have found applications ranging from synthesis of advanced materials, reaction kinetic studies, nucleic acid assays to cell-based analysis. For detection in droplet microfluidics, various detection methods have been used including laser-induced fluorescence, mass spectrometry, Raman spectrometry and absorption spectroscopy.[2] Although these techniques offer highly selective, sensitive and accurate determinations, their main drawback is the cost of instrumentation and the challenge of implementing miniaturized systems for on-site applications.

Electrochemical detection is an attractive and alternative approach which can be easy integrated on microfluidic chips for real-time measurements. Electrochemical methods in droplet microfluidics can be performed to count droplets or to evaluate their size and velocity. Only a few reports dealt with the electrochemical detection of droplet contents. Due to the discontinuous property of diphasic flow, direct electrochemical detections often lead to transient signals which are difficult to analyze.

We report here the electrochemical detection of droplet contents by chronoamperometry. A specific microfluidic device was designed to generate reproducible droplets on-demand with large aspect ratios. Each droplet was characterized in size and velocity before being detected by a microchannel electrode located downstream. The influence of droplet size and velocity on the electrode response was investigated as well as the device geometry. We showed that steady-state current was controlled by convective mass transfer to electrode. A comparison with known operating regimes of microband electrode in continuous pressure-driven flow[3] evidenced the internal recirculating convection within droplets.

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Coupling Ion Channels to Mobile Nanofluidic Devices (Nanopipettes)

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Integration of dual-barrel membrane patch-ion channel probes (MP-ICPs) to scanning ion conductance microscopy (SICM) holds promise of providing a revolutionized approach of spatially-resolved chemical sensing. However, to fully exploit the MP-ICP platforms for concurrent topography and chemical sensing, a comprehensive characterization of the analytical performance of this newly-developed platform is needed. A series of experiments were performed to further our understanding of the system and to answer some fundamental questions, in preparation for future developments of this approach. First, we constructed MP-ICPs that contained different types of ion channels including TRPV1 channels and BK channels to establish the generalizability of the methods. Next, we proved the capability of the MP-ICP platforms in single ion channel activity measurements, and demonstrated that the channel behaviors can be faithfully obtained with this approach. In addition, we studied the interplay between the SICM barrel and the ICP barrel. An interesting phenomenon that's related to the charge of the ligand molecules was discovered, for ion channels gated by uncharged ligands, channel activity at the ICP barrel is unaffected by the SICM barrel potential; whereas for ion channels that are gated by charged ligands, enhanced channel activity can be obtained by biasing the SICM barrel at potentials with opposite polarity to the charge of the ligand molecules. Finally, a proof-of-principle experiment was performed and site-specific molecular flux sensing was demonstrated at single-ion-channel level.

Microfluidic experiments on enrichment of paramagnetic metal ions in aqueous solutions by applying inhomogeneous magnetic fields

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Magnetic separation is a well-established technology for separating magnetic particles from solutions. The magnetic gradient force scales with the magnetization density and the volume of the particle.

The magnetic moment of paramagnetic metal ions in solution could be utilized as well for separating ions from solutions in strong magnetic fields of large spatial gradients. This idea dates back to early work of Noddack et al[1], where firstly separation effects were found for rare earth metal ions in aqueous solution. However, the effect is limited, as the ratio of magnetic to thermal energy is small. Recently, separation of paramagnetic ions from gel[2] and homogeneous solution[3,4,5] in inhomogeneous magnetic field were reported.

Triggered by these findings, microfluidic experiments were performed. The setup consists of a small reactor printed by 3D technology where a spiral pipe flow is exposed to an inhomogeneous magnetic field created by an iron wire the spiral of which is close to the pipe, and which is magnetized in an external magnetic field, thus creating strong gradients near the pipe. Flow experiments were performed for different salt solutions. At the outflow, the flow volume was separated into a near-magnet and a far-magnet half, the concentrations of which was analyzed by UV/VIS spectrophotometry and by ICP-MS.

The absorption spectrum of 0.1 M HoCl3 solution was shown in Fig.1. According to Lambert-Beer Law, the concentration of ions could be determined depending on the absorbance in the highest peak.

$$C = A_\lambda / (\varepsilon_\lambda \cdot l)$$

where Aλ is the absorbance in the peak maximum, ε_λ is the molar absorption coefficient of Ho ions and l is the thickness of the sample cuvette. The concentration difference from the two outlets was measured based on the spectrum, and the effects of the magnetic field gradient and flow rate were studied.

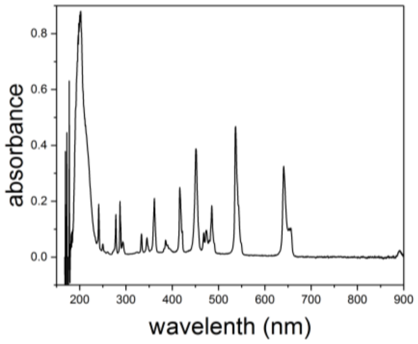

Fig.1. Absorbance spectrum of 0.1 M $HoCl_3$ solution.

Acknowledgements:

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Electrochemical Surface Functionalization of Microsystems: Towards a Selective and Sensitive Analytical Platform

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The current increase in healthcare costs and the global population ageing have generated a growing demand of small, rapid and robust analytical tools for the monitoring of patients.[1] However, the selective analysis of real samples represents a bottleneck in the development of personalized diagnostic devices. Due to the considerable amount of potential interfering species present in biological samples, the use of highly selective sensors is of major importance.

Our present work is focused on the development of a rapid and easy method to customize integrated platinum microband electrode surfaces for the construction of analytical microfluidic platforms.[2] Platinum microbands were first functionalized by electrochemical reduction of aryl diazonium salts combined to click chemistry reaction to attach ferrocene molecules, as a model system for further tailored functionalization.[3] Also, we developed poly(eugenol) and platinum-black modified Pt microband electrodes within microfluidic devices to endow them with the desired sensitivity and selectivity for the detection of analytes of interest such as nitric oxide NO and H_2O_2, respectively. Such devices are aimed at characterizing and interpreting the key components in terms of reactive oxygen species (ROS) and reactive nitrogen species (RNS) to provide data that accurately reflect their concentration in living cells.

This research based on microband surface modifications is of great interest for the development of multi-target screening in the same microchip. It thus allows a single run analysis in the same microchip of mixtures of analytes in biological matrices for biomedical applications.

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Carbon Nanotube Based Flow-Through Electrode: Why and How?

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The detection limit in electroanalytical methods is usually governed by mass transfer. To increase the sensitivity it is essential to increase the collection efficiency, which is the ratio between the charge required to deposit the analyte onto the electrode surface and the charge that passes through the electrode. The essence of this work is to develop a flow-through electrode, which substantially increases the collection efficiency of the analyte, thus increasing the sensitivity and decreasing the analysis time.
Specifically, a novel approach is proposed for the electrochemical detection of both organic and inorganic pollutants in water. The properties of multi-walled carbon nanotubes (MWCNT) membrane, such as porosity, water permeability and electrical conductivity are exploited for preparing an ultrathin electrode whereby the analyte solution is pumped through the electrode while performing electrochemical or adsorptive deposition of the analyte. The porous flow-through electrode is prepared by filtering a stable MWCNT dispersion through a PTFE filter membrane. The membrane electrode was installed in a syringe filter connected to a pumping system (figure 1). Membranes made of MWCNTs with two different outer diameters have been characterized by different surface techniques (figure 1) as well as by their performance in detecting low concentrations of copper ions. We found that while the sheet resistance of the two types of membranes was not significantly different, however, membranes made of MWCNTs with bigger outer diameter showed better water permeability that allowed higher analyte flow through the electrode. The deposition efficiency of the system was evaluated by performing linear sweep ASV of Cu^{2+}. The collection efficiency could reach values that were close to 100%, yet, with sharp and clear stripping peaks. The system allowed the detection of 6.4 ppb of copper in 30 seconds of deposition time. The lecture will describe the formation and characterization of the flow-through system. We are currently working on the optimization of the system towards a variety of inorganic and organic pollutants in natural samples.

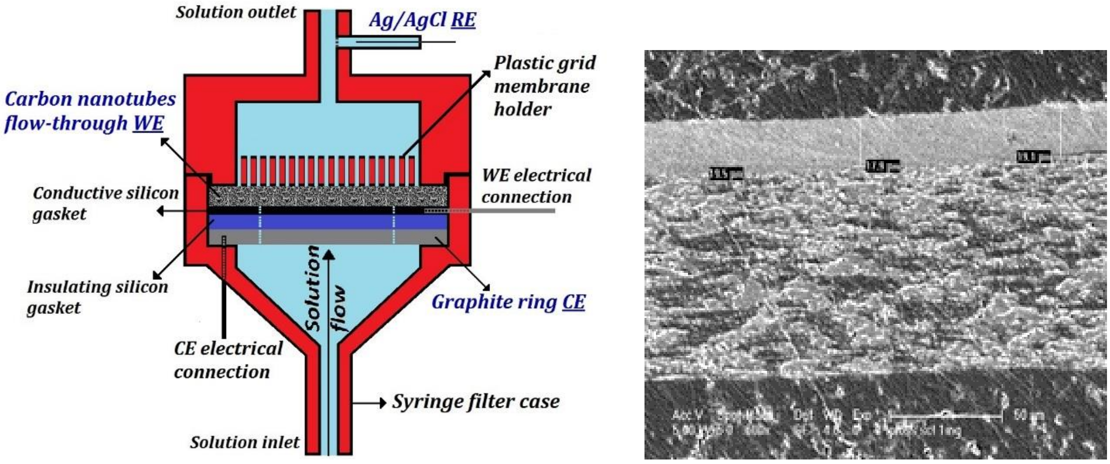

Figure 1: Left – schematics of the flow-through system, right – SEM image of a cross-section of the membrane (the membrane was embedded in epoxy and cut, the upper grey part is the CNT while the lower part is the membrane PTFE support.

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Combining magnetic forces for contactless manipulation of fluids and electrochemical detection in highly integrated microfluidic systems

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New technologies based on transport, actuation and manipulation of fluids and objects in the micro- and nanometer scale are rapidly developing. The enormous scientific and technological interest focuses on lab-on-a-chip approaches which are applicable in analytics and monitoring in medicine, in biology and in the environmental sector. Avoiding mechanical forces, alternative pumping concepts gain in importance. Contactless external driving forces such magnetic fields and field gradients for tailored fluid manipulation and electrochemical and analytical approaches are of interest.

Several microfluidic approaches were employed to prove the concept of fluid manipulation by overlaying magnetohydrodynamic (MHD) effects generated by the Lorentzforce (F_L) and the magnetic field gradient force ($F_{\nabla B}$) [1]. For this purpose suitable microstructures were designed and applicable materials were chosen to generate high magnetic field gradients in the immediate vicinity of the surface of the microfluidic chip. Either soft magnetic or permanent magnetic materials of high saturation or remanent magnetization, e.g. CoFe or FePt, respectively, are electrochemically deposited in microstructured templates. They are utilized to manipulate liquids with paramagnetic ions (e.g. Mn^{2+}) or superparamagnetic particles in microfluidic devices. Potential time transients as a measure for concentration changes between the electrodes with and without superimposed magnetic field gradients are recorded and the enrichment [2] is detected by fluorescence microscopy supported by magnetic field gradient simulation. For driving fluid flow the redox system $K_3Fe(CN)_6/K_4Fe(CN)_6$ which is commonly used for redox-MHD [3] was employed and superimposed by high magnetic field gradients. These are generated by magnetic field gradient templates consisting of µm-thin CoFe stripes which are saturated by a permanent NdFeB magnet. Then, a fluid flow can be controlled by on-off-switching of the cell current originating from the electrodes which is generating a Lorentz force. In combination with the magnetic field gradient template a desired change of velocity and flow direction is realized as well as localized enrichment of ions. To clarify the impact of the magnetic field gradient, the template can be positioned in different orientation and distances in between the electrodes facing each other to reduce or enhance the fluid flow. Video microscopy illustrates the localized "channel-like" flow of the particles); particle velocity measurements quantify the effects further supported by magnetic field gradient and Lorentz-force simulations. The observed change in fluid flow and enrichment is discussed considering the impact of $F_{\nabla B}$ and F_L.

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Development of an Electrophoresis Microchip Coupled to Amperometry for the Analysis of Nitrosothiols

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S-Nitrosothiols (RSNOs) are an important class of compounds due to their role as NO donors in a biological environment. The requirement for their quantification is related to their important pathological and physiological functions [1]. RSNOs are easily decomposed by light, temperature and metal ions, as mercury (Hg^{2+}) and copper (Cu^{+}), and their quantification is mainly based on the detection of the released compounds. Decomposition of RSNO with mercury generates nitrite being detected by colorimetric and electrochemical methods [2]. Herein we propose, for the first time, the analysis of GSNO, an RSNO compound, through its degradation with Hg^{2+} and posterior detection of nitrite by amperometry on an electrophoresis microchip. Experiments were performed in a commercial microfluidic platform and SU8/glass microchip both from *Micrux Technologies*. The decomposition procedure is performed by electrokinetic injection of GSNO (1 mmol/L) in gated mode, applying -800 and -1000 V to sample (S) and buffer reservoir (B), respectively, maintaining waste reservoirs grounded (SW, BW). The voltage was then turned off after 20 seconds and introduction of 5 uL of Hg^{2+} (0.03 mol/L) into BW reservoir was performed (see figure 1A). When the voltages are reestablished, Hg^{2+} migrates backward the channel, since negative polarity is used. Nitrite, resulting from GSNO decomposition in the microchannel diffuses to the BW reservoir and it is detected by amperometry on platinum electrodes positioned at the end of the microfluidic channel. Detection was performed by applying 1.0 V *vs.* Pt. To verify the reliability of the proposed methodology detection of nitrite (1 mmol/L) and analysis of controls experiments, including buffer, Hg^{2+}, and GSNO without decomposition were performed. In all control analysis, no amperometric signals were observed. Therefore, after decomposing GSNO, the observation of any peak should be related to the generated nitrite. The obtained electropherograms are shown in Figure 1B &C. Despite the low intensity of the signal related to nitrite, the viability of the detection of GSNO in a microchip using electrophoresis coupled with amperometry is proved. Next steps should be devoted to the improvement of the signal intensity and the separation of two or more RSNOs before their decomposition.

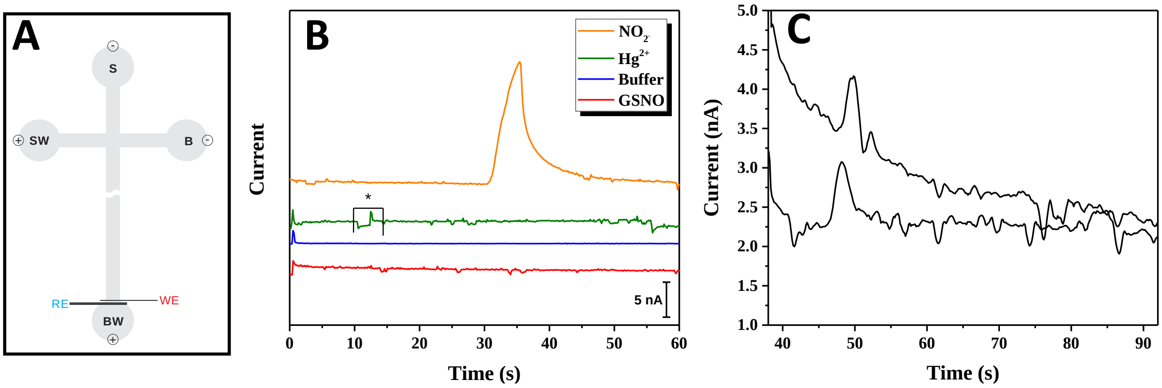

Figure 1 - (A) Scheme of the microfluidic device. (B) Electropherograms obtained for nitrite and control analysis. The area marked with * corresponds to the addition of mercury to BW reservoir. (C) Electropherograms obtained for nitrite from GSNO decomposition with $\mathbf{Hg^{2+}}$. Buffer: Arginine 20 mmol/L pH 5,4 adjusted with acetic acid. Experiments were performed by electrokinetic injection in gated mode, applying -800 and -1000 V to sample and buffer reservoir, respectively, maintaining waste reservoirs grounded. For injection, the voltage on buffer reservoir was turned off by 2 seconds. Detection: 1.0 V vs. Pt.

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New Approaches of Microchip-based Electrochemical Detection for Cellular Analysis

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Our lab has long been interested in the development of robust microfluidic devices that integrate cell culture and analysis, with electrochemistry being used to detect neurotransmitters/modulators in close-to-real-time. This includes the integration of PC 12 cell culture with microchip based analysis (to monitor stimulated exocytosis of multiple neurotransmitters) as well as creation of an endothelium mimic with integrated electrodes for nitric oxide detection. This talk will detail recent technology we have developed around these applications. This includes the fabrication and use of polystyrene-based microfluidic devices, where encapsulation of materials (tubing and electrodes) can be used to improve cell viability and device performance. We will show that a unique feature of this encapsulation approach is the ability to create planar membranes from 3-dimensional pillar electrodes. Work towards using this type of device to monitor cell-to-cell interactions will be discussed. Finally, more recent work on the development of more realistic, 3-dimensionsal cell culture models for microfluidics will be presented. This includes the use of 3D-printing to create an air sheath device to dynamically focus electrospun fibers into a fully closed fluidic channel, with a fibrous scaffold being created on the inner channel wall. We will discuss these results and how electrospinning can be used to easily and quickly create 3D scaffolds that can improve the culture conditions in microfluidic devices.

Automated Microcontrolled Microfluidics with Electrochemical Prostate Cancer Diagnostics

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Designing systems with microfluidics rather than conventional laboratory analysis procedures can lead to miniaturisation, increased throughput and reduced reagent consumption. However, most existing fluid manipulation techniques rely on manual or semi-automated hardware. We describe a system for fully programmable microcontrolled automation of microfluidic platforms that is simple and uses very suitable inexpensive mass produced components; the Arduino microcontroller, high torque servos, commercial syringe pumps and electronically commutated motors. This method greatly reduces both input requirements and labour-intensiveness of microfluidic experimentation. Furthermore, because programmable microcontrollers allow complex processes to be planned, ordered, actioned and stored, the flow performance across different experiments is reproducible. To demonstrate system performance a multiplexed magnetic-particle based immunoassay is performed. Multiplexing biomarkers increases predictive power compared with singleplexing in any cancer. Therefore the system isolates and captures a panel of 8 proteins heavily associated with prostate cancer or progression including PSA, CD-14, ERG, GOLM-1, PEDF-1, IGF-1, VEGF-D and IGFBP-3. The system requires only rudimentary instruction to use and performs integrated amperometric detection in about 30 mins. Results from a 100µL sample volume with ultra-low detection limits in the sub fg ml^{-1} range are possible[1]. Demonstration of diagnostic and prognostic capability will be discussed alongside prostate cancer patient samples.

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PLGA microspheres modified with gold-198 radioisotope - polymer carriers of anticancer drug doxorubicin

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Hybrid spheres consisting of organic polymer and inorganic components have enjoyed great interest in recent years. [1] This is related to the possibility of using such structures in many areas, including in medical therapy and diagnostics. [2] In particular, it is extremely interesting to integrate diagnostic and therapeutic functions, called theranostics. [3] Such spheres may for example be used as drug carriers, and at the same time be used to locate the affected parts in the body.

In the following presentation we report on the novel method of fabrication PLGA microspheres modified with gold-198 radioisotope as a model drug delivery system. The nanoparticles deposited on the surface of the microspheres consist of two gold isotopes: stable (197), and radioactive (198). The gold nanoparticles play several functions. First, they can be used to attach thiol derivative of folic acid, which is intended to facilitate penetration of the PLGA carriers into the tumor cells. Second, the gold-198 isotope emits β^- radiation that can be used for the treatment of tumors. Finally, due to the emission of gamma rays by gold-198, the drug carriers can be used in SPECT imaging (single-photon emission computed tomography). The resulting microspheres can be additionally loaded with an anticancer drug (doxorubicin).

Polymeric drug carriers have been precisely characterized by a number of physicochemical techniques such as transmission electron microscopy, X-ray photoelectron spectroscopy, fluorescence spectroscopy, thermogravimetry, gamma spectroscopy, electron tomography. Additionally, based on FRAP measurements, the permeability of PLGA microspheres on doxorubicin in different pH environments was determined. Furthermore, electrochemical studies allowed to determine the release profile of doxorubicin from drug carriers as a function of temperature and pH of the environment.

In vitro studies of the cytotoxic activity of drug carriers (radioactive and non-radioactive) have been performed to investigate the effect of β^- radiation and doxorubicin on human tumor cell MCF-7 line and human normal cell CRL-1790 line. Cell viability was determined by MTT assays. Synergy between doxorubicin and β^- radiation were also investigated to determine whether such combination of therapeutic compounds would enhance antitumor action while increasing selectivity between tumor and normal cells.

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The Development of a Mathematical Model for Electrochemical Impedance Response of Continuous Glucose Monitor

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Enzymatic biosensors commonly used for management of diabetes must be maintained in good working condition to provide reliable real-time data. Electrochemical impedance spectroscopy has potential applications in *in-vivo* sensor diagnostics and sensor calibration.

In the present work, a mathematical model for the impedance response of glucose oxidase electrochemical biosensors has been developed [1]. The coupling between the homogeneous reactions and heterogeneous reaction has been considered in the model, which involves four homogeneous enzymatic catalytic reactions transforming glucose and oxygen into gluconic acid and electroactive hydrogen peroxide and one heterogeneous reaction of electrochemical oxidation of hydrogen peroxide on the electrode.

The electrochemical system was modeled mathematically as a one-dimensional boundary value problem and solved by using Newman's BAND algorithm [2]. This model accounts for two layers, a layer adjacent to the electrode where the glucose oxidase is immobilized and the glucose-limiting membrane (GLM), which controls the amount of glucose participating in the enzymatic reaction. The steady-state concentrations of reacting species were calculated, including the concentrations of glucose, oxygen, hydrogen peroxide, oxidized and reduced enzyme, and enzymatic-complex intermediates. The solution of the nonlinear coupled set of differential equations for the steady-state was used as input for the set of coupled linear differential equations for the frequency-domain calculations. The corresponding impedance was calculated for each specified frequency [3].

The model was used to explore the influence of system parameters such as interstitial glucose concentration and enzymatic rate constants on limiting current, reaction profiles, and diffusion impedance.

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Telomerase Activity Sensing from Cancer Cells using Label-Free Electrochemical Impedimetric Microchip

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The enzyme Telomerase is present in about 85% of human cancers, which makes it an excellent biomarker for cancer detection. Using a single stranded DNA probe specific for Telomerase binding and reverse transcription tethered to an interdigital gold electrode array surface, the chromosome protection provided by the Telomerase was replicated and followed by Electrochemical Impedance Spectroscopy (EIS) as an unlabeled biosensor. Using a system designed in-house, easy and affordable, the impedance measurements were taken while incubating at 37 °C and promoting the DNA probe elongation. This resulted in up to 14-fold increase in the charge transfer resistance when testing a Telomerase-positive nuclear extract from Jurkat cells compared to the heat-inactivated Telomerase-negative nuclear extract. The electron transfer process at the Au electrodes was studied before and after the elongation, after 4 months in contact with the Telomerase-positive nuclear extract, and after desorption of the non-specific bindings. In this work, we designed and fabricated a small and robust biosensor microchip based on two interdigital electrodes and a temperature sensor, which were connected through a female USB type-A connector. Taking advantage of the Telomerase-positive nuclear extract (Jurkat cells) and nuclear lysis buffer, we showed the detection of Telomerase activity without the addition of redox or fluorescent labels or other reagents. Under 20 minutes, we obtained up to 14-fold increase in the electrochemical signal when testing a Telomerase-positive solution compared to a heat-inactivated Telomerase-negative solution, using EIS. We believe that translating this biosensor microchip into a more affordable substrate, with the addition of a simple impedance measurement circuit, can lead to an easy and fast cancer detection medical device for point-of-care applications.

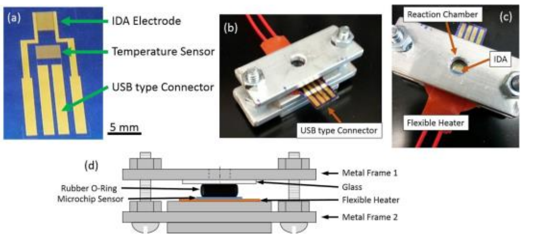

Figure 1. Images of (a) the biosensor microchip made by photolithography, (b) and (c) the system used for heating the connecting the biosensor, and (d) a scheme of our device closed and ready for measurements.

Acknowledgement

This research work was supported in part by NSF-Chemistry Grant No. CHE-1152940.

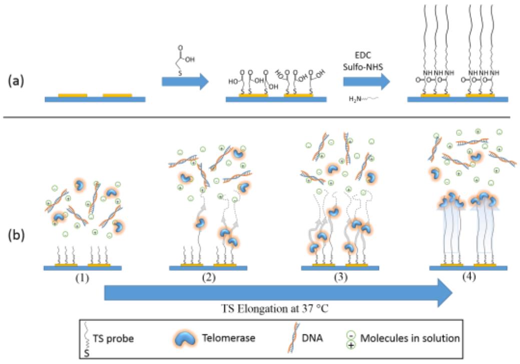

Figure 2. (a) Procedure for the tethering of the TS probes and (b) the mechanism responsible for the expected change in the impedance during incubation at 37 °C.

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Use of an electrochemical sensor in the detection of nitric oxide in periaqueductal gray during optogenetic stimulation

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The neuromodulator NO plays an important role in threat signalization for species survival which is known as innate fear[1]. In this context, the present work show the detection of NO released in rat brain after optogenetic stimulation using a Pt microelectrode. In this way, a Pt microelectrode (r = 3 µm) was fabricated and its external body was covered by silver epoxy to get a dual function microelectrode, where the silver coat acts as a pseudo reference electrode. Firstly, experiments involving the electrochemical behavior of NO was carried out (*in vitro*) recording voltammograms in an oxygen-free PBS solution saturated with NO (pH = 7,4). The voltammogram obtained showed an oxidation peak at around 0.8 V vs Ag (not shown). After that, *in vivo* experiments were carried out inserting the microelectrode in the dorsolateral periaqueductal gray area (PAG) of the rat brains and voltammograms were recorded before and after the laser stimulus (Fig. 1). The voltammogram at time zero corresponds to a basal situation with no optogenetic stimulation and no defined faradaic process was noticed (black line). A different situation was observed in voltammograms recorded after 40 minutes (red line) and 80 minutes (blue line) after optogenetic stimulus. In this situation, a current increase in the same potential range corresponding to NO anodic oxidation was obtained in *in vitro* experiment. The same procedure was performed in a non-infected rat and no current increase was noticed after the optogenetics stimulation (not shown). Based on results obtained in experiments performed with the microelectrode implanted in the brain region of the rat, one can conclude the current increase after the optogenetic stimulus can be regarded as due to an increase of NO released in the PAG region. Hence, the light stimulus mimics the situation of innate fear in animal.

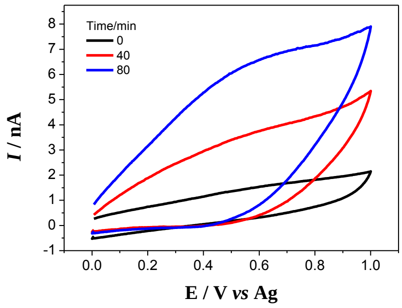

Figure 1: Voltammograms recorded at 3 different times: zero (black), 40 minutes (red) and 80 minutes (blue) after the stimulation. v=50mV s^{-1}

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Micro and Nano-structured Materials shape Living Cells: a Scanning ElectroChemical Microscopy study

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The shape and morphology are related to the health status of the cell. Diseases, senescence, and the presence of toxic compounds cause morphological changes. Mechanical forces involved in the interaction with the microenvironment and cell adhesiveness influence morphology. Variations of morphology and motility are present in all cancer cells and are involved in metastasis.

Cells adhesion to solid substrates is a multistep and complex process. It involves surface receptors, signalling elements and cytoskeleton. When a cell attaches to a solid substrate, it spreads over the surface. The degree of adhesion can be expressed in terms of shape parameters. Cells sense the chemistry of their microenvironment and modulate their shape.

We employed 2D nanomaterials: organic monolayers with a high surface coverage >90% [1] as culturing surfaces/environment for normal and cancer cells.

We used Scanning Electrochemical Microscopy (SECM) to study the local reactivity [2] and conductivity [3] of the surfaces. Using SECM, fluorescence microscopy and AFM we correlated the local physical chemical characteristics of the environments with the cancer and normal cellular shapes.

The investigation of the interactions of living cells with 2D environments can gain fundamental knowledge on the type of environment that retards or accelerates diseases and degeneration and can determine the chemical forces that drive cell recruitment on a bioactive surface.

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Interaction of nanoparticles with biomembranes

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Biological membranes, which protect all cells, tissues and organs, are natural barriers that drug carriers like nanoparticles must pass through before reaching the site of their action. In order to delivery drug modified nanoparticles into the specific tissues, before reaching such sites they must pass through biomembranes. Despite intensive studies in molecular biology and medicine at the present time, the mechanism of the nanoparticles' penetration through biological membranes and the influence of this process on the cell are not well understood. These results are of critical importance to understand the mechanism(s) responsible for the introduction of therapeutic agents into the cell and to determine their effect on the organization of the cell membrane constituents.

The nanoparticle carriers can interfere with the organization of the biological membrane, leading to passive penetration through their barrier. The study of the physicochemical properties of drug carrier and their interactions with biological membranes provide deeper understanding of the mechanisms involved in this phenomenon.

The purpose of our studies was to investigate the interactions of nanoparticles with model cell membranes for better understanding of drug carrier capabilities as well as possible cytotoxicity.

We have reported interactions between Superparamegnetic Iron Oxide Nanoparticles (SPIONs) or silver nanoparticles and different types of biomimetic membrane systems: monolayers on a water surface (Langmuir monolayers), monolayers after their transfer onto a solid substrate (Langmuir-Blodgett monolayers) and bilayer lipid membranes obtained by the Langmuir-Blodgett/Langmuir-Schaeffer method. A systematic experimental studies of such systems were carried out with complementary techniques, such as: Langmuir method coupled with the Brewster Angle Microscopy (BAM), Electrochemical Impedance Spectroscopy (EIS), Surface Enhanced Raman Resonance Spectroscopy (SER(R)S), Fluorescence Anisotropy Imaging Microscopy (FAIM) or Fluorescence Recovery After Photobleaching (FRAP) technique. Considerable effect of nanoparticles induction on the phase behaviour of mixed monolayers, increasing also the structural reorganization and inducing changes in the formation of domains was presented.

Characterization of Ti-30Nb-13Ta-2Mn Alloy for biomaterials applications

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Abstract

Development of T-based foams with low elastic modulus has increased its scientific and technological relevance due to the evident need to avoid the stress shielding problems related to stiffness mismatch with respect to bone. In this work we studied the synthesis and characterization of foams of CP-Ti and Ti-30Nb-13Ta-2Mn alloy. Foams were obtained using NaCl as space-holder. Powders and space-holder were mixed together and compacted from 200 to 800 MPa stress. NaCl particles were removed from the green compacts by submerging samples in distilled water at 60 °C (5 cycles of 4h). The green compacts were sintered at 1300 °C for 3 h in Ar atmosphere. Foams were characterized by surface analysis, such as X-ray diffraction and scanning electron microscopy. In addition, electrochemical measurements such as open circuit potential curves, polarization curves and electrochemical impedance spectroscopy were in Ringer solution. Results showed that Ti-based foams with tailored heterogeneous pore distribution may be obtained using space holder method. The electrochemical results showed that the corrosion potential was shifted to more positive values as a function of exposure time and not significant effect was observed in the corrosion current. In addition, the EIS data revealed a CPE behavior of the foams for all exposure time and the impedance modulus at low frequency range was influenced by the compaction stress, which could be related to the stress raiser.

Ackowledgements

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Voltammetric Ion-Selective Electrode for Potassium Ions

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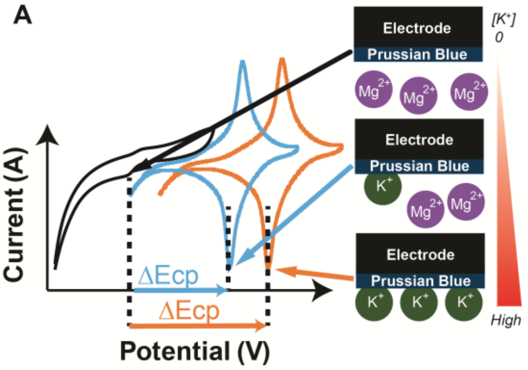
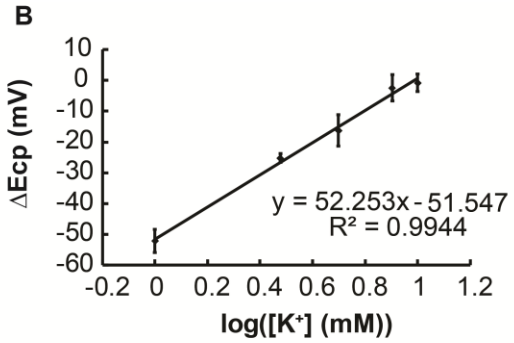
The quantification of electrolytes, such as magnesium, calcium, potassium, is relevant for identifying health conditions. In particular, potassium levels in blood outside of the “healthy range” (3.5 – 5.0 mM) are indicative of abnormal heart rhythms, and can be used to guide appropriate treatment in cardiac emergencies. For preventative care applications, micronutrients can also be used to assess dietary deficiencies. Ion-selective electrodes are currently used in clinics and laboratories for the quantification of different ions, but are fragile, subject to interference from biological samples, often expensive and require calibration and maintenance. We are developing a paper-based device for the electrochemical detection of potassium. Paper-based platforms are useful for point-of-care bioanalysis, particularly resource-limited settings, due to their simplicity, low cost, portability and disposability.

Our assay is not based on usual potentiometric methods, but on voltammetry; we are monitoring the shift in the redox potential of a sensing layer due to the concentration of the targeted ion in the sample. For potassium quantification, we quantified the redox reaction of an electrodeposited Prussian blue layer and observed a proportional shift in the potential of the cathodic peak due to the potassium ion concentration (Fig. A). We successfully tested solutions containing potassium ions in the health-relevant range (0-10 mM) on paper-based devices and obtained reproducible trend correlating the shift in potential to the concentration of potassium (Fig. B). We also observed negligible interference from sodium and magnesium ions. The quantification of potassium was possible in a mixture of biologically relevant electrolytes (sodium, calcium and magnesium) present at high concentration. The fabrication process of our sensors has been optimized in terms of pH, deposition of Prussian blue, and choice of filter paper. This voltammetric method for ion quantification also permits further miniaturization. Testing of human serum samples, as well as assessment of reproducibility and specificity of the paper-based devices is ongoing. This paper-based device for detection of potassium will represent the first of a collection of solid-state voltammetric micronutrient sensors our group is developing.





A point-of-care device and a cell phone app in the diagnosis of neurological diseases

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Each year an estimated 1.5 million people in the United States alone sustain a nonfatal traumatic brain injury. Approximately 80% of these injuries are classified as mild with loss of consciousness (LOC) lasting less than 30 minutes, an initial Glasgow Coma Score (GCS) of 13 to 15, and posttraumatic amnesia lasting less than 24 hours. Increasingly, mild traumatic brain injury (mTBI) has been recognized as a major public health concern with an economic impact accounting for about 44% of the $56 billion annual cost of TBI in the US. Recent research and the implemented Scandinavian guidelines show that serum S100B may serve as a good pre–head computed tomography (CT) screening test because of its high sensitivity (negative predictive value) for abnormal head CT scans. Since the vast majority of CT scans performed on victims of mTBI are negative (no findings), a test allowing to perform fewer scans would translate into substantial savings and a reduced amount of unnecessary exposure to X rays. In addition, if implemented where CTs are not available, such a test will greatly reduce the need to transport mTBI victims by ambulance or air.

S100B is used as a marker of good prognosis after traumatic brain injury in Europe and in a few US centers. The main problems are that this test is as of today not FDA approved, nor is there a point-of-care (POC) device available. While the use of S100B can be expanded to many neurological disorders, we decided to focus on concussions because of available data from Europe showing excellent results in people with minor TBI and a recent set of meta-analysis papers showing the same. We have purposefully chosen a condition in which standard evaluation at the site of injury is not possible. Methods exist to assess concussions in football (Impact test; SCAT2) but these are highly subjective and do not provide a clear cut picture of the risks the patients have after a head hit. Attempts have been made to predict cognitive decline after repeated mTBI or other neurological events, but results have been so far inconclusive.

In conclusion, we developed a blood test and a cell phone interface that allows to rule out acute or long-term consequences of concussive or mild head hits. A point of care measurement of the marker S100B will rapidly allow to rule out concussions or traumatic brain injury in athletes, soldiers, or civilian populations. An added feature consists of measuring antibodies against S100B in the same sample, which are indicators of poor long-term prognosis.

Electrochemical diagnostic devices based on organic and printed electronic integration

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Point of care diagnostics was completely revolutionised through the mass production of printed sensor strips in combination with electrochemical transduction. Glucose biosensors could be considered ahead of their time in the field of organic and printed electronics. With the development of a broad array of new functional materials with characteristics such as organic, nanostructured solution processability, in combination with printing and low cost 2D and 3D system integration approaches, the field is now developing rapidly, allowing the fabrication of novel, integrated systems for new diagnostic applications.

Our research group has been developing a number of point-of-care diagnostic devices based on the application and integration of electrochemical sensors in organic and printed electronics. Impedimetric sensors based on inkjet-printed polyaniline nanoparticle-modified electrodes have been used as the basis of a breath diagnostic device for measuring breath ammonia.[1] The sensors were capable of measuring ammonia down to several parts per billion in human breath and were studied in haemodialysis patients.[2] This technology is being commercialised and being used to address a number of healthcare challenges. This concept has also been extended to the measurement of ammonia in blood,[3,4] which has remained a challenging analyte in point of care diagnostics. Other print-processable materials are now also being developed to measure other trace breath gases such as acetone for monitoring diabetes.[5]

Fully integrated sensor systems for cholesterol[6-9] are also being developed by combining organic and printed electronic components such as biosensors, batteries[10], displays and organic circuits[11] to create fully integrated, instrumentless devices. The 'SIMS' device is being developed which aims to transform the simplicity with which blood cholesterol levels can be measured, with the aim of improving the management of hypercholesterolaemia.[12]

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Electrochemical detection of uric acid in human serum using glassy carbon electrodes modified by gold nanoparticles and poly(amidoamine) dendrimers and its application to the clinical diagnosis of hypertensive disorders of pregnancy

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Glassy carbon electrodes (GCE) were modified by cysteamine-capped gold nanoparticles (AuNp@cysteamine) and PAMAM dendrimers generation 4.5 bearing 128-COOH peripheral groups (GCE/AuNp@cysteamine/PAMAM), in order to evaluate their capabilities as electrochemical detector of uric acid (UA) in human serum samples. The results showed that concentrations of UA detected by cyclic voltammetry with GCE/AuNp@cysteamine/PAMAM were comparable (deviation <±10%; limits of detection and quantification were 1.7×10^{-4} and 5.8×10^{-4} mg/dL, respectively) to those concentrations obtained using the typical uricase-based enzymatic method [1]. Furthermore, results of UA detected by DC-potential amperometry demonstrated that the presence of dendrimers in the GCE/AuNp@cysteamine/PAMAM system minimizes ascorbic acid and serum proteins interferences during UA oxidation, thus improving the electrocatalytic activity of the gold nanoparticles [2]. On the other hand, GCE/AuNp@cysteamine/PAMAM were employed for detecting UA in serum donated by pregnant women having gestational hypertension or preeclampsia (the group of “cases”) and from health pregnant women (the “control” group). The new data confirmed significant differences between the detected UA levels ($p<0.001$) in the groups of “cases” (6.2±0.5mg/dL) and “control” (4.2±0.9mg/dL), respectively [3]. Therefore, the using of GCE/AuNp@cysteamine/PAMAM for applications in clinical diagnosis offers a non-enzymatic route to detect serum UA with a high reliability.

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Pt-Grown Carbon Nanofibers for Enzymatic Detection of Glutamate

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Vertically aligned carbon nanofibers (CNFs) have shown great promise when used as electrochemical biosensors [1]. However, it is often mandatory to treat CNFs with strong acids to remove residual metal catalyst particles before they can be used for sensing applications. Unfortunately, these leftovers cannot be completely removed as shown in [2]. Strong oxidative treatment can also damage the CNF structure. Instead of trying to remove the metal particles we have utilized Pt as the catalyst to fabricate application-specific carbon nanostructures for H_2O_2 sensors, where Pt is meant to stay in the structure and form an integral part of the sensor. We have recently demonstrated the high sensitivity of these materials towards H_2O_2 [3]. Here we will further characterize these novel Pt-containing CNFs and assess their use as a platform for enzymatic detection of glutamate, which is the most important excitatory neurotransmitter in mammalian brain. SEM micrograph in Figure 1 shows that the grown fibers formed a forest of vertically aligned fibers with height of approximately 400 nm. The Pt particles were located at the tips of the fibers. Initial results from XPS analysis revealed that the Pt content was approximately 7 %. Presence of Pt was further verified electrochemically as the samples show clear Pt features in 0.1 M $HClO_4$ with distinct oxide and hydrogen regions (Figure 2A). Moreover, Pt-CNFs showed reversible behavior in 1 mM $Ru(NH_3)_6Cl_3$ in 1 M KCl (Figure 2B). Amperometry was utilized to assess the sensitivity and response time of these materials towards various amounts of glutamate.

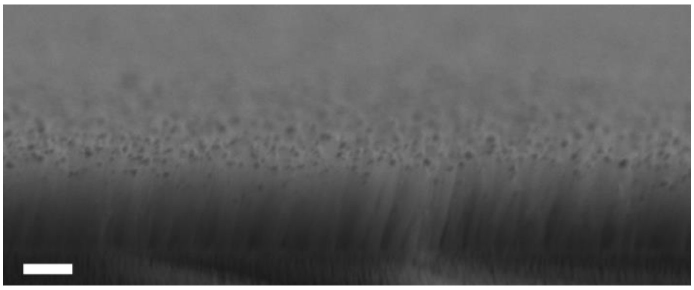

Figure 1. SEM micrograph of Pt-CNFs. Scale bar is 200 nm.

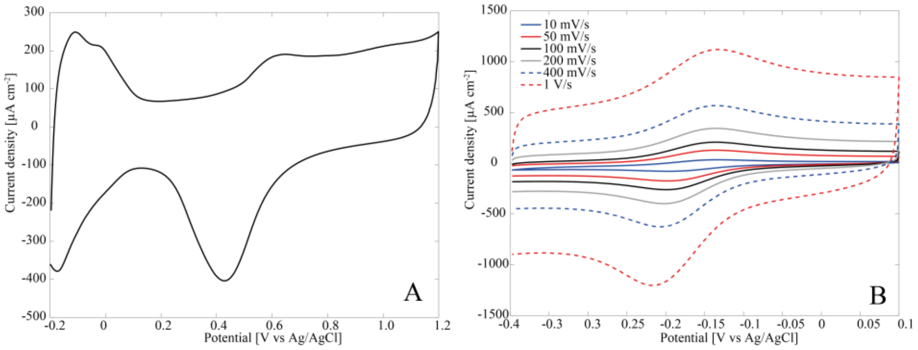

Figure 2. A) Cyclic voltammograms of Pt-CNF sample in 0.1 M $HClO_4$ showing clear Pt features. B) Pt-CNFs show reversible behavior in 1 mM $Ru(NH_3)_6Cl_3$ at several scan rates.

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Understanding electrified interfaces as a prerequisite for improved DNA hybridization detection

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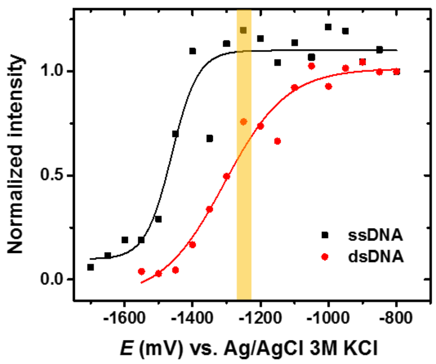
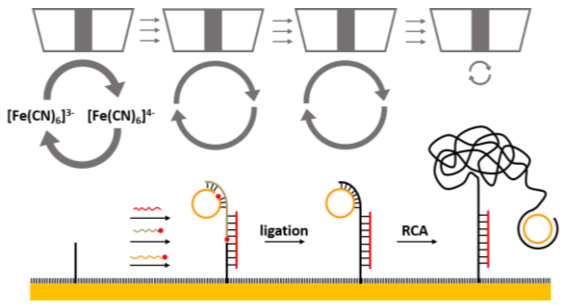
Understanding the properties of an electrified interface at which a single-stranded capture DNA strand has to be immobilized at a well-defined surface coverage, followed by hybridization of a target strand and an – if possible label-free - hybridization detection with high sensitivity and accuracy is undisputable of high interest. Related DNA assays are becoming even more important considering the progress of multi-resistant organisms and the lack of suitable antibiotics.

In this presentation, we want to demonstrate that preparation of DNA chips for detection of multiple DNA sequences becomes feasible in which the whole 32-electrode chip is exposed simultaneously to each solution during the modification with different DNA probes using Au-S chemistry and potential-assisted surface modification procedures[1,2]. The procedure is based on ion stirring created by fast switching between carefully selected potentials, positive and negative from the potential of zero charge of the DNA-modified Au surface. Ion stirring leads to significantly accelerated immobilization of both charged and uncharged molecules and hence allows to reproducibly control surface modification in a very short time. Both DNA immobilization with desired coverage and subsequent thiol passivation are achieved in the range of seconds to minutes. In addition to the very efficient surface passivation, fast potential pulse-assisted surface cleaning prevents cross-talk between electrodes.

One possibility to unequivocally detect single nucleotide polymorphisms is based on dehybridization and the thermodynamic stability of double-stranded (ds) DNA defines the threshold of DNA dehybridization. We demonstrate a specific dehybridization potential which allows SNP analysis by observing dsDNA dehybridization kinetics on a Au nanovoid modified SERS-active electrode surface using in-situ SERS measurements. Cy3-labeled target DNA was employed as a Raman reporter to observe dehybridization.

In another approach, an isothermal DNA amplification approach such as rolling circle amplification (RCA) using a circular DNA sequence as a template for DNA polymerase produces a long repeating product that can be used for modulating the properties of the electrified interface as a basis for high-sensitive DNA detection. Coupling RCA with scanning electrochemical microscopy (SECM) read-out for label-free DNA hybridization detection becomes possible with at least micrometer resolution. Significant increase in the blocking of the electron-transfer rate of a free-diffusing and negatively charged redox species at the DNA-modified surface by the formed RCA product is the basis of this approach.





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ELECTROCHEMICAL DETECTION OF BIOFILM DISPERSION

Antibiotic resistance due to bacterial biofilms is a major health concern. Biofilms are a protective layer of DNA, proteins, polysaccharides, and/or other macromolecules that act to block and/or remove foreign antibiotics from accessing underlying bacteria. [1-3] An estimated 80% of human bacterial infections are biofilm related, resulting in 500K annual deaths.[2] Several different compounds have been developed to treat biofilm-related infections, which act through various mechanisms to disperse the biofilm allowing use of established antibiotics. Electrochemical methods can be used to accelerate anti-biofilm compound discovery by providing improvements to established assays.

We will present a simple electrochemical method designed to assay biofilm dispersal from a variety of established anti-biofilm compounds, both small molecules and antimicrobial peptides. Layer by layer (LbL) techniques were utilized to immobilized medically important biofilm forming bacteria on pyrolytic graphite (PG) electrodes. Both redox active (*Pseudomonas aeruginosa*) and redox inactive (*Streptococcus mutans*) bacteria were immobilized on the electrode. Detection strategies were tailored to the specific bacteria utilized, but in both cases, anti-biofilm activity was monitored via square wave voltammetry (SWV) peak current changes at representative potentials as a function of anti-biofilm compound exposure time. Validation of the electrochemical method was performed utilizing an established 96-well plate biofilm dispersal assay. Overall, dispersal kinetics data generated using the electrochemical assay were consistent with inhibition and established biofilm dispersal constants determined using the 96-well plate assay. Therefore, monitored electrochemical changes were based on biofilm dispersal by the test compounds; however, material use and significant analysis time improvements were realized with the electrochemical approach.

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Glucose Monitoring: Enzymatic vs. Non-enzymatic

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A (bio)sensor is an analytical device which integrates a chemical or biological recognition element with a physical transducer to generate a measurable electrochemical, optical, acoustical, mechanical, calorimetrical, or electronic signal proportional to the concentration of the analytes. It has been studied intensively and utilized extensively in various applications ranging from public health and environmental monitoring to homeland security and energy-related area.

Diabetes is a metabolic disorder and a major world health problem. As stated by International Diabetes Federation, there are over 382 million people worldwide living with diabetes in 2013. Due to the extremely large financial burden caused by diabetes and its serious health complications, the detection of glucose is becoming incredibly important in managing diabetes and reducing its financial costs.

This presentation will first outline the challenges for in vitro and in vivo glucose monitoring in battling diabetes, and then discuss our recent research activities for the development of enzymatic and non-enzymatic glucose sensors based on electrochemical and optical methods. Finally, the future research direction for in vivo, long-term glucose monitoring will be laid out and discussed.

Surface- and Core-Modified Nanoferrites as Tools for Magnetic Field-Assisted Targeted Drug Delivery. Electrochemical and Spectroscopic Studies

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Superparamagnetic nanoparticles (SPNs) have attracted wide attention due to their unique magnetic properties, high surface area-to-volume ratio, and the ability to control their core and surface chemistry. The superparamagnetic behavior makes SPNs ideal candidates as carrier platforms in magnetically-driven targeted drug delivery and hyperthermia. In such a therapeutic approach, the drug/SPN carrier conjugate can be guided to the specific site with an aid of magnetic field, release the drug payload or/and become localized sources of heat, leading to the cell death. If the SPN core is labelled with “soft” β^- emitting radionuclide (e.g., ^{161}Tb), it will allow for simultaneous direct irradiation of tumor, solely from within its tissue. This combined, multimodal approach is particularly promising in the treatment of tumors resistant to classical therapies.

We present here three examples of applications of SPNs: **i**) hydrophilic nanoparticles conjugated covalently with biologically active molecule - a “vector” peptide targeting specific tumors, **ii**) hydrophobic SPNs confined only within the bilayer lipid membranes of liposomes and cubosomes, **iii**) Tb-doped SPNs – initial studies of their behavior from the point of view of synergic effect of radiotherapy and hyperthermia. For the first type of studies, (**i**), we used an anti-angiogenetic heptapeptide – ATWLPPR (A7R), recognizing selectively the co-receptor neuropilin-1 (NRP-1) on the endothelial cells and blocking the vascular endothelial growth factor A (VEGF A). For the second mode, (**ii**), the hydrophobic SPNs were confined within the lipid bilayers of magnetoliposomes and magnetocubosomes loaded with doxorubicin – a potent anti-cancer drug. Such systems appeared to be prone to mechanical rupture and drug release in a low-frequency alternating magnetic field. The kinetics of drug release was followed with electrochemical (CV and DPV) and fluorescence techniques. We show that the drug release proceeds through the rupture of lipidic carriers, induced by mechanical vibration of SPNs, rather than through the localized heating of nanoparticle vicinity. Finally, the initial studies of “cold”, Tb-doped magnetic nanoparticles, (**iii**), are presented, showing their luminescent behavior. Apart from preserving their superparamagnetic behavior, luminescent properties of Tb-doped SPNs can be used for labelling of living cells, monitoring carrier distribution both *in vitro* and *in vivo*.

All three types of systems were tested against the selected normal and tumor cell lines *in vitro*, showing their potential suitability for magnetically-driven targeted drug delivery.

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Electrochemical Quantification of Neurotransmitters in Live Embryonic Zebrafish

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Understanding the mechanisms involved in neurological signaling and function is of great physiological importance. Such studies require the availability of effective methods to accurately detect and quantification of biological markers in relevant biological models. This presentation will describe the use of zebrafish embryos as a model biological target for detecting physiological biomarkers and mechanisms of neurotransmission in the digestive system. We used differential pulse voltammetry with implanted carbon fiber microelectrodes to monitor serotonin and nitric oxide release in intact zebrafish embryos during early development (5 dpf). The microelectrodes were implanted at various locations in the intestine of zebrafish embryos. Measurements were performed in intact live embryos without additional perturbation beyond electrode insertion. The sensor was able to quantify pharmacological alterations in serotonin and nitric oxide release and provide the longitudinal distribution of these species along the intestine with high spatial resolution. The variation of neurotransmitter levels was confirmed by immunohistochemical analysis. Results of these assays and the potential of this method to quantify biomarkers of inflammation and oxidative stress will be discussed. This work demonstrates the potential of electrochemical microsensors for in vivo monitoring of intestinal neurotransmitter levels in intact zebrafish embryos.

Development of Miniaturized Non-gassing Electroosmotic Pump for Drug Delivery

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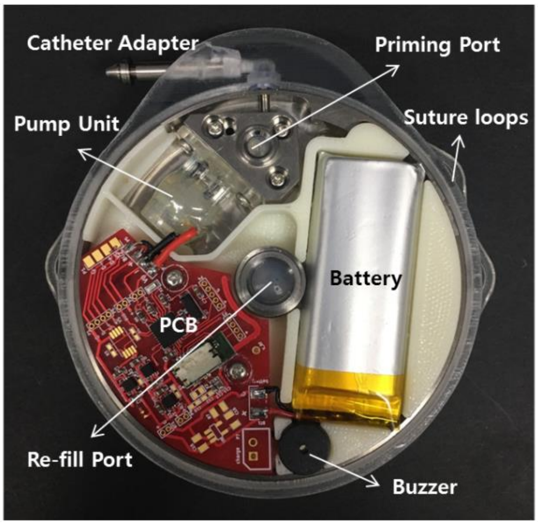
Non-gassing electroosmotic pump is developed and applied for implantable intrathecal pump. The pump aims for the delivery of morphine directly into the space between the spinal cord and the protective sheath surrounding the spinal cord. Medications delivered in this manner can minimize the side effects often associated with the higher doses used in oral or intravenous delivery. The electroosmotic pump could control the dosing of 0.05~4.0 mL/day delivery by controlling the pulse width, pulse height and resting time. In addition to the wide range of flow rate, low-power operation and long-term stability were obtained and confirmed the electroosmotic pump is suitable for intrathecal pump. The prototype is developed as shown below (top opened).



Enabling Bioelectrochemistry for In Vivo Analysis

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The development of new strategies and methodologies to directly, selectively, and sensitively record chemical signals of neurons involved in brain functions has drawn more and more attention because recording of the dynamic change of chemical signals affords a platform to understanding the chemical essence involved in various brain functions, for example, neurotransmission and the diagnosis and therapy of diseases. Electrochemical methods based on bioelectrochemical mechanisms are particularly attractive for probing brain chemistry with a high temporal and spatial resolution. This topic will focus on our attempts on enabling bioelectrochemistry for in vivo analysis, covering the fundamental aspects of bioelectrochemistry with direct electron transfer of laccase as example, recent updates in biofuel cells, and new electrochemical methods for in vivo analysis based on new biosensors and biogenerators. The biogenerators are envisaged to be one kind of novel neurochemical sensing technology, providing a new tool to understanding chemical essences underlying physiological and pathological processes. With the development of the interfacial bioelectrochemistry and energy conversion technologies, some kinds of new biogenerators will be developed to work efficiently in living systems.

Keywords: Bioelectrochemistry, Biosensors, In Vivo Electrochemistry

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Assessing CD62L Protein as a Biomarker in Bladder Cancer Patients

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Bladder cancer patients face a 5-year survival rate of 80% or less than 35% depending on early or late stage diagnosis of the disease respectively; making early detection critical to patient outcome. A prior study identified L-selectin (CD62L) as a potential protein biomarker for aggressive bladder cancer. Here we describe a previously established bead-based microfluidic immunoarray to quantify soluble CD62L expression in patients with varied stages of the disease, as high-grade muscle invasive tumor cases may exhibit overexpression of this protein. Detection antibody and enzyme-label decorated magnetic beads capture the protein antigen online, followed by incubation with surface bound capture antibody on an 8-electrode screen-printed carbon array. A hydroquinone/hydrogen peroxide activator/mediator mixture is injected for amperometric signal detection. Our analysis of 40 patient samples shows an overall increase in CD62L concentration with progression of disease stage but observes a drop-off for late stage, high-grade metastatic tumors.

On demand release of antibiotics from porous reduced graphene oxide modified flexible electrodes

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The development of a general platform for efficient on-demand delivery of a variety of drugs remains an unachieved task. While a large variety of stimuli responsive vehicles for drug delivery at the nano- and microscale have been designed and tested, for each drug, special formulations have to be designed taking into consideration the physico-chemical properties of the therapeutics. The development of a loading matrix allowing the integration of a variety of active principles would consequently be of high interest. Considerable efforts have been directed in recent years towards the use of porous structures as drug loading matrices due to their high surface area, tunable pore size and well-defined surface architectures.[1-3] Porous graphene-based nanostructures such as porous reduced graphene oxide (prGO) have shown to provide next to high mechanical strength also superior electrochemical properties when compared to rGO. As the resident porosity increases the specific surface area, higher drug loadings are expected to be achieved on such nanostructured materials.

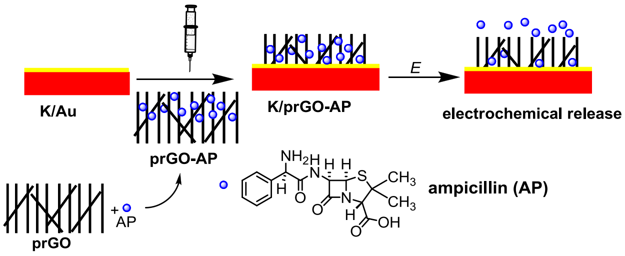

Figure 1: Schematic illustration of the fabrication of flexible electrical interfaces modified with antibiotic-loaded porous reduced graphene oxide (prGO) for electrochemical triggered on demand release.

In this work, we demonstrate the interest of porous reduced graphene oxide (prGO) for loading with different drugs with a special focus on antibiotics as therapeutic loading agents. Drop-casting a prGO-antibiotic loaded matrix onto electrodes made of gold coated Kapton (K/Au) (**Figure 1**) results in flexible interfaces, which can be electrochemically addressed. Indeed, despite all advantages that electrochemistry offers, such as low-cost, excellent control over applied potential or current, miniaturization etc., only a handful of electrochemical-based delivery systems have been shown to release drugs at therapeutic relevant concentrations.[4-5]

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Reliable and Non-invasive Electroanalytical Biosensing of Cancer Biomarkers for Early Diagnosis

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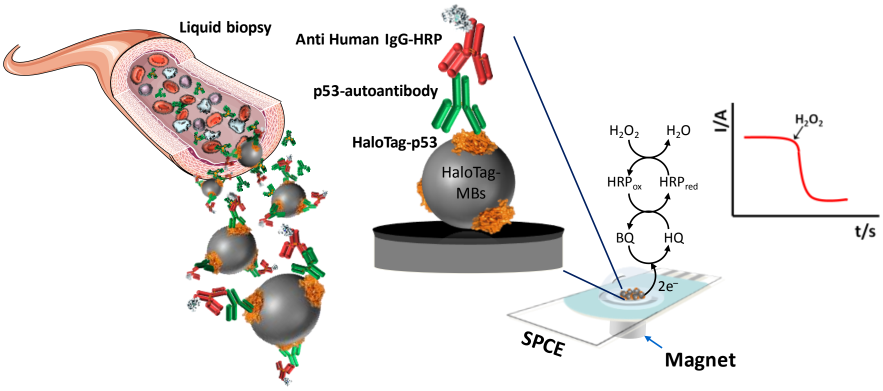
Nowadays, it is widely accepted that the prompt diagnostic of a certain disease is a key factor in the patient survival. Among the many diseases affecting mankind, cancer is of great relevance due to its high incidence, prevalence and mortality worldwide. Cancer is the cause of over 8 million deaths worldwide and the second leading cause of death just behind cardiovascular disease. Although, substantial progress has been made in the last years for prevention and treatment of different cancer types, cancer incidence and prevalence is increasing worldwide due to the continuous growth and aging of the global population and the maintenance or the increase in smoking, obesity, and risky dietary patterns. Therefore, the implementation of non-invasive massive population screening programs could help reducing cancer mortality due to the detection at early stages, when the disease can be efficiently treated and cured in more than 90% of patients of the eight most common cancer types. Therefore, the demand of efficient, simple and disposable devices with short response times, low-cost, and suitable to perform decentralized and reliable determination of cancer biomarkers has increased tremendously during the last years.

Within this context, different strategies implying the development of electrochemical platforms for the sensitive, selective and rapid biosensing of single or multiplexed cancer-related biomarkers of different molecular levels will be discussed in this lecture. In particular, the main features of novel sensing platforms for determination of miRNAs [1-3] and autoantibodies [4] against tumor associated antigens (TAAs) (see scheme depicted in the Figure), both biomarkers of great relevance at present and considered of early diagnosis, will be discussed. The developed methodologies, based on the appropriate use and coupling of novel bioreceptors, functionalized magnetic microcarriers, attractive bioassays formats and electrochemical disposable transducers, allow the accurate determination of the target analytes at clinically relevant levels in challenging biological samples: cancer cells, human tissues, both fresh and formalin-fixed, paraffin-embedded (FFPE) and human serum.



These easy handling single- or multiplexed platforms provided results in agreement with conventional methodologies but with lower cost and in remarkably shorter times which make them suitable alternatives in the implementation of user-friendly and affordable devices, particularly feasible to perform routine determinations in clinical and basic research settings which facilitate predictive diagnostics and personalized medicine. Moreover, the developed methodologies can easily be extended to the determination of other biomarkers of relevance in other types of cancer or major diseases.

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Prostate Cancer Biomarker Detection Using a 16-Sensor Electrochemical Microfluidic Immunoarray

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Online capture and detection using a semi-automated multiple biomarker-based diagnostic microfluidic device is described herein. The lifetime risk of a man developing prostate cancer in the United States is 1 in 7. The process of detecting detection and staging of prostate cancer includes prostate specific antigen (PSA) test, digital rectal exam (DRE) and biopsy. Such practices also are not adequate in terms of sensitivity, specificity and inability to distinguish between aggressive and indolent forms of prostate cancer. These inaccuracies can lead to unnecessary treatments that adversely affect the patients' quality of life. Measurement of small panels of molecular biomarkers in serum holds tremendous potential for cancer diagnostics and personalized therapy. The protein panel includes PSA, CD-14, ERG, GOLM-1, PEDF-1, IGF-1, VEGF-D and IGFBP-3, which are in one form or another indicative of prostate cancer or progression. The protein analytes are captured from serum samples in a two channel on-line microfluidic chamber by magnetic beads labeled with antibodies and signal transducing elements. Captured analytes are then magnetically separated, washed, and introduced into a two channel detection chamber housing an array of 8 or 16 nanostructured, antibody-labeled electrodes. Ultra-low detection limits in the sub fg ml^{-1} range was achieved for the protein panel. Using this strategy, 8-16 proteins can be detected simultaneously in 30 minutes. Measurements of the selected biomarker panel will be tested with prostate cancer patient samples to assess its diagnostic capability.

Bioelectrochemical Systems as Biosensors for Real-Time Environmental Monitoring

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Environmental monitoring is often based on labour-intensive laboratory analysis, which is expensive and features significant delays. This study compares performances of Microbial Fuel Cells (MFCs) and Microbial Electrolysis Cells (MECs) as biosensors for real-time monitoring of organic and inorganic contaminants in surface and ground waters. MFC and MEC response to changing concentrations of organic materials, ammonium, metal sulfates, and other environmental pollutants was evaluated. The biosensor response was evaluated in terms of current (MFC and MEC) and power production (MFC). To improve biosensor accuracy the perturbation-and-observation algorithm for maximizing MFC power production is used. Furthermore, we show that the measurement accuracy can be improved by using a simple equivalent circuit model and estimating model parameters in real time (soft-sensor approach). In this approach, the internal resistance and the capacitance are estimated in real time and linked with concentration changes. Our results show better response time and sensitivity of an MFC-based sensor as compared to an MEC. High correlation of MFC power output and current (providing MFC is operated at an optimal external resistance) with chemical oxygen demand (COD) concentration enables the development of on-line COD and BOD sensors. Also, MFC power output sensitivity to changes in dissolved metal concentrations enables the development of an MFC-based toxicity sensor suitable for real-time monitoring of acid mine drainage.

Real time monitoring of the flavin gate in the ETC of *Shewanella MR-1* by planar waveguide experiments

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Shewanella MR-1 is of interest for its applications in microbial fuel cells (MFC). The microbial film that operates as the catalytic site for the fuel cell application is a highly complex and diverse 3 dimensional structure. Microorganisms must both manipulate and adapt to proton production in anodic end of electron transfer chain anaerobic respiration and terminate electrochemical activity on reduction. Here we introduce and validate a method to monitor the differential activity at the surface of the electrode of the flavin in its bound and free states via spectro-electrochemistry in a planar waveguide (SE-PWG). We observe the characteristics of the final microbial film after two hours of anodic loading to the indium tin oxide (ITO) waveguide. Optical peaks are verified against both free flavin and free cytochrome c. The assigned peaks are further verified against the CV currents indicative of the bound and free flavins by monitoring the spectra at the beginning and switching potentials of a series of 6 cyclic voltammograms (CVs). We demonstrate for the first time, to our knowledge, the observation of the semiquinone 1e transfer associated with the catalytic OMcA/MtrA site. We further demonstrate that the charge transfer band of the cytochrome c is enhanced substantially, presumably by the action of a surface plasmon phenomenon. Alterations in the CT band are indicative both of reduction and/or signal pH changes occurring at the ITO/microbial film interface.

Kinetic Monte Carlo Study of Channeling in Synthetic Bioreaction Networks

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Quantitative understanding and control of reaction networks requires detailed knowledge of thermodynamic, kinetic, and transport properties associated with individual reaction steps. In bioactive systems, this information is relevant at multiple time and length scales, associated with atom-atom interactions, molecular-scale kinetic processes, and mesoscale diffusion phenomena. Combination of these phenomena in a single model is made possible by Kinetic Monte Carlo modeling, which is event-based rather than time-based and allows a random sampling of events such as molecular transport and reaction steps based on their likelihood which is proportional to rate. We have taken this approach to study reaction-diffusion processes in molecular-scale networks that exhibit intermediate channeling. Specifically, we have studied a hexokinase–glucose-6-phosphate dehydrogenase system in which the enzymes are complexed via a charged polypeptide. Taking inputs from DFT and molecular dynamics models, the KMC model predicts reaction dynamics that are directly comparable to experimental results. We will present this model with comparison to experiment and discuss extension of the KMC approach to larger systems involving multi-step networks.

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Nitric Oxide Reductase Based-Biosensor Modified with Liposomes and Gold Nanoparticles for Nitric Oxide Detection

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Nitric oxide reductase (NOR) isolated from the denitrifying organism *Pseudomonas nautica* is a membrane-bound enzyme containing one heme *c*, two hemes *b* and one non-heme iron. This enzyme is involved in the denitrification pathway, catalyzing the reduction of nitric oxide radical (NO) to nitrous oxide: (N_2O): $2^{\bullet}NO + 2e^- + 2H^+ \rightarrow N_2O + H_2O$ [1]. The specificity of NOR towards NO makes it an ideal target to develop a biosensing device to monitor NO, and possibly other reactive nitrogen species, in biological systems, namely in humans [2]. Electrochemical techniques are the approach of choice for selective, sensitive, direct and real-time measurements, for both *in vitro* and *in vivo* studies of NO metabolism and homeostasis [3]. The principal condition to develop enzymatic sensors is to succeed in the stabilization of the enzymes on solid supports. In this study, electrodeposition of gold nanoparticles (AuNPs) was performed and combined with liposomes to obtain enhanced immobilization of NOR on a pyrolytic graphite electrode (PGE). To electrodeposited AuNPs on the PGE surface, the electrode was immersed in 0.1 M KNO_3 solution containing 3 mM $HAuCl_4$ while a −200 mV working potential was applied to the electrode. Liposomes have been used to increase the signal and also to serve as a membrane mimetic (since NOR is a membrane-bound enzyme). Liposomes (POPC:Cholesterol – 2:1) with 125 ± 1.42 nm diameter were synthetized using the lipid film hydration method [4]. Direct electrochemical measurements by cyclic voltammetry and impedance spectroscopy were used to characterize the multiple steps of surface modification and the performance of the developed biosensor through NO catalysis (figure 1). A reduction peak was obtained for NO reduction at around -0.68 V *vs.* Ag/AgCl. NOR/Liposomes/AuNPs/PGE biosensor performance, namely, regarding the linearity range, limit of detection and quantification, reproducibility, repeatability and stability was characterized.

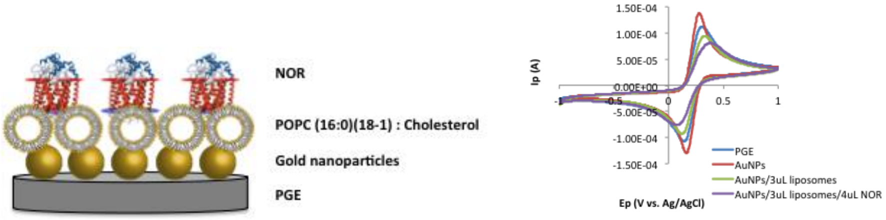

Figure 1. Biosensor construction and cyclic voltammograms (100 mV/s) for NOR/Liposomes/AuNPs/PGE biosensor in 2.5 mM $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ and 100 mM KNO_3.

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detection in biological and environmental samples” is also acknowledge.

Electrochemical behavior of membrane proteins reconstituted in lipidic liquid crystalline cubic phases

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Lipidic cubic and hexagonal phases are advantageous materials for hosting biologically relevant molecules since they are biocompatible, stable in excess water and can accommodate relatively large loads of such molecules due to a high internal surface area of ca. 400 m^2/g. The highly structured reverse bicontinuous lipidic cubic phase (LCP), composed of two sets of noncommunicating but interpenetrating three dimensional periodic water channel network separated by lipid bilayers exhibits interesting properties for applications as a drug and protein carrier [1]. Because of their internal structure, LCPs can incorporate hydrophilic, amphiphilic and hydrophobic molecules.

Retaining the activity of proteins incorporated in the artificial membranes essential for their use in membrane - based sensors or biofuel cell devices remains a true challenge. Direct adsorption at electrode surfaces often results in loss of their activity. Membrane proteins, generally are not stable outside the cell membranes, however, we reveal their stabilization by encapsulation in LCP - a matrix that resembles natural lipidic environment. Selected proteins: fructose dehydrogenase [2], Na$^+$/K$^+$-ATPase transmembrane protein and chloride-conducting ion channel from *Escherichia coli* (EcClC) were incorporated into the monoolein (MO) based LCP and studied using cyclic voltammetry, chronoamperometry and chronocoulometry. The structures of the LCPs without and with the proteins were determined by small-angle X-ray scattering (SAXS).

The Na$^+$/K$^+$-ATPase activity in LCP was studied spectroscopically and using electrochemistry, The enzyme activity evaluation was based on the ability of Na$^+$/K$^+$-ATPase to hydrolyze ATP and form ADP and free phosphate, which reacted with ammonium molybdate under acidic conditions. The detection was performed in the presence of ascorbic acid, where the voltammetric response at around +0.2 V *vs.* Ag/AgCl/3M KCl was monitored in the presence or absence of ouabain, a Na$^+$/K$^+$-ATPase specific inhibitor.

Since ecCLC is a potential dependent chloride-conducting ion channel protein, chronocoulometry was used to study the charge passing through the LCP film as a function of potential applied to the electrode. From the charge vs. potential plots the difference between charge passing through the LCP and LCP with ecClC channel protein was evaluated. Results indicate that more negative charge is transferred through the electrode covered with LCP containing ecClC which confirms that ecClC acts as Cl$^-$ ions transporter. Diode-like behavior of the cubic phase containing the protein is observed. More negative charge was found to flow through the LCP covered electrode loaded with ecClC at pH 4.5 than at pH 7.4. These results demonstrate that the membrane proteins reconstituted in the lipidic cubic mesophase not only retain their structure, but they retain their functions in this biomimetic environment.

Acknowledgements The financial support of Sinergia project no. CRSII2_154451/□1 “Design, synthesis and characterization of lipidic nanomaterials for biomedical and biosensing applications” is acknowledged

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Mechanistic Insights into Nitric Oxide Reduction Catalyzed by Bacterial Nitric Oxide Reductase

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In microbial denitrification process, nitrate (NO_3^-), which is the main nitrogen-containing pollutant in ground water, is stepwise reduced to harmless dinitrogen (N_2) thorough nitrite (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O). Although ideally no intermediate metabolite is lost to the environment, certain soil bacteria release N_2O into the atmosphere. N_2O is known to be one of the contributors to the green house gas effect and to ozone depletion. The largest emission source of N_2O is bacterial breakdown of nitrogen compounds and the key enzyme in the N_2O production is a metalloenzyme of nitric oxide reductase (NOR). NOR is a membrane-integrated protein and catalyzes the reduction of NO to N_2O at active sites of iron co-factors of the non-heme Fe_B and/or the heme b_3.[1] The NO reduction involves the N−O bond cleavage and the N−N formation. The reaction mechanism is interesting from a chemical point of view because the NO reduction is known to govern the selectivity of the final product, N_2 or NH_3, in electrochemical nitrate reduction.[2] Three possible reaction mechanisms are proposed: *trans*-mechanism, *cis*-heme b_3 mechanism and *cis*-Fe_B mechanism.[3] However, the molecular mechanism of the NO reduction catalyzed by NOR still remains to be solved.

Herein, we report protein film voltammetry (PFV) and surface-enhanced infrared absorption (SEIRA) spectroscopy of NOR to gain mechanistic insights into the NO reduction. PFV allows us to apply bias potentials to redox-active enzymes including NOR on the electrode surface[4] and to initiate electrocatalytic reactions by the enzyme. SEIRA spectroscopy is a powerful technique to understand reaction mechanisms of enzymes at the electrode surface.[5] In this work, a cytochrome *c*-dependent NOR was isolated from *Pseudomonas Aeruginosa* and then immobilized directly on the surface of a gold-coated Si hemicylinder prism[6] or via self-assembled monolayers for cyclic voltammetry and SEIRA spectroscopy. Cyclic voltammograms of NOR-modified electrodes showed reduction current under NO but not under Ar, suggesting that NOR on the electrode surface catalyzed the NO reduction to N_2O. Potential-dependent SEIRA spectra of NOR-modified electrodes were recorded under NO and characteristic two bands were observed in the range from 1600 cm^{-1} to 1800 cm^{-1}. NO molecules bonded to the non-heme Fe_B and to the heme b_3 are known to show absorption bands in this IR range.[6] Thus, it is most likely that NOR on the electrode may catalyze the NO reduction in the *trans* mechanism.

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Engineering of Redox Potential of Direct Electron Transfer Type Glucose Dehydrogenase

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In this presentation, we report our recent success in the engineering redox potential of the direct electron transfer type glucose dehydrogenase, and its electrochemical characterization.

We have been engaged in the isolation and characterization of flavin adenine dinucleotide glucose dehydrogenase complex (FADGDH) from *Burkholderia cepacia*1). FADGDH is comprised the following three distinct subunits: the catalytic subunit that has an FAD cofactor in its redox center2); the small subunit, a hitch-hiker protein of the bacterial TAT secretion system, which is necessary for the proper folding and secretion of the catalytic subunit3); and the multi-heme cytochrome *c* subunit that is responsible for the electron transfer between the active-site cofactor and external electron acceptors4). The presence of the multi-heme cytochrome *c* subunit makes this enzyme complex possible to facilitate the direct electron transfer type enzyme electrode. Based on this superior feature, glucose sensing system and as well as power generation systems based direct electron transfer have been reported. Recently, we reported on the presence of a 3Fe–4S-type iron–sulfur cluster in its catalytic subunit, which plays as the primary electron acceptor of FAD, consequently transfers electron to the multi-heme cytochrome *c* subunit5). These features appear to be conserved in the other three-subunit type dehydrogenases having an FAD cofactor.

We focused on the protein structure and hemes which are responsible for the intra- and inter-molecular electron transfer. Based on the extensive analyses its structural features of FADGDH and the information obtained based on site directed mutagenesis studies of the multi-heme cytochrome *c* subunit, we designed an engineered electron transfer subunit. This designed molecule, a “miniaturized” electron transfer subunit, was recombinantly produced together with catalytic- and small- subunit. These three components are self-assembled to form soluble and an active glucose dehydrogenase complex, showing similar catalytic features of wild type FADGDH. The direct electron transfer properties of thus constructed engineered FADGDH harboring miniaturized electron transfer subunit were characterized. The results revealed that the engineered FADGDH showed direct electron transfer under much lower oxidation potential compared with the wild type. Therefore, thus constructed engineered FADGDH will be utilized for glucose sensing operating with much lower potential, which is beneficial to avoid the effect of the presence of electro-active ingredient in the sample solution.

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Multi-Enzyme Modified Bioanode Utilizing Maltose as Fuel

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1. Introduction

Enzymatic biofuel cells (EBCs) are a type of fuel cells which use enzymes as catalysts to oxidize fuels (saccharides, alcohols, etc.) and reduce oxygen molecules. EBCs are expected to be applied as small-sized power sources for portable medical instruments, etc., as they can operate at mild condition, use renewable energy sources with enzymatic reactions, and do not need separators because of substrate specificity. Although monosaccharides are commonly used as biofuel, we have already studied on a bioanode to oxidize sucrose for biofuel cells.¹⁾ In this study, we focus on maltose to extend our idea towards disaccharides. Maltose is a dimer of α-D-glucose and one of the most common edible disaccharides, however, there are no reports on multi-enzyme modified bioanodes for maltose oxidation. Therefore, we attempt to fabricate bioanodes to utilize maltose and glucose as fuel by using multi-enzyme system containing three enzymes, and also report further improvement by electrode materials.

2. Experimental

The multi-enzyme bioanodes were prepared as follows; 1) aqueous multi-walled carbon nanotube (CNT) dispersion, containing cethyltrimethylammonium bromide (CTAB) or Triton X-100 as dispersant, was dropped on a carbon-felt (CF) electrode, 2 mm thick and 8 mm in diameter, 2) tetrathiafulvalene (TTF) acetone solution was added to the electrode as a mediator, 3) each enzyme solution of maltase (MAL), mutarotase (MUT) or glucose oxidase (GOD) was dropped on the electrode. Thus prepared bioanode was used as a working electrode. Pt-wire and Ag/AgCl electrodes were used as counter and reference electrodes, respectively. We conducted electrochemical measurements in phosphate buffer solution (PBS, pH 7.0) including 25 mmol dm^{-3} maltose at 37℃.

3. Results and discussion

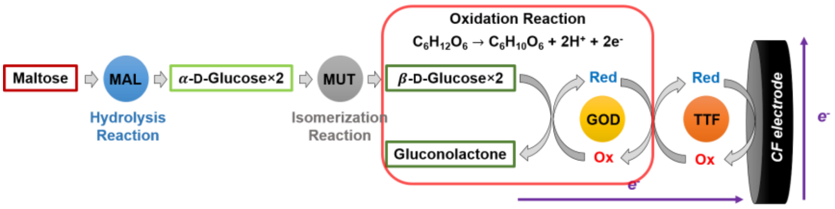

Fig. 1 Maltose oxidation scheme in multi-enzyme modified electrode.

Fig. 1 shows our concept of multi-enzyme bioanode system for the oxidation of maltose. The maltose anodic oxidation process involves three enzymatic reactions; 1) one maltose molecule is catalytically hydrolyzed into two α-D-glucose molecules by MAL, 2) α-D-glucose is isomerized to β-D-glucose by isomerase, MUT, 3) β-D-glucose is oxidized by GOD and electrons are transferred by TTF mediator. Figure 2 shows cyclic voltammograms of two types of multi-enzyme bioanodes: CNT/CTAB electrode, and that with Triton X-100 as CNT dispersant. The former demonstrates oxidation currents from the potential of -0.05 V in maltose solution, while the latter achieves a high current density in the whole potential range, i.e. 17 mA cm^{-2} at 0.34 V (vs. Ag/AgCl), which is mostly due to good dispersion of CNT in CF and suppressed deactivation and elution of the enzymes. We are also to demonstrate the dependence of electrolyte concentration and full cell performance by combining the anode and a cathode in the presentation.²⁾

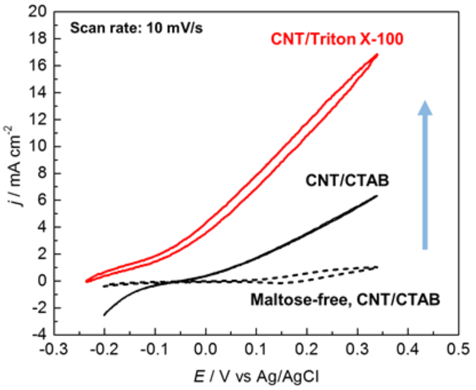

Fig. 2 Cyclic voltammograms of bioanodes examined in 40 mmol dm^{-3} PBS (pH 7.0) containing 25 mmol dm^{-3} maltose at 37 °C.

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Detection of Ionic Neurotransmitters from Single Neuronal Structures via Versatile Nanosensor Probes

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Nanoelectrodes have the advantage of low background charging current, when coupled with scanning electrochemical microscope,[1] it can provide nanometer spatial resolution imaging with high temporal resolution. My group use the Nano-Interface between Two Immiscible Electrolyte Solutions (ITIES) as a unique analytical platform for the study of ionic species of biological interest such as neurotransmitters on living bio-structures.[2, 3, 4] A typical nanopipet electrode consists of a laser pulled pipet with an orifice in the few nm range that can be filled with an immiscible organic solution for its immersion into biologically-relevant fluids, thus forming a liquid/liquid interface. Upon electrochemical polarization, charged neurotransmitters can be transferred from one phase to another, which is the basis for quantitative ionic species sensing. This is particularly useful for the detection of non-redox active neurotransmitters, especially those whose detection on carbon microelectrodes is challenging. This versatile technique is capable of detecting species such as dopamine, acetylcholine, serotonin and tryptamine.[2, 3, 4]

Scanning electrochemical microscope coupled with nanoelectrodes have been a very useful technique providing chemical information of nanostructures with unprecedented nanometer spatial resolution and high temporal resolution, e.g. ion transfer properties across a single nanopore,[5] catalytic properties of single nanoparticles,[6] dynamic processes of nanobubbles.[7] We studied acetylcholine neurotransmission activity at single neuron structures from the model organism *Aplysia californica*. We employed scanning electrochemical microscopy for accurate positioning of our nanoprobes on selected regions of cells and their synapses. By using the liquid/liquid approach, we circumvent challenges in the evaluation of redox inactive neurotransmitters using electrochemical methods. Our results show that our nanoprobes, with a typical diameter of 30 nm, can detect acetylcholine neurotransmission both qualitatively and quantitatively and in real time, with excellent signal to noise ratios and in biologically-relevant fluids. The strategy presented here suggests an exciting analytical pathway to study of the mechanisms of neurotransmission.

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Probing the Physiological Redox Role of Selenocysteine

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Selenium is an essential trace element, primarily found in the amino acids selenomethionine and selenocysteine. Proteins containing selenocysteine in their active site are known to play an integral role in key physiological processes. Several fundamental questions remain, however, regarding the unique redox chemistry afforded by selenocysteine in the cellular environment. Using surface and solution electrochemical and spectroscopic techniques, the selenocysteine / selenocystine redox couple has been examined under physiological conditions at gold and platinum electrodes. Voltammetric behavior is indicative of a two-step process, in which the metallic substrate is modified by the diselenide analyte prior to observation of diffusionally controlled, proton-coupled electron transfer. The selenium-based adsorbate can be removed via anodic stripping voltammetry and subsequently regenerated, displaying high recyclability with little to no loss in signal restoration. Electrochemical and spectroscopic characterization data will be presented and biosensing applications of selenium-modified electrodes will be discussed.

Towards Continuous Self-empowered Glucose Detection

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Wearable chemical sensor technologies enable the opportunity to continuously collect physiologically information on an individual's health status. This is in contrast to traditional blood draws and subsequent analysis. Using glucose oxidase as a model enzyme, we compare and contrast several fabrication methods, and describe an optimized glucose monitoring sensor, which works in open circuit potential with good selectivity and sensitivity (>2000 nA/mM) over a concentration range of 50 to 300 µM (Figure 1). The sensors can continuously operate for a few hours with minimal loss of sensitivity over time. Key steps, procedural details, and findings will be discussed.

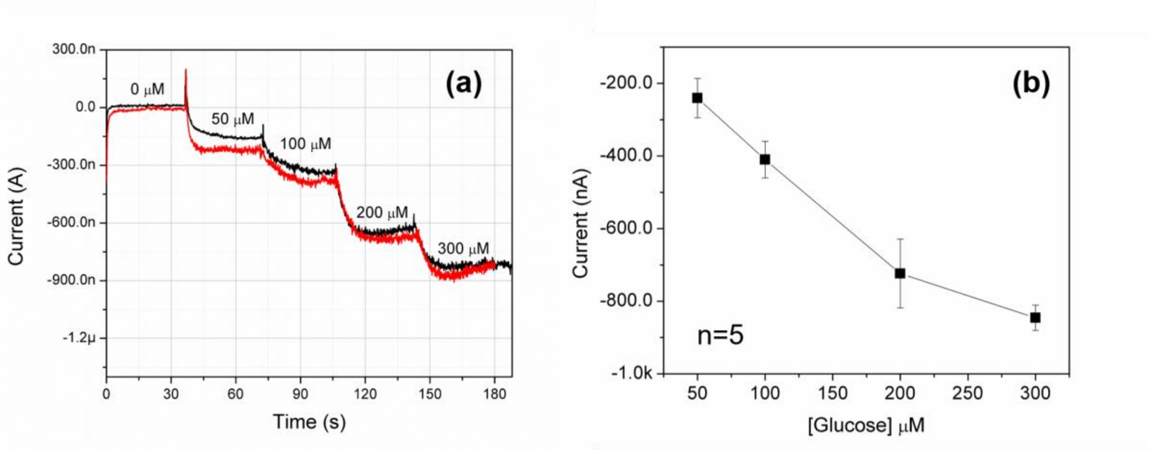

Figure 1. (a) The open circuit potential chronoamperometric response of glucose to the glucose oxidase sensor in phosphate buffered saline (b) calibration curve.

Electrochemical Molecular Imprinting for Selective Determination of Chosen Biomarkers

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Electrochemical molecular imprinting in conducting polymers was applied for preparation of recognition units of chemical sensors for selective determination of chosen biomarkers including a D-arabitol sugar alcohol fungal infection biomarker,[1] the carnosine dipeptide cancer biomarker,[2] the oxytocin nonapeptide autism biomarker[3] as well as the neopterin cancer and HIV biomarker.[4] Different functionalized bithiophenes and *bis*-bithiophenes were used as functional monomers. These comprised boronic acid substituted bithiophene,[1] carboxy and 18-crown-6 ether derivatives of *bis*(2,2'-bithien-5-yl)methane,[2] 4-bis(2,2'-bithien-5-yl)methylbenzoic acid glycol ester,[3] 1-methylamide-4-[bis(2,2'-bithienyl)methane[3] and bis(2,2'-bithienyl)-(4-(2-hydroxyethoxy)phenyl)methane[3] as well as *bis*-bithiophene derivatized with cytosine and bithiophene derivatized with boronic acid[4] while 3,3′-bithiophene[1] and 2,4,5,2',4',5'-hexa(thiophen-2-yl)-3,3'-bithiophene[3,4] served as cross-linking monomers. For pre-polymerization complex formation in solution, weak covalent bonds,[1,4] hydrogen bonds,[2-4] and inclusion interactions,[2] were generated between functional monomers and analytes, which played the role of templates at this step. Structures of these complexes were optimized and Gibbs free energy changes due to complex formation were calculated using DFT at the B3LYP/6-31G(d),[2] B3LYP/3-21G*,[3] and B3LYP/6–31G*,[4] level confirming complex stability sufficient to survive electropolymerization. These complexes were electropolymerized under potentiodynamic conditions with resultant MIP thin film deposition on a conducting transducer surface. An extended-gate field-effect transistor for source-drain current trunsduction,[1] a gold film coated quartz crystal resonator of an electrochemical quartz crystal microbalance for piezoelectric microgravimetry transduction,[1,2] a Pt disk electrode for impedimetric capacity (CI) measurements under flow-injection analysis (FIA) conditions,[2] an Au thin film electrode in an electrochemical miniaturized microfluidic cell for CI determinations,[3] and a Pt disk electrode for open-circuit potential transduction under FIA conditions[4] were used as these transducers. The templates were then extracted from the MIP films with 0.1 M HCl for 2 h at 40 °C,[1] 0.1 M NaOH,[2] 0.01 M NaOH at 0.50 V vs. Ag/AgCl for 8 h,[3] and 0.1 M carbonate buffer (pH=10.0), which was 0.1 M in KF, at 0.50 V vs. Ag/AgCl with superimposed ac voltage of the 10 mV amplitude and 20 Hz frequency for 90 min,[4] thus leaving in MIPs empty molecularly imprinted cavities ready to attract analyte molecules. Embedding templates in MIPs, and then completeness of template extraction was confirmed by XPS,[1-3] the "gate effect" using the 0.1 M $Fe(CN)_6^{4-/3-}$ redox probe[1,2] as well as Raman[2] and fluorescence spectroscopy.[4] Thickness and morphology of MIP films were determined with AFM imaging. Prevailingly, the films were robust; they changed their morphology after template extraction only slightly. Thus devised chemosensors were selective to interferences of similar structures. Other analytical parameters reached met requirements of determination of these biomarkers in body fluids.

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Model phospholipid membranes mimicking healthy and cancer cells to study the interactions with anticancer drugs - electrochemical, spectroscopic and neutron reflectivity studies.

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Phospholipid monolayers prepared by the Langmuir technique at the air-water interface can be successfully employed as simple models of one leaflet of cell membranes and are commonly used in the studies of the interactions of drugs, toxins and other biologically important species [1]. Although very simplified, this system has already proved to be useful to investigate the interactions of anticancer drugs [2,3]. The main advantage of such an approach is the fact that the composition of a model layer may be adjusted to mimic different types of cellular membranes. In order to obtain a better model of a real biological membrane, the phospholipid monolayers may be also transferred onto solid support to form a bilayer, which also allows one to employ other techniques such as spectroscopy and electrochemistry to investigate the model membranes.

We have studied the influence of selected model anticancer drugs, doxorubicin (DOx) and daunorubicin (DNR), on the properties of phospholipid layers treated as simple models of healthy and cancer cell membranes. DOx and DNR are anthracycline antitumor drugs, which find application in the treatment of various types of cancer [4]. Results of Langmuir studies show that those drugs incorporate into the 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) monolayers at the air-water interface treated as a simple model of healthy cell membranes. The incorporation leads to the changes in such properties of model membranes as area per molecule and reciprocal of compression modulus. Interestingly, the effect of DOx and DNR on the model monolayers composed of 1,2-dimyristoyl-sn-glycero-3-phospho-L-serine (DMPS), a phospholipid occurring in an elevated level in cancer cell membranes [5], is much more pronounced compared to the interactions with model DMPC layers. It may be explained by the presence of electrostatic interactions between negatively charged polar heads of DMPS and positively charged DOx and DNR, which are not that significant in case of neutral polar headgroups of DMPC. Additionally, in case of DMPS model system the effect of the pH of the subphase was also proved to be crucial. Brewster angle microscopy studies for both healthy and cancer model membranes also confirmed the changes in the morphology of the layers due to the presence of the anticancer drugs.

In order to get more insight in the nature of the interactions of anthracyclines with phospholipid membranes, the layers were transferred onto solid support and electrochemical methods were employed. Due to the electrochemical activity of the drugs it was possible to confirm the incorporation of the drugs into both DMPC and DMPS supported bilayers, compare the interactions of anthracyclines with these two types of model systems and observe the influence of the pH of the supporting electrolyte on the redox signal from the anthracycline drugs. PMIRRAS studies performed for supported DMPC/DOx system showed a significant decrease in the tilt angle of DMPC molecules in the bilayer, which may imply that the drug interacts strongly with polar heads of phospholipids. The differences in the interactions of DOx with the two types of model membranes were confirmed by neutron reflectivity studies performed on monolayers at the air-water interface, which showed that the drug incorporates into the headgroup region of DMPS membranes replacing the lipid, while penetration of DMPC membranes is not as favored.

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Effect of Heavy Water on Redox-switching of DNA Self-Assembled Monolayers observed by EQCM and Cyclic Voltammetry

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We have investigated the interaction of 50 µM hexammine ruthenium(III) (RuHex) and hexammine cobalt(III) (CoHex) with DNA on gold electrodes by electrochemical quartz crystal microbalance (EQCM). Both complexes are known for interacting with DNA both electrostatically and by formation of hydrogen bonds. The large frequency change of ca. 30 Hz (Fig. 1A, B) upon 450 mV potential jumps could not be explained by a loss or gain of RuHex cations or counter anions. The EQCM response was 20 Hz with CoHex. It occurred only when a proper potential jump around the redox potential of RuHex or CoHex was applied. For CoHex, it took 30 seconds to reach a new stable frequency in contrast to only 240 ms in case of RuHex. Without RuHex and CoHex, a very small frequency response occurred within 80 ms. Viscoelasticity of the DNA-SAM may be influenced by the interaction with the different complex ions. CoHex is known to influence the secondary and tertiary structure of DNA forming intermolecular bridges between strands.[1] Accordingly, the involved hydrogen bonds can be influenced by kinetic isotope effects. We think this was confirmed for CoHex by experiments in heavy water, where EQCM response was diminished by 50%. With RuHex, this D_2O-effect was significantly smaller. Cyclic voltammetry revealed dramatic isotope effects regarding both redox potential and reversibility of CoHex, but no such differences with RuHex. This contribution discusses the possible redox-switching of the viscoelasticity of a DNA-SAM induced by CoHex and influenced by kinetic isotope effects.

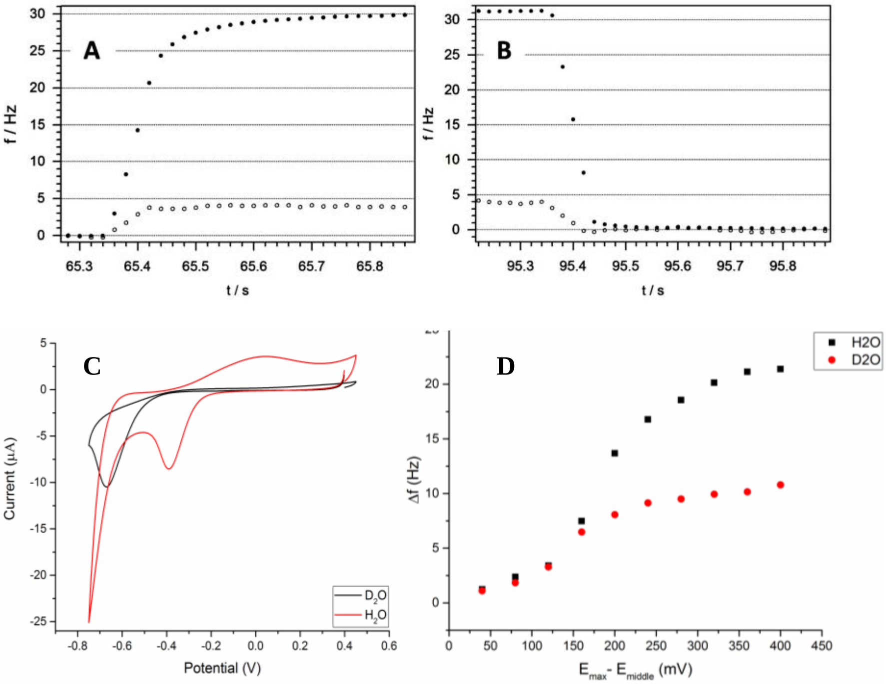

Figure 1. EQCM frequency transients recorded with ssDNA-SAM in H_2O (10 mM TRIS, pH 7.4) in presence of (black circles) and without (open circles) 50 µM RuHex upon potential jump from -0.35 V to 0.1 V vs. Ag/AgCl (A) and back (B). Below panels depict the effect of D_2O as solvent upon both CV (C) and EQCM (D) response at different potential jumps in presence of 50 µM CoHex compared with H_2O.

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Hierarchical OCNT- $NiFe_2O_4$ composites for sensitive non-enzymatic electrochemical sensing of cholesterol

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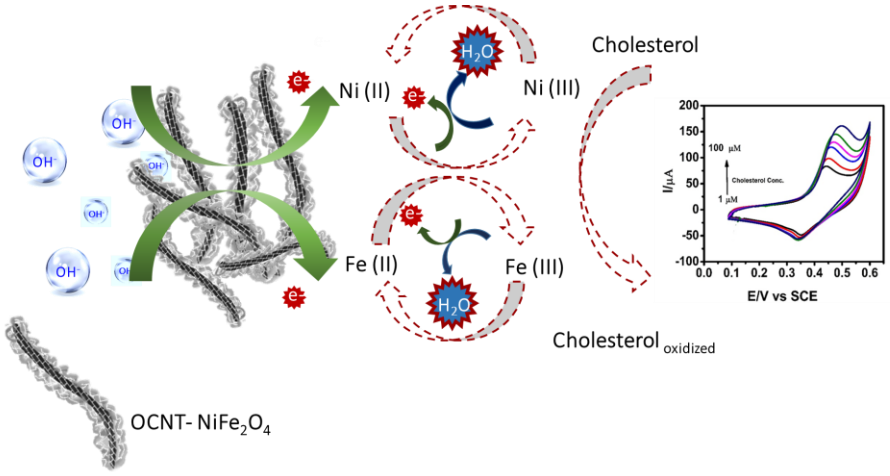
Abstract

Increased prevalence of hypertension and cardiovascular diseases within recent years, has drawn considerable attention towards sensitive and selective determination of cholesterol [1]. However, conventional electrochemical sensing of cholesterol, utilizing efficient immobilization of cholesterol oxidase (Ch_{Ox}) suffers from integral drawbacks like poor reproducibility, complex immobilization procedure and denaturation of expensive enzymes due to pH, humidity and temperature [2]. To device an "enzyme free" solution, we here demonstrate the application of hierarchical $NiFe_2O_4$ flakes supported onto oxidized carbon nanotubes (OCNT-$NiFe_2O_4$) as an active catalyst material towards non-enzymatic electrocatalytic oxidation of cholesterol. For this purpose, OCNT- $NiFe_2O_4$ were synthesized by a novel, surfactant free, template less microwave assisted synthesis procedure. Cyclic voltammetry and chrono-amperometric measurements suggests superior sensitivity of OCNT-$NiFe_2O_4$ with a wide linear detection range of 0.5 µM- 1000 µM and lowest detection limit of 0.01 µM (S/N=3) towards electrocatalytic oxidation of cholesterol. Furthermore, OCNT-$NiFe_2O_4$ possess excellent selectivity towards the determination of cholesterol, even in presence of commonly known interferences like ascorbic acid, dopamine, uric acid and glucose, confirming the enormous potential of OCNT- $NiFe_2O_4$ towards enzyme-less electrochemical sensing of cholesterol.



Keywords: OCNT- $NiFe_2O_4$, cholesterol, ascorbic acid, uric acid, dopamine, glucose

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Polymer Pencil Graphite Electrode in the Study of Electrochemical Processes of Guanine Analogues

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Understanding the oxidation processes of purines and their derivatives is primary for the improvement of electrochemical methods of genetic and food materials analysis. However, it is generally known that guanine (G) is one of the four main nucleobases found in the nucleic acids DNA and RNA, but it is less known that G, G-based purines, including the nucleoside and the nucleotide monophosphate (GMP) play an important role in diet-related diseases (gouty arthritis), health of cardiovascular and digestive systems (heart function including blood flow and oxygen delivery) and in neurodegenerative diseases (oxidative stress) [1,2].

Electrochemical techniques in connection with carbon electrodes are powerful methods for analysis of G and its derivatives [3-5]. Our previous research revealed that a polymer pencil graphite electrode (pPeGE, Tombow or Koh-i-noor) can serve as a sensitive and disposable sensor for purines, including G and its derivatives [6-8]. In this work, the electrochemical oxidation processes of G, guanosine (Guo), guanosine monophosphate (GMP) and their deoxy-derivatives (dGuo and dGMP) were investigated. Chronoamperometric technique was used for electrochemical pretreatment of the pPeGE surface by applying a potential of 1.4 V for 60 s in the supporting electrolyte (phosphate acetate buffer solutions), which substantially improved the limit of detection of guanine analogues. The dependence of oxidation signals on experimental conditions such as scan rate, electrode surface pretreatment, addition of Cu(II) ions, adsorption, pH and the presence of structural increments (ribofuranosyl-, deoxyribofuranosyl-, and phosphate group) allowed us to evaluate: (i) kinetics and mechanism of G and GMP oxidation (electron and proton numbers, coefficients of electro-transfer, the role of electrode surface), (ii) the effect of adsorption and (iii) the effect of oxo, deoxy, and phosphate groups on oxidation responses. According to the results, pPeGE exhibits higher electron transfer rates and at the same time lower double layer capacitance values in comparison with the common carbon electrodes (glassy carbon, pyrolytic graphite). The composition of pPeGE surface studied by electron microscopy, Raman spectroscopy and XPS indicates a low degree oxygenation, high content sp^3 carbon and the presence of substoichiometric silicon oxide (SiO). We can conclude that the polymer pencil lead is a prospective electrode material with good stability and reproducibility not only for analysis of G and its analogues but also for whole purine group. Since the interaction between the pPeGE surface and nitrogen-rich molecules results into fast electron transfer reactions and low detection limits the origin and cause of this interaction is discussed.

Acknowledgement

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Invited Talk in Symposium 4: Bio-Electrocatalysis Using Magnetic Nanoparticles and Carbon Nanostructures

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Cost-effective methodologies involving precious enzyme catalysts for biocatalytic and biosensing applications represent considerable significance. In this presentation, we will discuss our research contributions on the efficient use of enzymes by utilizing poly(acrylic acid)-functionalized magnetic nanoparticles (MNPs)-enzyme bioconjugation with characterization of electro and biocatalytic features. Our studies started with a simple redox protein model, myoglobin, to understand direct electron transfer and electrocatalysis in films of covalent and noncovalently bound enzyme with the MNPs. Later, we extended this knowledge to assess scalability of such conjugates for enzyme bioassays and sensitivity enhancement of electrochemical biosensors. At present, we are investigating catalytically more significant membrane-bound liver cytochrome P450 (CYP) enzymes attached to amine functionalized MNPs as a novel bioelectrode platform useful for drug metabolism assays, metabolite synthesis, and biosensing. Additionally, we obtained fundamental insights of the CYP and its reductase electrocatalytic pathways in these bioconjugates. Along this line, we examined various carbon electrode materials and carbon nanostructure modified electrodes for studying electrocatalytic properties of membrane-bound liver CYPs, model peroxidases, and bilirubin oxidase enzymes. Our results demonstrate that by appropriate selection of functionalized MNPs, and by quantitative understanding of the functionalization of CNT-modified electrodes, one can achieve stable, scalable, and reusable biocatalytic systems for synthesis, renewable energy, and sensitive and selective biosensing applications.

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Combining Experimental and Computational Approaches in the Design of Synthetic Catalytic Cascades

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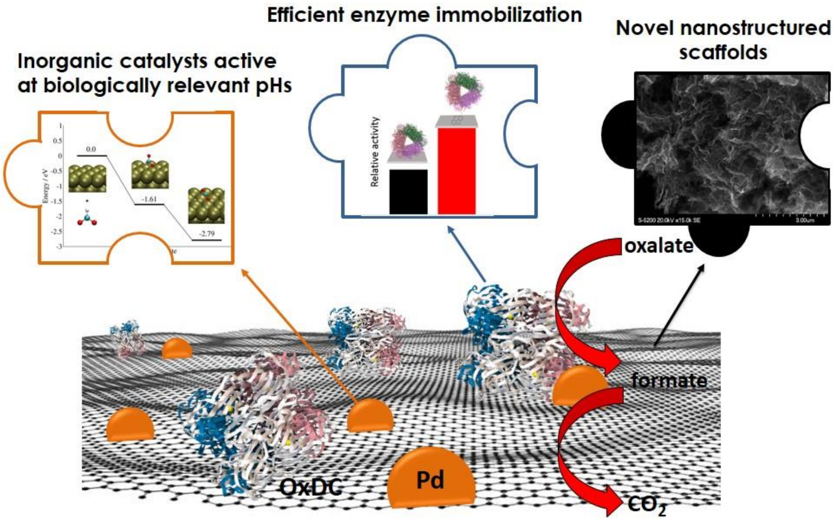
Biomimetic catalysis and cascade catalytic systems are viewed as an approach to increase efficiency of the conversion of complex fuels into electrical power at low to medium temperatures and diversify the integration of unusual fuels into the energy carriers' portfolio. The integration of different catalytic modalities into the framework of synthetic cascades is one of the most promising areas for creating such advanced catalytic systems with optimized performances. We will use the example of cascade for complete oxidation of glycerol to demonstrate how computational and experimental strategies can be combined in order to optimize the activity and selectivity of individual catalytic components and help their integration into multi-component multi-step catalytic cascades.

Integration of inorganic and enzymatic catalysts still represents a significant challenge. Namely, the traditional ways of preparing hybrid enzyme-metal nanoparticle systems rely on physical adsorption or chemical conjugation of enzyme and an inorganic catalyst, which result in the reduced enzyme activity. In addition, the development of inorganic catalysts that will replace or complement naturally occurring enzymatic systems in multi-step catalytic cascades requires the design of selective catalysts with high activity at biologically relevant pHs. Density functional theory was used to study the activity of different inorganic catalysts toward oxidation of oxygenated molecules such as oxalic and formic acid at different pHs. Studied catalysts included Pt and Pd-based materials as well as N-3D-Graphene with atomically dispersed Mn. It was found that Pd nanoparticles have high activity for oxidation of small organic acids and that their selectivity for the targeted intermediates in the glycerol oxidation cascade can be tuned by varying the applied potential. 3D-Graphene nanosheets (3D-GNS) had been synthetized and explored as a novel platform that enabled the incorporation of Pd nanoparticles with oxalate decarboxylase (OxDC). Moreover, we have demonstrated that Pd nanoparticles can be successfully integrated with oxalate decarboxylase using 3D-GNSs in a way that leads to enhanced two-reaction throughput (Figure). Furthermore, we will show how computational docking simulations can be used to predict the unexpected activity of the enzymes. Molecular docking simulations allowed us to predict the promiscuity of formate dehydrogenase from *Candida boidinii*, which enabled combining this enzyme with a molecular catalyst to produce a hybrid cascade for oxidizing glycerol to carbon dioxide.



On the influence of antibiotic lipopeptides on model biological membranes – Langmuir-Blodgett, QCM-D and Electrochemical Studies

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Antibiotic-resistant bacteria are an important health concern worldwide, focusing researchers on the development of novel classes of antibiotic compounds. Antimicrobial peptides (AMPs) are small molecules present in virtually all living organisms as a part of the innate immune system. AMPs exhibit a broad spectrum of activity against various bacteria strains, viruses and fungi.[1] However, they are very susceptible to peptidases action, which reduces their viability as internal drugs.[2] Another class of compounds, i.e. antimicrobial lipopeptides (AMLPs) can overcome this problem. AMPLs are composed of a lipid chain attached to a linear or cyclic peptide backbone.[3] They are expressed in bacteria e.g. from Bacillus or Pseudonomas groups and exhibit antibacterial, antifungal and surfactant activity. The naturally occurring lipopeptides contain in their peptide backbone at least one D-amino acid residue, which makes them less susceptible to degradation but also substantially increase their antimicrobial potential.

Here we present the results of our studies on the interactions of both natural (i.e. surfactin) as well synthetic (i.e. 2,4-diaminobutyric acid-containing ultra-short lipopeptides) with model biological membranes. The models of two cell membranes were employed, reflecting the eukaryotic and bacterial cell membrane. The first one was composed of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) and cholesterol. The latter membrane was prepared with lipids extracted from Escherichia Coli cells, i.e. L-α-phosphatidylethanoloamine (PE) and L-α-phosphatidylglycerol (PG). Results of Langmuir studies show that lipopeptides incorporate into PE:PG monolayers at the air-water interface, whereas the effect on eukaryotic film is less pronounced. The experiments performed using Langmuir through allowed us to determine the affinity of peptides to particular lipid components of the cell membranes. The changes in the morphology of the lipid layer in the presence of lipopeptides were also monitored by Brewster Angle Microscopy.

In order to obtain a better model of the natural cell membrane, phospholipid monolayers may be transferred onto solid substrate to form a bilayer.[4] We employed the combination of Langmuir-Blogdett and Langmuir-Schaefer techniques to immobilized model lipid membranes on solid support. The supported lipid bilayers were used to obtain more detailed information on the interactions of lipopeptides with model membranes. Electrochemical impedance spectroscopy and cyclic voltammetry were utilized to monitor the changes in the permeability of membranes upon the addition of lipopeptides. Quartz crystal microbalance with dissipation (QCM-D) allowed us to observe the kinetics of the membrane-lipopeptide interactions and to verify the mode of actions of lipopeptides to model membranes of different composition. Our results clearly show that the presence of D-amino acid residue(s) in the lipopeptide structure is crucial for its antibacterial activity. Moreover, lipopeptides present a different kinetics and the mode of action on membranes of different composition.

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Immunoassay read-out system based on Electrolyte-Gated Organic Field-Effect Transistors

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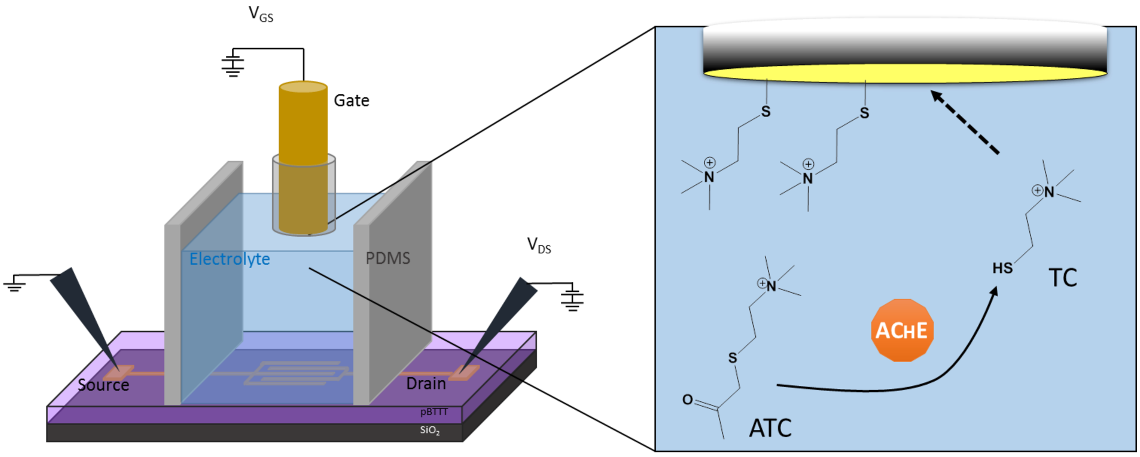
Highly sensitive, robust and miniaturized transduction systems could overcome the typical problems associated with the early diagnostic of diseases that requires the simultaneous identification and quantification of several biomarkers (proteins) at the trace level. A **new** kind of organic field-effect transistor architecture, the so-called "Electrolyte-Gated Field-Effect Transistor" (EGOFET)[1] offers a **new** analytical tool with extremely high sensitivity electrical characteristics toward any physicochemical phenomenon occurring in the vicinity of the gate and / or transistor channel[2].

To perform simultaneously a precise quantification of proteins at the trace level, we propose to adapt the standard ELISA (Enzyme-Linked Immunosorbent Assay) setup by replacing the conventional enzyme label (i.e., usually an enzyme producing a chromophore detected by UV-Vis spectroscopy) by an acetylcholinesterase (AChE). This enzyme converts the acetylthiocholine (ATC) into thiocholine (TC). The TC has a thiol group that spontaneously chemisorbs on the EGOFET gate (Au), leading to a drastic change of the transistor characteristics. The proof of concept of an ELISA read-out performed using an organic field-effect transistor will be presented as well as the device electrical figures of merit. This work paves the way to the development of new ultra-sensitive protein sensors that are compatible with the integration of microfluidic systems as well as large-scale and low-cost fabrication processes.



Scheme: Principle of the immunoassay read-out system based on EGOFETs

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Electrolyte Gated Reduced Graphene Oxide-Based Field-Effect Transistor Sensors

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Field effect transistors (FETs) are very sensitive tools for the detection of surface potential modulations hence showing high sensitivity for the detection of a variety of different analytes [1]. From all different FET architectures, the electrolyte-gated configuration seems to be the most promising for biosensor development. Graphene and graphene-related materials are considered materials of the future and due to their switchable charge-carrier mobility an ideal material for FET fabrication. Different sensing mechanisms are described for graphene-FET sensors, one of them being the potential drops at interfaces [2].
Recently, we showed the fabrication of needle-type FETs using double-barrel carbon nanoelectrodes (dbCNEs) as source (S) and drain (D) electrodes [3]. In the present work, reduced graphene oxide (rGO)-based needle-type FET sensors were fabricated using dbCNEs. Reduced graphene oxide (rGO) was deposited as channel between the two carbon nanoelectrodes by electrodeposition and simultaneous reduction of the graphene oxide on the dbCNEs. Detection of different analytes, like dopamine, was done at the gate electrode, while the FET device was used to amplify the response of the sensors. Modifications of the gate electrode in order to increase the specificity/sensitivity of the device will be presented.

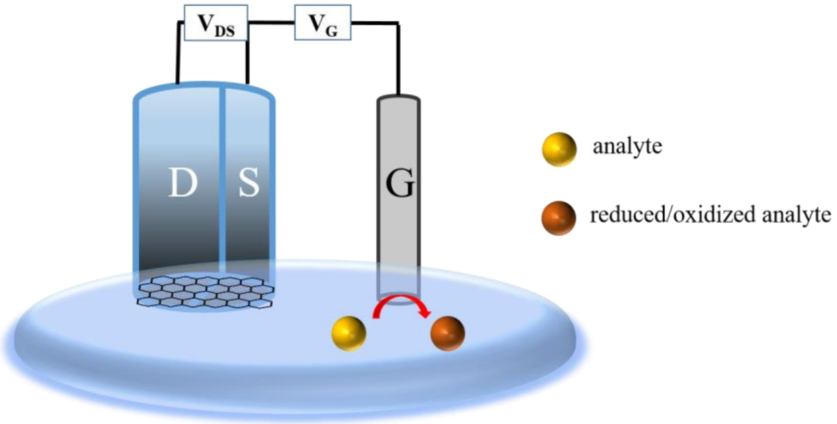

Figure 1: Needle type rGO-FET architecture used for the detection of different analytes

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Sickle Cell Disease, SCD, is a consequence of homozygous haemoglobin S in the red blood cell and is associated with crises and mortality. Cyclic voltammetry has been found useful in the characterization of some human haemoglobin phenotypes (1). In some previous reports the effects of compounds used in clinical practice in the management of SCD on values of the cathodic peak current at -273.3mV for haemoglobin S were presented (2,3). In this study the results of such values using 4-hydroxy- and 4-fluoro- benzoic acid, plant-based antisickling compounds which are derivatives of benzoic acid, at concentrations of 0.4, 0.8 and 1.6 mg / ml are presented. The electrode system is GCE / Ag, AgCl / Pt and the settings are: initial and final potential, -400 mV, switching potential, 300 mV, scan rate 50 mV/s. For 4-hydroxy benzoic acid, the percentage increase in cathodic peak currents are 88.7, 102.3 and 2.4 for 0.4, 0.8 and 1.6 mg/ml of reagent respectively. The corresponding values for 4- fluorobenzoic acid are 69.5, 122.7 and 85.4 respectively. The maximum value of peak current is at the same concentration for the two reagents. Mechanistic organic chemistry will be applied in the analysis of these results. The values of the peak current and the voltammograms obtained in these results will be compared with those of hydroxyurea, piracetam and phenylalanine, compounds used in the clinical management of SCD.

Key words: Cyclic voltammetry, haemoglobin S, antisickling agents, peak current.

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Electrochemical Impedance Spectroscopy of Tethered Bilayers: Effect of Random Distribution of Defects in Membrane

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Phospholipid bilayers are one of the major building blocks of life. They provide compartmentalization as well as localization of the protein machinery responsible for a wide spectrum of organism functions from signaling, defense, and energy generation to maintenance of cell electric potentials and the electric pulse generation in nerve cells. Tethered bilayer membranes (tBLMs) are solid-supported, self-assembled phospholipid systems used as simple-to-prepare and stable models of biological membranes. From the electrochemical standpoint the surface immobilized bilayer is a dialectic sheet that may host ion conducting pathways associated with the presence of natural defects or reconstituted ion channels (artificial defects).

Electrochemical impedance spectroscopy (EIS) is one of the major techniques used to study the electrical properties of tBLMs. To date, most of the analyses of the EIS response are based on an explicit or a tacit assumption that the distribution of defects in tBLMs is homogeneous [1, 2]. Recently, we attempted to assess the effects of the heterogeneity which is expected being present in the “real-world” samples of tBLMs. Our approach was based on the assumption that the real surface can be divided into patches with near-ideal distribution of defects inside. The probability of the occurrence of a patch with the particular defect density is defined by the log normal distribution function. While such an analysis allows one to explain several qualitative features of the EIS spectra, the underlying assumptions of the structure of the tBLM surface includes uncertainties related to boundary effects that were not taken into account [3].

The current communication discusses the electrochemical impedance of tBLMs populated with randomly distributed defects (pores). In contrast to [3], the surface heterogeneity is designed by a random generation of lateral coordinates of defects. The analysis of the distribution indicates that the radii of occupancy of an individual defect obey Rayleigh probability distribution law pattern. For calculations of the impedance spectra we used a finite element analysis (FEA) approach for solving the electrostatic differential equation for stationary conditions under the ac perturbation as described in [2]. Because the computational resources increase drastically in three dimensional FEA analysis with the size of the object we aimed at establishing the minimal surface patch, which is enough to obtain the converging solution for the EIS spectra. Another important aspect of the work was to establish the minimum number of defects that is enough to reflect the properties of the population distributed according to a Rayleigh distribution.

Comparison of the EIS spectra in systems with random and even defect distributions revealed several important facts. tBLMs with random defect distribution appears more electrically insulating compared to the tBLMs with even distribution of defects, at the same number of defects per area. As we will demonstrate in this work, pore-forming toxins attack tBLMs forming randomly distributed lesions. To assess the extent of the damage exerted by these toxins using tBLMs as a biosensor the effect of the heterogeneous/random distribution of defects needs to be assessed. We will provide simple empirical algorithms for such an assessment which can be incorporated into the bioanalytical devices.

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Development of novel cathode materials for the bioelectrocatalysis of oxygen reduction reaction by laccase from *Trametes versicolor*

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Biocatalysts such as enzymes or bacteria constitute an attractive alternative to transition metal catalysts. They have several advantages as they often possess a better selectivity and higher catalytic performances and they can be used in different types of electrochemical devices such as fuel cells or batteries [1]. We are focusing here on the cathode of a biofuel cell working with enzymes acting as biocatalysts. In the cathodic compartment, the oxygen reduction reaction (ORR) occurs. Most of the enzymes used to catalyse this reaction belong to the multi-copper oxidase family. Among multi-copper enzymes, laccase, an extra-cellular blue copper enzyme, is the most widely used biocatalyst. This enzyme contains four copper atoms shared in two different areas of the protein. The T1 site is responsible for the oxidation of phenolic substrates while T2/T3 is responsible for the ORR [2, 3, 4]. The particularity of the cathode developed in this work is first that the enzymes are directly grafted on the electrode material and no redox mediator is therefore required to shuttle the electrons between the support and the enzyme. We have defined and exploited several strategies to immobilize the enzyme on the electrode surface, by modifying either the grafting procedure, the structure of the laccase or the electrode material. The goal of all these strategies was to optimize the kinetics of the oxygen reduction reaction. In some of those strategies, we have used an amorphous carbon nitride (a-CNx) thin film deposited on rough graphite as an electrode. a-CNx thin films contain in their pristine form surface amine groups [5] suitable for enzyme grafting but carboxylic acid type surface functional groups can also be produced by an electrochemical treatment. Moreover, they can be easily deposited on various substrates by using the cathodic reactive magnetron sputtering technique. In other strategies, the surface area of graphite was increased considerably by depositing carbon nanowalls (CNWs) by using the plasma-enhanced chemical vapour deposition technique in a CO/H_2 microwave discharge. The CNWs were then functionalized by atmospheric plasma to ensure efficient enzyme grafting. Both sets of strategies are innovative as neither amorphous carbon nitride nor carbon nanowalls have been studied as biofuel cell electrode materials in the literature to the best of our knowledge. The resulting a-CNx@graphite and CNW@graphite electrodes were characterized by electrochemical measurements (cyclic voltammetry and chronoamperometry), UV-visible spectrophotometry, and XPS techniques to characterize the electrocatalytic activity and to quantify the amount of grafted enzymes. A better characterisation of the electron transfer between the electrode and dioxygen was further developed by using the electrochemical impedance spectroscopy (EIS) technique.

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Electrochemistry of Alzheimer Disease Amyloid Beta Peptides

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Alzheimer's disease (AD) is a widespread form of dementia that is estimated to affect 44.4 million people worldwide. AD pathology is closely related to the accumulation of amyloid beta (Aβ) peptides in fibrils and plagues, the small oligomeric intermediate species formed during the Aβ peptides aggregation presenting the highest neurotoxicity. The use of electrochemical methods for the investigation of Aβ peptides is continuously increasing, and become an important complementary tool in biochemical studies related with Aβ peptides aggregation, and clarification of Alzheimer's disease (AD) neurodegeneration mechanisms.

The time-dependent structural modifications and oxidation behaviour of the synthetic $A\beta_{1\text{-}40}$ and $A\beta_{1\text{-}42}$ peptides, by atomic force microscopy (AFM) and voltammetry, were investigated [1, 2]. The $A\beta_{1\text{-}40}$ and $A\beta_{1\text{-}42}$ peptides contain five electroactive amino acid residues: one tyrosine (Tyr^{10}), three histidine (His^{6}, His^{13} and His^{14}), and one methionine (Met^{35}). The Aβ peptides oxidation at a glassy carbon electrode occurs in two steps, the first electron transfer reaction corresponding to the Tyr^{10} amino acid residue oxidation, and the second to the His^{6}, His^{13}, His^{14} and Met^{35} amino acid residues oxidation.

During the $A\beta_{1\text{-}40}$ and $A\beta_{1\text{-}42}$ peptides fibrilization process, changes in the Tyr, His, and Met amino acid residues oxidation currents occur. The Aβ peptides aggregation and amyloid fibril formation was electrochemically detected via the electroactive amino acids oxidation peak currents decrease that occurs in a time dependent manner [2]. The Aβ peptides redox behavior was correlated with changes in the adsorption morphology, from initially random coiled structures, corresponding to the Aβ peptide monomers in random coil or in α-helix conformations, to aggregates and protofibrils and two types of fibrils, corresponding to the Aβ peptides in a β-sheet configuration, observed by AFM.

Using control sequences that: *(i)* do not aggregate (inverse $A\beta_{40\text{-}1}$ and $A\beta_{42\text{-}1}$ peptides, and $A\beta_{1\text{-}40}$Rat peptide), and *(ii)* Aβ peptides specially designed to lack specific electroactive amino acids (mutant $A\beta_{1\text{-}40}Phe^{10}$ and $A\beta_{1\text{-}40}Nle^{35}$ peptides), it was demonstrated that the decrease of the Aβ peptides oxidation peak currents is effectively due to aggregation and not to another process. All these control Aβ peptide sequences do not aggregate, no protofibriles or fibrils were observed, and the oxidation peak currents did not change, by increasing the incubation time from 24 h to 48 h.

Using different short fragments of the $A\beta_{1\text{-}42}$ peptide complete sequence, $A\beta_{1\text{-}16}$, $A\beta_{1\text{-}28}$, $A\beta_{10\text{-}20}$, $A\beta_{12\text{-}28}$ and $A\beta_{17\text{-}42}$, a strong correlation between the time-dependent changes on the Aβ peptides aggregation and the presence of an intact highly hydrophobic LysLeuValPhePhe aggregation core was observed. The hydrophobic C-terminal domain IleIleGlyLysMetValGlyGlyValVal present in the $A\beta_{1\text{-}40}$ and $A\beta_{1\text{-}42}$ peptide sequences, also contributed to accelerate the formation of Aβ peptide aggregates and fibrils.

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Printed Combinatorial Sensors with Graphene Oxide Nanoribbons and PEDOT:PSS for Detection of Ascorbic Acid, Dopamine, Uric Acid, and Nitrite

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Ascorbic acid (AA), dopamine (DA), uric acid (UA) and nitrite (NO_2^-) usually coexist in biological matrixes, and they were considered as crucial molecules for physiological processes in human metabolism. For instance, AA is a vital component in human diet and the animal and plant kingdoms. DA is a neurotransmitter that is widely distributed in the mammalian central nervous system for message transfer, and it plays an important role in the function of the central nervous, renal and hormonal systems. UA, a major final metabolite of purine metabolism, is a significant biological molecule which appears in human urine and blood. Nitrite in physiological systems can form nitrosamines by interacting with amines, which are toxic and carcinogenic substances, and thus brings serious problems. Therefore, the development of a sensitive and selective biosensor for their simultaneous determination is highly desirable for analytical applications and diagnostic researches.

Generally, the improvement of the simultaneous determination is obtained by the synthesis of new materials in the literature. In this study, we modified graphene oxide nanoribbons and PEDOT:PSS on single electrode for sensing based on printing technology. By combining these two materials of excellent detection characteristics for different substance, the simultaneous determination of the sensor can be enhanced. Printing technology can accurately position in the desired location and control the working area. Moreover, the ability to distinguish complex mixtures, detection limit, stability and repeatability with potential applications of the printed sensors will be carefully examined to demonstrate the feasibility of printed sensors for accurate simultaneous determination of AA, DA, UA, and NO_2^-.

Entrapment of Biomolecules in Tunable Nanoporous Gold Networks: A Strategy for Improved Rates of Electron Transfer

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Nanoporous gold (NPG) is a material of emerging interest for the immobilization of enzymes. NPG materials provide a high surface area onto which biomolecules can either be directly physisorbed or covalently attached after first modifying the NPG with a self-assembled monolayer. The immobilization of enzymes on NPG is of interest for applications in sensors[1], assays, catalysis and biofuel cells[2]. By controlling experimental parameters such as the composition and thickness of the alloy and the dealloying conditions, the surface area and morphology[3] of NPG electrodes can be tailored to the desired application. The entrapment of enzymes, such as glucose dehydrogenase, bilirubin oxidase[2], laccase and fructose dehydrogenase[1], in the porous network can lead to enhanced protein loadings and favorable orientation of the active site of the enzyme, resulting in significantly improved current densities. In addition, rates of direct electron transfer can be enhanced removing the need for redox mediators, paving the way for implantable biodevices such as sensors and fuel cells. Comprehensive studies have been performed on fructose dehydrogenase modified NPG electrodes. The biosensor was successfully used to detect D-fructose in a wide range of natural sweeteners and beverages. In a biofuel cell, glucose dehydrogenase and bilirubin oxidase modified NPG electrodes showed improved stability and significantly increased power outputs in comparison to planar electrodes. The response of a wide variety of bilirubin oxidases immobilized on NPG electrode has been examined in detail.

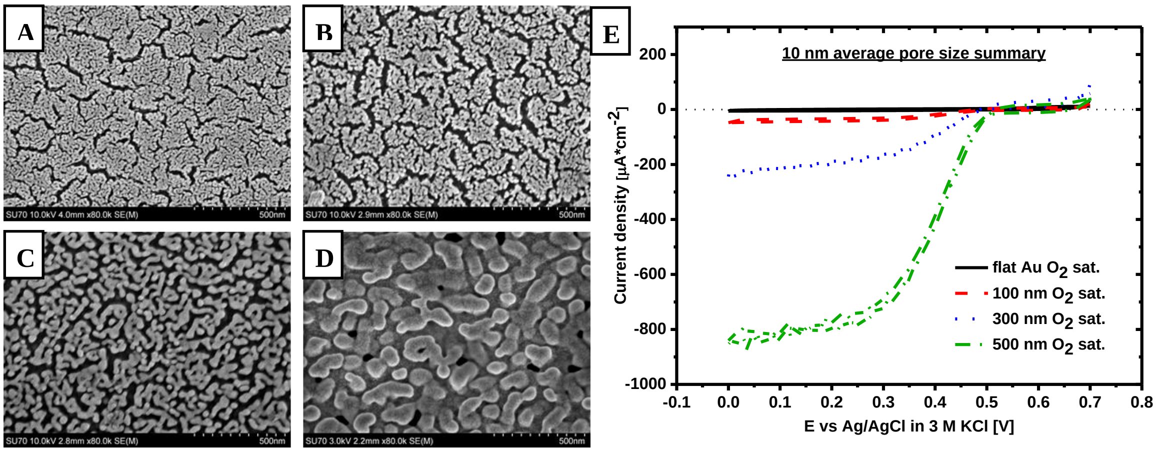

Figure 1. SEM images of NPG electrodes prepared using differing dealloying conditions resulting in A: 10 nm, B: 20nm, C: 40 nm and D: 60 nm average pore size. E: After immobilization of *Mv*BOD through covalent attachment on 100, 300 and 500 nm thick NPG sheets with 10 nm average pore size the electrocatalytical response could be improved drastically.

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Redox Matrices for Redox Bio-Catalysts - Film Thickness and Film Thickness Distribution

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Redox hydrogel films built from polymeric materials are among the most commonly used matrices for the immobilization, electrical wiring as well as protection of redox (bio-)catalysts in electrochemical systems for sensing or energy conversion. Since the film thickness defines the contributions from mass transport, electron transfer and catalysis, reproducible formation of films with controlled and homogeneous thicknesses is essential. We introduced in-situ gelation procedures for the formation of viologen modified hydrogel films for the integration and protection of hydrogenase as catalyst for H_2 oxidation (1-3) and H_2 evolution. We demonstrate precise control of the average film thickness in the range of 0.1 to 300 µm. However, straightforward assessment of the electroactive film thickness distribution was not accessible by classical surface roughness characterization methods such as AFM. Therefore, we developed a simple electroanalytical approach based on linear sweep voltammetry to extract the electroactive film thickness distribution. This powerful method is in principle applicable to any redox-active matrix involving diffusion-like processes such as electron hopping or counter ion transport.

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Lipid Bilayers on Gold Electrodes: Mechanism of Formation and Interactions with Membranolytic Peptide-Based Compounds

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Lipid bilayers supported on solid substrates are often considered as simplified models mimicking the architecture of biological membranes. Properties of lipid films are determined by numerous factors which include lipid composition, length and the saturation of the hydrocarbon chains and the identity of polar head groups. Nature of the solid substrate is equally important as it may substantially affect the mechanism of the bilayer formation and its molecular arrangement. Hydrophilic surfaces like glass, quartz and mica are most commonly used as supports for bilayer deposition. However, metal surfaces were demonstrated to be useful as well.[1] Immobilization of the lipid bilayers on gold brings several advantages, for example the membrane may be exposed to static electric fields in the range of 10^7 - 10^8 V m^{-1}, which is comparable to the static electric field experienced by natural biological membrane. Importantly, the structure of the supported film as well as lipid-lipid and lipid-protein interactions can be probed in full electrochemical conditions.

One of the most popular methods to obtain supported lipid bilayer involves fusion and spreading of small unilamellar vesicles (SUV).[2] This process is well understood on hydrophilic surfaces, but little is known about the mechanism of SUV spreading on gold surface. The most direct way to address this problem is the use of nanoscale imaging techniques such as scanning probe microscopy (SPM) combined with electrochemical setup. By following the changes in the topography and thickness of lipid film as a function of time, it was possible to propose the detailed mechanism of SUV spreading on Au(111) surface and compare it with hydrophilic supports. It was found that the mechanism of the bilayer formation on gold involves several steps including accumulation of the vesicles followed by release lipid molecules which adsorb on Au(111) surface giving rise to appearance of highly ordered stripe-like domains. The latter serve as a template for the buildup of hemimicellar film, which facilitates further adsorption and rupture of the vesicles leading to formation of the single bilayer.

Regardless of the mechanisms of bilayer formation and the nature of the solid substrate, supported lipid membranes can serve as platforms for evaluation of the activity of membrane-disrupting agents like antimicrobial peptides or lipopeptides.[3,4] Such compounds have ability to aggregate in the cellular membrane and form pores or fluidize the lipid films. The mechanism of their action and the changes in permeability of the lipid bilayers can be evaluated using AFM and electrochemical methods. It was found that the strength of interactions depends on peptide/lipopeptide concentration and lipid composition of the membranes as demonstrated for supported lipid bilayers mimicking either mammal or bacterial cell membranes.

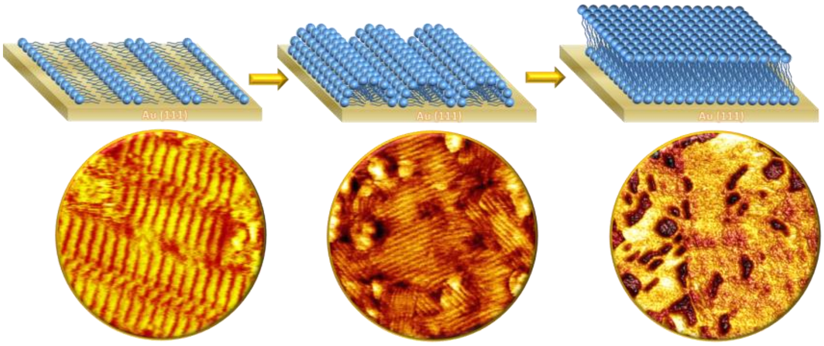

Figure 1. Sequential mechanism of formation of lipid bilayer on Au(111) surface.

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The catalytic reaction of proteins from the respiratory chain immobilized on gold nanoparticles studied by bioelectrochemistry and vibrational spectroscopies

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Integral membrane proteins account for approximately one third of the coding capacity of the genes in an average organism. They are critically important for multiple central functions in any living cell. It is estimated that membrane proteins provide 80 to 90% of the targets relevant for the chemical and pharmaceutical industries. It is thus highly interesting to develop experiments that help to understand their function and at the same time, that allow identifying inhibitors.

Here we will focus of the terminal oxidases from the respiratory chain from *E. coli*. Whereas cytochrome *bo*$_3$, works at 'normal' oxygen level, cytochrome *bd* becomes active at microaerobic conditions. Both enzymes have at least one quinone binding site that is critical for their function. The quinone binding was correlated with the catalytic oxygen reaction in wild type and mutant enzymes immobilized on gold nanoparticles, or on other nanostructures surfaces and studied by electrochemical, Raman and infrared spectroscopic approaches as well as surface enhanced techniques. [1-5]

The catalytic reaction of cytochrome *bo*$_3$ was found to be strongly dependent on the type of quinone. Electrochemically induced FTIR difference spectroscopic data reveals that D75 is protonated upon quinone reduction, whereas other residues are mostly present to stabilize the radical form of the quinone. No evidence for a second binding site is seen.

The second quinol oxidase from *E. coli* studied, cytochrome *bd* was also successfully immobilized on nanostructured electrodes. In combination with infrared spectroscopies it was found that the enzyme can function with both, mena- and with ubiquinone and that the deprotonation of an acidic residue takes place to accommodate the menaquinone. The inhibition of the oxygen reaction was studied for different inhibitors.

It is noted that quinone binding sites seems to differ strongly between organisms and enzyme types. They are thus an interesting target for specific inhibitors, i.e in order to function as antibiotics.

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Enhanced Microbial Electrocatalysis with Naphthoquinone Redox Polymer Modified Electrodes

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Extracellular electron transfer (EET)[1] from microorganisms to electrode surfaces is one of the greatest challenges in microbial electrochemistry. In microbial electrochemical systems (MESs), *Shewanella oneidensis* MR-1 is widely studied due to its electrogenic properties and versatile metabolism. Direct electron transfer (DET) from *S. oneidensis* MR-1 to electrodes has been documented, however, the electrical performance of a DET-based system is usually lower when compared to a system based on mediated electron transfer (MET). Polymeric mediators are preferred in MESs due to their efficient electron shuttling properties. A naphthoquinone (NQ)-based redox polymer[2], having a relatively low formal potential ($E^{0\prime}$= -0.3 V *vs.* SCE) was reported as an alternative mediator for enzymatic bioelectrocatalysis. Recently we have demonstrated NQ-functionalized linear polyethylenimine (NQ-LPEI) for photo-bioelectrocatalysis of chloroplasts[3]. Here we report on improved electrocatalysis of *S. oneidensis* MR-1 on NQ-LPEI modified Toray carbon paper electrodes and carbon felt. Experiments were conducted either in a three electrochemical cell configuration or in air-breathing single chamber microbial fuel cell (MFC). In the presence of 18 mM lactate, *S. oneidensis* MR-1 immobilized on a bare Toray carbon paper electrode generated a biocatalytic current of 0.3 ± 0.1 µA cm^{-2}. On NQ-LPEI modified Toray electrodes, the biocatalytic current is improved to 42 ± 8 µA cm^{-2} and further improved to 370 ± 40 µA cm^{-2} on a carbon felt modified with this polymer. The complete MFCs, equipped with the NQ-LPEI modified carbon felt anode and Pt-free cathodes, achieved a maximum power output of 530 ± 20 mW m^{-2}, compared to 190 ± 50 mW m^{-2} achieved in the MFCs with DET based anodes. These findings suggest that NQ-LPEI modified polymers could be used to further improve the EET capabilities of known natural electrogenic bacteria.

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Direct and mediated electrochemistry of immobilized cellobiose dehydrogenase

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Cellobiose dehydrogenase, CDH, (EC 1. 1. 99. 18) is a flavocytochrome that is of interest as a catalytic redox enzyme for application in the bioanode of a biofuel cell [1]. The enzyme contains both heme and flavin domains joined by a flexible peptide chain [2], Figure 1. In this work we have immobilized mutants of cellobiose dehydrogenase from *Myriococcum thermophilum* at electrode surfaces by coupling engineered cysteine residues on the surface of the enzyme to maleimide groups covalently attached to the electrode surface, Figure 2.

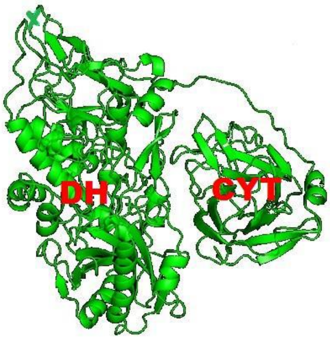

Fig. 1. Cellobiose dehydrogenase.

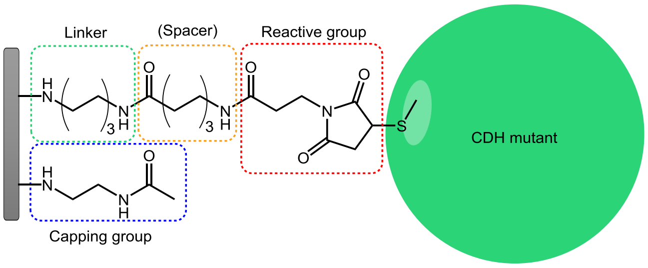

Fig. 2. Attachment scheme.

Maleimide and capping groups were immobilized onto the electrode surface using amine oxidation and solid phase synthesis approaches as described in our earlier work [3]. The maleimide groups were diluted on the surface to ensure efficient CDH immobilization, Figure 2.

The immobilized CDH mutants were found to show both direct electrocatalytic oxidation of substrate around -0.15 V *vs.* SCE through the heme, and mediated electrocatalytic oxidation of substrate using ferrocene carboxylic acid at around +0.15 V *vs.* SCE. The electrodes show excellent stability allowing detailed comparison of the kinetics of the reactions for the different mutants and investigation of the effects of calcium ion and pH on the reaction kinetics.

In this talk we will discuss the kinetics of the immobilized enzyme and the effects of the choice of mutation site.

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Bioelectrochemical Haber-Bosch Process: Coupling Hydrogenase And Nitrogenase To Create An Ammonia-Producing H_2/N_2 Fuel Cell

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Nitrogenase is a metal-containing enzyme that is able to facilitate the biological fixation of N_2 to $2NH_3$, as well as being able to reduce alternative substrates such as alkynes (*i.e.* acetylene), CN^-, R-CN, R-NC, CO, CO_2, N_2O, N_3^-, NH_2NH_2, OCS and CS_2.[1] Nitrogenase comprises a reducing component (Fe protein) and a catalytic component (MoFe protein), where the transient association of both components affords ATP-hydrolysis-coupled electron transfer (ET) and subsequent substrate reduction. The immobilization of the MoFe protein onto a carbon electrode was previously demonstrated, where the use of cobaltocene as an electron mediator was able to support the reduction of H^+ to H_2, and N_3^- and NO_2^- to NH_3.[2] N_2 reduction, however, was not achieved.

In this study, the use of methylviologen (MV, N,N'-dimethyl-4,4'-bipyridinium) as an electron donor to nitrogenase is initially reported, whereby bioelectrochemical reduction is able to support H^+ reduction to H_2 and N_2 reduction to NH_3. Short (1 h) bioelectrosynthetic experiments at -0.85 V (*vs.* SCE) resulted in the production of 2.1 ± 0.5 µmol NH_3 mg^{-1} MoFe protein, operating at a Faradaic efficiency of 59 ± 6 %.

Following the successful bioelectrochemical production of NH_3 from N_2, this MV-mediated nitrogenase biocathode was coupled with a H_2-oxidizing hydrogenase bioanode to yield a H_2/N_2 enzymatic fuel cell (EFC). In order to enable the simultaneous production of electrical energy and NH_3, MV was also used as the anodic mediator resulting in an open circuit potential of 228 ± 28 mV. The H_2/N_2 EFCs possessed maximum current and power densities of 48 ± 3 µA cm^{-2} and 1.5 ± 0.1 µW cm^{-2}. To demonstrate the ability of the EFCs to simultaneously produce electrical energy and NH_3, a low potential difference (10 mV) was applied for approximately 2 h resulting in the passage of ~ 60 mC of charge across the EFC, where 286 nmol NH_3 mg^{-1} MoFe protein was produced at a Faradaic efficiency of 26 %.

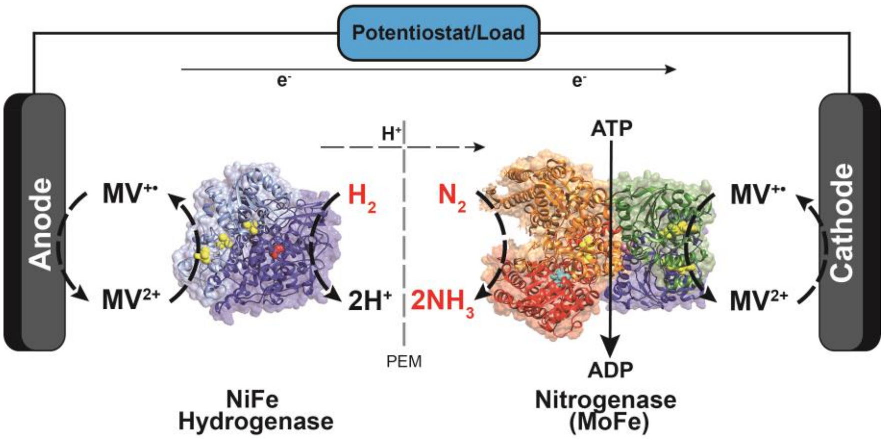

Figure 1 – H_2/N_2 enzymatic fuel cell utilizing hydrogenase at the anode and nitrogenase at the cathode. MV is used as the anodic and cathodic mediator.

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An energy-harvesting device based on supercapacitive enzyme-modified nanoporous gold electrodes: an autonomous pulse generator

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Integration of biological fuel cells (BFCs) with electrochemical capacitors (known as supercapacitors), can enable high specific power density combined with more durable fuel cells[1-3]. These hybrid devices can generate cyclic, scaled up power pulses from the discharge of the supercapacitor, which is then recharged via the BFC in open-circuit mode. We describe a supercapacitor/biofuel cell hybrid device obtained by the facile, one-step electrodeposition of PEDOT/Os polymer/enzyme onto dealloyed nanoporous gold electrodes[4]. The device can generate a current density pulse of 2 mA cm^{-2}, with an instantaneous maximum power density of 608.8 μW cm^{-2}, a power output 468 times higher than that of the BFC alone. The modification layer shows reasonable stability without visible leakage of redox mediators over 50 cycles of operation at 0.2 mA cm^{-2} for approximately 7 hours. A proof-of-concept pulse generator, simulating the requirements of a pacemaker (0.02 Hz pulse at 10 μA for 0.5 ms), has been successfully demonstrated using a series of connected cells[4].

On replacing the enzymatic cathode with an abiotic, solid-state NPG/MnO_2 electrode, a rechargeable biobattery with a maximum power density of 2.3 μW cm^{-2} and an OCV of 0.49 V (in 10 mM glucose) was obtained. Power recovery of the cathode has been observed, resulting in an oxygen-independent biobattery/supercapacitor hybrid device. A stable performance (50 cycles of discharge/charge) at a current density of 0.1 mA cm^{-2} was obtained over a period of 25 hours. The device can be discharged at various current densities up to 2 mA cm^{-2} supplying a maximum instantaneous power density of 676 μW cm^{-2}, 294 times higher than that from the biobattery alone. The mechanism of operation of the biobattery is described in detail.

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Redox-Pair-Defined Electrochemistry: Simple Biamperometric Setup for Enzymatic and Immunochemical Biosensors (and Not Only)

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A routine, large scale monitoring, such as point-of-care systems, requires inexpensive and simple analytical schemes [1,2]. An electroanalytical concept of biamperometry has been overlooked for such sensing systems for decades due to the widespread potentiostat-controlled methods. Herein, this technique is introduced as a powerful tool [2].

In particular, its ability to eliminate electrochemical interferences is highlighted on a case-study where $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$, aminoferrocene($Fe^{2+}$)/$[Ru(NH_3)_6]^{3+}$ and ascorbic acid are employed as two redox pairs and one interfering compound, respectively. A 15-times higher specific vs. non-specific signal was observed even at such unfavorable conditions as a molar ratio 1:5 of specific-to-interfering redox entities. It has to be emphasized that the ascorbic acid (vitamin C) was present in an abnormally high 5 mM concentration. This simple system was successfully used for the determination of glucose in blood plasma without any significant interferences (Fig. 1) [2].

Biamperometry provides superiority in the rejection of interferences and possibility of tuning of the redox system by utilization of complementary redox partner with suitable oxidation/reduction potential. Moreover, biamperometry is also very interesting for immunosensing applications. Detection of immunoreaction occurring at the electrode surface using impedance measurement combined with biamperometric setup provides very simple and low-cost analytical system. This will be documented on a model determination of anti-human serum albumin antibody.

A further promising sophisticated usage of biamperometry will be illustrated on the study of an unstable redox system – oxygen dependent oxidation of $[Ru(NH_3)_6]^{2+}$ in an aqueous environment.

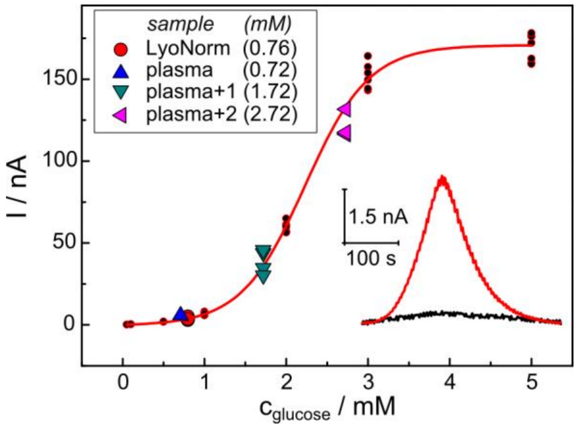

Fig. 1 Calibration curve for the biamperometric glucose biosensor (black data points). Blood plasma samples (originally with 0.72 mM glucose, and glucose-fortified, +1 and +2 mM) were 1:4 diluted with buffer containing 5 mM $Ru(NH_3)_6^{3+}$. Right lower corner: comparison of the signal of GOD (red curve) and BSA (black curve) modified electrodes to plasma sample (0.72 mM glucose) is depicted.

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Polymer-supported enzyme – electrode contacts as basis for the construction of bioelectrocatalytic sensing electrodes

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Polymers are valuable materials for immobilizing enzymes, but they can also be used to “wire” proteins with electrodes. For this purpose often redox polymers with defined redox centres and conducting polymers with electronic conductivity are applied. With focus on intrinsic conductivity we have studied the interaction of sulfonated polyanilines with dehydrogenase enzymes. Besides (PQQ)glucose dehydrogenase (PQQ-GDH) [1,2] and fructose dehydrogenase (FDH) [3] recently xanthine dehydrogenase (XDH) has been studied.

XDH is a complex enzyme comprising different redox active cofactors: a mononuclear, five-coordinated molybdenum center, two [2Fe-2S] clusters, and a flavin adenine dinucleotide. For these investigations a copolymer PMSA1 (poly(2-methoxyaniline-5-sulfonic acid)-co-aniline has been synthesized chemically and characterized. First, the polymer-enzyme interaction has been studied in solution with UV/Vis and cyclic voltammetry indicating that electron transfer from the substrate-reduced enzyme to the polymer is feasible.

Second, the bioelectrocatalytic reaction has been analysed in dependence on the solution pH at ITO electrodes. Two processes can be identified: (i) A polymer supported enzyme electrocatalysis and (ii) a product-mediated communication of the enzyme with the electrode. The polymer supported bioelectrocatalytic process starts already at rather low pH and becomes inefficient at basic pH values – mainly because of decrease in conductivity of the polymer.

Third, different types of enzyme electrodes are constructed based on the feasibility of electron transfer between XDH and the polymer. XDH is here immobilized on planar ITO electrodes by means of a polymer layer. These enzyme electrodes exhibit well-defined, substrate-induced bioelectrocatalytic currents starting at potentials below 0 mV vs. Ag/AgCl. The magnitude of catalytic currents can be enhanced, when porous ITO electrodes with pore sizes of ~ 300 nm are used. The open pore structure allows incorporation of high amounts of polymer and enzyme. A current increase of at least one order of magnitude is found compared to flat ITO.

The investigations demonstrate that sulfonated polyanilines are valuable tools in connecting enzymes with electrodes and that the polymeric environment can also modify the properties of the enzyme as has already been found for FDH and PQQ –GDH.

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Enhanced Bioelectrocatalytic Reduction of Oxygen Using Hybrid Biocathodes Containing Anthracene-modified MWCNTs Decorated With $Ni_{90}Pd_{10}$ Nanoparticles

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The oxygen reduction reaction is at the core of several renewable energy conversion technologies, such as fuel cells, metal-air batteries, water electrolysis, among others. Particularly in fuel cells, this reaction is of major interest because it has limited the output power density of many of these systems, either in those using metal-based catalysts or in biological devices. In this investigation, we report the preparation of hybrid biocathodes containing enzymes and metallic nanoparticles targeting the bioelectrocatalytic reduction of oxygen in buffered solutions. The goal was to immobilize either laccase or bilirubin oxidase onto anthracene-modified multi-walled carbon nanotubes (MWCNTs) decorated with $Ni_{90}Pd_{10}$ metallic nanoparticles [1-3]. The electrochemical characterization showed that the presence of the hydrophobic moieties does not affected the synthesis protocol, attesting for the possibility of obtaining a bifunctional material containing both the metallic nanoparticles and the aromatic moieties employed for enzyme orientation (Figure 1A). Based on the electrochemical data obtained with the hybrid biocathodes, enhanced direct bioelectrocatalytic reduction of oxygen could be clearly noticed by both laccase and bilirubin-based biocathodes, being more evident the improvement provided to the hybrid bioelectrode prepared with the enzyme laccase. In such bioelectrode, the targeted reaction occurs at lower overpotential and provide about 50 % higher current density (Figure 1B), thus showing the benefit of incorporating small amounts of $Ni_{90}Pd_{10}$ metallic nanoparticles into enzymatic cathodes for the oxygen reduction reaction.

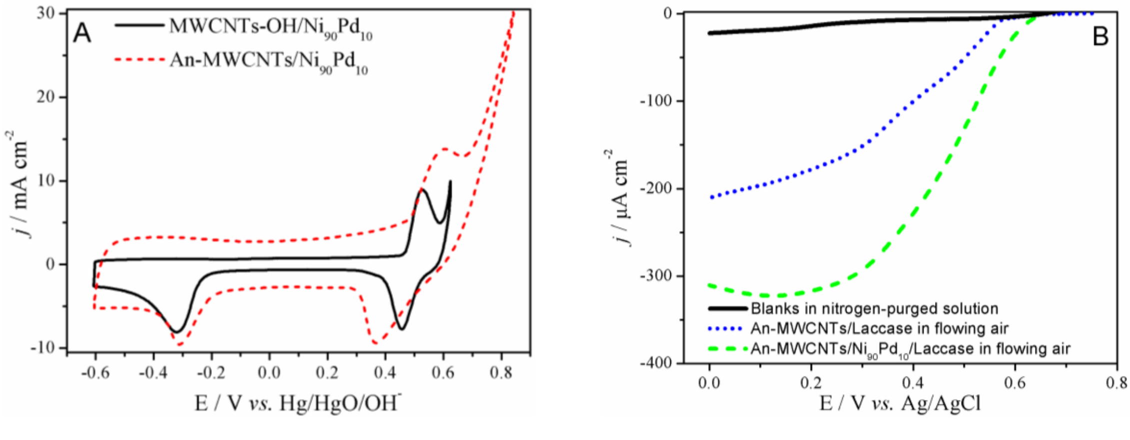

Figure 1. (A) Representative cyclic voltammograms obtained for the synthetized An-MWCNTs/$Ni_{90}Pd_{10}$ and the control MWCNTs-OH/$Ni_{90}Pd_{10}$ registered in 0.1 mol L^{-1} NaOH at 20 mV s^{-1}. (B) Representative cyclic voltammograms performed at 1 mV s^{-1} from 0.8 to 0.0 V vs an Ag/AgCl, in the presence and in the absence of oxygen, which was obtained with the hybrid biocathodes in citrate/phosphate buffer solutions at pH 4.5 for laccase-based biocathode.

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Artificial Synapse between Surface Modified Electrode and Neuron

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Knowledge and technology on neural interface have remarkably advanced along with the increasing social and scientific interests in the brain and nerve system. The main objective of neural interface technology is to establish connections between the outside world and the nervous system, to acquire neural information or to understand neural networks. Most of neural interface techniques rely on the physical contacts simply placing bare electrodes near the nervous system to let them sense electric field and/or detect neurotransmitters in given model systems. However, neuronal cells in the real neurobiological system communicate via synapses, which are narrow intercellular gap junctions between neurons. Neural information such as chemical neurotransmitters and electrical signals transmits through synapses and specificity of the synaptic transmission (excitatory or inhibitory synapse) is determined by trans-synaptic cell adhesion molecules (CAMs) that are intensively located on the membrane of neurons in the synaptic clefts. As recent studies have revealed the structures and functions of such CAMs, we suggests an artificial synaptic interface closely connecting an electronic device and a neuron. To construct the proposed artificial synapse, we engineer the fluorescent protein and biotin-tagged neuroligin 1 (NL1), neuroligin 2 (NL2) and slitrk 3 (SL3) among well-known post-synaptic CAMs, and then modify a microelectrode surface with them. Firstly, we confirm that the engineered postsynaptic CAMs can be immobilized on microbead surface selectively induced the excitatory (glutamatergic) and inhibitory (GABAergic) presynaptic differentiations when contacted with primary hippocampal neurons. Then, we fabricate the chemically modified microelectrode arrays, on which the engineered postsynaptic CAMs allow us to investigate the electrochemical properties of the modified surface. The engineered proteins are immobilized on gold surface electrodeposited on TiN microelectrode array. The artificial synapses consisting of pre-synapse and the modified electrode can work as an active electrode even with multiple stacks of functional units. This work is expected to provide a new platform of studies on neural interfaces, which enable direct investigation of electrochemical behavior inside synaptic clefts and thus bilateral transmission of synaptic-based neural information.

Redox Enzymes Engineering Using Synthetic Biology and Synthetic Chemistry

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Redox enzymes are the main catalysts in biosensors and biofuel cells, however, their activity and electron transfer (ET) pathway that takes place when in close contact with an electrode is not well defined, as oppose to their biocatalytic activity when in solution. Synthetic biology is a relatively new field in Chemistry and Biology, where different standard genetic "parts" are combined together to generate a new functionality in a living cell. Among the different new functions, is the ability to expand the genetic code in a way that enables the insertion of new functional chemical groups into proteins in a site-specific manner and in a controlled way.

We have utilized our knowledge in this technology to modify several redox enzymes such as Copper Oxidase from *E. coli* (CueO), FAD dependent Glucose dehydrogenase (GDH), Alcohol dehydrogenase from *Zymomonas mobilis* (ADHII) and to generate an enzymatic cascade of reactions in an anode of a biofuel cell. The modifications we have conferred to these enzymes include, their site-specific attachment to electrodes in order to have a single population relative to the electrode surface, to control ET kinetics, to control substrate channeling and to photo activate an enzyme that is displayed on the surface of *E. coli*.

I will demonstrate the different applications we have developed in our lab using site-specific modifications of redox enzymes with unnatural amino acids (UAAs) that served as bio-orthogonal chemical handles for the further modification of these redox enzymes, by redox active groups, linkers for electrode attachment with a defined distance, and in order to photo-activate the enzymatic redox activity of an enzyme in a site-specific manner (depending on the mutant that was generated).

Construction of Direct Electron Transfer-Type Bioelectrodes with High Performance

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Direct electron transfer-type (DET-type) bioelectrocatalysis has attracted significant attention worldwide in recent years. Because a DET-type system is constructed only with an enzyme and an electrode without the use of an ionically conducting membrane as a separator, it is possible to miniaturize devices to extremely small sizes and to minimize the thermodynamic overpotential required in a mediated electron transfer-type system between the redox center of the enzyme and a mediator in solution. To date, DET-type reactions of several oxidoreductases have been demonstrated, and applied to enzymatic biofuel cells and biosensors.

When we consider an oxidation of a substrate as follows:

$$\mathrm{S} \xrightarrow{k_{\mathrm{mt}}} \mathrm{E_R} \xrightarrow{k_{\text{elec-enz}}} \mathrm{E_O} \quad \text{and} \quad \mathrm{E_R} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{E_O} \underset{k_{-2}}{\overset{k_2(=k_2(2)c_{\mathrm{S}}}{\rightleftarrows}} \mathrm{ES} \xrightarrow{k_3} (\mathrm{E_R})$$

the steady-state current density of DET-type bioelectrocatalysis is given by [1]

$$\frac{1}{j} = \frac{1}{j_{\mathrm{mt}}} + \frac{1}{j_{\text{elec-enz}}} \quad \text{and} \quad \frac{1}{j_{\text{elec-enz}}} = \frac{1}{k_1} + \frac{1}{K_2 k_3} + \frac{1}{K_1 K_2 k_3} + \frac{1}{k_3} (= n_{\mathrm{S}} F k_{\mathrm{E(2)}} \mathit{\Gamma}_{\mathrm{E}} c_{\mathrm{S}} = n_{\mathrm{S}} F k_{\text{elec-enz}} \mathit{\Gamma}_{\mathrm{E}})$$

$$\text{with } j_{\mathrm{mt(RDE)}} = 0.62 n_{\mathrm{S}} F D_{\mathrm{S}}{}^{2/3} \nu^{-1/6} \omega^{1/2} c_{\mathrm{S}}, \quad K_1 = \frac{c_{\mathrm{E_O}}}{c_{\mathrm{E_R}}} = \frac{k_1}{k_{-1}}, \quad k_1 = k^\circ \eta_1{}^{1-\alpha}, \quad k_{-1} = k^\circ \eta_1{}^{-\alpha},$$

$$\eta_1 \equiv \exp\left(\frac{n_{\mathrm{E}} F (E - E^{\circ\prime}{}_{\mathrm{E}})}{RT} \right) = K_1, \text{ and } K_2 = \frac{c_{\mathrm{ES}}}{c_{\mathrm{E_O}}} = \frac{k_2}{k_{-2} + k_3}.$$

In order to increase the standard rate constant of interfacial electron transfer (k°) and the surface concentration of an adsorbed enzyme with orientations suitable for DET ($\mathit{\Gamma}_{\mathrm{E}}$), construction of mesopore-structured electrodes with pore sizes close to the size of an enzyme for DET-type bioelectrocatalysis [2,3] and surface modification to induce electrostatic attractive interaction with an redox center of an enzyme for DET-type bioelectrocatalysis [4-8] are very important. In the case of bilirubin oxidase (BOD), negatively charged part and hydrophilic part are required at electrode surface with suitable mesopores [4], and diffusion controlled condition was achieved under rotating disk conditions ($j \cong j_{\mathrm{mt(RDE)}} (\cong 8.4\,\mathrm{mA\,cm^{-2}}{}_{\omega = 4000\,\mathrm{rpm},\,25\,^\circ\mathrm{C}}) (<< j_{\text{elec-enz}})$ [5]. However, because of low concentrations (c_{S}) of gaseous substrates including O_2, it is essential to construct gas diffusion-type bioelectrodes. The j value at an optimized gas diffusion-type BOD-adsorbed electrode reached about 30 mA cm^{-2} under quiescent and passive conditions [6]. Copper efflux oxidase [4] and hydrogenase (H_2ase form *Desulvovibrio vulgaris* Miyazaki F) [6] prefer positively changed electrodes, while D-fructose dehydrogenase (FDH) prefers CH_3O-group [7]. High speed supply of H_2 to H_2ase in a gas diffusion system can suppress an oxidative inhibition of H_2ase [8]. A protein engineered variant of FDH without one of three heme *c* moieties was very effective to reduce the over potential of D-fructose oxidation [9]

By combining DET-type biocathodes and bioanodes, several biofuel cells were constructed with high performance under quiescent and passive mode: 8.4 mW cm^{-2} at an H_2/O_2 biofuel cell at 40 °C [8], 6.1 mW cm^{-2} at an H_2/air biofuel cell at 25 °C [6], and 2.6 mW cm^{-2} at a D-fructose/O_2 at 25 °C [9].

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Li/S Cells with Cetyltrimethylammonium Bromide Modified Sulfur-Graphene Oxide-Carbon Nanotube Electrodes

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In recent years, the lithium/sulfur (Li/S) cell has been spotlighted as a next generation Li rechargeable cell for high specific energy applications, especially the electrical vehicle (EV) due to its high theoretical specific energy of 2680 Wh/kg. The challenges to maximize the performance of the Li/S cell have mainly related to overcoming the drawbacks of the sulfur electrode. Previously, we have developed a cetyltrimethylammonium bromide modified sulfur-graphene oxide-carbon nanotube (S-GO-CTA-CNT) nano-composite that showed promising electrochemical performance. To maximize the ability of the S-GO-CTA-CNT electrode for high specific energy applications, it is important to optimize the cell system by understanding the electrochemical behavior of the S-GO-CTA-CNT electrode under various experimental conditions such as electrolyte composition and electrode structure.

First of all, we have investigated the effect of the electrolyte composition on the electrochemical behavior of the S-GO-CTA-CNT electrode. Electrodes using S-GO-CTA-CNT active material with a 3-dimensional (3-D) aluminum foam as current collector were evaluated in type 2032 coin cells with two different electrolytes; an ionic liquid based electrolyte and conventional electrolyte (the compositions of the electrolyte are given in the Figure 1 caption). As shown in Figure 1a and 1b, higher charge and discharge overpotentials were observed at both 0.2 and 0.8 mA/cm^2 when the electrolyte contains ionic liquid. The discharge specific capacity of the ionic liquid electrolyte cell was a little lower than that of the conventional electrolyte cell for 23 cycles, however ionic liquid cell showed slightly better capacity retention with a higher Coulombic efficiency above 99 % than those of the conventional electrolyte cell (96~98 %) for 30 cycles. These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

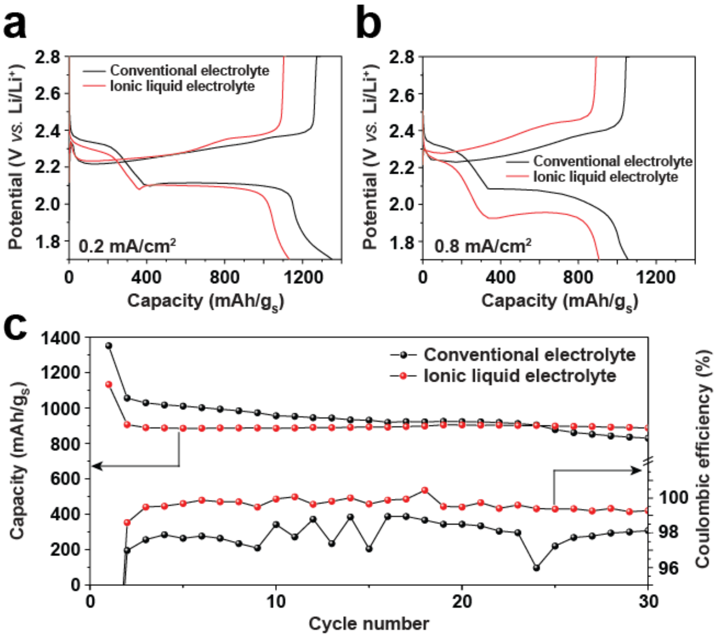

Figure 1 Electrochemical test results of the S-GO-CTA-CNT electrodes. Voltage profiles of the electrodes (a) at 0.2 mA/cm^2 for the first cycle and (b) at 0.8 mA/cm^2 for the second cycle. (c) Cycling performance of the electrodes with ionic liquid based electrolyte (1 M LiTFSI in $PYR_{14}TFSI$/DOL/DME (1:1:1, *v/v*) with 0.5 M $LiNO_3$) and conventional electrolyte (1 M LiTFSI in DOL/DME (1:1, *v/v*) with 0.5 M $LiNO_3$). Average sulfur loading of the electrodes was ~ 3.7 mg/cm^2.

Design principles for self-forming and self-healing stable SEI layer for Li metal anodes

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Abstract:

The driving range of electric vehicles are currently severely limited by the energy density of the current Li-ion batteries. The energy density of Li-ion batteries can be improved by replacing graphite anodes with lithium metal anode. However, the main issue with lithium metal anodes is that they form dendrite like structures, which grow on cycling and eventually short the battery. It has been shown that forming stable SEI layers on top of lithium metal anodes can stop dendrite formation.[1] It is well known that electrolyte components play a crucial role in formation of stable SEI as the SEI components primarily comprise of decomposition products of the solvent, the salt and the additives in the electrolyte. Ethylene Carbonate leads to the formation of stable SEI components in the case of graphite anodes. The major properties of the SEI components that determine stable deposition of lithium are overpotential of lithium deposition, shear modulus, ionic and electronic conductivity and the morphology (porosity) of the SEI component.

In this work, we will discuss a new approach to forming a stable SEI layer shown in Figure 1 with sufficient ionic conductivity and mechanical strength and at the same time maintaining a uniform morphology of the SEI layer. This is achieved by choosing appropriate solvents, salt anions and additives in the battery, which will form a spatially homogenous SEI layer during a forming step of the battery. The detailed formation steps will be discussed. Using the appropriate solvent, salt and additives in the desired proportion leads to a spontaneously formed SEI layer. The SEI component must possess low electronic conductivity but at the same time have high lithium ion conductivity. Low electronic conductivity will result in passivation and in turn the formation of a stable SEI layer. It is worth highlighting that most SEI components in batteries such as LiF, LiOH, Li_2O, Li_2CO_3, etc are insulators and have low electronic conductivity. The design principles associated with the selection of the electrolyte additives and salt components will be discussed.

The battery under cycling conditions will unavoidably form cracks in the SEI layer. Our approach is to provide a persistent source of dissolved additive salt components for self-healing of these defects formed in the self-formed solid electrolyte during battery cycling. Depending on the additives and the solvent, there is a large window for tuning the dissolution rate of some SEI components. The under-coordinated defect sites will possess a significant driving force for deposition from the solution phase. An important consideration is that the dissolved species in the electrolyte should also be stable to the potentials at the Li-ion battery cathodes. Unstable species will result in a shuttling reaction of the species in the along with parasitic processes which will result in poor cycling efficiency.

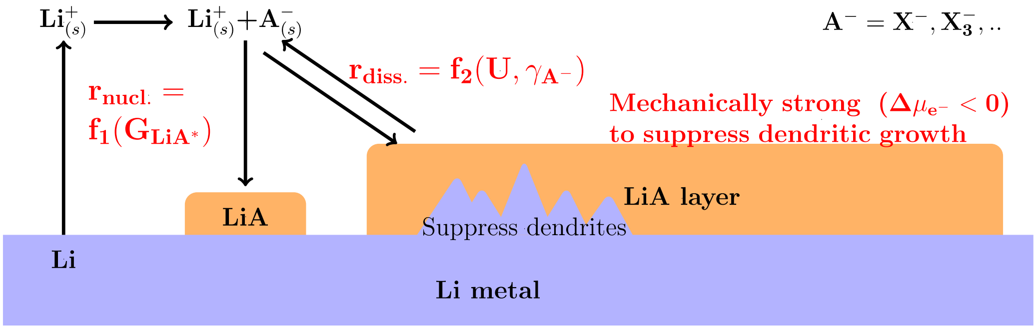

Figure 1: Schematic of the self-forming scheme for stable SEI formation at lithium metal anode.

We gratefully acknowledge support from the U.S. Department of Energy, Energy Efficiency and Renewable Energy Vehicle Technologies Office under Award Number DE-EE0007810.

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Improved Anode Performance of Nut-shaped Pristine Li_3VO_4 for High Capacity Lithium-ion Batteries

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Recently, Li_3VO_4 has been investigated as a promising anode material for LIBs[1-3]. Li_3VO_4 showed intercalation/deintercalation of Li^+ ion at voltages ranging between 0.5 –1.0 V versus Li^+/Li[2], which is lower than $Li_4Ti_5O_{12}$. The theoretical specific capacity of Li_3VO_4 (394 mAhg^{-1}) is higher than that of the commercial graphite anode (370 mAhg^{-1})[4]. Despite having many advantages, such as, safe voltage, high specific capacity and high Li^+ ion conductivity ($\approx 10^{-4}$ S m^{-1})[5], low electrical conductivity limits the use of Li_3VO_4 as a suitable anode material for LIBs. Many attempts have been made to improve the electrical conductivity of Li_3VO_4[6-9]. Moreover, Li_3VO_4 prepared by solid state reaction[1,2], sol-gel[7] and hydrothermal method[10] result in larger particle sizes. Low surface area and slow Li^+ ion diffusion are the main drawback with the large particle sizes. Herein we report a rapid synthesis of nut-shaped Li_3VO_4 via a low temperature modified hydrothermal method. The pristine material is highly crystalline and phase pure without any post calcinations as ascertained by the powder-XRD pattern analysis. The refined lattice parameters, a = 5.444(3), b = 6.313(3) and c = 4.943(3) Å, conform to the reported orthorhombic Li_3VO_4. SEM analysis showed formation of nut-shaped microstructure in addition to the presence of porous networks formed by interconnected nanocrystals of Li_3VO_4 inside the nut-shells. Electrochemical performance of the pristine Li_3VO_4 anode material is investigated in the potential range 0.2 – 2.0 V at different C-rates. The charge/discharge studies show the highest discharge capacity of 613 mAhg^{-1} and charge capacity of 385 mAhg^{-1} at 0.1C for the first cycle. Further, a discharge capacity of 168 mAhg^{-1} at 0.2C after 10 cycles and 117 mAhg^{-1} at 0.5C after 40 cycles are exhibited by the nut-shaped pristine Li_3VO_4. The electrochemical performance of the nut-shaped Li_3VO_4 is considered to be either superior or comparable to those reported with bare, nanostructured or carbon coated Li_3VO_4.[3,6,10,11]

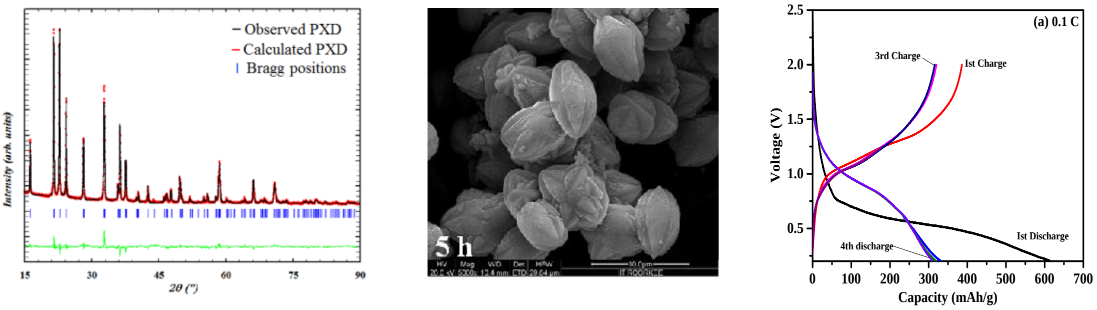

Figure 1 Rietveld refined P-XRD pattern (left), SEM micrograph (middle) and electrochemical charge-discharge characteristics (right) of pristine Li_3VO_4.

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Advanced Li-O_2 Battery Utilizing Free-Standing Meso-pores Carbon Nano-tubes (CNTs) Tissues-Perfluorocarbons (PFCs) Hybrid Air-electrodes

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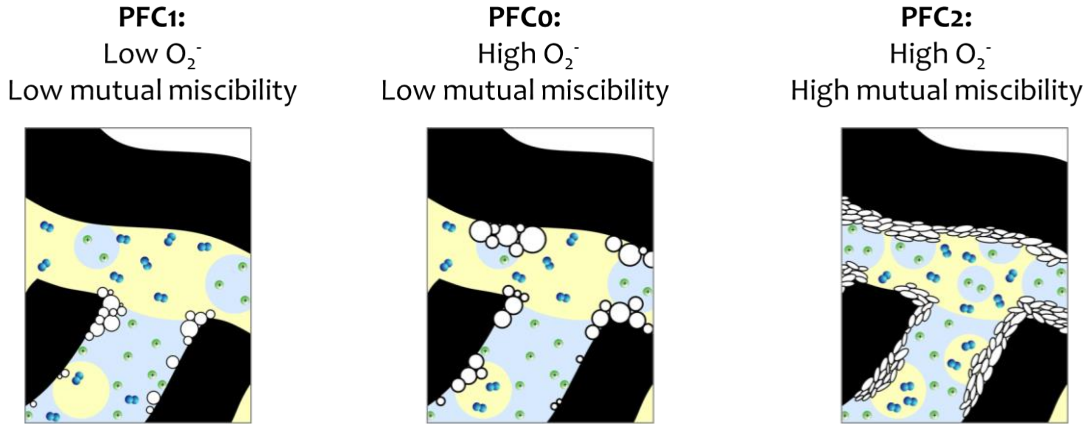
Adding immiscible perfluorocarbons (PFCs) possessing superior oxygen solubility and diffusivity to a free-standing (metal-free and binder-free) CNTs air-electrode tissues having a meso-pore structure, allows to fully maximize the advantages of PFCs as oxygenated-species' channels-providers. The discharge behavior of hybrid PFCs-CNT Li-O2 systems demonstrates a drastic increase in cell capacity at high current density (0.2 mA cm^{-2}), where oxygen transport limitations are best illustrated. The results of this research reveal several key factors affecting PFCs-Li-O_2 systems. The incorporation of PFCs with higher superoxide solubility, but more importantly higher PFCs/electrolyte miscibility, in an air-electrode with meso-pores structure, rather than an interconnected meso and micro-pore structure, allows a better exploitation of the PFCs potential and consequently, enhances the utilization of the air electrode' surface area via the formation of an artificial three phase reaction zone. Associated mechanisms are discussed along with insights into an improved Li-O_2 battery system



PFC1: Low O_2^- Low mutual miscibility

PFC0: High O_2^- Low mutual miscibility

PFC2: High O_2^- High mutual miscibility

Schematic representations of CNT air cathodes after Li-air batteries discharge with the addition of different PFC's (yellow), possessing modified $O_2^{\bullet -}$ solubility and mutual miscibility with the electrolytes (blue). (PFCO=Perfluoro-n-octane; PFC1= Perfluorodecalin; PFC2= Perfluoro-n-nonane; Electrolyte=1M LiTf/triglyme).

Glass-type Li_2S-P_2S_5 based electrolytes for next generation lithium sulfur batteries using novel composite cathodes

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The conversion reaction of sulfur to form lithium sulfide is characterized by a high theoretical specific capacity of 1672mAh g^{-1}, translating in a theoretical energy density of c.a. 2500 Wh kg^{-1}, a value 2.5 times higher than that of commercial state-of-the-art Li-ion cells, using transition metal oxide based cathodes[1]. Lithium-Sulfur batteries based on this conversion reaction may therefore represent the power source of choice for the future. The Li-S system is, however, still far from commercialization. In conventional organic electrolytes the conversion reaction is, in fact, characterized by the formation of soluble polysulfides, resulting in the shuttling mechanism, a major issue causing low coulombic efficiency and high self-discharge rates[2]. This reaction is also associated with large volume changes. This can lead to cell failure, due to the alteration of the cathode and anode structure and the favored formation of lithium dendrites[3]. Moreover, sulfur and lithium (di)sulfide possess rather poor electron conductivity[3]. Glassy Li_2S-P_2S_5 based solid electrolytes, characterized by a high ionic conductivity and chemical and electrochemical stability, are used to overcome the limitations of the systems employing organic based liquid electrolytes[4]. At the same time, the use of composite cathodes, incorporating carbonaceous materials and transition metal sulfides, can help improve cell performance by buffering volume changes, while creating effective electron conduction pathways and enhance sulfur utilization by catalytic effects. This work aims at demonstrating the feasibility of these Li-S all-solid-state batteries (Li-S ASSBs) employing said composite cathodes, explore the effect of metal sulfides in the cathode composition, while elucidating some of the key concepts necessary for the realization of said devices. Li-S ASSBs show enhanced performances, with stable reversible capacities over 1.6Ah g_S^{-1} coupled with relatively high mass loadings.

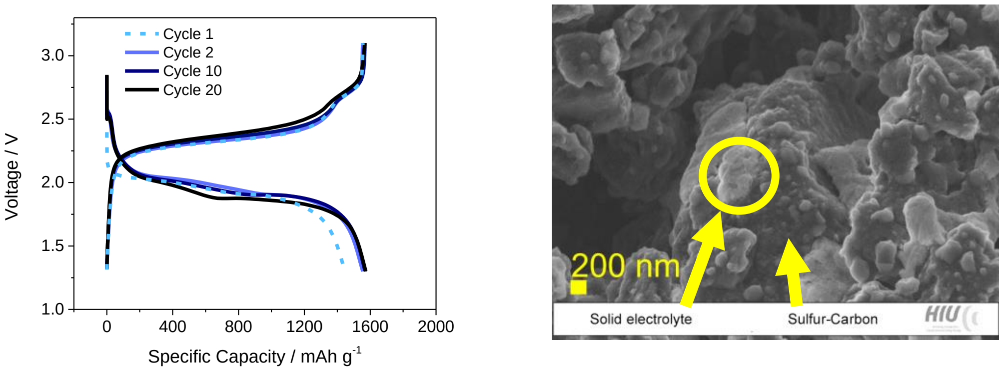

Figure 1: Voltage profile of a Li-S all-solid-state cell, using a sulfur-carbon composite as the cathode and lithium metal as the anode (left). SEM micrograph of the cathode composite (right).

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Dendrite Growth Rate of Li Electrodeposited in PC and Ionic Liquid

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Lithium-ion batteries have almost approached to its technological limitation. Several researchers believe that inherent limitations make it difficult for Li-ion chemistries to meet the growing demands for smaller scale portable electronics, powerful electric vehicles and large scale grid-type energy storage (1, 2). Metallic Li may become one of the most favoured choices for next-generation Li batteries.

Electrochemical processing of Li metal was reported.(3, 4). The dendrite growth behavior of Li metal galvanostatically electrodeposited on Ni substrate in a $LiClO_4$– or $LiPF_6$-propylene carbonate electrolyte solution as well as in 1.0 M LiTFSI–ionic liquid (N-methoxymethyl-Nmethylpyrrolidinium) bis(trifluoromethane-sulfonyl) imide was in-situ measured under a view of laser scanning confocal microscope. The effects of salt concentration, current density and temperature were investigated.

A Li dendrite precursor is stochastically evolved on Ni substrate probably through a solid electrolyte interphase layer produced by the surface chemical reaction between a reduced Li metal and an organic electrolyte/ionic liquid. The measured length of randomly growing Li dendrite arms was statistically analyzed. Dendrite growth process can be classified into two regions depending on its growth rate: the initiation period and the growing period with swinging behavior probably caused by residual stress. The initiation period of the dendrite precursor becomes shorter with increasing current density and decreasing salt concentration. Once it has been initiated, the ionic mass transfer rate starts to govern the growth process of the dendrite arm length, exceeding over the surface chemistry controlling step. The dendrite arm length averaged over the substrate surface grows linearly proportional to the square root of time. The lower the salt concentration, the steeper the inclination of the line at 5 mA cm^{-2}, whereas the concentration dependence of inclination is not evident at 0.5 mA cm^{-2}.

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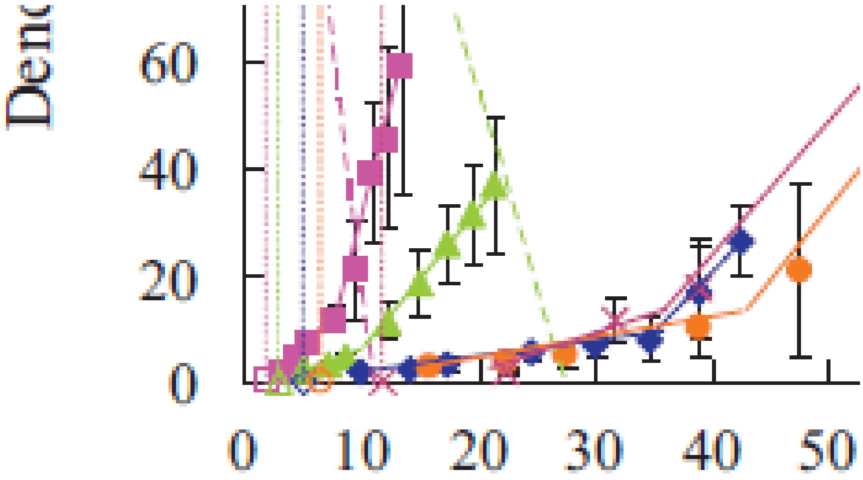
Denc
60
40
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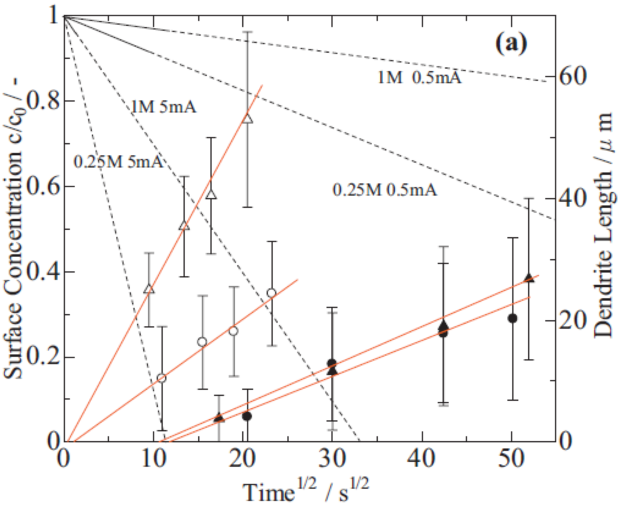
(a)
1M 0.5mA
1M 5mA
0.25M 5mA
0.25M 0.5mA
Surface Concentration c/c_0 / -
1
0.8
0.6
0.4
0.2
0
Dendrite Length / μ m
60
40
20
0
Time$^{1/2}$ / s$^{1/2}$
0
10
20
30
40
50

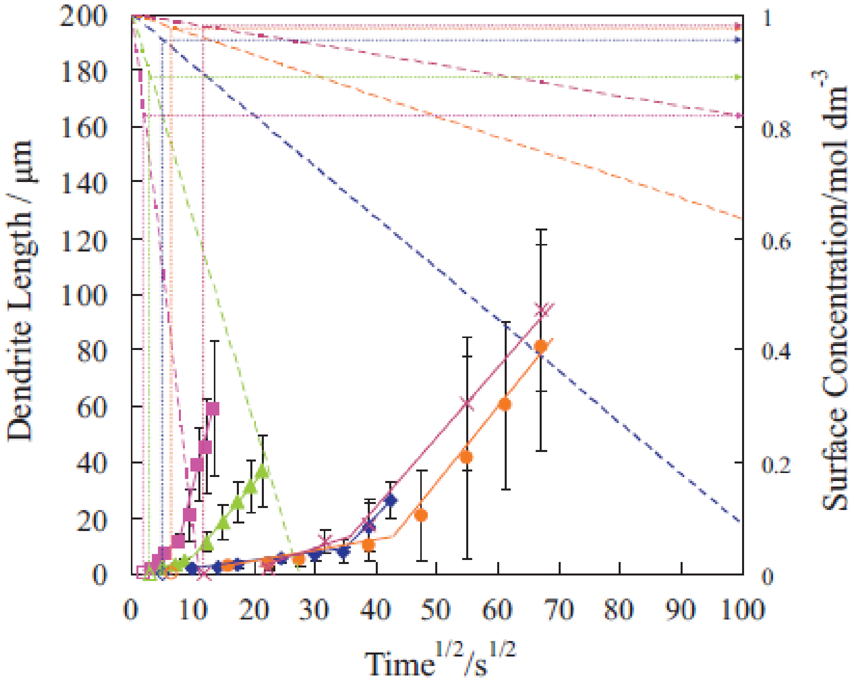

Fig. 11. Time transient of Li dendrite length and calculated Li$^+$ surface concentration with the square root of time. Solid markers represent the mean dendrite length at 5 mA cm^{-2} (■), 2 mA cm^{-2} (▲), 0.5 mA cm^{-2} (◆) 0.2 mA cm^{-2} (●) and 0.1 mA cm^{-2} (×), respectively.

Designing Performance of O3-type Na$_x$[Ni,Mn,Fe,Ti]O$_2$ for Practical Na-Ion Batteries

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P2-type sodium layered oxide materials have attracted attention as positive electrode materials for Na-ion batteries because of the relatively high working voltage and large reversible capacity.[1] However, considering the potential window of the electrolyte, sufficient energy density is still a challenging issue for the P2-type materials in the limited voltage range of 2.0 – 4.1 V vs. Na$^+$/Na.[2] In this study, we synthesized O3-type Na$_{2/3+x}$[Ni$_{1/3}$Mn$_{2/3-x-y}$Fe$_x$Ti$_y$]O$_2$ (x = 1/9 – 1/3, y = 0 – 5/9) by Fe- and Ti-substitution for Mn and increase in Na content from P2-type Na$_{2/3}$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ which delivers large reversible capacity of ca. 160 mAh g^{-1} with high working voltage of 3.6 V. Electrode performance of the samples is examined in Na cells and relation between the composition and performance is investigated.

The samples were synthesized by solid-state reaction. Na$_2$CO$_3$, Li$_2$CO$_3$, α-Fe$_2$O$_3$, Ni(OH)$_2$, Mn$_2$O$_3$, and TiO$_2$ were mixed, pelletized and then heated at 800 – 1000 °C for 24 h in air. Galvanostatic charge/discharge tests were conducted using coin-type cells. Positive electrodes consisted of the active material, acetylene black and PVdF with a gravimetric ratio of 80:10:10. Metallic sodium was used as a counter electrode. The electrolyte used was 1.0 mol dm^{-3} NaPF$_6$ / PC.

Fig. 1 shows XRD patterns of Na$_{2/3+x}$[Ni$_{1/3}$Mn$_{2/3-x}$Fe$_x$]O$_2$ (x = 1/6, 1/4, and 1/3) samples. Diffraction peaks of the samples can be indexed with R-3m, and O3-type materials were successfully synthesized without any impurities. Fig. 2 shows galvanostatic charge/discharge curves of the samples in the voltage range of 2.0 – 4.1 V. Reversible capacities of Na$_{2/3+x}$[Ni$_{1/3}$Mn$_{2/3-x}$Fe$_x$]O$_2$ (x = 1/6, 1/4, and 1/3) were 151, 144, and 152 mAh g^{-1}, respectively with modification of voltage curves. Reversible capacities in 2.5 – 4.1 V were, however, 117, 134, and 148 mAh g^{-1}, respectively, and increased with increase in Fe content. In addition, Ti-substituted samples with P2-type structure exhibited higher energy density resulting from elevated discharge voltage. Influence of Ti-substitution on electrode performance and phase transition will be discussed in detail at the conference.

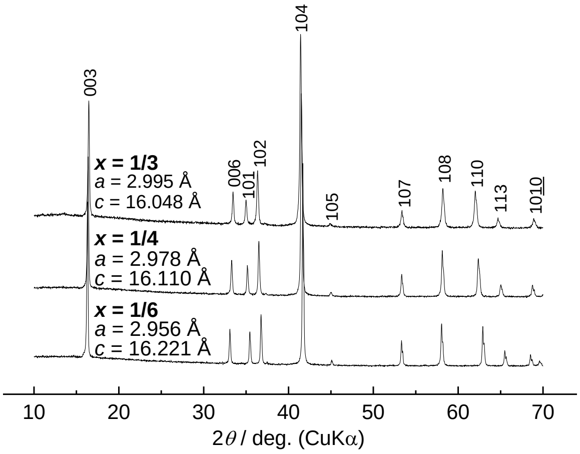

Fig. 1. X-ray diffraction patterns of O3-type Na$_x$[Ni$_{1/3}$Mn$_{2/3-x}$Fe$_x$]O$_2$ (x = 1/6, 1/4, and 1/3).

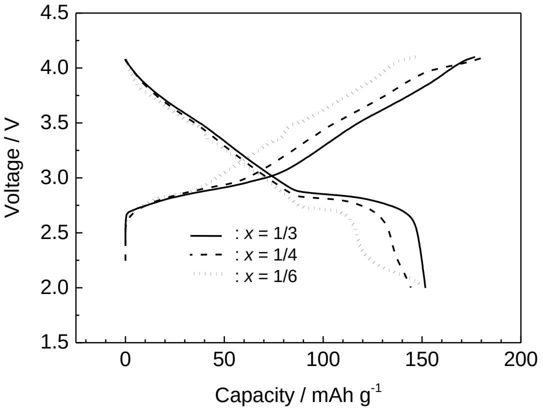

Fig. 2 Galvanostatic charge and discharge curves of Na // Na$_{2/3+x}$[Ni$_{1/3}$Mn$_{2/3-x}$Fe$_x$]O$_2$ cells (x = 1/6, 1/4, and 1/3) in the voltage range of 2.0 - 4.1 V.

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Real-Time Monitoring of Phase Boundary Propagation in Electrode Materials through Picosecond Ultrasonics

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Study of phase boundary kinetics in electrode materials requires accurate measurement of phase boundary velocity under well-defined electrochemical conditions. Current approaches include methods such as *in situ* transmission electron microscopy (TEM) and substrate curvature method. The former enables visualization of the atomic scale details of the phase transformation; however, controlling/measuring the applied potential and lithium flux at such small scales has been a challenge. The latter approach employs uniform, wafer-like sample geometries that facilitate excellent control of the electrochemical parameters, but requires some assumptions to infer the phase boundary mobility. Here we introduce a non-invasive, *in situ* method that combines the desirable features of the above approaches, i.e., measurement of the position of the advancing phase front at a resolution of tens of nanometers and well-controlled voltage and lithium flux conditions. By integrating picosecond ultrasonics with a custom-designed electrochemical cell, this new approach enables direct measurement of the position of the phase front. Figure 1 shows the experimental setup and Figure 2 shows a representative result of the arrival time of signals reflected from the Si/Li$_x$Si interface and the Li$_x$Si/electrolyte interfaces. A moving phase boundary model is used to analyze the experimental results in order to extract the relevant kinetic parameters.

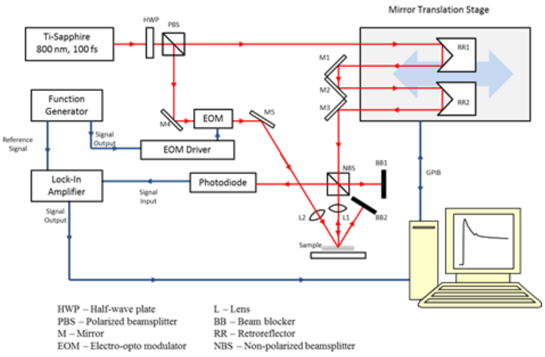

Figure 1. Schematic experimental setup to measure the position of the advancing Si/LixSi phase boundary during lithiation using pico-second ultrasonics.

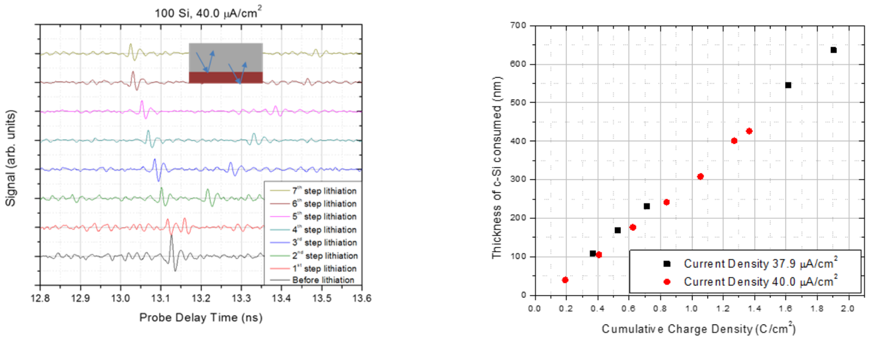

Figure 2. (Left) Reflected ultrasonic pulses from the phase boundary and the free surface at different stages of lithiation; the progressive change in the arrival times show the advancing phase boundary position. reflection Schematic experimental setup to measure the position of the advancing Si/LixSi phase boundary during lithiation using pico-second ultrasonics. (Right) Measured position of the phase boundary as a function of charge density.

Optimization of electrode pore size for 1mm thick binder-free electrodes fabricated by Spark Plasma Sintering (SPS)

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Micro fabrication of thick electrodes for lithium ion batteries is done increasingly faster than in the past because of the increasing demand for higher energy density and far less volume consumption for the portable electronics.[1] Theoretically, the volumetric energy density of the intrinsic active materials is 100 times higher than the energy density of the complete industrial batteries. However, the addition of the electrochemically inactive materials (binders, conductive carbon and current collector) occupies almost half of the total battery mass and two thirds of the battery volume, which results in the overall reduction of the energy density as well as the increase in the overall cost of the battery.[3]

Spark plasma sintering (SPS) is an efficient, rapid technology to make the dense sintered electrodes by applying high pressure (200 MPa) and temperature (650 C) in a short interval of time (5 min). In this technique, binders are neglected because of the high applied pressure and temperature ensuring high compactness of the electrodes. As a consequence, no porosity will be present in the as-formed electrodes for the electrolyte to flow inside the total volume of the electrodes. This problem can be solved by using a pore-forming agent sintered along with the active material that will be dissolved later to create porosity.

A few years ago, we proposed our idea of using commercial NaCl as a pore-forming agent to fabricate 1 mm thick electrodes using SPS with LFP or LTO active materials (AM) mixed with conductive carbon in the ratio 50 (AM):40(NaCl):10(sp-Carbon) volume %. The electrochemical performance of 1 mm thick LFP and LTO sintered electrodes against lithium at C/20 rate using liquid electrolyte was found to 4 times higher than the conventional Li-ion batteries. A full battery was assembled and operating at 1.9 V was made using LFP and LTO electrodes (Results submitted in EES). In an extension to our previous work, we focused on the optimization of the electrode pore size by using different particle sizes of the pore-forming agent. In the aim of finding the best architecture (optimum pore size and pore volume) for 1mm thick electrodes, micro tomography using Transmission X-ray microscopy was done for LFP and LTO electrodes each with different average pore sizes (20 µm, 10 µm & 2 µm). Important properties such as pore size distribution, tortuosity and effective diffusivity of lithium ions are determined. Surprisingly, fabrication of these 3D porous electrodes creates a low tortuous path (1.54) for the 10 micron pore sized electrodes, well in line with the Bruggeman model compared to the other 2 pore sized electrodes which is confirming the better electrochemical performance. Rate capability tests were also carried out for LFP with three different pore sizes (20, 10 and 2 µm) Vs Li using conventional LP30 as electrolyte.

To conclude, in this presentation, we will show the fabrication and characterization of three different LFP and LTO electrodes, each having 20, 10 and 2 µm average pore sizes at a fixed pore volume (40%) using SPS. The electrode pore size was optimal at 10 µm on a fixed porosity (40%) for LFP electrodes. Thanks to the tomography measurements, we obtain a correlation between tortuosity and electrochemical performance of our sintered electrodes to optimize the electrode pore size for 1 mm thick LFP and LTO electrodes. Finally, Spark Plasma Sintering (SPS) is a rapid and efficient approach that can be also applicable to other lithium and sodium ion battery systems.

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Electrode Fabrication: Think Electrodes from Slurry to Laminate

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There is essentially two ways to increase the energy density of a Li-ion battery of a particular chemistry: 1.) push the cathode to higher voltages, removing more lithium form the structure in hope that the material remains stable in the electrolyte for several cycles and at top of charge, 2.) increasing the fraction of active material in the cell. This work is focused on the second method, which can also be broken down into two paths: 1) reduce the amount of binder and conductive additive from the electrode laminate, or 2) make the electrode laminates thicker such that the fraction of laminate increases relative to the fraction of separator and current collector. Presented here are preliminary findings in both directions.

To start, the laminate, which is the part of the electrode that is cast onto the current collector and consists of active material, an electronically conductive agent (*e.g.* acetylene black), and a polymer binder (which, for Li-ion cathodes is typically PVDF) begin as a slurry in a high shear mixer where its three components are thoroughly mixed through wet-mixing *via* a solvent (typically N-methyl pyrrolidone.) Wet-mixing improves the thoroughness of the mixing and the solvent is chosen based on its ability to dissolve the binder. The addition of solids to a binder allows one to think of the resultant slurry as a polymer composite, although, one with a very small fraction of polymer, typically less than 5% by weight. Although the conductive agent consists of particles that are small enough (< 65 nm) that surface forces dominate and the particles agglomerate to form networks, it is the polymer that provides structural integrity to the laminate. Without the polymer, the other two powders would not adhere strong enough to each other nor to the current collector.

PVDF, the polymer of choice in Li-ion batteries is considered a stiff polymer with a high Young's modulus of around 1.1 GPa. This polymer was chosen not based on stiffness but on its resistance to oxidation and ability to be applied like a lacquer in a roll-to-roll process. One property that an electrode must have, especially if it is to be wound around a mandrel, as is done for cylindrical cells, is to have some flexibility to prevent it from delaminating from the current collector substrate. The amount of flexibility must increase as the film is thicker because the hoop stress is greater as a thicker film is wrapped around a mandrel of a given radius. The inherent modulus of the binder makes this a stiff electrode but the addition of active material and conductive agent (fillers) and the presence of void volume left behind in the drying process, reduces the effective Young's modulus of the laminate. Finding an optimum of the amount of polymer one needs for making thick electrodes, that adhere to the current collector, hold all the particles together and still wrap around a thin mandrel is just one of the factors we will be discussing.

Mechanical Degradation and Optimization of Solid Electrolyte Interphases in Li Ion Batteries

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The stability of the solid electrolyte interphase (SEI) is critically important in rechargeable Li-ion batteries. In particular, the volume changes that occur in the active electrode materials during lithiation and delithiation can create significant mechanical deformations in SEI layers. It is difficult to probe the mechanical response of the SEI directly in complex electrode microstructures that consist of powdered active components and other constituents. However, thin films provide an opportunity to investigate fundamental processes more directly. This approach has been used to investigate SEI formation on silicon and carbon electrodes. To accomplish this, we employed *in situ* stress, AFM, conventional *in situ* electrochemistry, and *ex situ* surface characterization. These experiments allowed us to investigate SEI behavior in different electrolytes and with different cycling conditions. Significant differences between Si and graphitic carbon were observed in SEI growth and passivation mechanism. Both the electrolyte composition and the formation conditions had significant effects on the SEI structure and properties. The results from these experiments and corresponding models also suggest that stresses can be engineered during SEI formation, to enhance the electrochemical and mechanical integrity of these critical passivation layers.

Potassium Intercalation into Graphite: Electrochemical Properties and Phase Transition

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In recent years, the demand for Li-ion batteries has been increasing for large-scaled applications such as a stationary energy storage system. However, Li resources are limited in lopsided producing area, potentially leading to unstable supply and price increase. On this background, our group study on K-ion batteries as one of promising candidates of next generation secondary batteries because K resources are abundant in the Earth's crust, moreover, redox potential of K is lower than Li in carbonate ester-based electrolyte [1]. Furthermore, K^+ ion diffuses faster than Li^+ and Na^+ ions in electrolyte solution because of its low Lewis acidity resulting in weaker coulombic interaction. From these reasons, K-ion batteries are expected as high-voltage/-power batteries. Our group have demonstrated highly reversible potassium intercalation into graphite by electrochemical charge/discharge in a potassium cell [1,2]. At fully charged state, KC_8 is formed as stage-1 structure. However, the phase transition during electrochemical (de) potassiation is not elucidated explicitly so far. Here, we investigate K intercalation mechanism into graphite electrodes and their electrochemical properties.

The electrochemical measurements were conducted by using 2032 coin cells assembled in an argon-filled glove box. The working electrode, consisting of graphite (SNO3, SEC Carbon Ltd.) and sodium polyacrylate (PANa) binder in 95:5 weight ratio. The counter electrode was potassium metal and the electrolyte solution used in this study was 1 mol dm^{-3} potassium bis (fluorosulfonyl)imide (KFSI) or 0.8 mol dm^{-3} potassium hexafluorophosphate(KPF_6) / ethylene carbonate (EC): diethyl carbonate (DEC) mixture at 1:1 (v/v). Galvanostatic charge/discharge was carried out in the voltage range of 0.0 – 2.0 V vs. K/K^+ at a current density of 25 mA g^{-1}.

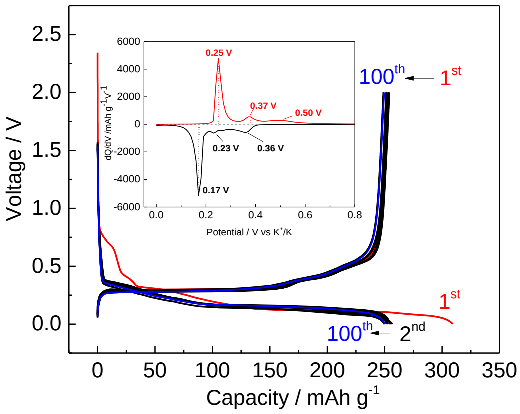

Figure 1 Charge/discharge profiles of graphite electrode in a K cell with 1 mol dm^{-3} KFSI /EC:DEC (1:1 v/v); insert dQ/dV curves of 3rd cycle.

Fig.1 shows charge/discharge (K-insertion/extraction) curves with a reversible capacity of ca. 252 mAh g^{-1} corresponding to 91% of the theoretical capacity with good capacity retention of 98.8% after 100 cycles. Phase evolution during the intercalation was investigated with *operando* XRD as shown in Fig. 2. Reversible phase transitions are observed from graphite to staging compounds. Considering interlayer distances of graphene layers and K-intercalated layers, diffraction peaks can be assigned as stage-1, stage-2, and stage-3, which could be corresponding to KC_8, KC_{24}, and KC_{36}, respectively[3]. Despite of +60% volume increase from graphite to KC_8 on charge, graphite demonstrates no capacity decay during 400 cycles by selecting proper binder and electrolyte. We will further discuss the formation of a solid electrolyte interphase (SEI) and its evolution during cycling by using powerful surface characterization techniques, such as SEM, time-of-flight secondary ion mass spectrometry, and hard/soft X-ray photoelectron spectroscopy.

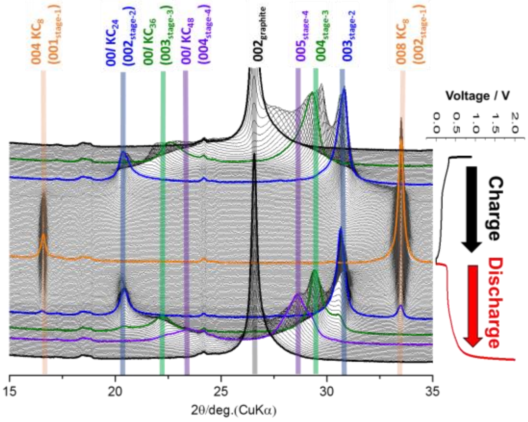

Figure 2 *Operando* XRD patterns of graphite electrode in a K cell.

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Coherently Integrated Layered-Spinel Cathodes for Lithium-Ion Batteries

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Layered $LiMO_2$ and spinel LiM_2O_4 oxides (e.g., M = Co, Mn and/or Ni) are important cathode materials for rechargeable lithium-ion batteries, the electrochemical properties of which are dictated largely by their structure (atomic arrangement) and composition. For example, layered $LiMO_2$ structures have alternating layers of lithium and transition metal planes that provide 2-D diffusion pathways for the lithium ions. While high specific capacities can be delivered by highly-delithiated layered electrodes, their structures are prone to destabilization when charged to high electrochemical potentials. Spinel LiM_2O_4, on the other hand, has cubic symmetry that offers 3-D channels for lithium-ion diffusion, which enables stable and fast lithium extraction/insertion reactions without jeopardizing the transition metal-oxide framework of the structure. However, the lower utilizable lithium content per MO_2 unit in spinel compositions (i.e., $0.5Li/MO_2$ compared to $1.0Li/MO_2$ in layered oxides) limits their theoretical capacity – at least for high voltage reactions, typically >3V). The different, yet complementary, structural and electrochemical properties between layered and spinel materials provide an opportunity to design new electrode materials. Indeed, blending layered and spinel cathode particles in commercial lithium-ion battery products has already been used widely by industry. We have extended this approach over the past several years by pursuing a strategy to design new cathode materials by integrating layered and spinel structures at the atomic level [1]. Compared to physically blended cathodes, structurally-integrated layered-spinel cathode materials appear to offer synergistic properties that may be advantageous for advancing lithium-ion battery technology. In this presentation, the relationships between synthesis control, atomic structure, and electrochemical properties in simple, model, layered-spinel materials, such as in Li-Mn-O and Li-Co-O systems, will be discussed; in addition, the structural complexity of multi-cation compositions in Li-Mn-Co-Ni-O systems will be highlighted.

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Oxygen Loss and Stress Evolution During Electrochemical Cycling of Lithium-Rich Cathodes

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Lithium-rich layered oxides ($Li_{1+x}M_{1-x}O_2$, M= Ni, Mn, Co) are attractive cathode materials for next generation lithium-ion batteries due to their high reversible capacity (over 200 mAh/g). During electrochemical cycling, structural changes cause compositional stresses that lead to performance degradation. In this study, we characterize these structural changes using $Li_{1.2}Mn_{0.55}Ni_{0.125}Co_{0.125}O_2$ (LR-NMC) thin-films prepared by sputtering on sapphire substrates and characterized using x-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM). A multibeam optical stress sensor (MOSS) is used to quantitatively measure the average stress in the cathode film during electrochemical cycling. A unique and unpredicted stress signature is observed during the first charge. Initially, a tensile stress is observed, consistent with volume contraction from lithium removal, however, the stress reverses and becomes compressive with continued charging beyond ~4V vs Li/Li+, indicating volume expansion; this phenomenon is present in the first cycle only. The origin of this irreversible stress during the first charge is thought to be oxygen loss and the resulting cation reordering. Subsequent cycling exhibits reversible stresses, with volume expansion during lithiation and volume contraction during delithiation. Raman spectroscopy provides evidence of the layered-to-spinel phase transition after cycling. After reannealing cycled samples in an oxygen environment, the original Raman spectra is recovered and the re-annealed samples show the same compressive first charge behavior. Density functional theory modelling supports the experimental findings. The compressive stress that is induced near the surface of these cathodes can potentially improve the stability of these materials during initial electrochemical cycling. This study shows that in situ stress measurements can be used to track oxygen loss, providing valuable information in support of efforts designed to improve the performance of lithium-rich cathodes through the suppression of oxygen evolution.

Bio-Inspired Active Materials for High-Stability Nonaqueous Redox Flow Batteries

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With integration of intermittent, renewable energy sources, such as solar and wind, into the electrical grid, matching generation-capability and demand becomes more challenging. As such, large, rechargeable batteries are an increasingly important component of infrastructure. Among several strategies for meeting the growing need for grid storage capacity, non-aqueous redox flow batteries (NRFB) are a promising technology. Compared to their aqueous counterparts, these systems have the potential for much wider electrochemical windows and improved range of operating temperature, while maintaining their benefits, including decoupled power and capacity.

Despite the promise of NRFB, currently these systems are limited by poor stability of solution-phase, charge-carrying active materials. In most cases, this has led to low active-material concentration, low current density and substantial capacity fade. Since improved stability would extend cycle-life and facilitate optimization of NRFB components, interest has recently developed in understanding the fundamental factors that control decomposition.[1, 2]

Herein, we present a bio-inspired approach to solve the problem of instability of NRFB active materials using a family of molecules that is naturally occurring and produced biologically. These compounds, an example of which is shown in Figure 1, are analogues of Amavadin, which is found in mushrooms of the *Amanita* genus. Biosynthesis of this molecule evolved over millions of generations to bind vanadium selectively and with the highest stability ever reported, using a unique tetradentate, bis-carboxylato-ε-2-hydroxyimino- binding motif.[3] Ligand-substitution is suppressed in this compound, shutting down a major mechanism of decomposition. In this way, natural selection serves as a toolkit for molecular design, elucidating a scaffold for optimized NRFB active materials.

We will present evidence that an analogue of Amavadin that we call CVBH is stable even in the presence of water (Figure 2) and is oxygen tolerant. Further, we will demonstrate stability to extensive, deep redox cycling in a static cell. Finally, we will discuss synthetic modifications that result in improved solubility and electrochemical properties.

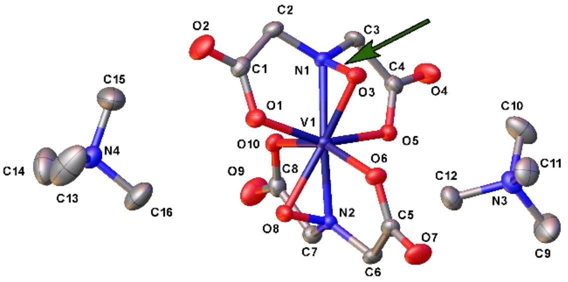

Figure 1. $[TMA]_2[VBH]$ crystal structure with hydrogen atoms and solvent molecules removed for clarity. Green arrow indicates ε-2 hydroxyimino- group (N1-O3).

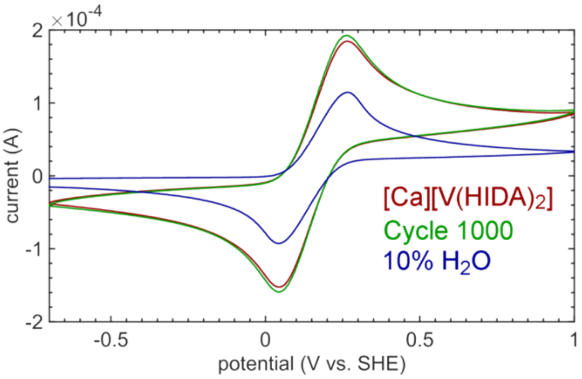

Figure 2. Cyclic Voltammetry of 10 mM CVBH in DMSO, 0.2M TBAPF6, Glassy-C WE.

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Magnesium Battery: The Untold Story

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Without a doubt the Holy Grail of battery research is the development of a post lithium ion technology. This may require a shift towards batteries containing a pure metal anode. Li metal is an attractive metal anode in part due to its high volumetric capacity (2062 mAh cm^{-3}), a high reductive potential of -3.0 V vs. NHE and the wide availability of lithium electrolytes. However, its deposition occurs unevenly with formation of dendrites which leads to safety concerns during cycling. In contrast to lithium metal, magnesium metal deposition is not plagued by dendritic formation. Additionally, magnesium is more stable than lithium when exposed to air, more abundant in the earth crust and provides a higher volumetric capacity (3832 mAh cm^{-3}). However, magnesium has a reductive potential of -2.36 V vs. NHE and has a unique electrochemistry which prohibited the use of magnesium analogues of lithium electrolytes. Since the oxidative stability of electrolytes governs the choice of cathodes it is of paramount importance to develop non-corrosive magnesium electrolyte with wide electrochemical windows which will permit discovery of high voltage cathodes. In this talk we will present the latest developments and future challenges which must be overcome.[1,2,3,4,5,6,7]

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Aging Analysis in Cylindrical Graphite/LiFePO$_4$ Batteries Cycled at High Current Densities

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Nowadays lithium ion battery technology is playing a crucial role in the development of portable devices, stationary energy storage systems and electric vehicles (EVs) due to their high power and energy densities. To encourage the wide spreading of this technology, it is fundamental to gain a deeper understanding of the causes leading to the battery end of life and performance losses. One of the major problems for Li-ion battery manufacturers concerns the cells aging, in order to ensure long-term reliability and safety. In this respect, determination of specific degradation mechanisms and their correlation with cell performances is crucial for working on cell concepts that can meet targeted lifetimes [1-3].

An evaluation of the cycling performances of LiFePO$_4$-based cylindrical batteries at high discharge current (6C) and around a limited DOD range (60%) is discussed in this study.

The combination of temperature, charging C-rate and end-of-charge voltage are very important to define and understand the aging mechanism in cycled Li-ion cells. A study on the degradation mechanisms of the battery is realised by post-mortem analysis in order to identify the main degradation mechanisms following a well-defined protocol [4].

Systematic degradation mechanisms are evaluated by microstructural (SEM) and crystallographic (XRD) analyses. Elemental analysis of the electrode composition was determined by EDS and ICP techniques. The electrochemical performances of selected areas of the harvested electrodes were determined by galvanostatic testing in half-cell configuration and electrochemical impedance spectroscopy. Figure 1 and Figure 2 show the cell state of Health (SOH) evolution referred to the capacity and internal resistance, as a function of Full Equivalent Cycles (FEC). These results were combined with non-destructive cell electrochemical measurements to provide a global view of the main degradation processes.

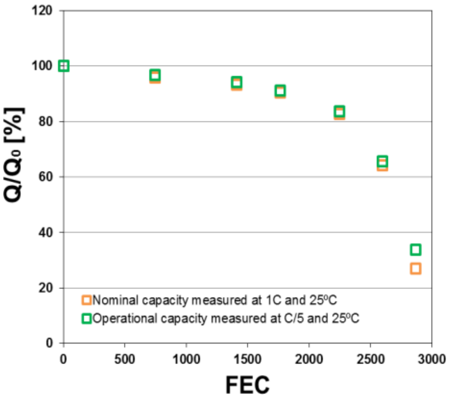

Fig. 1. Capacity (Q) loss evolution, referred to the initial capacity (Q0) (%), as a function of Full Equivalent Cycles (FEC) measured at different C-rates

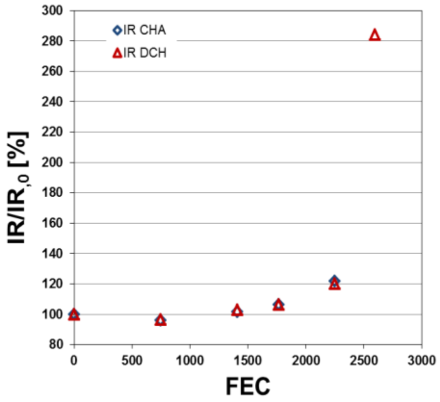

Fig. 2. Internal resistance (IR) increase evolution, referred to the initial internal resistance (IR,0) (%), as a function of Full Equivalent Cycles (FEC) measured at different C-rates

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Chemical Reactivity of Reduced Oxygen Species in Alkali-Oxygen Batteries

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Because of its high theoretical specific energy, that is far beyond what the current and even future Li-ion technology can achieve, the Li-O_2 battery has attracted a great deal of interest in the past few years.[1-4] However, realization of a practical Li-O_2 battery is a major challenge because the overwhelming majority of current Li-O_2 batteries suffer from limited chemical reversibility, due to the parasitic side reactions between the reduced oxygen species O_2^-, LiO_2 and Li_2O_2 involved in Li-O_2 batteries and the battery components such as the cathode materials and electrolytes.[5,6]

In this presentation, we compare the chemical reactivity of intermediates of O_2^-, LiO_2 and Li_2O_2 in liquid NH_3 at cryogenic temperatures (typically -78 ºC). It was found that LiO_2 has the highest reactivity among the reduced oxygen species involved in Li-O_2 electrochemistry. It was also found that the reduced oxygen species O_2^-, NaO_2 and KO_2 involved in aprotic Na/K-O_2 batteries are less reactive than LiO_2, explaining why Na/K-O_2 batteries have less side reactions than their Li-O_2 siblings. The identification of LiO_2 as the most reactive oxygen species in Li-O_2 batteries has important consequences for the development of Li-O_2 cells with better reversibility. For instance, by selecting electrolyte solvents, in which LiO_2 can rapidly disproportionate to Li_2O_2, and by optimizing cell operating conditions to promote the electro-reduction of LiO_2 to Li_2O_2, Li-O_2 cells having less side reactions could be realized.[7]

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X-ray and Optical Spectroscopy and Imaging of the SEI Layer on Intermetallic Anodes

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Silicon has received significant attention as a viable alternative to graphitic carbon as the negative electrode in lithium-ion batteries due to its high capacity and availability [1]. Elemental silicon can theoretically store ~3800 mAh/g (or ~8800 mAh/mL), nearly an order of magnitude higher than graphite (372 mAh/g and 818 mAh/mL, respectively). However, several problems have been identified that limit its utility including large crystallographic expansion (~320%) upon lithiation, which translates to particle cracking, particle isolation, and electrode delamination issues, as well as electrolyte side reactions, which affect cycling.

The key problems that have hindered practical application of silicon and other silicon alloy anodes in commercial Li-ion batteries are: (i) the large volume changes during cycling, which results in cracking and decrepitation of the active material, and loss of electronic connectivity and mechanical integrity in the composite electrode, (ii) inherent non-passivating behavior of silicon in organic electrolytes, which results in large irreversible capacity loss and gradual electrolyte consumption during the electrode operation [2.3]. However, despite extensive research in the past four decades, the intrinsic behavior and the corresponding barriers to implementation of silicon anodes have in Li-ion systems have not been fully understood and remedied.

This study involves diagnostic evaluations of silicon composite electrodes as well as studies of the properties of the individual components and their interfaces. Unraveling the basic function and operation of the SEI layer on Si and Sn anodes at the length-scale that corresponds to its basic building blocks is the primary focus of this work. Surface characterization techniques such as FTIR, Raman, x-ray and NMR spectroscopy and microscopy have provided valuable information regarding the SEI chemical composition and structure at a micrometer scale. In this research effort we leverage the use of model experimental systems and novel characterization techniques to investigate and evaluate intrinsic properties of individual components such as additives and advanced binders and their effects on the composite silicon anode electrochemical performance. For instance, using far- and near-field IR spectroscopy, AFM imaging and LIBS depth-profiling, we correlate the improved passivating properties of silicon in the presence of LiBOB to the formation and incorporation of ion conductive $Li_xByC_nO_{2n}$ oligomers in the SEI layer. This study also demonstrates a unique ability of the synchrotron infrared nanospectroscopy to probe individual chemical building blocks at electrochemical interfaces at the spatial resolution of ca. 20 nm with an exceptional surface sensitivity, chemical selectivity and specificity.

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Study of a $LiMn_2O_4$/Polypyrrole hybride battery-selective capacitor system for the extraction of lithium chloride from natural brine

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The current evaporation method, by which lithium is extracted from salt flats is simple but relatively inefficient with environmental costs. With the current technology, approximately 0.5 million liters of water are evaporated and lost per ton of extracted Li_2CO_3. Moreover, the soda-lime method is rather slow, taking 1-2 years to evaporate water by solar radiation and wind. The Electrochemistry group at INQUIMAE has developed an electrochemical method to extract lithium chloride from brine, which is fast, efficient, has low environmental impact, and low energy consumption.

The method uses an electrochemical asymmetric lithium ion battery electrode and a chloride selective polypyrrole capacitive electrode. Lithium ions are inserted in the crystal structure of a battery-type lithium insertion electrode (e.g., λ-MnO2) as a cathode in the extraction step from natural brine. The inserted lithium ions are then released from the crystal structure of $LiMn_2O_4$ in a concentration step in which the battery-type lithium insertion electrode functions as the anode and the electrolyte is a diluted aqueous solution [1,2]. The counter electrode is a chloride reversible electrode that comprises an electrically conductive polypyrrole electrode. The respective electrode reactions are:

At the cathode:

$$xLi^+(brine) + Li_{1-x}Mn^{III}_{1-X}Mn^{IV}O_2 + xe^-(cathode) \leftrightharpoons LiMn^{IV}Mn^{III}O_4$$

At the anode:

$$xCl^-(brine) + xPP^o(anode) \rightleftharpoons x[PP^+Cl^-] + xe^-(anode)$$

In the present study we have examined the exchange of lithium ions at the $Li_{1-x}Mn_2O_4$ ($0 \leq x \leq 1$) by electrochemical impedance spectroscopy and the lithium surface composition by x-ray electron spectroscopy. The competition of lithium and sodium ions present in the brine has been examined during the extraction process.

We have also implemented a laboratory scale electrochemical reactor for the extraction of lithium from brine comprised of two packed bed porous electrodes loaded with the active materials, respectively $Li_{1-x}Mn_2O_4$ ($0 \leq x \leq 1$) and polypyrrole. Both porous electrodes are separated by a porous non conductive matrix containing natural brine or recovery electrolyte.

Experiments at different reactor geometries, current densities, flow rates, etc. have been compared with digital simulations using COMSOL® finite elements software to get an insight into the concentration and potential gradients within the porous electrodes and separator. This reactor differs from a hybrid supercapacitor described recently by Hao et. al. (3) since the PPy electrode is selective to the adsorption/desorption of chloride ions and not a double layer capacitor with electrostatic adsorption/ desorption of lithium ions. As a consequence LiCl is extracted at both electrodes and the concentration decays in the separator gap.

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Novel Lithium-ion Cell Architecture

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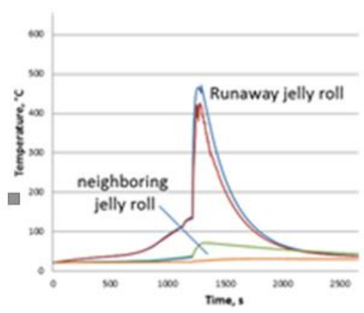
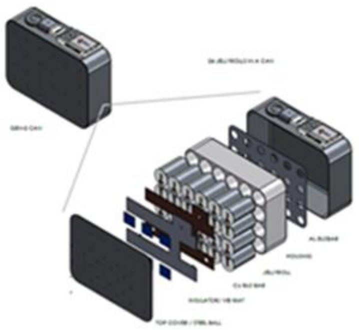
A novel Li-ion cell architecture (*Super-Cell*), which includes multiple open electrode assemblies mounted inside a ceramic support housing will be presented. Due to the technology's unique and robust safety properties, the Super-Cell technology enables high energy density at low product cost. It is anticipated that this technology will enable meeting the US Department of Energy cost goals of $125/kWh for an electric vehicle battery. The presentation will display key design properties of the Super-Cell technology and its ceramic housing support member.

The Super-Cell technology packages standard cylindrical electrochemical assemblies, such as 18650 jelly rolls, in a tight array narrowly separated by a newly developed ceramic housing material from Morgan Advanced Materials. This ceramic composite has unique materials properties for the isolation and heat absorption of jelly rolls. The ceramic is designed to crumble into a powder upon mechanical abuse, isolate jelly rolls for even thermal profile during normal battery use, and isolate and absorb heat produced by a jelly roll that is put into thermal runaway. The latter design property protects the cell and battery from cascading thermal propagation, should a jelly roll experience an internal short. Critical to this operations is the incorporation of a heat absorbing fire retarding component, aluminum tri hydrate (ATH), which is loaded into a molded matrix of high temperature ceramic fibers that are stable up to temperatures of about 1000ºC. The ATH endothermically decomposes at approximately 200-220ºC, which quenches the incident electrochemical unit when thermal runaway is initiated, and creates steam. These unique features of the ceramic support, along with an effective venting mechanism and pressure disconnect device (PDD) allow for closely packaged electrochemical units of high volumetric energy density in a non-expanding and contracting large prismatic cell format.

Thermal and mechanical modeling, along with safety and electrochemical test results on high capacity Super-Cells, will be presented that illustrates this new technology.



Temperature of jelly rolls in Super-Cell during thermal runaway



Super-Cell

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Synthesis of T-Nb_2O_5 /N, B-Codoped Graphene for Lithium-Ion Hybrid Supercapacitors

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Advanced energy storage systems are anticipated to satisfy the requirements for fast-growing electrical vehicle applications with high power and energy density. Combining the features of high-energy Li-ion batteries and high-power supercapacitors, lithium-ion hybrid supercapacitors (Li-HSCs) was recently proposed [1, 2]. The orthorhombic niobium oxide (T-Nb_2O_5) with high power and theoretical capacity (~200 mA h g^{-1}) has become a candidate for the anode materials of Li-HSCs. However, the poor electrical conductivity is the major obstacle for its rate capability and electrochemical utilization. One strategy to overcome this barrier is to use conductive carbon materials such as carbon nanotubes (CNTs) and graphene, which can improve rate capability and cycle stability. Herein, we synthesized T-Nb_2O_5/nitrogen and sulphur co-doped graphene (NS-G) hybrid via a two-step hydrothermal method followed by annealing treatment. The morphology and chemical composition of the hybrid were examined by the TEM, XRD, Raman spectra and XPS. Compared to the individual T-Nb_2O_5 and T-Nb_2O_5/reduced graphene oxide, it exhibited better cycling stability (a low capacity fading of ~6.4% after 1000 cycles at 0.5 A g^{-1}) and more superior rate capability (capacity retention of 63% from 0.05 A g^{-1} to 5 A g^{-1}). The NS-G with good conductivity can efficiently enhance the electron transport and the T-Nb_2O_5 nanosheets are uniformly anchored on the NS-G surface, leading to the short ion diffusion paths. Additionally, their synergetic effects play a dual role to improve the electrochemical performance. Furthermore, a Li-HSCs device, assembled with the T-Nb_2O_5/NS-G hybrid and activated carbon, exhibits high energy density and excellent cycling stability. Therefore, the T-Nb_2O_5/NS-G hybrid shows potential application as Li-HSCs.

Acknowledgements
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In-situ Electrochemical ATR-SEIRAS Investigation of the Solid-Electrolyte Interphase in a Lithium-ion Battery Configuration

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Lithium-ion battery (LIB) has been developed for wide applications including electric vehicles, plug-in hybrid electric vehicles and portable devices. Reducing cost, increasing capacity, prolonging cycle life and improving the efficiency are the current goals of advancing their development.[1] A solid electrolyte interphase (SEI) forms on the graphite/electrolyte interface during the first charge of LIB, which is essential to the performance of LIB in terms of capacity, self-discharge, cycle life and safety.[2] However, the underlining chemistry that governs the SEI's impact on the LIB performance is far from unclear. Although the lithium inorganic and organic salt has been identified inside SEI derived from the side faraday or non-faraday reactions on electrolyte and graphite,[2] the morphology, composition and structure of SEI is not fully unveiled. Because SEI is highly air and humidity sensitive, the results obtained from ex-situ methods are largely irrelevant to understanding the SEI's functionalities in real batteries, especially when it is out of LIB stable potential window, 2.5~4.2 V. Herein, we present a novel in-situ electrochemical Attenuated Total Reflection Surface Enhanced Infrared Reflection Absorption Spectroscopic (ATR-SEIRAS) study of the SEI in a real LIB configuration. The information we obtained is associated with the very process inside the LIB.

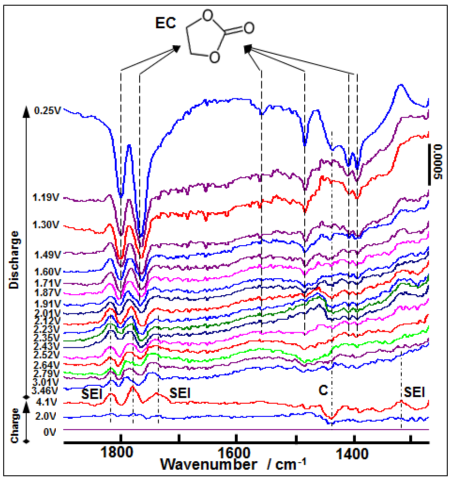

Figure 1. in-situ electrochemical ATR-SEIRAS spectra for the charge and discharge processes on graphite/electrolyte interface of lithium-ion battery anode. Electrolyte is $LiPF_6$/EC/DEC(1:1:1, 1M).

Figure 1 shows in-situ electrochemical ATR-SEIRAS spectra for the charge and discharge processes on the graphite/electrolyte interface of a lithium battery anode. Using the reference spectrum at initial cell potential of 0V, four bands at 1820, 1780, 1736 and 1316 cm^{-1} were observed at 4.1 V (cell potential) during charging and are associated with the formation of SEI. The first 3 bands are assigned to carbonyl group (ν(C=O) of different composition inside the SEI and the last one is from the ν(C-O) single bond vibration. The decreasing of the band at 1435 cm^{-1} is corresponding to the ν(C-H) from the graphite due to the lithium intercalation from its edge.[2] When the LIB discharged from 4.1 V to 2.52 V (Figure 1), the bands of ν(C=O) at 1736 cm^{-1} gradually disappeared. A further discharge from 2.52 V to 0.25 V (Figure 1) evidences the significant loss of ethylene carbonate (EC) on the anode surface. The irreversibility of this process could impede lithium intercalation since lithium ion in electrolyte mainly coordinates with the most polar EC molecules. Our results demonstrate that the *in-situ* ATR-SEIRAS is a powerful technique to unravel the chemical information of SEI and therefore will benefit the LIB community for advancing the battery development.

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Tailoring the Surface Chemistry of Li-Ion Battery Anodes through the Use of Water-Soluble Functional Binders

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The key for long cycle life in Li-ion batteries is intrinsically connected to the formation of a stable solid-electrolyte interphase (SEI) on the surface of the negative electrode. More control over the surface layer can be gained if the layer is generated *prior* to the battery operation. Such a layer can be more easily tailored, and can reduce loss of lithium inventory considerably. In this context, water-soluble electrode binders, e.g. sodium carboxymethyl cellulose (CMC-Na) and poly(acrylic acid) (PAA), have proven themselves exceptionally useful. Since the binder is a standard component in composite electrodes, its integration into the electrode fabrication process is easily accomplished.

Here, some of the parameters that govern binder distribution in electrode coatings, control the stability and electrochemical performance of the electrode, and that determine the composition of the surface layer are discussed. A number of commonly used anode materials (graphite, silicon and lithium titanate) are applied in order to study the impact of the binder on electrode morphology and the different electrode-electrolyte interfaces. The results are correlated with the electrochemical performance and with the SEI composition, which is studied by in-house and synchrotron-based photoelectron spectroscopy (depth profiling).

The results demonstrate that the poor swellability of the water-soluble binders leads to a protection of the active material when the surface coverage is high and the binder well distributed. This can generate functionality of sensitive anode materials, such as graphite, also in aggressive solvent environments such as propylene carbonate (Fig. 1) [1]. This, in turn, can render graphite electrodes useful in novel battery chemistries such as graphite-sulfur [2]. For anode materials which undergo large volume changes during cycling, for example Si, the SEI layer formation increases substantially, rendering the binder properties increasingly important for the surface chemistry of the electrodes [3]. As the binder content is decreased, complete surface coverage is more difficult to achieve. Thereby, the benefits provided by CMC-Na and PAA at the electrode surface are compromised and the performance differs less distinctly from electrodes fabricated with the conventional PVdF binder. Composites of alloying and conversion materials, on the other hand, typically employ binders in larger amounts. Despite the frequently noted resiliency to volume expansion, which is also a positive side-effect of the poor swellability of the binder in the electrolyte, the protection of the surface and the formation of a more stable interphase is the major cause for the improved electrochemical behaviour, compared to electrodes employing PVdF binders.

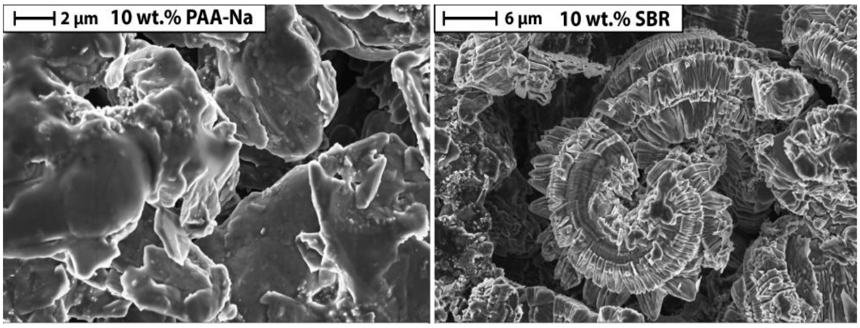

Fig. 1. Cycled graphite electrodes in PC-based electrolytes. The different binders applied display distinctive differences in graphite exfoliation.

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Job-Sharing Storage in Composite Electrodes

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Mass storage processes are widely used in energy storage devices such as Li and Na batteries. To achieve higher energy density and higher power density, it is essential to understand the fundamentals of storage processes in electrodes. Conventional mechanisms including insertion, phase-change, and conversion reaction homogeneously accommodate the component M (=Li, Na, etc.) in the bulk phase [1]. In this contribution, we will report an alternative mechanism that allows the storage occurring at interfaces of composite materials. This is realized by a job-sharing way: M^+ is accommodated by an ionic conductor while e^- is injected into an adjacent electronic conductor. Not only can an excess of M be realized, but a deficiency can be created in this way. Such storage can be treated in the framework of defect chemistry and space charge effects [2]. As these composites behave like classic mixed conductors that convey both electrons and ions, they are termed artificial mixed conductors.

Besides treating the thermodynamic and kinetic background, we will also highlight recent examples of Li, H_2, and Ag storage in composite materials [3-5]. In particular, the kinetics of Ag storage in the composite of superionic conductor $RbAg_4I_5$ and electronic conductor graphite is extremely fast. The solid-state chemical diffusion rate exceeds the values for any other solids at room temperature. This study does not only describe the transition from bulk to supercapacitive storage, but also potentially pave the way for reconciling energy density and power density.

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Si alloy/graphite coating design principles for Li-ion battery with high energy density

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Abstract

The development of Li-ion cells with high volumetric energy density is of great technological importance for consumer electronics [1], and also crucial in automotive applications [2]. Much attention has been given to Si-based materials due to the high theoretical capacity of Si (2194 Ah/L, compared to 764 Ah/L of graphite) [3]. With moderate cycling performance now collectively achieved for Si alloy materials, a shift in focus needs to be made towards incorporating Si alloys in anode coatings and increasing energy density of a lithium-ion full. Thus, a rational design strategy must be developed regarding the volumetric energy density of Li-ion cells.

Since Si-based materials are on the roadmaps of all major cell manufacturers, the objective of this study is to develop a Si alloy/graphite coating design model with the motivation of improving the volumetric energy density of full cells. Such information is scarce and is not adequately covered in the most recent version of BatPac model [4]. The effect of volume change on cell performance is discussed at both a materials and cell level, providing an opportunity for the development of practical Si alloy/graphite coatings with higher energy density, lower particle expansion, and lower cell expansion.

In this study, a Si alloy/graphite coating design model is established based on several well-established conclusions for high-energy-density Li-ion batteries. (1) lithiation of silicon alloys follows Vegard's law that molar volume of lithium takes 9 mL/mol [1]; (2) porosity in the Si alloy/graphite coating remains constant during charge/discharge [5]; (3) lithiation of Si alloy and graphite particles are independent of each other; (4) volumetric capacity and energy density have to be calculated at fully expanded (lithiated) state [5].

Two competing factors of volumetric capacity and average voltage are discussed to achieve high energy density. To achieve the same energy density improvement, either high capacity Si alloy at a lower weight ratio in Si alloy/graphite coating can be used or low capacity Si alloy at a higher weight ratio can be used. However, the volume expansion of high capacity Si alloys leads to low Coulumbic efficiency due to the parasitic reaction from repeated SEI destruction and repair. Low Coulumbic efficiency of 99.75-99.85% gradually attenuates the energy density improvement of the cell during cycling. The use of low capacity Si alloys leads to high volume expansion of the cell stack; therefore, Si alloy/graphite anode designers must make trade-off considerations between particle level expansion and cell level expansion.

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High power thin film $LiCoO_2$ for wireless sensor applications.

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Billions of wireless distributed sensors are envisaged as the environmental interface to provide data for the ‘Internet of Things’. Commercial wireless sensors in use today typically utilise large non-rechargeable batteries as the energy source and as such require frequent battery replacement. Hybrid devices with combined energy harvesting and storage are desirable to enable intervention-free operation over the lifetime of the device [1]. The critical energy provision issues also require significant advances in low power electronic circuit design and low power sensor elements. [2]

Silicon integrated on-chip energy storage is an attractive goal for the hybrid solution but is limited to low power and energy outputs in the typical 2D planar thin format demonstrated to date. One of the issues with solid state thin film microbatteries is the high resistance of the electrolyte which can lead to significant potential drop when powering devices during operation and interrogation. The ability to provide high currents in a small form factor is a critical need for the development of realistic long life devices.

In this work we will describe the use of Comsol finite element simulations, showing material utilisation and electrochemical cell behaviour of a rechargeable Li-ion microbattery and the influence of electrolyte type on the output characteristics of the non-porous additive free sputtered $LiCoO_2$. The sputter deposited 100 nm thick film of $LiCoO_2$ is capable of delivering 13 mA/cm^2 in pH 7 electrolyte as shown in figure 1. Cyclic voltammograms recorded at 100 mV/s indicate 100 mA/g active material utilisation in 3.6s or an approximate C rate of 1,000.

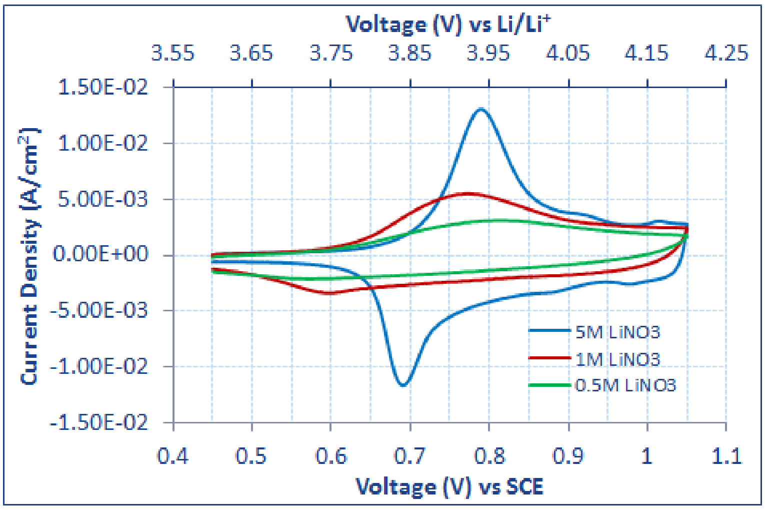

Figure 1. Cyclic voltammograms for 100 nm $LiCoO_2$ in aqueous lithium nitrate solutions, recorded at 100 mV/s.

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A Highly Stable Solid-State Battery-Supercapacitor Hybrid Device based on Three-Dimensional Nanostructured Array Electrodes and a Gel Polymer Electrolyte

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Lithium-ion batteries (LIBs) and supercapacitors are two important rechargeable electrical energy storage (EES) systems. LIBs are known for their high specific energy due to the Li-intercalation or alloying reactions in the bulk electrode materials. But their power density is limited by the sluggish Li-ion diffusion kinetics in the solid materials. In contrast, supercapacitors can deliver a much higher specific power, however, their specific energy is low since surface redox reactions only involve a small portion of total electrode materials. Many applications demand for hybrid EES systems that combine the advantages of both LIBs (high specific energy) and supercapacitors (high specific power), which critically depend on novel electrode materials and unconventional architectures that combine multiple functionalities [1]. This paper demonstrates a unique method to produce three-dimensional (3D) nanostructured electrodes consisting of vertical core-shell array which can effectively interface with a solid-state gel polymer electrolyte film toward flexible thin-film unconventional energy storage devices.

A novel solid-state battery-supercapacitor hybrid device was fabricated using a silicon (Si) anode and a titanium dioxide (TiO_2) cathode in conjunction with a solid-like gel polymer electrolyte film as the electrolyte and separator. The electrodes were fabricated as three-dimensional nanostructured vertical arrays by sputtering active materials as conformal shells on vertically aligned carbon nanofibers (VACNFs) which served as the current collector and structural template. Such nanostructured vertical core-shell array-electrodes enable short Li-ion diffusion path and large pseudocapacitive contribution by fast surface reactions, leading to the hybrid features of batteries and supercapacitors that can provide high specific energy over a wide range of power rates. The soft gel electrolyte film can effectively infiltrate the vertically aligned 3D nanostructured electrodes, forming stable electrode-electrolyte interfaces with all active shell materials at both electrodes [2]. Such infiltrated composite structures provide an excellent structural stability during high-rate tests and long cycling. The hybrid cell shows excellent cycling stability and is able to retain more than 95% of the original capacity after 3500 cycles. More importantly, this solid-state device can stably operate in a temperature range from -20 to 60 ^{o}C with a very low self-discharge rate and an excellent shelf life. The combination of the 3D nanoarchitectured electrodes and the gel polymer electrolyte is promising for the development of highly stable energy storage devices for unconventional applications in largely varied power, wider operation temperature, long shelf-life.

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Electrolytes for sodium ion batteries: can ionic liquids be alternative additives?

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Sodium ion batteries (SIB) are currently being developed as an alternative to the lithium ion batteries (LIB). Regarding the foreseen lithium penury, sodium is attractive due to a large abundance in the earth crust and, therefore, a lower cost. However, the higher redox potential of sodium combined with a heavier weight decreases the potential energy density of SIB. Different positive and negative electrodes are being proposed for increasing this density [1,2].

Electrolytes are a very important part of the cell in order to guarantee ionic transport and the formation of suitable electrode/electrolyte interfaces. They consist of an alkaline salt dissolved in an adequate solvent generally containing additives that stabilize the interfaces. Especially interesting is the recent use of glymes in the case of sodium [3] that allows sodium plating/stripping process to occur in a very reversible manner. However, glymes are highly viscous and the charge transport would be penalized.

Concerns about chemical, thermal and electrochemical stability of the electrolytes attracted attention on room temperature ionic liquids, RTIL, one decade ago. Consequently, they have been proposed as solvents for both, LIB and SIB [4,5] although their high cost penalize the price of the final device.

In this work, we investigate the possible application of RTIL as additives in contents not surpassing 10% in weight. For this study, we have chosen EMIFSI (1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide) as it is a suitable electrolyte solvent for negative electrodes designed in advanced batteries [6]. We will compare the physicochemical properties of electrolytes based on EC/PC and containing EMIFSI with those doped with glymes [7] or FEC [8] additives. We will also examine the sodium plating/stripping reversibility and the sodium charge storage in hard carbons and correlate their physicochemical and electrochemical properties.

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High-Stability Mushroom-Based Electrolytes for Non-Aqueous Redox Flow Batteries

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Among several types of redox flow batteries under development, non-aqueous redox flow batteries (NRFBs) have recently gained significant interest due to their wide electrochemical potential windows, offering high performance operation compared to aqueous chemistries [1]. However, the poor stability of electrolytes and related lifetime issues hinder their widespread implementation as an emerging technology. Molecular redox couples that have been evaluated for application as NRFB active materials have displayed significant capacity fade after only modest cycling [2-3]. Several decomposition mechanisms are possible and it has been noted that these are difficult to predict a priori [4].

To address the instability issues of these systems, we demonstrated a new class of high-stability NRFB active materials that is based on a molecule known as Amavadin. This compound is produced by mushrooms in the *Amanita* genus, and exhibits the most stable metal-ligand interaction ever elucidated for a vanadium (iv) ion. We evaluated the performance of calcium vanadium (iv) bis-hydroxyiminodiacetate (CVBH), an analogue of Amavadin, as an active material for NRFB electrolytes. Preliminary results using CVBH in a symmetric flow cell architecture indicated that the proposed system can be cycled extensively without loss of active materials (Fig. 1). In this presentation, we will demonstrate the performance characteristics of the proposed NRFB system using charge/discharge cycling, capacity fade and efficiency analyses. Additionally, our efforts to reduce area specific resistance and improve current density applied during operation will be discussed.

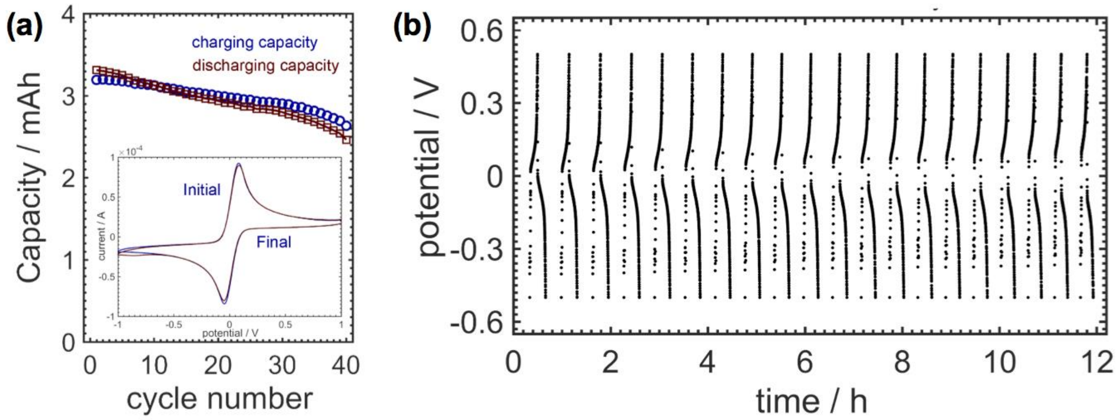

Figure 1. (a) Charge and discharge capacity over 40 cycles (inset: CV of sample before and after cycling) and (b) charge/discharge potential profiles for cycles 1 – 40, with every other cycle removed for clarity for 10 mM CVBH in DMSO with 0.4 M TEAPF$_6$.

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Safe and Highly Conducting Polymer Electrolytes for Ageing Resistant Li-ion Energy Storage

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Profoundly ion conducting, self-standing and tack-free ethylene oxide based polymer electrolytes are successfully prepared via a rapid and easily up-scalable UV/thermal curing process. Free radical polymerization (UV/thermal-curing) can be an interesting alternative to produce polymer electrolytes, being highly advantageous due to its easiness and rapidity in processing, high efficiency and eco-friendliness as the use of solvent is avoided. All of the prepared materials are thoroughly characterized in terms of their physico-chemical, morphological and electrochemical properties.

The crosslinking produced during curing allows the incorporation of high amount of RTIL (e.g., imidazolium, pyrrolidinium) or tetraglyme and lithium salt ($TFSI^-$ anion), leading to a material with remarkable homogeneity and robustness. The polymer network can efficiently hold plasticizers without leakage. Samples are thermally stable up to 375 °C under inert conditions, which is particularly interesting for application in Li-ion batteries with increased safety. Excellent ionic conductivity (>0.1 mS cm^{-1} at 25 °C), wide electrochemical stability (> 5 V vs. Li), stable interfacial properties and dendrite nucleation/growth resistance are obtained. The lab-scale Li-polymer cells assembled with different electrode materials (e.g., $LiFePO_4$, Li-rich NMC, $LiCoPO_4$, TiO_2) show stable charge/discharge characteristics with limited capacity fading upon very long-term reversible cycling [1-3].

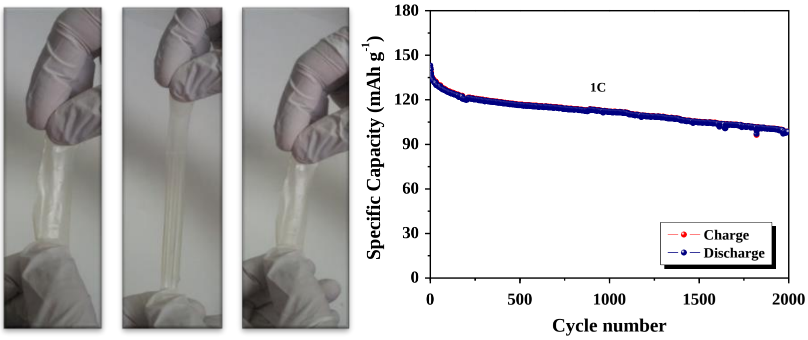

Fig. 1. Typical appearence of a cross-linked polymer electrolyte with truly elastic characteristics (left) and long-term reversible cycling at ambient temperature in $LiFePO_4$/Li lab-scale polymer cell (right).

The overall remarkable performance of the novel polymer electrolytes postulates the possibility of effective implementation in the next generation of safe, durable and high energy density secondary Li-ion polymer batteries working at ambient and/or sub-ambient temperatures.

Acknowledgements

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Sulfur-Microporous Carbon Composite Positive Electrode for Rechargeable Li/S Batteries

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A sulfur positive electrode is known to have some crucial problems for realistic application as Li/S battery, which are mainly dissolution of intermediate product species in its charge-discharge processes, insulation property of sulfur and lithium sulfide, and relatively large volume change of a sulfur positive electrode, although a sulfur positive has a high theoretical capacity (1,672 mAh g^{-1}).

During discharge process of a sulfur positive electrode, S_8 molecule goes through a series of lithium polysulfides (Li_2S_n [n =1-8]). Li_2S_8, Li_2S_6, and Li_2S_4 can easily dissolve to a liquid electrolyte. Moreover, insoluble Li_2S_2 and Li_2S also transform to a soluble lithium polysulfide by being oxidized during a charge process. These processes cause a redox shuttle reaction in a liquid electrolyte, which may induce rapid capacity decay and low charge-discharge efficiency. Also, a dissolved lithium polysulfide into a liquid electrolyte reacts with various electrolyte components (carbonate solvents, anions, *etc.*) and hence generates unnecessary products. Therefore, a simple sulfur positive electrode limits the choice of liquid electrolytes, which is one of some problems preventing from practical using Li/S batteries.

There have been at least two approaches to overcome the above issue. One is embedding sulfur into less than about 1 nm-sized micro pores by diffusion melt [1]; the other is covalently bonding sulfur onto de-hydrogenated polyacrylonitrile by heat treatment. These types of sulfur composite electrodes show better cycle stability and higher charge-discharge efficiency than those of other types of sulfur composite positive electrodes and avoid the necessity to use a special electrolyte because they can completely prevent dissolution of a lithium polysulfide into a liquid electrolyte. This should be an advantage for a Li/S battery. It is interesting to note that these types of composites show similar charge-discharge behavior in spite of undergoing different synthesis routes. To enhance the energy density of a Li/S cell, we think that sulfur-microporous material composites would be more investigated as a better choice.

In this study, we synthesized sulfur-microporous activated carbon (AC) composite material and systematically researched battery performance with different ACs, electrolytes (glyme-solvated ionic liquid electrolyte, carbonate-type electrolyte, etc.), and negative electrode materials (lithium negative electrode and partly silicon negative electrode). our efforts would enhance a possibility of a sulfur-microporous composite as positive electrode material for a next generation rechargeable battery.

We confirmed that the present sulfur-AC positive electrode shows relatively better low-temperature performance and prevents self-discharge at 60ºC by blocking dissolution of lithium polysulfide, which induces a redox shuttle reaction. According to the present results, a micro pore structure of 1 nm-sized strongly retains sulfur inside the pores, which indicates that some problems of sulfur as positive electrode material should be overcame by this simple synthesis method. Moreover, safety and reliability of the battery containing a sulfur positive electrode will be further improved by changing negative electrode material from lithium to silicon or carbon material. Further research on sulfur-microporous AC positive electrode is currently proceeding in our laboratory.

This work was partly supported by “Advanced Low Carbon Technology Research and Development Program, Specially Promoted Research for Innovative Next Generation Batteries (ALCA-SPRING)” from Japan Science and Technology Agency (JST). We thank Mr. Takuya Takahashi for his contribution in the early stage of our work.

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Visualization of Lithium Plating and Dissolution via in Operando Transmission X-ray and Optical Microscopy

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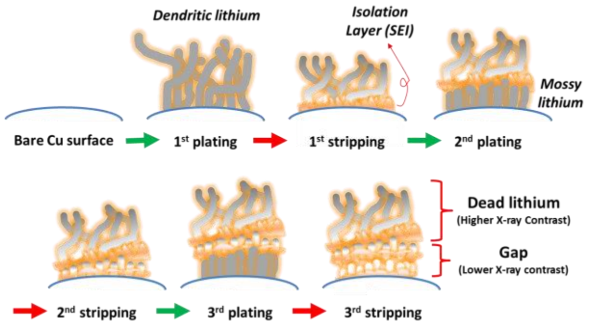
Lithium dendrite growth dynamics on Cu surface is first visualized through a versatile and facile experimental cell by *in operando* transmission X-ray microscopy (TXM). Lithium plating and stripping cycles in different current densities are also envisaged to show the dynamics of dendrite formation. During plating, dendritic/mossy lithium structures grow and shrink as the stripping proceeds, leaving dead lithium and SEI complex structure. It is interesting to note that the aspect ratio (height/width) of deposited lithium has increased with charge passed during plating. The different shapes of lithium metal either dendritic or mossy type have been observed when various current density was applied, and a growth mechanism for dendritic/mossy lithium is proposed. This work explores TXM as a useful tool for *in operando* dynamic visualization and quantitative measurement of lithium dendrite which is difficult to achieve with *ex situ* measurements and other microscopy techniques. The understanding of growth mechanism can be beneficial for the development of safe lithium ion and lithium metal batteries. The lithium plating and dissolution phenomena are also observed by optical microscope. The mechanism for Li-plating and dissolution is proposed as Scheme 1.



Scheme 1 Li-plating and dissolution mechanism

A New Ionic Network for Aqueous Polymer Binder for Enhancing the Electrochemical Performance of Li-Ion Batteries

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Abstract

Binders play a critical role in the mechanical stabilization of electrodes. However, commercial-grade adhesive polyvinylidene fluoride is soluble in N-methyl-2-pyrrolidone, which is an organic solvent that is both toxic and expensive. Therefore, water-soluble binders have recently been considered a promising alternative. In this study, an aqueous polymer with an interpenetrating network was introduced as a binder. Poly(acrylic acid), polyvinyl alcohol, and lithiated sulfosuccinic acid precursors were employed for crosslinking through an esterification reaction at a high temperature to form a long-chain polymer. This gel-like binder exhibited excellent cycling stability and high coulombic efficiency even at high current densities because of the promotion of ionic conductivity. This ionic polymer was systematically connected with active materials to ameliorate the electrochemical polarization of interfacial resistance. On the basis of these advantages, as well as its low cost, facile manufacturing process, and high performance, this simple method provides a pathway for achieving a commercial-grade high-capacity for Li-ion batteries. The electrochemical performance of $LiFePO_4/C$ electrodes maintained a specific capacity of 160 $mAhg^{-1}$ over 300 cycles at first charge, coupled with a coulombic efficiency of approximately 99% reversibility. In brief, an $LiFePO_4/C$ cathode with water-based binders demonstrated superior electrochemical performance in a half-cell test. The development of aqueous processing should provide considerable potential for meeting the requirements of next-generation high-power Li-ion batteries.

Keywords: ionic conductivity, aqueous binder, lithium battery

Effect of Controlled-atmosphere Storage and Ethanol Rinse on $NaNi_{0.5}Mn_{0.5}O_2$ for Sodium Ion Batteries

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$NaNi_{0.5}Mn_{0.5}O_2$ is a promising sodium ion batteries cathode material and has been extensively studied. It is important to understand the air-sensitivity of this material, which is not well studied or understood. Here, we present a detailed study of the air-sensitivity of $NaNi_{0.5}Mn_{0.5}O_2$ and a simple ethanol rinse method to improve its electrochemical performance.

$NaNi_{0.5}Mn_{0.5}O_2$ powders were stored in different atmospheres (oxygen, argon, carbon dioxide, compressed air), each being either dry or wet, for 5 days. XRD and FTIR were used to characterize materials before and after controlled-atmosphere storage. Figure 1 shows XRD patterns of $NaNi_{0.5}Mn_{0.5}O_2$ powders after being stored in different dry atmospheres. It was found that when stored in dry atmosphere, $NaNi_{0.5}Mn_{0.5}O_2$ itself do not participate in the reaction with ambient gas. The sodium residues in the sample (e.g. surface Na_2O_2) can react with dry CO_2 to form Na_2CO_3. However, when stored in wet atmosphere, drastic structural changes could be observed (Figure 2). Therefore, it was determined that water plays a crucial role in the desodiation process during air exposure. Combined with the results of FTIR, possible reaction mechanisms were proposed.

Finally, it was found that ethanol washing to remove residual surface impurities had significant beneficial effects on $NaNi_{0.5}Mn_{0.5}O_2$ structural stability and electrochemical performance. These effects will also be discussed.

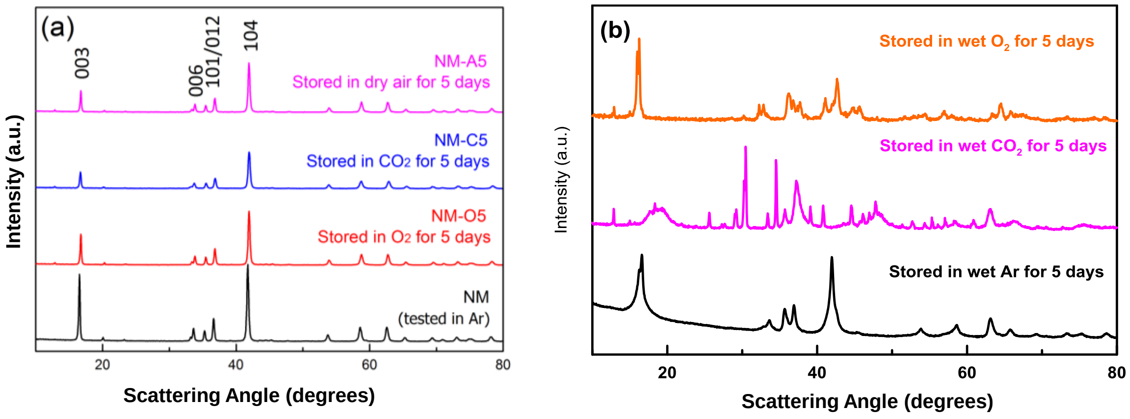

Figure 1 XRD patterns of $NaNi_{0.5}Mn_{0.5}O_2$ powders after being stored in different (a) dry and (b) wet atmospheres.

Method to Increase the Speed of EIS Series Measurements on Battery Stacks During Cycling while Avoiding Dramatic Loss of Measurement Accuracy

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The amount of time expended while running experiments is a crucial factor to consider when screening new materials as candidates for improving battery performance. Electrochemical impedance spectroscopy (EIS) is among the most appropriate evaluation tools for collecting in-situ information about electrochemical processes occurring inside battery systems. However, during charging and discharging cycles, the electrodes, electrolytes, and related materials comprising battery systems are continuously undergoing changes in state over time, even at timescales shorter than the amount of time required to run a single charge-discharge experiment. For instance, voltage is changing during constant current load. Here, the application of EIS can become restricted because the prerequisite of steady state as a foundational principle to interpret the resulting EIS spectra is violated due to changes of state in between the time it takes to sweep through frequencies of interest. Trying to yield significant results accounting for drift effects requires implementing particular modeling measures.

This abstract presents an ensemble of solutions to combat this issue. Parallel EIS, automatic drift correction of the measured time dependent signals, time interpolation by series measurements, and the application of the Z-HIT algorithm as post-processing of the data are the tools of choice. Simultaneous EIS is an effective time saving procedure. Otherwise, sequential EIS evaluation of *n* single cells in a stack increases time consumption by the factor *n*. Also, comparing the results for each individual cell to other cells is no longer directly comparable to an exact degree because the measurement drifts due to time effects are difficult to correct for. Second, precautions must be provided during the data acquisition phase in order to suppress the erroneous assignment of drift signals to the system response [1]. Furthermore, “non causal” spectra in the meaning of the Kramers-Kronig relations can be converted into correct spectra by interpolation of spectra series vs. time and, by removal of residual non-causalities with the help of the Z-HIT transform, which has the capability to reconstruct drift-affected data [2]. In many cases, the user would favor the comfortable possibility to significantly reduce the time for recording the EIS spectra by the application of multi-sine excitation. However, conventional multi-sine excitation normally is accompanied by significant losses of accuracy. An advanced technique provides the features of automatic drift correction and error detection known from single-sine excitation [3]. As a result, substantial loss in accuracy can be avoided.

Experimental data obtained from a four-cell Li-$FePO_4$ stack (13.2 V / 40 Ah) using this new multi-sine algorithm will be presented upon approval of this abstract for presentation.

Keywords: Multi-sine, Battery stacks, EIS, True parallel measurements, Z-HIT

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Gel Polymer-Ceramic Composites with an Asymmetric Configuration as Functional Electrolyte for Full-Cell Lithium Ion Batteries

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The leakage of liquid solvent posts a threat on the safety in the application of lithium ion batteries (LIBs). Gel polymer electrolytes (GPEs) overcome the leakage problem as the polymer functionalities strongly absorb the solvent molecules. The incorporation of ceramic-filler particles has been used to facilitate polymer-chain motion in GPEs. The choice of ceramic-filler particles to meet the requirements for charge transfer at the cathode- and anode-electrolyte interfaces is critical to the charge storage dynamics.

To capitalize the functions of ceramic nanoparticles in GPE-based LIBs, we take into account the difference in the interfacial characteristics of the anode and cathode. We proposed an asymmetric configuration for GPEs to comply with the interfacial characteristics of the cathode and anode of LIBs, for facilitating ion transport at both the cathode and anode interfaces. Silica (SiO_2) nanoparticles and TiO_2 nanoparticles are used to assemble the asymmetric GPE membrane for animating the anode and cathode, respectively, in ion transport.

The present study used poly(acrylonitrile-co-methyl acrylate) to construct the framework for the GPE membrane. When incorporated with SiO_2 and TiO_2 nanoparticles, the resultant asymmetric membrane presents outstanding performance in a full-cell graphite|electrolyte|$LiFePO_4$ battery, which exhibits a high-rate capacity retention of 62% at 7 C-rate (based on 0.1 C) and a cycling retention of 87% after 500 cycles of charge and discharge at 5 C.

Insertion / De-insertion of Magnesium into the Sb, Bi and Sn Modified Au Electrode

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Magnesium based secondary batteries have been regarded as a viable alternative compared to the immensely popular Li-ion systems owing to its high volumetric capacity [1]. One of the largest challenges is the selection of Mg anode material since the insertion/extraction processes are kinetically slow because of the large ionic radius and high charge density of Mg^{2+} compared with Li^{+}.

Bulk electrodeposition of Sb, Sn and Bi[2, 3] on polycrystalline Au has been investigated by cyclic voltammetry and electrochemical quartz microbalance (eQMB). Au(111) has been used as a substrate for STM study of monolayer (UPD) and bulk (OPD) deposition.

The cyclic voltammogram for Mg insertion/de-insertion from MACC/tetraglyme electrolyte [4] into/from an Sb modified electrode shows a positive shift (640 mV) of the onset potential of Mg deposition compared to that at bare Au electrode. The number of moles of Sb and Mg verify the stoichiometry of Mg_3Sb_2 alloy formation. The diffusion coefficient of Mg-insertion in Sb -multi-layers has been estimated by using two electrochemical techniques. At the steady state in the chronoamperommetry measurements, the apparent diffusion coefficient of Mg into the Sb layers are in the range of $2.5\text{-}4.7\times10^{-14}$ $cm^2\ s^{-1}$. Cyclic voltammetry at different sweep rate shows a value of 3.37×10^{-15} $cm^2\ s^{-1}$. Insertion of Mg into electrodeposited Bi and Sn and their effect on the decomposition of tetraglyme has been studied by DEMS. Mg diffusion coefficients have been also determined in the previous metal modified electrodes.

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Understanding of the Relationship between Electrode Structure and Electrochemical Performance in Li Ion Batteries

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Two novel electrode structures were designed to arrange active materials and porosity with greater precision inside the electrodes in order to improve Li ion transport and the electrodes were fabricated by scalable manufacturing techniques.

For the negative electrode, a two layer electrode structure was fabricated by atomisation spray processing [1]. A layer of porous TiO_2 particles was first sprayed on the current collector to improve Li ion transport through the internal pores of the porous TiO_2 particles in the electrode region where Li ion diffusion is usually limited. A second layer of non-porous TiO_2 nanoparticles was then sprayed to increase volumetric capacity (Fig. 1a). The volumetric capacity of the two layer electrode was 80% higher at a relatively fast (dis)charge rate of 2C compared with the electrodes with random structures of the same materials by a conventional slurry casting method.

Local Li ion concentrations through the negative electrode thickness were measured directly by X-ray photoelectron spectroscopy (XPS) depth profiling and clearly showed the improvements of Li ion diffusion in the layered electrode structure over its alternatives.

For the positive electrode, a thick (1.1 mm) $LiCoO_2$ electrode with vertical pores through the electrode thickness was fabricated by ice templating (Fig. 1b). The vertical pores reduced electrode pore tortuosity and consequently improved ion transport, compared with the electrodes with randomly structures of the same materials by slurry casting.

Electrochemical impedance spectroscopy (EIS) data showed that charge transfer resistance R_{ct} was decreased from 33.2 Ω cm^2 for the randomly structured electrode to 2.2 Ω cm^2 for the vertically porous electrode with the same total porosity, indicative of fast ion transport in the vertically porous electrode structure.

The general approach to electrode structuring combined with scalable processing could find wider applications to both existing industrial Li ion battery materials and next generation battery materials.

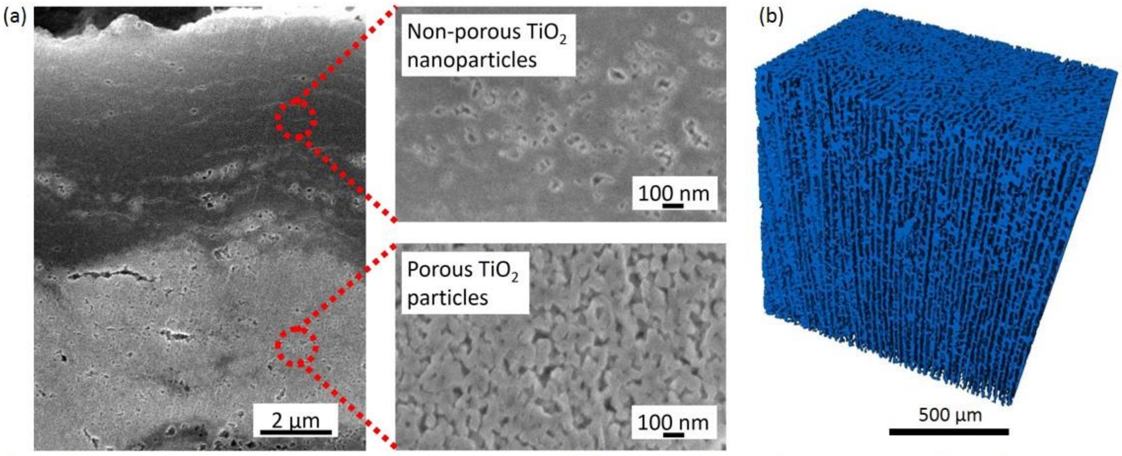

Fig. 1: (a) Cross sectional scanning electron microscopy (SEM) image of a two layer negative electrode; and (b) X-ray microtomography (XMT) 3D reconstruction of a vertically porous positive electrode.

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Test of $AlCl_3$-based electrolytes for the rechargeable Al-air battery

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Because of their higher theoretical energy density, lower toxicity, less expensive electrode materials and non-affinity to thermal runaway like e.g. Li-based systems, metal/air batteries such as Al-air (8040 *vs.* 2046 AhL^{-1} for Li) are potential candidates for sustainable energy storage applications. However, large scale commercialization is hindered by some inherent drawbacks related to the metal electrode such as irreversibility (not electrochemically rechargeable), passivation and parasitic hydrogen evolution as well as low energy efficiency [1]. In this context, recent developments in aprotic ionic liquids (ILs) and eutectic solvents based electrolytes open new perspectives for Al deposition/dissolution, especially with respect to suppression of passive layer formation and self-discharge due to hydrogen evolution [2,3]. Most of the ILs, however, are highly viscous and consequently have a very low ionic conductivity that drastically limits reaction kinetics. Other crucial aspects are related to their low surface tension compared to water that commonly hinders 3-phase boundary formation in the gas diffusion electrode.

In a preliminary screening, activity of Al stripping/deposition on pyrolitic graphite (PG) and O_2 reduction/evolution (ORR/OER) at Pt/C was investigated in numerous triflate, acetate or chloride anion-based ILs with corresponding salt mixtures, as well as in two $AlCl_3$-based eutectic solvents under half-cell conditions by cyclic voltammetry. Highest current density for ORR/OER was recorded in EMImOAc. As expected, Al deposition/stripping was found to be clearly more efficient in $AlCl_3$ containing electrolytes so that full-cell investigations were carried out first in EMImCl+$AlCl_3$(1:1.5), urea+$AlCl_3$(1:1.6) and acetamide+$AlCl_3$(1:1.6). All the cells successfully ran during 15 cycles (~100h) with 3h discharging/charging steps each at 100 μAcm^{-2} in dry synthetic air. Capacity fading was attributed to influence of residual moisture. Best performances were yielded with acetamide+$AlCl_3$. Average coulombic efficiencies of 55, 75 and 80% and energy efficiencies of 45, 50 and 52% were calculated for tests in EMImCl-, urea- and acetamide-containing electrolyte, respectively.

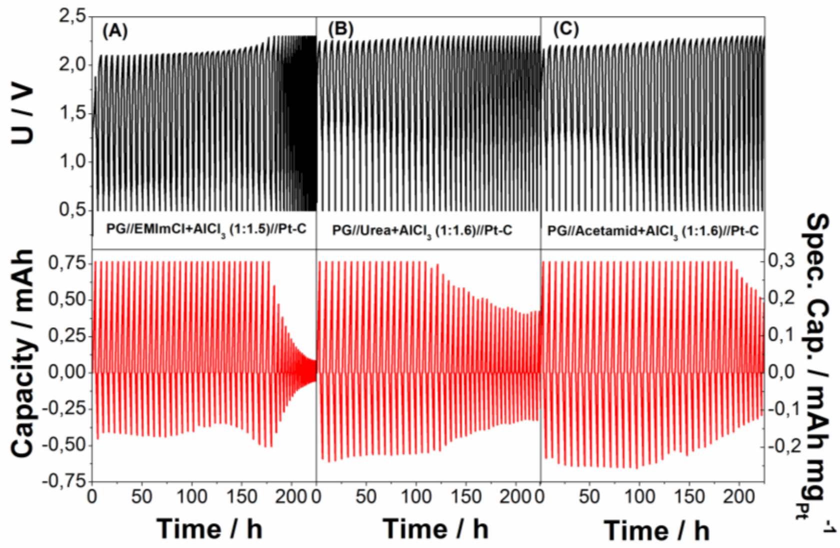

Figure 1: Charge/discharge (up) voltage and (down) capacity curves of PG//electrolyte//Pt-C cells at 100μAcm^{-2} for 3h with 2 $mlmin^{-1}$ dry synthetic air. Cut-off limits were 2.3 V for charge and 0.5 V for discharge step.

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Addressing the Controversial Mechanism of Na^+ Reversible Storage in TiO_2 Nanotube Arrays: Amorphous versus Anatase TiO_2

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Among a wide range of applications (e.g., dye-sensitized solar cells, lithium-ion batteries, supercapacitors, etc.), in its amorphous as well as most common polyphases including anatase, rutile, brookite and various metastable phases, TiO_2 is under intense investigation as anode candidate for advanced electrochemical energy storage based on the sodium-ion (Na-ion) technology. Na-ion batteries (NiB) are attracting the widespread interest of the scientific community because they may offer the most convenient alternative to current leading-edge Li-ion technology (LiB) for large-scale grid energy storage, where size does not matter and cost, safety and reliability are the stringent requirements [1,2].

In the recent years, various hypotheses have been proposed on the real mechanism of reversible insertion of sodium ions into the TiO_2 structure and literature reports are often controversial in this respect. Interestingly, when tested as binder- and conducting additive-free electrodes in lab-scale sodium cells, we experience intrinsically different and peculiar electrochemical response between amorphous and anatase TiO_2 nanotubular arrays obtained by simple anodic oxidation. In particular, after the initial electrochemical activation, anatase TiO_2 shows excellent high rate capability and very stable long-term cycling performance at larger specific capacities, thus definitely better response as compared to the amorphous counterpart. To reach deepen insights into the subject, materials are thoroughly characterized by means of scanning electron microscopy and *ex-situ* X-ray diffraction, and the mechanism of sodium ion insertion in the TiO_2 bulk phases is systematically modelled by density functional theory (DFT) calculations, which may significantly contribute to get a more systematic selection of proper active material configurations for highly efficient sodium-based energy storage systems.

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The Controversial Surface Reactivity of $Li_4Ti_5O_{12}$ in the Aprotic Electrolyte Disclosed with XPEEM

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Whether $Li_4Ti_5O_{12}$ (LTO) electrodes can induce reduction of the commonly used aprotic electrolyte and develop a stable surface layer at 1.55 V vs. Li^+/Li remains a subject of controversy. Understanding the reactivity of both electrode and electrolyte is considered to be a key step to ensuring a stable electrolyte/electrode interface and thus a long-life span of Li-ion batteries. Here, we make use of x-ray photoemission electron microscopy (XPEEM) to gain information on individual particles composing a commercial-like LTO electrode (Figure1.A) to determine the nature/origin of the LTO interface instability. In XPEEM, maps of the x-ray absorption spectra (XAS) of the sample are acquired with nm spatial resolution to yield surface-sensitive local electronic and chemical characteristics. The local XAS spectra acquired at the C K-edge on carbon (Figure 1.B) and LTO particles (Figure 1.C) show that reduction of the electrolyte occur only on the latter particles and exclusively during lithiation. Simultaneously, we detect a second reaction at the same potential, leading to a partial dissolution of the organic/inorganic species covering the LTO particles. This behavior correlates strongly with the Li^+ insertion/de-insertion and the thermodynamic stability of the electrolyte. With the support of DFT calculations, we conclude therefore that the origin and the mechanism of the electrolyte reduction relates to the adsorbed solvent on the LTO outer plans, driven by their co-insertion with solvated Li^+. The adsorption of solvents leads to a shift of their LUMO to energies below the operating potential of LTO and favoring a reductive electron transfer process (Figure 1.D). This study highlights the potential of XPEEM to investigating the complex electrode/electrolyte interface reactions for improving our understanding and the development of solutions to engineering the surface of Li-ion battery electrodes.

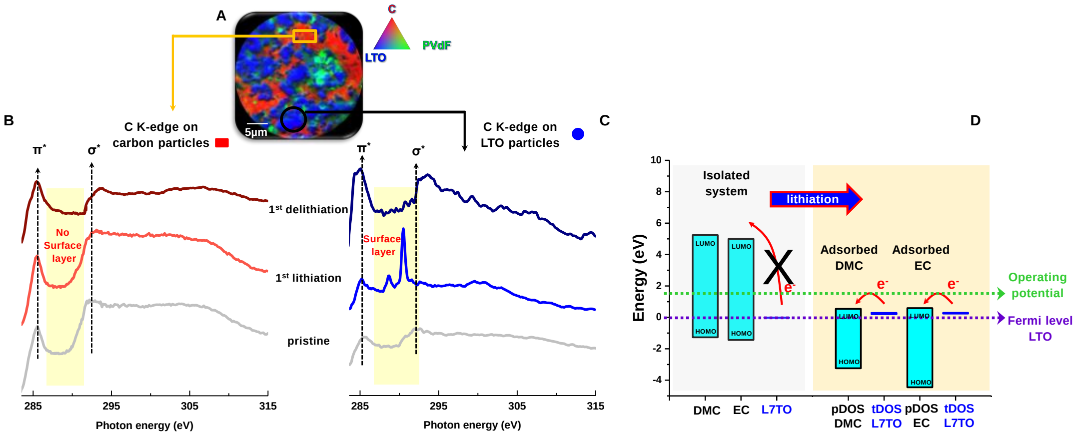

Figure 1: (**A**) XPEEM elemental map showing the distribution of carbon (red), active material (blue) and PVdF binder (green) on LTO pristine electrode. Local XAS at the C K-edge carried out on individual particles of carbon (**B**) and LTO (**C**) in pristine, lithiated and delithiated electrodes. (**D**) HOMO/LUMO levels of DMC, EC and L7TO (lithiated anode) calculated before (on isolated systems) and after lithiation (adsorption of DMC and EC on L7TO surface).

Li-S battery mechanism in sparingly soluble electrolytes

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Post Li–ion battery technologies are being quickly developed to accommodate an increasing world's energy demand. Lithium–sulfur batteries are a promising system, although they are facing several issues. Among them, the most pressing one is high solubility of polysulfides in traditionally used electrolytes, which causes material loss, low Coulombic efficiency and faster lithium degradation.

Since polysulfide dissolution is essential for the battery cell performance, most efforts are focused on minimizing the polysulfide shuttle extent. For this, several approaches have been proposed. One of the novel ways of reducing polysulfide shuttle problem involves the use of electrolytes that sparingly solute polysulfides (Cheng et al.; Gu et al.). Those types of electrolytes enable better capacities and coulombic efficiencies by impeding polysulfide diffusion away from the cathode. Furthermore, high-energy lithium-sulfur battery cells could be constructed with higher sulfur loadings and low electrolyte amounts.

We propose a novel electrolyte composition with diminished polysulfide solubility, which outperforms traditional electrolyte mixtures. Since we found a substantial difference of the operating high voltage potential between traditional electrolyte (1M LiTFSI TEGDME:DOL) and sparingly soluble electrolytes , we investigated the mechanism with X-ray absorption and UV/Vis spectroscopy. Both techniques prove the presence of polysulfides. Although the high voltage plateau is at a lower value, the reaction mechanism seems to be the same as previously determined for electrolytes with higher polysulfide solubility (Dominko et al.). Different compositions of the electrolyte were also tested to see the influence of the both solvents.

Finally we demonstrate that sparingly soluble electrolytes can substantially decrease required electrolyte loading normalized per sulfur without losing battery performance and this is a step forward to obtain high energy Li-S batteries.

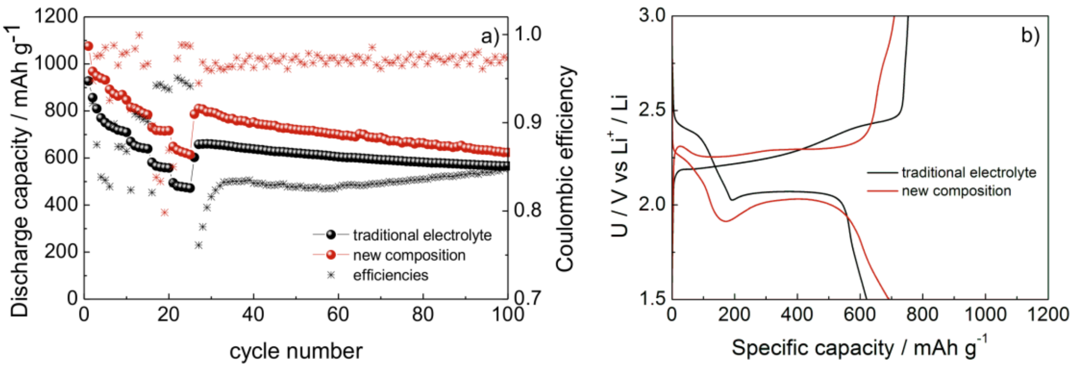

Figure 1: a) Comparison of electrochemical performance of the traditional electrolyte with the proposed new composition, note the difference in coulombic efficiency b) galvanostatic voltage profiles of both compositions (50th cycle)

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The Kinetic Study of Self-terminated Oligomer Branched Architecture (STOBA) in Lithium Ion Battery

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Surface plasmon resonance (SPR) is the optical technique that ensures high surface sensitivity, versatile, real-time monitoring and label-free detection [1-4]. This paper revealed the physical, optical and kinetic properties of self-terminated oligomer branched architecture (STOBA) synthesized from N,N'-bismaleimide-4,4'-diphenylmethane (BMI) with barbutiric acid (BTA) in the presence of hydroquinone (HQ). The STOBA was used to prevent the short circuit problem in lithium ion battery [5].

The STOBAs were spin coated on Au electrode and characterized by the SPR at Au-gas interface in 353K and 403K. The polymerization rate of the aforementioned polymers was determined using the appropriate kinetic model [6]. Accordingly, a unique SPR main peak was observed at lower reflection angle (θ) for BMI/HQ thin film while for BMI/BTA were observed at higher θ for 670nm and 785nm wavelength of incident light.

According to the literature [7], the BMI/BTA/HQ has two reaction mechanisms, including Michael reaction and Aza-Michael reaction. Table 1 shows that SPR reveals only one reaction rate constant (k1) in the value of $2.82*10^6$ $M^{-1}s^{-1}$ on BMI/BTA at 353K, indicating the reaction on this temperature contains only one mechanism (the first-reaction). In addition, the second-reaction rate constant (k2, $5.25*10^6$ $M^{-1}s^{-1}$) on BMI/BTA at 403K has been displayed, representing the second-reaction triggers at the higher activation. However, from the table, the rate of second-reaction reacts fast twice than the first reaction. We expect that the second-reaction dominates the key in preventing the short circuit problem of lithium ion battery. Furthermore, the molecule interaction of above STOBAs from room to high temperatures is under investigating in order to evaluate and design a new kinetic control safety additive. Those SPR results are used to compare with the information of differential scanning calorimetry.

In this research, we calculated the rate constant, activation energy and frequency factor from isothermal and non-isothermal processes. Using these two promising techniques, we investigated the polymerization reaction behavior of each polymer at surface and interface very well.

Table 1 Film thickness, refractive index, absorption coefficient and rate constant for STOBA materials.

Composition	**Polymerization Temperature/ k**	**Coating thickness/ nm**	**Rate constant/ $M^{-1}s^{-1}$**	
			k1	**k2**
BMI/BTA w/ HQ	353	105.38	$2.82*10^6$	-
BMI/BTA w/ HQ	403	105.37	$6.33*10^4$	$5.25*10^6$
BMI w/ HQ	403	105.44	$5.86*10^2$	-

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Growth Mechanisms and Safety Boundaries of Lithium Metal Anodes in Liquid Electrolytes

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Next-generation high-energy batteries, such as Li–O2, Li–S, and other Li metal batteries using intercalation cathodes, will require rechargeable lithium metal anodes, but lithium dendrites tend to form during recharge, causing short-circuit risk and capacity loss. Our experimental results from novel miniature capillary cells, junction cells and realistic sandwich cells reveal three distinct growth mechanisms that are sensitive to the applied current density. When a current density larger than the system-specific limiting current density J_{lim} is applied, concentration of lithium ions near the electrode surface will be depleted to zero at Sand's time, beyond which tip-growing lithium dendrites shoot out to form a fractal structure similar to the classic copper dendrites. When a current density well below J_{lim} is applied, the formation of robust solid electrolyte interphase (SEI) layers leads to the buildup of compressive pressure in the lithium metal anode and eventually the root-growing whiskers through pinholes of the SEI layers, which interweave with each other to form a mossy structure but fortunately can be blocked by nanoporous ceramic separators [1]. In the regime that the applied current density is below but close to the limiting current density J_{lim}, the competing reactions between lithium electrodeposition and SEI formation lead to whiskers growth in areas with thick SEI, but isotropic surface growth in other areas. The latter, under sufficient mechanical and electrochemical driving forces, can penetrate the nanoporous ceramic separator [2]. In our sandwich cells, where the distance between the two electrodes is 300 μm, the critical current J_{cc}, beyond which surface growth can penetrate the nanoporous ceramic separator, is determined to be 6 mA cm^{-2} [2]. Our work demonstrates that precision understandings of the distinct growth mechanisms during lithium electrodeposition is the premise of the realization of safe rechargeable lithium metal anodes. Our results suggest three layers of safety boundaries for the design and management of rechargeable lithium metal batteries. It is critical to monitor the degradation of transport properties (J_{lim}) of the aged batteries to avoid the short-circuiting risk at work.

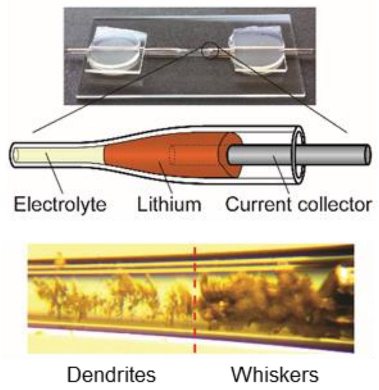

Figure 1. A capillary cell used to observe the transition from mossy lithium (collection of lithium whiskers) to lithium dendrites [1].

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Analysis on Growth Process of Irregular Shaped Zn Electrodeposits and Roles of Metal Additives

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Zn negative electrode is one of the promising candidates for large scale batteries applied in the power distribution system in terms of abundant resources and low cost. Despite long history of Zn for primary batteries, its applications in secondary batteries are still limited due to evolution of irregular shaped Zn during charge-discharge cycles. Notable fact is that not only dendritic deposits formed at high current density (c.d.) but also highly filamentous, mossy structures formed under low c.d. charging are major causes of battery failure [1]. In this study, in order to understand fundamental mechanisms behind irregular morphological evolutions, growth process of mossy structure was investigated, especially focusing the comparison with that of the dendrites. In addition, the roles of Sn additives, which were advantageous for smoothly depositing Zn, in deposition process were analyzed in detail.

Zn electrodeposition was mainly performed under galvanostatic conditions from alkaline zincate solution (6.0 mol dm^{-3} KOH + 0.10 - 0.50 mol dm^{-3} ZnO). As an additive, 1.0 - 50 mmol dm^{-3} $K_2SnO_3 \cdot 3H_2O$ was also dissolved into electrolyte. Electrochemical measurements were performed with three electrodes, Cu working (diameter = 0.80 cm), Zn counter and Hg/HgO reference electrodes. For the *in-situ* observation of the Zn growth behavior by CCD camera, μ-meter sized electrodes were also used. These electrodes were prepared by embedding 100 - 500 μm diameter Cu wire in epoxy resin. Mirror finishing on exposed surface was performed by chemical mechanical polishing (CMP).

First, the growth process of mossy structure was investigated. Compared to the dendritic growth at high c.d., mossy structure formation was characteristic in deposition potential and concentration dependence. In chronopotentiograms at c.d. = -5 mA cm^{-2}, the potential eventually shifted toward positive value. This is stark contrast with the dendritic growth accompanying concentration polarization prior to its initiation. Prior to the positive potential shift, the observation with scanning electron microscopy (SEM) showed relatively flat deposits with stacking of layer-like structures (microsteps). Then, filamentous structures evolved from the microsteps [2]. By decreasing zincate concentration from 0.25 mol dm^{-3} to 0.10 mol dm^{-3} at same c.d., the filaments disappeared and microsteps horizontally expanded (crystal size increased). Mossy structure formation process was significantly influenced by the periodic process of locally repeated nucleation and microsteps growth toward lateral direction. Such a growth process was quantitatively discussed by *in situ* observation of deposits growth behaviors, too.

As a method to suppress the mossy structure, we recently reported effects of Sn addition [2]. In the present study, the roles of Sn in Zn deposition process were further investigated. First, composition of deposits with Sn additive was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). As a result, Sn content in deposits was less than 1 at%. X-ray diffraction showed no peaks assigned to Sn. Then, the roles of such a trace amount of Sn in the Zn growth process was analyzed by focusing to morphological variations at early stages of deposition. At initial stage (<200 s), the deposits showed variety of microsteps structures dependent on crystallite of underlying Cu, which was same trend without additive. After 400 s, these microstep structures were hardly observed and Zn deposits uniformly grew over entire surface. These observations indicated that trace amount of Sn suppressed stacking of microsteps (locally repeated nucleation) and following mossy structures.

This work was partly supported by the "Research & Development Initiative for Scientific Innovation of New Generation Batteries (RISING II)" from the New Energy and Industrial Technology Development Organization (NEDO) of Japan. T.O. acknowledges the Leading Graduate Program in Science and Engineering, Waseda University from MEXT, Japan.

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Poly ionic liquid solid electrolyte interphase (SEI) formation in 5V class lithium ion batteries

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Electric vehicles (EVs) are poised to dominate the next generation of transportation, but meeting the power requirements of EVs with lithium ion batteries is challenging because electrolytes containing $LiPF_6$ and carbonates do not perform well at high temperatures and voltages. However, lithium benzimidazole salt is a promising electrolyte additive that can stabilize $LiPF_6$ through a Lewis acid–base reaction [1]. The imidazole ring is not eligible for high-voltage applications owing to its resonance structure, but in this research, electron-withdrawing ($-CF_3$) and electron-donating ($-CH_3$) substitutions on imidazole rings were investigated. According to the calculation results, the CF_3 substitution facilitates a high electron cloud density on imidazole ring structures to resist the electron releases from bezimidazole in oxidation reactions. In addition, through CF_3 substitution, electrons are accepted from the lattice oxygen (O^{2-}) in Lithium-rich (Li-Excess) layer material and O^- is converted by electron to a great quantity, which catalyzes the electrolyte reduction and forms a new polyionic liquid solid electrolyte interphase on the cathode’s surface. Furthermore, the cycle performance tested at 60 °C and 4.8 V showed that the CF_3 substitution maintains the battery retention effectively and exhibits almost no fading compared with both the blank electrolyte and the CH_3 substitution. In addition, the results of this study confirm that bezimidazole salt greatly catalyzed the reduction of EC to a stage II reaction, and therefore less Li_2CO_3 formation was found. A possible reaction mechanism is shown in Figure 1.

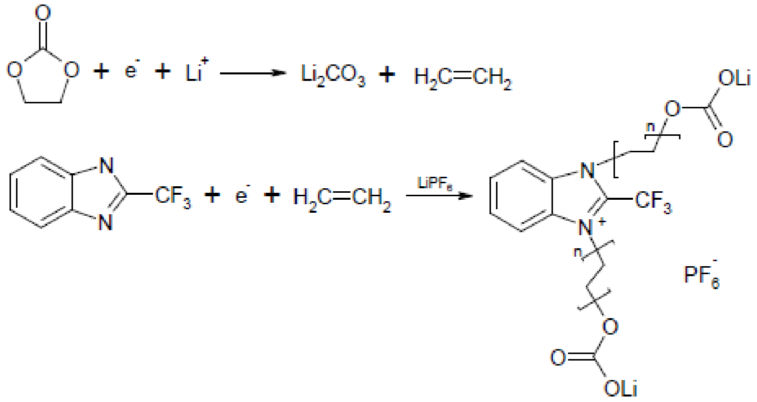

Figure 1 The proposed reaction mechanism of poly ionic liquid SEI formation on LLNMO electrode with bezimidazole salt additive [2].

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A revolutionary green approach for recyclable lithium ion battery

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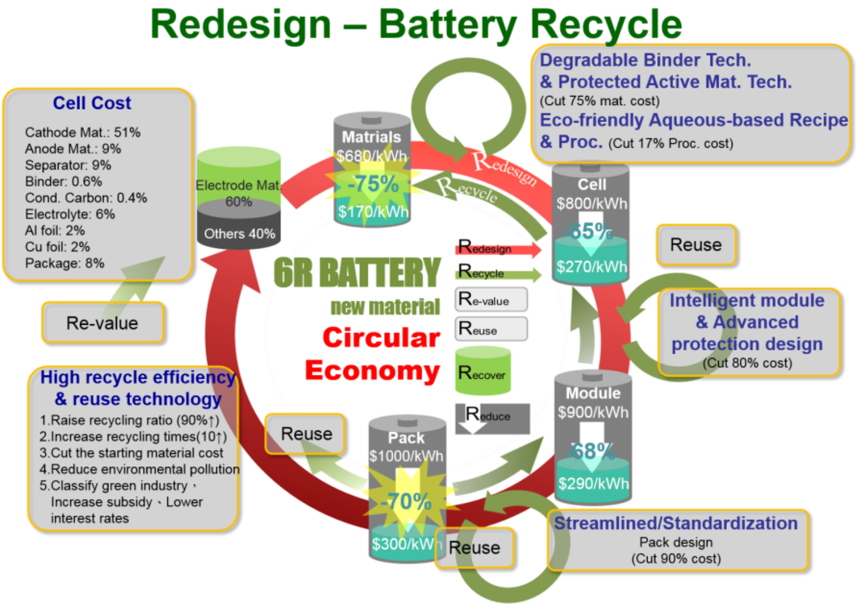
As demand for lithium-ion secondary batteries has increased tremendously, it also raises the serious problem from tons of waste year by year. Although rechargeable batteries in smartphones, cars and tablets can be charged again and again, they don't last forever. Lithium batteries are not currently being collected by manufacturers for recycling. They are currently disposed of after their use. Old batteries often wind up in landfills or incinerators, potentially harming the environment. And valuable materials remain locked inside. While other methods exist to separate lithium, cobalt and other metals, they require high temperatures and harsh chemicals. It also costs a lot of energy and very time-consuming. All in all, the greener method for battery recycling is a big challenge and still under a long-term development. A revolutionary technology to revive the battery waste is urgently needed.

Now, this study is turning to drive an environmentally friendly recycling process to extract the active material from disused lithium ion batteries. The detailed powder purification will take place after completing battery recycling. In fact, the remaining material can be reused in low-end batteries or other storage component without disposal. The key to achieve this goal is based on the employment of functional polymers as a new binder system to replace the currently used PVdF/NMP system, due to the problem that PVdF is very hard to be recovered. Aqueous manufacturing process has attracted a great attention for its low cost and non-toxic environment. Herein, the application of water-dissolved binders is critical for the renewable battery technology and some selection principles are needed to be pre-clarified. On the first hand, these binders need to have a good adhesive property with both active material and current collect. On the second hand, it should be easy to remove from the electrode matrix by a non-destructive way after prolonged usage. We have successfully established a systematic recycling flow and an effective binder degradation method. The recovery rate of the electrode material is generally over 80% and the purity can be raised to 90% or more. Hope that the as-provided green approach will become an alternative solution in contributing to our sustainable future.

Keywords: lithium ion battery; renewable; recycle; binder



Oxide Double-Coating Layers on the Surface of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ Cathode Material of All-solid-state Lithium Ion Battery

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All-solid state batteries (ASSBs) have been attracting great interest because of the concerns on safety issues. However, there are some particular challenges in the development of ASSBs. One is the large interfacial resistivity between solid electrolyte and cathode, which is believed to be induced through mutual diffusion of constituent elements creating a diffusion barrier [1] or a Schottky barrier at the interface [2]. Some coating layer candidates have been proposed to modify the cathode particle surface to mitigate above issue [3-4]. Recently we proposed a new protective layer of diamond-like carbon, and showed that preventing reaction between solid electrolyte and cathode can be effective to decrease interface resistance [5]. In this study, we report the application of some cathode surface coatings as protection layers, and analyze the influence of these coating layers on the local structure of the sulfur and phosphorus atoms of the solid electrolyte by Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) technique. We also propose a new type of oxide double-coating layer to improve the cell performance.

We prepared the cathode material of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ coated with lithium zirconium oxide (LZrO), lithium germanium oxide (LGeO). The oxide double-coating of LZrO (inner layer) and LGeO (outer layer) has also been prepared. Amorphous Li_2S-P_2S_5 (75:25 mol%) electrolyte was used for solid electrolyte, and graphite was used for anode. The discharge rate was set at 0.05C, 0.5C and 1C. The charge condition was fixed at 0.1C constant current with constant voltage at 4.0 V. The cell performances clearly show significant improvement in the cell using the coated samples, especially in the cell using the oxide double-coated cathode. The discharge capacity of the double-coated cell at 0.05C was 137 $mAhg^{-1}$ while those of LZrO-coated and LGeO-coated samples were 136 $mAhg^{-1}$ and 131 $mAhg^{-1}$, respectively. At 1C discharge rate, the capacities were 103 $mAhg^{-1}$ (double coat), 88 $mAhg^{-1}$ (single LZrO coat), and 90 $mAhg^{-1}$ (single LGeO coat). Also, the impedance measurements show a decrease of resistance in the following order: bare, LZrO, LGeO and double-coating of LZrO+LGeO. These results show that the cell performance can be improved using oxide double layer in comparison with a single layer. The TOF-SIMS analysis has revealed that the coating layers, in particular LGeO, prevent the interfacial reactions after charge-discharge, especially the PO_3^-, PO_4^-, SO_3^-, SO_4^- formation at the interface. The LGeO layer on the surface of cathode material has a positive effect on the stabilization of the sulfide solid electrolyte in ASSBs.

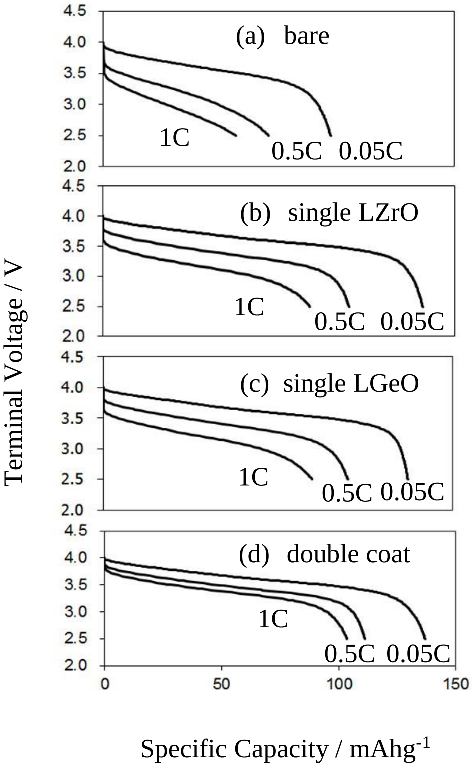

Fig. Discharge curves of the ASSBs using (a) bare (b) single LZO (c) single LGeO (d) double coating at different discharge rates at 25 ºC.

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Reversible Capacity Deterioration of 18650-type Lithium-ion Secondary Cell Investigated by d*Q*/d*V*-*V* Curve at 5-25°C

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A charge/discharge capacity of a lithium ion secondary cell deteriorates by a repeated charge/discharge operation in a low temperature environment[1]. We measured the capacity of a lithium ion secondary cell at 25-5°C, found that the capacity markedly deteriorated at 5°C as shown in Fig. 1; however, the capacity is recovered when the temperature raised at 25°C. To understand this temperature-dependent capacity change, the d*Q*/d*V*-*V* curve and AC impedance analysis can be powerful tools. The purpose of this study is to measure a d*Q*/d*V*-*V* curve by changing the cell temperature, and conduct AC impedance measurement to elucidate the performance deterioration of a commercially available 18650 type lithium ion cell at 5°C.

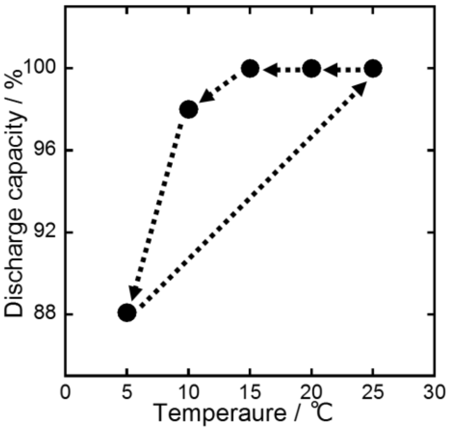

Fig. 1. Temperature dependence of discharge capacity for 18650-type lithium-ion secondary cell.

The lithium-ion secondary cell consisting of $LiCoO_2$ for the positive electrode and graphite for the negative electrode was used in the experiment. After a conditioning the cell, charge/discharge at a rate of 0.05C was carried out at 25°C and 0°C to evaluate the d*Q*/d*V*-*V* curve [2].

The d*Q*/d*V*-*V* curve obtained at a rate of 0.05C at 25°C is shown in Fig. 2. We define each peak by comparing to d*Q*/d*E*-*E* curves of the positive and negative electrodes of the half-cell, which both previously reported [3,4]. The A and B peaks during the charge are considered to be originated in the crystal structure change of $LiCoO_2$, where A corresponds to a structural change from Hexagonal-I to Hexagonal-II and B corresponds to a structural change from Hexagonal-II to Monoclinic. As for the anode, the four peaks of a, b, c, d represents the change of graphite stage structure. From a d*Q*/d*V*-*V* curve at 5°C, we found that a decrease in the differential capacity observed in the low SOC region affects of the decrease of discharge capacity shown in Fig. 1. To clarify this phenomena, AC impedance was measured for evaluating an activation energy and an exchange current.

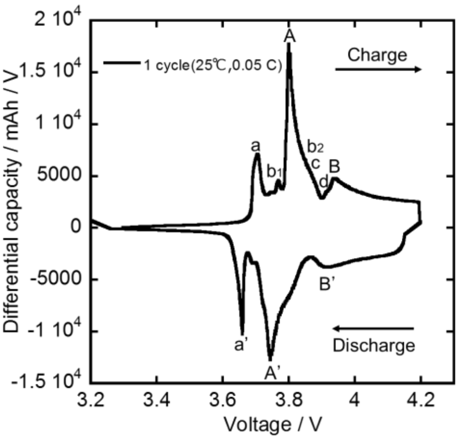

Fig. 2. Differential capacity vs. voltage recorded during charge/discharge cycling at 0.05 C and at 25°C.

Acknowledgement

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Understanding Electrolyte Decomposition of High Ni-NCM at Elevated Operating Voltage

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For the application in electronic devices as well as in electric vehicles, Li-ion batteries achieving high energy densities are required. Thus, the layered cathode material NCM ($LiNi_xCo_yMn_{1-x-y}$) with a high nickel content is a suitable candidate due to its high capacity in combination with a high operating voltage. However, operating cells at elevated voltage leads to severe electrolyte decomposition and effects the high Ni-NCM material. As a consequence, the cell suffers from gas evolution and capacity fading.[1,2]

In order to improve the electrochemical stability of high voltage cells, additives are widely used. Nevertheless, a deep understanding of the electrolyte decomposition is necessary to choose an additive for the corresponding cell system.
During electrochemical cycling the electrolyte decomposition leads to gas evolution. Thus gas analysis, such as online electrochemical mass spectroscopy (OEMS) can help to understand the composition of such gaseous products.[3,4] In addition, it was found that already at lower voltage ethyl methyl carbonate (EMC) - which can be a co-solvent in the electrolyte - undergoes a transesterification reaction towards dimethyl carbonate (DMC) and diethyl carbonate (DEC) while ethylene carbonate (EC) can undergo dimerization reactions with DMC, DEC or EMC. These electrolyte reactions can be quantitatively analyzed by GC/MS measurements.[5–7] Here, observations which were made already at operating voltages below 4.3 V are even more severe applying a higher voltage.
In understanding the decomposition mechanism of the electrolyte, suitable additives can be found to improve the cycling stability at elevated voltage.

Here, the correlation of transesterification/dimerization of the electrolyte solvents and gas-evolution of Ni-rich NCM / graphite cells during high voltage operation is investigated. An electrochemical investigation on the rate, efficiency and impedance of these cells at different cut-off voltages is performed in combination with a gas analysis during cycling. Furthermore, GC/MS analysis of the electrolyte after high voltage operation is implemented. Electrolytes with and without additives are analyzed in order to understand the reaction mechanism of the electrolyte decomposition (no additive) as well as the suppression of this decomposition by the reaction of the additive. FTIR and XPS measurements after cycling are made to get a full picture of the working principle of the used additives at elevated voltage.

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Non-Aqueous Copper Battery for Heat-to-Power Conversion and Storage

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In this presentation, we will describe a new approach for conversion of heat into chemical energy, stored in a battery. A thermo-electrochemical system with a redox flow battery (RFB) is proposed to allow the conversion of heat at relatively low temperature into chemical energy. The electroactive species of the battery are copper ions in an organic solvent mixture containing acetonitrile (ACN) as a complexing agent. Water is avoided because its presence influences considerably the voltage that can be achieved by the cell. During the process of charging, the Cu(I) complex with acetonitrile can be destabilized by a heat source around 150°C (or more) and it leads to the disproportionation of Cu(I) in Cu and Cu(II). In this charged state, the chemical energy can be converted into electricity with the Cu oxidation and Cu(II) reduction in the different half cells. This battery can also store energy as a conventional hybrid RFB with a purely electrical charging [1]. For a better understanding, the electrochemistry of copper in acetonitrile and propylene carbonate (PC) mixtures has been investigated. The thermodynamic properties of the copper electrolytes, as well as the heat required for the thermal regeneration has been evaluated by differential scanning calorimetry (DSC).

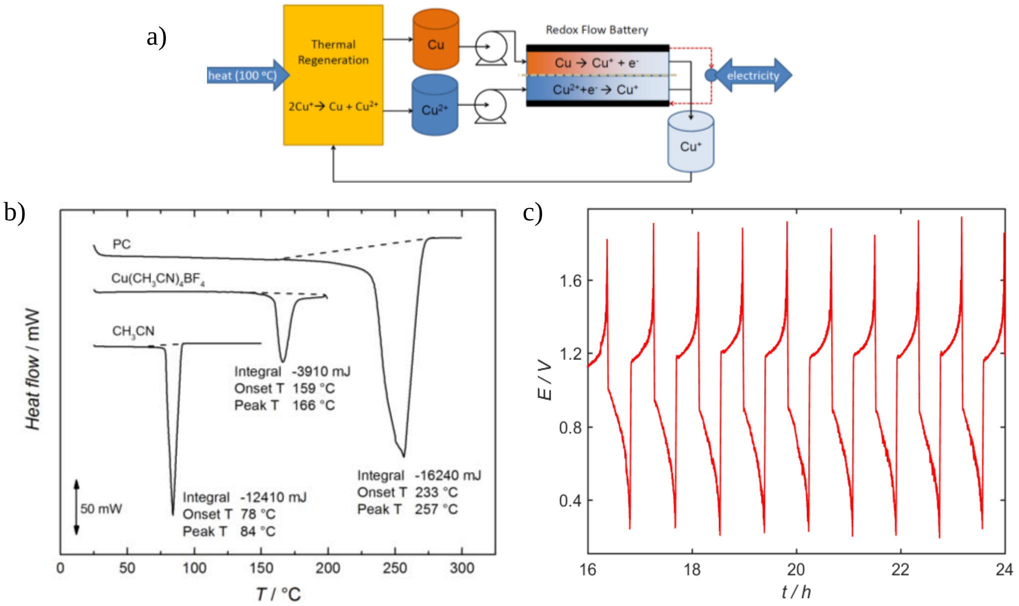

Fig. 1: a) the concept of heat conversion into chemical energy stored in an all-copper battery. b) DSC curves of ACN, PC and $[Cu(CH_3CN)_4]BF_4$ at 5°C·min^{-1} c) IR corrected charge/discharge cycles at 60°C with 10 mA·cm^{-2} regarding the potential of a cell with 0.15 M $[Cu(CH_3CN)_4]BF_4$ and 0.15 M $TEABF_4$.

The theoretical battery efficiency should reach 28%, if a thermal charging is applied. For the battery performance with an electrical charging, the Coulombic efficiency is around 95% and the energy efficiency stays between 45 and 60% with charging current in a range going from 1 to 15 mA·cm^{-2}. Different counter anions (BF_4^-, PF_6^- …) for the $[Cu(CH_3CN)_4]^-$ complex have been tested to increase the solubility and performance of the CuRFB.

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Zinc Batteries with Novel Electrolytes

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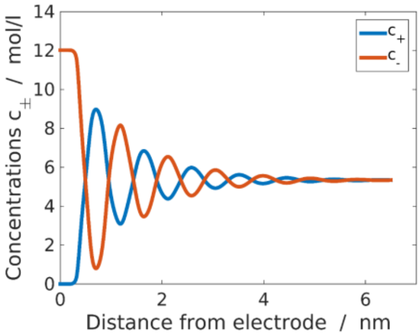
Zinc metal is a non-toxic, cheap, and abundant anode material with a great tradition in battery applications. Today, zinc batteries are among the few candidates for efficient and low-cost devices required for stationary grid storage. The development of rechargeable zinc batteries with high capacity and high cycling stability is challenging because of hydrogen evolution, dendritic growth of zinc, and low tolerance to ambient air. Commercial zinc batteries employ aqueous alkaline or aqueous neutral electrolytes. We investigate room temperature ionic liquids (RTILS) as alternative concepts for zinc-ion batteries and neutral aqueous solvents for zinc-air batteries.

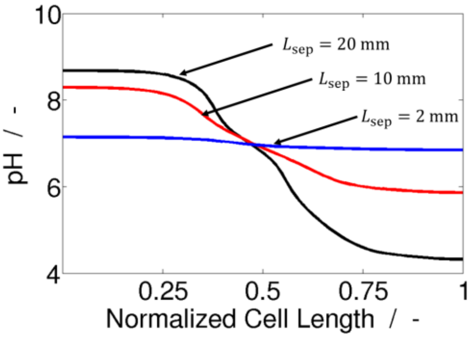
Previously, we presented a modeling framework for metal batteries [1,2] and a methodology to derive a consistent description of electrolyte transport based on non-equilibrium thermodynamics [3,4]. Here, we combine these approaches to model zinc batteries and compare our simulation results with experimental measurements. These models describe the cycling behavior of macroscopic battery cells as well as microscopic surface phenomena [5,6].

RTILs were shown to minimize dendrite growth [9] and allow cycling of zinc ion batteries [10]. We derive the first consistent electrolyte transport theory for RTILs that takes into account the important charge and volume constraints in these molten salts. We validate our transport theory against a Prussian blue battery cell [10]. The electrochemical double layer of RTILs shows a quasi-crystalline surface structure. Based on the hardcore nature of molecules, our model explains this structure [11]. To summarize, our model accurately describes macroscopic a well as microscopic effects.

Neutral aqueous solvents enable a long cycle life and homogeneous zinc deposition for zinc-air batteries, too [7,8]. For coping with the variety of aqueous zinc-ligand complexes in the $ZnCl_2$-NH_4Cl electrolyte, we assume fast homogeneous reactions and introduce a quasi-particle concept. We find that the distribution of zinc-ligand complexes shifts significantly with small changes in concentration. Our model shows that the pH may strongly vary locally and accelerate cell degradation. We optimize the cell architecture to maintain a stable, neutral pH during cycling.

This work is supported by the Federal Ministry of Education and Research (BMBF) via the project LuZi and the European Commission through the Horizon2020 project ZAS!.





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Generation and evolution of materials in the anode Solid Electrolyte Interphase (SEI) of lithium ion batteries

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A solid electrolyte interphase is generated on the anode of lithium ion batteries during the first few charging cycles. The presence and stability of the solid electrolyte interphase (SEI) is critical to the performance of the battery. Despite thorough investigation of the SEI for over 20 years, the mechanism of formation and function are still relatively poorly understood. We have investigated the structure of the initial SEI on graphite and silicon electrodes along with changes which occur to the SEI upon additional cycling via a combination of ex-situ surface analysis techniques. The investigation of SEI provides significant insight into the structure and properties of the anode SEI.

The one electron reducing agent, lithium napthalenide has been used to independently prepare the reduction products which constitute the SEI. The initial reduction product of ethylene carbonate is lithium ethylene dicarbonate (LEDC). However, the thermal decomposition of LEDC and related lithium alkyl carbonates in the presence of LiPF6 generates a intricate mixture of compounds which greatly complicates the structure of the SEI. The reduction products and their subsequent thermal decomposition products have been thoroughly investigated via a combination of NMR, XPS, IR-ATR, TGA, and GC-MS. Mechanisms for the generation of the complicated mixture of products will be discussed.

Thermal behavior of the SEI on a silicon electrode for Lithium ion batteries has been investigated by TGA. In order to provide a better understanding of the thermal decomposition of the SEI on silicon, the thermal decomposition behavior of independently synthesized lithium ethylene dicarbonate (LEDC) was investigated as a model SEI. The model SEI (LEDC) has three stages of thermal decomposition. Over the temperature range of 50~300oC, LEDC decomposes to evolve CO2 and C2H4 gasses leaving lithium propanoate (CH3CH2CO2Li) and Li2CO3 as solid residues. The lithium propanoate decomposes over the temperature range of 300~600oC to evolve pentanone leaving Li2CO3 as a residual solid. Finally, the Li2CO3 decomposes over 600oC to evolve CO2 leaving Li2O as a residual solid. A very similar thermal decomposition process is observed for the SEI generated on cycled silicon electrodes. However, two additional thermal decomposition reactions were observed characteristic of LixPOyFz at 300oC and the polyimide binder at 550oC. TGA measurements of Si electrodes after various numbers of cycles suggest that the LEDC on Si electrodes thermally decomposes during cycling to form lithium propanoate and Li2CO3, resulting in increased complexity of the SEI. The initially formed SEI and the evolved SEI after additional cycling are depicted in Figure 1.

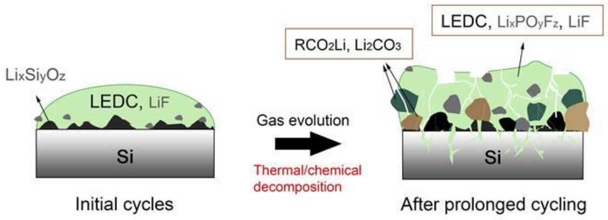

Figure 1. Illustrations of (a) thermal decomposition mechanism of LEDC and (b) compositional change of SEI during cycling on Si electrode.

Effect of stack pressure on the performance and ageing of lithium-ion batteries

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Lithium-ion batteries are subjected to stack pressure from such sources as the rigid cans of cylindrical and prismatic cells, and externally applied pressure in mechanically less stable pouch cells. The extent of the stack pressure is known to affect the battery life-time [1] and is linked to non-uniform ageing when it is non-homogenous [2]. It has been reported that prismatic cells age faster than cylindrical cells made from identical electrodes and the difference was attributed to the higher pressure in former [3]. On the contrary, the work by Arnold et al. on commercial pouch cells shows that high stack pressure causes higher capacity fade, and that a small stack pressure (0.1MPa) is important to extend the life-time [1]. Furthermore, non-homogeneous stack pressure has been linked to non-uniform ageing in lithium-ion batteries [2, 4]. The work by Klett et al. [4] and Bach et al. [2] indicate thicker and thinner SEI layer respectively towards the core of a cylindrical cell jelly roll where stack pressure is expected to be higher. Additionally, pressure has been shown to affect lithium plating differently - the work by Ptzel et al. [5] reported thinner lithium platting towards the core of a cylindrical cell than the surface while that of Bach et al. indicate thicker lithium plating at characteristic areas of high pressure. Hence, the above discrepancies in the effect of pressure calls for further investigation on ageing of model systems with single layer electrode cells subjected to different levels of constant pressure. Such model system has the advantage of excluding the additional and non-uniform pressure caused by the jelly winding.

In this work, the effect of stack pressure on the performance and ageing of single layer NMC/graphite pouch cell is presented. To this end, we constructed a simple custom built high precession spring loaded blocks for a controlled stack pressure application. Cells are aged at 3C charge/discharge rate at 25 °C. In order to model the outside and the core of a cylindrical or prismatic cell in non-uniform ageing; two pouch cells subjected to different levels of pressure are connected in parallel, current distribution measured as a function of cycle number, and capacity fade compared against a control group of parallel connected cells at the same pressure level. Capacity fade is analyzed by differential voltage (dV/dQ), differential capacity (dQ/dV), and post-mortem analyses. Electrochemical impedance spectroscopy (EIS) technique is used to study changes in impedance both at full cell and electrode level. Separator materials are analyzed for any morphological changes using scanning electron microcopy (SEM).

Results show that there is an optimum pressure a bit higher than 1 MPa which extends the battery life-time, and that any lower and higher pressure than the optimum accelerates battery ageing as shown in figure 1. The difference in the capacity loss as a function of pressure is caused by lithium-inventory loss, and similar amount of graphite active mass loss and no NMC active mass loss is observed irrespective of the pressure level. SEM images on the separator indicate non-uniform separator pore deformation at all pressure levels which might contribute to the difference in capacity fade. Comparison of capacity fade of cells subjected to different pressure level and connected in parallel against the control group indicates that the resulting current distribution caused by pressure distribution is not the cause for the non-uniform ageing, and that the effect of pressure is a local phenomenon. Electrochemical impedance spectroscopy (EIS) measurement indicates that pressure level affects the interfacial transport properties. Impedance rise of the cells with ageing is mainly caused by the impedance rise in the positive electrode.

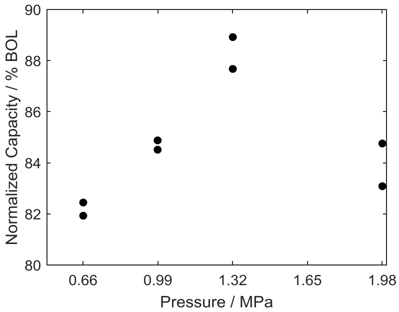

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Figure 1. Normalized C/25 discharge capacity of cells at the end of 600 cycles aged at different stack pressure levels.

Advanced Sodium-ion Batteries Based on NASICON-type Materials

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Na-ion batteries (NIBs) have attracted rapidly increasing attention because sodium is abundant resources, low cost and their better safety. However, the development of NIBs is greatly hampered due to the lack of appropriate active materials for both cathodes and anodes, because of the large radius of Na+. NASICON-type $Na_3V_2(PO_4)_3$ (denoted as NVP) has recently been investigated as a promising cathode material for NIBs. While it is difficult to reach high rate performance of $Na_3V_2(PO_4)_3$ cathode due to the poor electronic conductivity of phosphates. For anode materials, $NaTi_2(PO_4)_3$ has shown promising electrochemical performance.

Here, we reported electrode materials for NIBs based on porous carbon with excellent rate performance: Carbon-coated nanosized $Na_3V_2(PO_4)_3$ embedded in the porous carbon matrix.[1] [2-5] The double carbon coating NVP could deliver high rate performance (44 $mAhg^{-1}$ at 200C). This ultrahigh rate performance is comparable to that of supercapacitor, but with much higher energy density. We also designed $NaTi_2(PO_4)_3$ particles embedded in micro-sized 3D graphene network to improve its electrochemical performance.

The outstanding electrochemical performance of electrode materials with porous carbon network for NIBs is attributed to the special structure design, which confined a variety of advantages: hierarchical porous channels facilitating fast ions and electrons transport, carbon coated structure resulting in low resistances, good mechanical properties leading to the excellent morphology stability.

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Silicon Nanowire Cocooned in Graphene like Carbon With One-Dimensional Si Anode for Lithium-ion Battery

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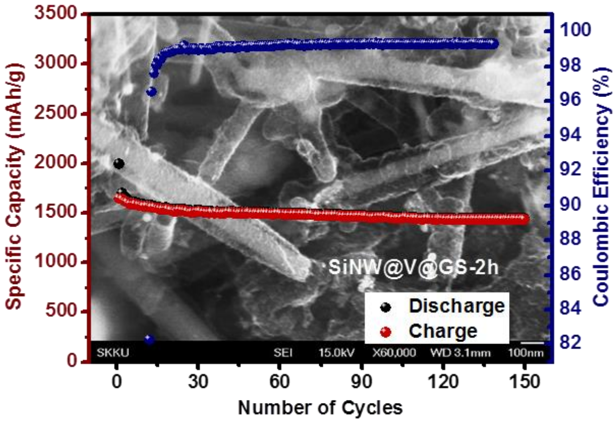
Silicon (Si) is considered as next-generation material of the anode because it is rich in nature resource and its high theoretical capacity (4200 mAh/g), which is ten times higher than of commercial graphite anode (372 mAh/g). However, Si suffers a large volume expansion (approximately 400 %) during cycling process. As a result, it induces pulverization of silicon and causes to rapid capacity fading. This study describes controlled fabrication of one-dimensional silicon nanowires (SiNW) cocooned in graphene-like carbon sheath (SiNW@V@GS) for the improved electrochemical performance of Si anode. The specific new advances demonstrated are included in this work. First, the design of the one-dimensional morphology (SiNW@V@GS) for highly conductive network with Si core for high capacity, graphitic carbon sheath for better electrical conductivity and void space for compensation of large volume expansion during the cycling process. Second, we controlled void space between Si core and graphitic carbon sheath by adjusting oxidation time of Si core during CVD process and enabled electrode fabrication with high capacity and stable cycling performance. Finally, we developed facile and scalable synthesis of the prepared SiNW@V@GS materials by using the SiO_2 template through successive CVD growth and chemical vigorous etching process.



Conductivity, Viscosity and Ionic Dissociation of LiTFSI-1,3 Dioxolane Electrolyte Solutions: a Case Study for Li-S Battery Applications

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Lithium-Sulfur batteries (LSBs) are considered one of the main candidates for the “post-lithium-ion” battery generation.[1] Unfortunately, despite the progresses made so far, there are still problems associated with this system.[2] In this respect, it is necessary to focus on the basic properties of each active components of the LSB system (*e.g.*, cathode active material and electrolyte), thus allowing for possible exploitation in practical applications.[1] Particularly, the role of the electrolyte is crucial. Indeed, it has been proven that by tuning the amount of salt in the electrolyte, remarkable battery performances can be obtained.[3] However, as the reasons for such performances improvement are still unclear, extensive studies of the fundamental physicochemical properties of the electrolyte are required.

In this talk, the systematic study of various physicochemical properties of the lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)–1,3 dioxolane (DOL) salt–solvent system will be presented. By means of a complete screening from extremely diluted (*e.g.*, < $2*10^{-3}$ molal) to highly concentrated (*e.g.*, > 1.5 molal) electrolyte solutions, the physicochemical behavior of the solution’s ions will be uncovered. Interestingly, when the molal conductivity is taken into account with respect to the more commonly used conductivity,[4] the ions association behavior could be observed (Figure 1).[5–7] In fact, at extremely diluted concentrations the single ions (*e.g.*, Li^+) seem to be the predominant charged species, while at the diluted stage the increasing effect of the ion pairs can be observed. Ranging from the diluted to the concentrated stage, the interpretation of the conductivity data suggests triple ion associations (*e.g.*, $Li_2(TFSI)^+$) as predominant charged species. Surprisingly, as indicated by the experimental results, at the highly concentrated stage the electrolyte solutions start behaving as molten salts[8] (*e.g.*, ionic liquids) and the molal conductivity can be described by the viscosity (*i.e.*, Walden’s rule).[9,10]

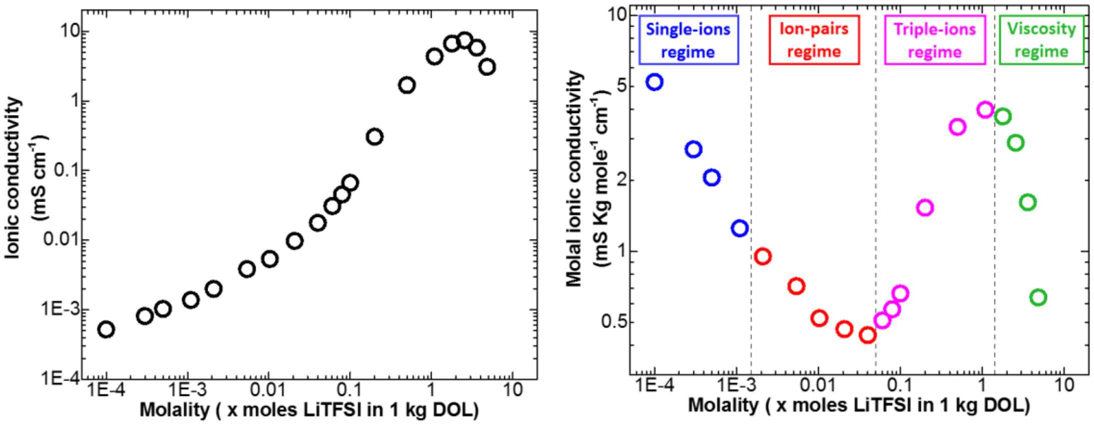

Figure 1: Ionic conductivity (left) and molal ionic conductivity (right) of different LiTFSI-DOL electrolyte solutions (T = 25°C).

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Interface Stability and Redox Activity of Argyrodite Li_6PS_5Cl as Solid Electrolyte in Bulk All-Solid-State Batteries

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Solid electrolytes for lithium-ion batteries provide increased safety and wider operating temperature range than liquid electrolytes. Bulk all-solid-state batteries are thus a safer alternative to Li-ion battery and allow storing more energy than microbatteries, but need very good ionic conductors for their solid electrolytes. Sulfide-based solid electrolytes show good ionic conductivities, but on the other hand reactivity issues towards active materials.[1,2] Their reactivity towards metallic lithium has been extensively studied, however less studies have been focused on their reactivity towards positive electrode materials. [3,4] In this work we investigated argyrodite Li_6PS_5Cl as solid electrolyte in all solid state batteries with different active materials in the positive composite electrode. The reactivity of Li_6PS_5Cl towards $LiCoO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiMn_2O_4$ at interfaces was investigated using surface-sensitive techniques, namely X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). We show that Li_6PS_5Cl within the composite positive electrode is oxidized into elemental sulfur, lithium polysulfides, P_2S_5, phosphates and LiCl during cycling. In spite of this interface reactivity, it is possible to cycle argyrodite-based batteries for over 300 cycles.

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Interface and safety properties of phosphorus-based negative electrodes for Li-ion batteries

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Due to its tremendous theoretical specific charge and low cost, numerous publications report on the electrochemical performance of phosphorus-based electrode used as negative electrode in Li-ion and Na-ion batteries. Those works are mainly focused on improving the electronic conductivity of the material [1], [2] but the interaction between the electrode and the electrolyte is oftentimes neglected. Since phosphorus reacts with water to form the toxic phosphine gas (PH_3)[3], monitoring its electrochemical mechanism in an aprotic electrolyte containing traces of water is crucial to assess its safety upon cycling.
In this study, three surface characterization techniques are combined to monitor the 1st lithiation process of a red phosphorus electrode (P_{red}): scanning electron microscopy (SEM), on-line electrochemical mass spectroscopy (OEMS) and X-ray photoelectron spectroscopy (XPS). Figure 1 shows the evolution of the hydrogen (H_2), ethylene (C_2H_4) and PH_3 gases during the 1st lithiation obtained from the OEMS experiment. PH_3 and H_2 gases are already detected at potential higher than 2 V, which is far from the lithiation of the phosphorus expected below 1 V. The C_2H_4 signal, attributed to the decomposition of the electrolyte and the formation of the Solid Electrolyte Interphase (SEI), appears around 0.8-0.6 V. Interestingly, it correlates with the cessation of the release of PH_3, which reveals that the SEI plays a crucial role for preventing the formation of PH_3 along the first lithiation. Moreover, post-mortem SEM pictures of the electrodes reveal a change in the morphology of the particles along lithiation. The evolution of the C1s and P2p core levels at different state of discharge will be presented in order to link the formation of PH_3 with the surface species developed at the electrode/electrolyte interface. Finally, a mechanism including both chemical and electrochemical reactions will be proposed and the hazardousness of such battery will be discussed.

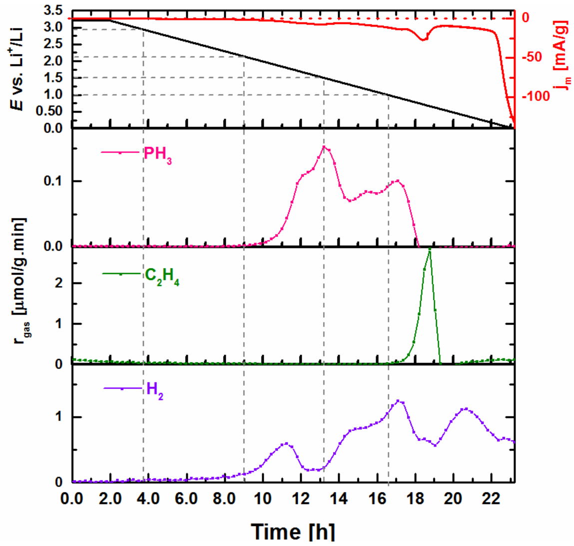

Figure 1. OEMS analysis during the 1st lithiation of the P_{red}-based electrode.

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Development of New Anion-Inserting Organic Electrode Materials for Rechargeable Lithium Batteries

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Nowadays, access to power sources is an essential factor for the increasing population. By the way, it is necessary to exploit more efficient and cleaner electronic energy-storage systems. Indeed, most of Li-ion batteries are based on the use of "inorganic" electrode materials, especially on transition metals. Despite relatively good electrochemical performances of these compounds, they have several disadvantages, like their expensiveness or their toxicity and difficulty to recycle at the end of life.

To tackle this issue, there is great interest in developing alternative low cost, high energy and environmentally friendly solutions for rechargeable batteries. Indeed, organic compounds are made of quite naturally abundant chemical elements (C, H, N, O) and if properly used, they could be revalorized, by combustion [1]. Consequently they appear as an interesting alternative to conventional active materials, especially for positive electrode of electrochemical storage devices. These organic molecules can easily be prepared using simple organic chemistry techniques from low cost precursors [2].

This study, led between IMN and CEA-Liten, focuses on the synthesis of new insoluble organic derivatives presenting a redox potential up to 3,2 V vs Li^+/Li, based on cationic dihydroxyterephthalic salt. Some fine characterizations (XRD, FTIR, SEM, TEM and electrochemistry) have been applied in order to evaluate their electrochemical performances. For the most promising structures, the formulation of the electrode will be optimized in order to integrate them in a stacked cell with a soft packaging.

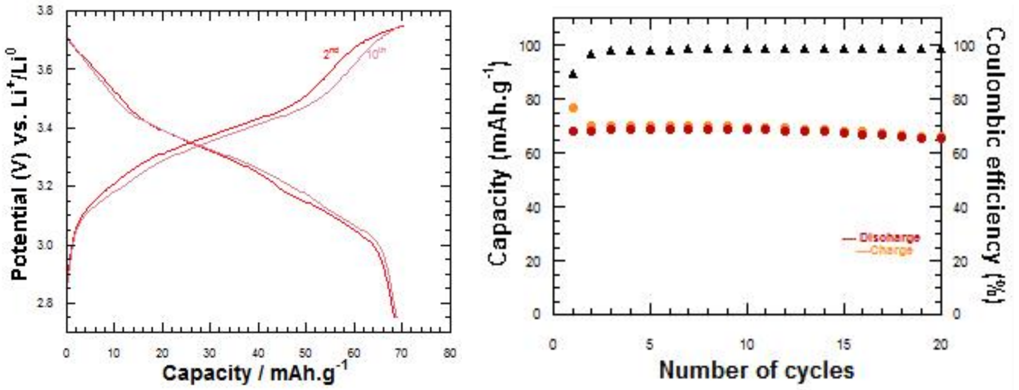

Figure 1: Potential curve of MgDAnT(C_{th}=72 mAh.g^{-1}) cycling at C/5 rate (left) and capacity curve (right).

Funding and acknowledgement: ANR Volta – CEA Liten (Grenoble)

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Impacts of the Electrode Fabrication Process on the Performances of Lithium-Oxygen Batteries

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Invented more than twenty years ago[1] lithium oxygen batteries are attracting a growing research interest world-wide for nomad applications, in view of their ultra-high theoretical energy density. Numerous characterization studies aiming at understanding the mechanisms occurring in these batteries have been reported so far.[2] The positive electrode, where a complex interplay occurs between electrochemistry, charge and oxygen transport, is recognized to be a key component determining the performance and maximal capacity of these devices.

In order to process the fabrication of efficient electrodes two main issues need to be taken into account: i) the Li_2O_2 discharge product is insulating and tends to passivate the electrode pores surface; ii) Li_2O_2 clogs the pores which reduce significantly the electrochemically active surface area and so the cell ability to further discharge and cycle. A wide diversity of fabrication techniques has been then implemented,[3] leading to positive electrodes with different porosities and specific surface areas which make difficult the comparison between results obtained in different groups.

In this communication we report a systematic experimental investigation of the influence of positive C-based electrode fabrication process on the resulting surface and electrochemical performances. Tradeoffs between electrode composition, porosity, tortuosity and specific area are determined and analyzed experimentally and with computational modeling.[4] Implications of the implementation of the prepared electrodes in practical Lithium-O_2 batteries are discussed.

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New 3D-Microbattery Designs on 3D-Printed Polymer Substrates

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The microelectronics industry is continually downscaling its products to produce micro devices for cognitive arthropods, subdermal drug delivery systems, wireless sensor networks (WSN), and self-powered integrated circuits for IoT applications. Such devices need rechargeable batteries with dimensions on the scale of 1–10 mm^3 (few to tens mm^2 footprint area of substrate) including all the components and all the associated packing. Generally, these devices have mission durations of an hour to a few years. The absence of effective miniature power sources producing micro-watts of steady-state power with peaks to tens milliwatts presents a substantial roadblock because the replacement of batteries is cost prohibitive. Furthermore, a battery that is large enough to last the lifetime of the device would dominate the overall system size and cost.

Batteries based on three-dimensional (3-D) microstructures are shown to offer significant advantages (e.g., small areal footprint, short diffusion lengths) in comparison to thin film devices. We present the quasi-solid rechargeable 3D-microbattery assembled on 3D-printed high-aspect-ratio perforated polymer substrates (3DMB-3DP) of different shapes and area gain. The interconnected perpendicular channels formed through XYZ planes provide an area gain of the substrate, which is 1.5 to 10 times that of the top-to-bottom perforated sample used by us in previous research. We wish to point out that the novel structure simplifies electrochemical insertion of consecutive battery layers which, in turn, enables fabrication of 3D microbatteries with an aspect ratio much higher than 10. The battery occupies a footprint area of only a few mm^2, while its height may approach a few cm. Simple and inexpensive electrophoretic-deposition routes are applied for the fabrication of all the thin-film active-material layers of the microbattery. Taking advantage of thin films, which conformally follow all the contours of the 3D-substrate and are composed of nanosize cathode and anode materials, like modified lithium iron phosphate, lithium titanate, and original polymer-in-ceramic electrolyte, enable the maintenance of high reversible specific capacity, long cycle life, and intrinsic safety of the microbattery.

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The long and winding road towards Ca-based batteries

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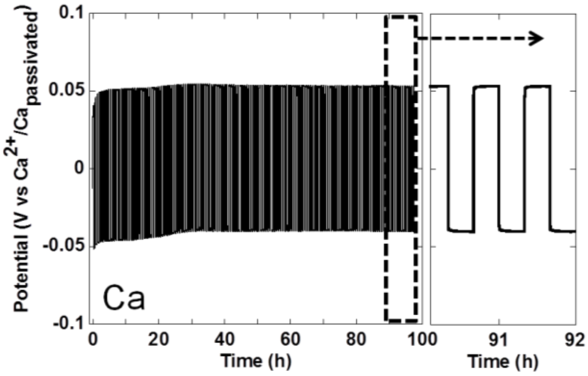
Amongst multivalent electropositive metals, calcium is especially attractive as it is the fifth most abundant element on earth crust and its standard reduction potential is only 170 mV above that of lithium, enabling significantly larger cell potential than that achievable with magnesium. Moreover, Ca^{2+} would hold promise for faster reaction kinetics than Mg^{2+} (and thus better power performance) due to its lower polarizing character. The electrochemical behavior of calcium electrodes in conventional organic electrolytes is surface-film controlled, and calcium deposition was for long thought to be impossible, which was attributed to the lack of calcium ion transport through the surface layer formed. Nonetheless, our results indicate that the main hurdle for reversible calcium metal plating/stripping in alkyl carbonate based electrolytes is tendency to ion pairing, which influences efficient migration of cations within the electrolyte, that can be mitigated by a moderate enhancement of temperature. [1] Symmetric cells assembled using 0.45 M $Ca(BF_4)_2$ in EC:PC tested at 100ºC exhibit good performance in terms of cyclability in spite of a somewhat high ohmic drop (ca. 50 mV).



The well known stability of these electrolytes at high potentials is maintained at 100ºC which paves the way to exploratory screening and testing of potential cathode materials which would reversibly insert and deinsert calcium to assemble a full calcium based cell and achieve proof-of-concept. Candidate compounds should have a redox center, typically a transition metal, and involve a couple operating within the stability range of the electrolyte. Moreover, the crystal structure must exhibit pathways to enable diffusion of calcium ions. Some compounds such as $CaMoO_3$ or $CaMn_2O_4$ which exhibit such features are found to exhibit too large barriers for calcium ion diffusion.[2,3] Results will be presented on the experimental exploratory screening of a range of compounds containing different transition metals, for which preliminary results seem to indicate electrochemical activity.

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Two-dimensional modeling and analysis of mass transfer losses in a Li-air button cell for different electrolytes

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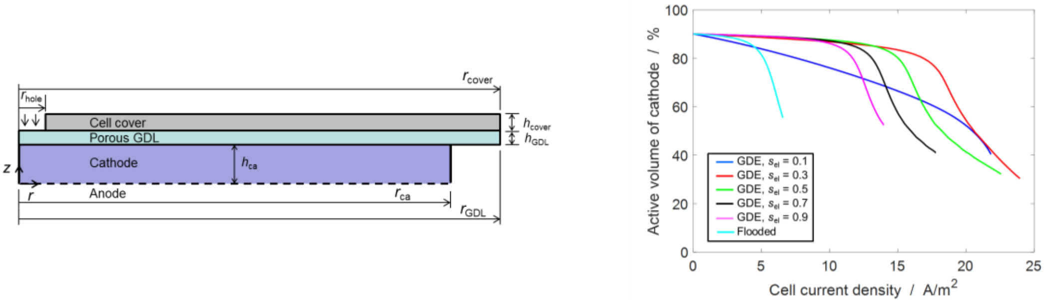
Practical bottlenecks associated with commercialization of Lithium-air cells include capacity limitation and low cycling efficiency. The origin of such losses can be traced to complex electrochemical side reactions and reactant mass transport losses [1]. The efforts to minimize such losses include exploration of various electrolytes with additives [2], and cell component geometry and material design. Given the wide range of options for such materials, it is almost impractical to experimentally setup and characterize all those cells. Consequently, modeling and simulation studies are efficient alternatives to analyze spatially and temporally resolved cell behavior for various combinations of materials [3]. In this study, with the help of a two-dimensional multiphysics model, we have focused on the effect of electrode and electrolyte interaction (electrochemistry), choice of electrolyte (species transport), and electrode geometry (electrode design) on the performance of a lithium-air button cell. Figure 1a shows the schematics of the 2D axi-symmetric computational domain. A comparative analysis of five different electrolytes was performed while focusing on the 2D distribution of local current density and the concentration of electro-chemically active species in the cell, that is, O_2 and Li^+. Using two different cathode configurations, namely, flooded electrode and gas diffusion electrode (GDE) [4] at different cathode thickness, the effect of cell geometry and electrolyte saturation on cell performance was explored. Further, a detailed discussion on electrode volume utilization (cf. Figure 1b) is presented via changes in the active volume of cathode that produces 90% of the total current with the cell current density for different combinations of electrolyte saturations and cathode thickness.



(a) (b)

Figure 1: (a) Schematics of the 2D axi-symmetric computation domain, (b) Comparison of active volume of cathode that produces 90% of the total current for different electrolyte saturations.

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Electrocatalysts for Lithium-Sulfur Energy Storage Systems

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Li-S- (Lithium-Sulfur-) battery systems theoretically provide very high specific gravimetric energy (2600 Wh/kg [1]) and volumetric energy density (2800 Wh/l [2]). Hence, Li-S batteries are one of the key technologies for both the upcoming electromobility and stationary applications. Furthermore, the Li-S battery system is potentially cheap [3] and environmentally benign [4]. However, the technical implementation suffers from cycling stability, low charge and discharge rates and incomplete understanding of the complex polysulfide reaction mechanism [5].

The aim of this work is to develop an effective electrocatalyst for the polysulfide reactions, so that the electrode kinetics of the sulfur half-cell will be improved. Accordingly, the overvoltage will be decreased and the efficiency of the cell will be increased. An enhanced electroactive surface additionally improves the charge and discharge rates. To reach this goal, functionalized electrocatalytic coatings are investigated to accelerate the kinetics of the polysulfide reactions.

To best of our knowledge no extensive screening of electrocatalysts has been conducted so far. In order to determine a suitable electrocatalyst, apparent exchange current densities of a variety of materials (Ni, Co, Pt, Cr, Al, Cu) have been evaluated in a polysulfide containing electrolyte by potentiodynamic measurements and Tafel plots. SEM studies of the samples after potentiostatic sulfur or lithium sulfide deposition have been performed.

Our work shows that sulfur containing nickel coatings from a modified Watt's nickel bath are promising candidates with good electrocatalytic properties for the polysulfide reactions. Furthermore, it is observed that coatings containing sulfur provide an autocatalytic effect superior to coatings without sulfur content.

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Conversion/Alloying Materials – Impact of the Choice of Elements

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Lithium-ion batteries are at present the electrochemical energy storage technology of choice for a wide range of applications, covering small-scale devices like mobile phones and laptops as well as large-scale applications as, for instance, (hybrid) electric vehicles [1,2]. Nonetheless, the ongoing development of "smarter" small-scale devices, accompanied by increasing mobility demands of electronic applications, and – last but not least – the urgent need for extended driving ranges for electric vehicles calls for further improvement regarding their power and energy density. While substantial advances have been realized in the past, largely benefitting of optimized battery engineering strategies, it is commonly accepted that the next leap forward will require the implementation of new electrode active materials. With respect to the cathode side, the most promising ones are presently oxygen [3] and sulfur [4], both following a conversion mechanism, i.e., the formation of lithium sulfide and oxide upon discharge. Similarly, for the anode side, the most studied lithium host electrodes follow either a conversion [5] or alloying mechanism [6], allowing for greatly enhanced gravimetric and volumetric capacities. However, both material classes suffer intrinsic challenges, such as a large voltage hysteresis for the discharge and charge process in case of conversion-type compounds or extensive volume variations upon de-/lithiation in case of alloying-type elements. In an attempt to overcome these issues, a new class of materials, combining these two mechanisms in one single compound has attained continuously increasing attention: conversion/alloying materials [7]. The great benefit for this materials' class is the *in situ* formation of alloying element nanograins embedded in a percolating network of highly conductive transition metal nanoparticles and reversibly formed lithium oxide, simultaneously preventing the aggregation of the alloying nanograins and buffering the occurring volume variations.

Herein, we will report our most recent results on this class of compounds, highlighting the impact of the choice of elements and their ratio on the electrochemical properties, including the lithium reaction voltage, the specific capacity and relative contribution of the conversion and alloying mechanism, as well as the eventual performance metrics, finally determining their suitability as lithium-ion anodes.

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In Situ Monitoring of F^- Formation in Lithium Ion Batteries by OEMS

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Fluorinated compounds are ubiquitous in modern lithium ion batteries (LIBs) because of their superior anodic stability. $LiPF_6$ is the most commonly used conducting salt in LIBs. Polyvinilydene fluoride (PVDF) is the standard binder for LIB cathodes. Fluorinated molecules, such as fluoroethylene carbonate (FEC), play also a role either as electrolyte co-solvent or additive. However, fluorine containing compounds also play a detrimental role for the performance of LIBs. LiF formed on the electrodes decreases the Li conductivity and leads to an increased cell impedance. HF, formed by $LiPF_6$ hydrolysis, leads to the decomposition of carbonate electrolytes and to the dissolution of the Li-ion cathode. Both are detrimental to LIB lifetime.

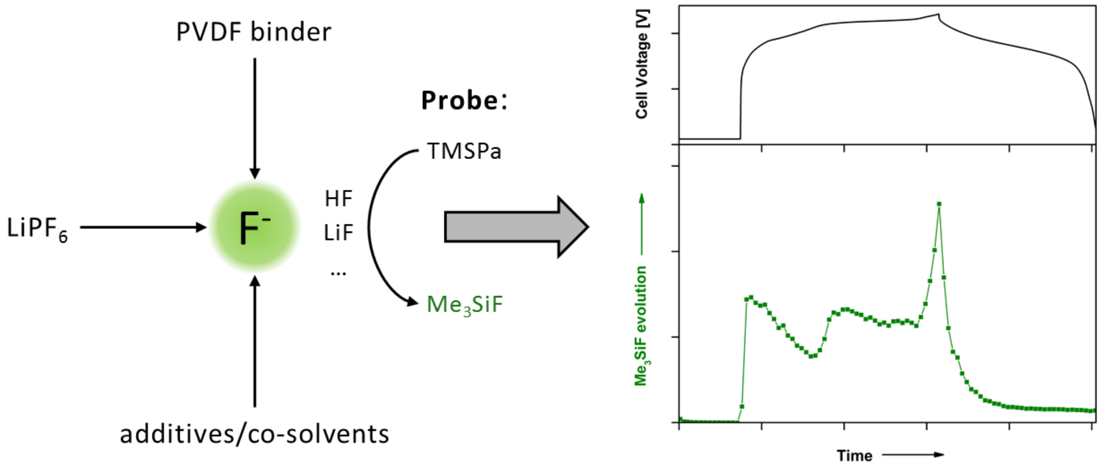

Figure 1: Fluoride formation in lithium ion batteries is monitored by using tris(trimethylsilyl)phosphate (TMSPa) as sacrificial probe (left) to detected Me_3SiF evolution by OEMS during the 1st galvanostatic cycle of HENCM/graphite (C/10, 4.7 V) full cells with FEC/DEC (12:88, 1M $LiPF_6$, 1 wt % TMSPa) electrolyte (right).

Online electrochemical mass spectrometry (OEMS) was previously shown to be a valuable tool to monitor the gas evolution in LIBs. It was applied to describe electrolyte decomposition processes,(1) the hydrolysis of the conducting salt,(2) the surface reconstruction of Ni-rich NCM cathodes,(3) and the effect of additives on the electrolyte decomposition.(4) During the latter work, it was shown, that the tris(trimethylsilyl)phosphate (TMSPa) additive acts as a F^- scavenger and forms gaseous Me_3SiF.

Applying TMSPa not as an additive, but as a probe for F^-, allows monitoring the formation of fluoride species during cycling of HENCM/graphite full cells with FEC/DEC (1M $LiPF_6$) electrolyte by detecting Me_3SiF by OEMS (Figure 1). In this contribution, several stages of fluoride formation during the cycling of full cells are identified and their relations to the different fluorinated cell components (FEC, $LiPF_6$ and PVDF) as well as the respective reaction mechanisms are discussed.

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Sulfur Electrochemistry in a Sparingly Soluble Electrolyte

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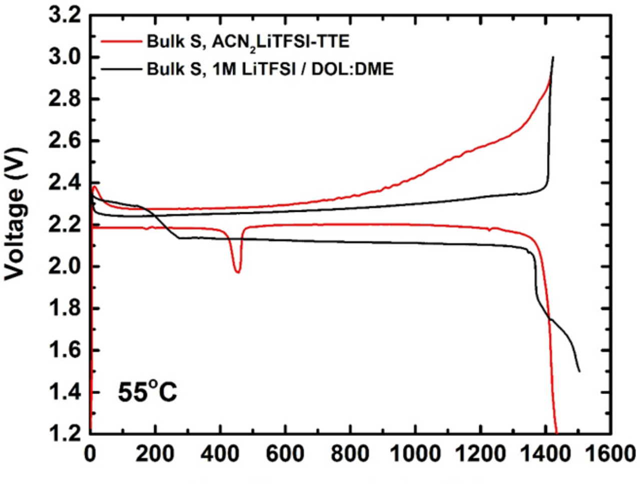
Owing to the low cost of sulfur and high theoretical materials-only energy density, Li-S battery chemistry continues to be studied worldwide. For Li-S chemistry to enable a truly disruptive technology for transportation applications, the ability to perform sulfur redox chemistry with high reversibility and high capacity under lean- or starved-electrolyte conditions is a critical requirement—as recently identified by techno-economic modeling carried out by JCESR.[1] Recent works using advanced electrolytes, referred to as solvates or nonsolvents,[2-5] show significant promise in minimizing the detrimental effects from polysulfide dissolution encountered in conventional Li-S batteries. The reduced dissolution allows for efficient, long-lived operation with high sulfur utilization. Additionally, these advanced electrolytes can potentially provide a path towards attaining lean-electrolyte operation. In this talk, we discuss recent fundamental studies aimed at developing an energy storage system that uses a sparingly soluble electrolyte.



First cycle voltage profile during galvanostatic cycling at C/30 rate (1C capacity = 1675 mAh/g$_s$)

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Stability evaluation of Li-ion batteries by forced destruction system

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The assessment of the safety in Li-ion cells is the most curious issue in electric vehicles (EV) and/or energy storage system (ESS) use. However, conventional safety tests were evaluated by the visual assessment (smoke, fire, or explosion). Though the cell temperature is the only quantitative indicator to evaluate the event, there is large dependence on the position of the sensor on the cell. Then, we propose to evaluate the event by monitoring pressure in the pressure-tight container as shown in Figure 1. In the equipment, named "forced destruction system", the test cell is placed on the hot plate (70^{o}C) to avoid the heat release in the event, and it is connected to charge / discharge system (50 V / 100 A), needle injector, and Web camera. The events such as overcharge or nail penetration is evaluated using the pressure change. The observed change in pressure has no dependence on sensor position so that we can evaluate the event quantitatively with sufficient reproducibility. In addition, the chamber is filled with N_2 gas. Therefore, we estimate the reaction occurs only between electrode and electrolyte. In other words, we can avoid the combustion reaction between oxygen in air and electrolyte in our test condition.

We compared various type lithium ion cells as follows; $LiCoO_2$ (LCO) / Graphite (Gr), $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC) / Gr, $LiFePO_4$ (LFP) / Gr, $LiMn_2O_4$ (LMO) base / Gr, and LCO / $Li_4Ti_5O_{12}$ (LTO). The cell capacities tested were between 10 Wh to 60 Wh. We prepared NMC/Gr cells with conventional liquid electrolyte and solid polymer electrolyte (SPE). All cells were charged up to SOC120%, and internally short circuited by stepwise (1 mm/step) nail penetration. The observed maximum pressure in event (ΔPe) was compared based on the capacity as shown in Figure 2. We confirmed followings from the results. (i) Cathode characters in events were reflected well in the common Gr anode. (ii) In the LMO base cathode, approximately 20 % of layer cathode was blended1) and the layer active material in LMO base cathode was overcharged more than 120%. Therefore, ΔPe of LMO base cell was larger than that of NMC. (iii) LTO acted as an insulator at the internal short circuit2) so that it prevented gas evolution from LCO. (iv) SPE did not react immediately with NMC in the event so that gas evolution was drastically suppressed3).

As pointed out above, our proposed system has a potential to estimate quantitative comparison of stability in various kinds of Li-ion cells in the abuse conditions.

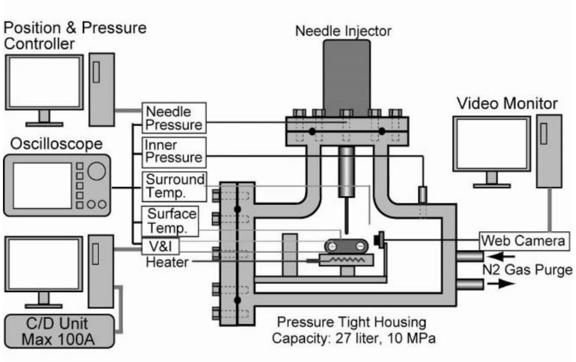

Figure 1 Proposed forced destruction system of Li-ion cells.

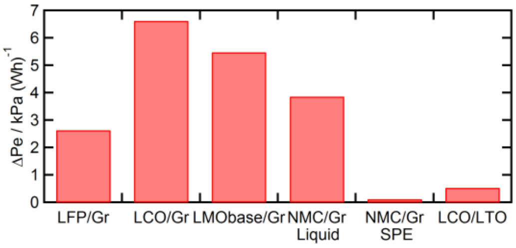

Figure 2 Observed maximum pressure of various Li-ion cells in the internal short circuit at SOC120%.

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Novel 3D nano-graphene-functionalized silicon anode for lithium ion battery with superior cycle stability and rate capability

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Silicon (Si), one of the most promising anode materials for next generation high-performance Li-ion batteries (LIB) is popularly studied recently because of its super high lithium capacity (4200 mAh g^{-1}). However, Si has a dramatic volume change (~300%) during charge-discharge cycling, leading to severe capacity decay and poor cycle stability originating from its structural collapse. Carbon or graphene-modified Si is an effective method to improve its performance. Traditional three models of carbon or graphene/Si-based core-shell, yolk-shell and physical wrapping have been reported recently.[1,2] However, they are still insufficient in structure to solve the silicon issues.[3] In our work, a multifunctional elastic nano-graphene shell is elaborately designed for silicon. The as-synthesized nano-graphene-functionalized silicon (Si@NG) composite shows unique functions to challenge the current silicon anode issues in LIB. The new functional nano-graphene shell gives the full consideration of Si issues such as Si conductivity, Si volume expansion, and mass transfer, which not only can supplement poor conductivity of Si, but also self-adaptively change their space to accommodate the lithiated Si with inflated volume by their elastic feature. More importantly, different with traditional large graphene flakes, the graphene sheets in nano size has less ions barrier effect to guarantee easy Li^+ and electrolyte paths. In addition, the graphene layer provides excellent protection for SEI film to guarantee high cycle stability.

As an anode electrode for LIB, the Si@NG composite exhibits excellent cycling performance with high reversible specific capacity (2330 mAh g^{-1} at 250 mA g^{-1} with an initial CE of 83.4%, and 1385 mAh g^{-1} at 500 mA g^{-1} after 510 cycles with a CE of 99.2%). A superior 95% capacity retention is achieved after 510 cycles. All the electrochemical performances get benefits from the well-designed functional elastic graphene shells. This work demonstrates a new direction towards the development of high efficient Si anode with high capacity and super cycle stability.

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Dilution of Concentrated Electrolyte Solutions for High Voltage Cathode Materials

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Highly concentrated electrolytes have many unique properties [1-7] such as Li^+-intercalation into graphite anode without EC [1,3], suppression of S_8^{2-} ion dissolution in Li-S batteries [2], etc., and is attracting much attention of many researchers. In highly concentrated electrolytes, all solvent molecules are strongly coordinated with Li^+ ions, and hence the stability of the electrolytes against oxidation is improved significantly. Yoshida et al. reported that $LiCoO_2$ can be charged and discharged in a LiTFSI/triglyme (1:1) electrolyte with good cycleability [3], though triglyme is an ether compound and usually cannot be used as solvent for 4-V class cathodes.

5 V-calss $LiNi_{0.5}Mn_{1.5}O_4$ spinel cathodes and high-Ni layered $Li(Ni,Co,Mn)O_2$ (Ni:Co:Mn = 5:2:3, 6:2:2, 8:1:1, etc.) are promising for the next-generation LIBs with high energy densities. We previously reported that highly concentrated propylene carbonate (PC)-based electrolyte solutions are highly stable against oxidation at $LiNi_{0.5}Mn_{1.5}O_4$ positive electrodes [5,6]; the use of nearly saturated $LiPF_6$/PC and $LiBF_4$/PC solutions resulted in an improved cycleability.

Concentrated electrolyte solutions have a serious problem, that is, very high viscosity. We have explored various kinds of fluoroalkyl ethers as diluents of the concentrated $LiBF_4$/PC system to obtain low-viscosity electrolyte solutions without losing high oxidative stability. Fluoroalkyl ethers have high stability against oxidation because they have electron-withdrawing fluorine atoms, and are suitable as diluents for the concentrated $LiPF_6$/PC and $LiBF_4$/PC electrolyte systems. We found that 1,1,2,2–tetrafluoroethyl 2,2,3,3–tetrafluoropropyl ether (HFE) is the most suitable diluent because of a high solubility of $LiBF_4$ [7].

2.50 mol kg^{-1} $LiBF_4$/PC+HFE (2:1) was obtained by diluting 4.10 mol kg^{-1} $LiBF_4$/PC with HFE, and hence it has an equal PC/Li ratio (2.39) to 4.10 mol kg^{-1} $LiBF_4$/PC. The HFE addition significantly reduced the viscosity from 302.2 to 51.7 mPa s. Raman spectra of $LiBF_4$/PC+HFE (2:1) revealed that the fraction of solvating PC molecules (56.8%) in 2.50 mol kg^{-1} $LiBF_4$/PC+HFE (2:1) was comparable with that (62.9%) in 4.10 mol kg^{-1} $LiBF_4$/PC that has an equal PC/Li ratio (2.39), whereas it was significantly higher than that in 2.50 mol kg^{-1} $LiBF_4$/PC (35.8%) that has an equal concentration of $LiBF_4$. These facts indicate that PC molecules preferentially solvated Li^+ ions when diluted with HFE.

$LiNi_{0.5}Mn_{1.5}O_4$ positive electrodes showed high charge/discharge performance with low irreversible capacities in the 2.50 mol kg^{-1} $LiBF_4$/PC+HFE as shown in Fig. 1. These results clearly show that the highly concentrated $LiBF_4$/PC system can be diluted with HFE without losing the high stability against oxidation.

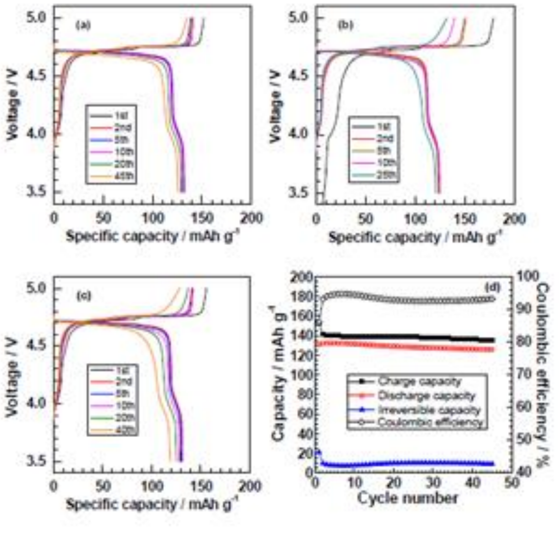

Fig. 1. Charge and discharge curves (a-c) and (d) variation of capacities and Coulombic efficiency with cycle number of $Li|LiNi_{0.5}Mn_{1.5}O^4$ cells. The electrolyte solution used was (a, d) 2.50 mol kg^{-1} $LiBF_4$/PC+HFE (2:1 by volume), (b) 2.50 and (c) 3.75 mol kg^{-1} $LiBF_4$/PC [7].

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Solid Electrolytes for Thin Film Li-ion Batteries with Si and SiC Based Anodes

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Miniaturization of electronic devices, recent progress in materials science and other technology fields have led to development of multifarious small-scale devices such as microelectromechanical systems, micromachines microsensors, and devices for medical application. These advances urge for next generation power sources, and rechargeable microbatteries are considered as the most promising for such applications. Micro lithium-ion batteries (MLIBs) with high energy density and low cost could lead such technologies and demand for new component materials to ensure high performance and low cost. Application of solid electrolyte avoids the leakage problems and improves both operation and safety of microdevices powered by MLIB. .

Si containing anodes have the advantages as anodes for MLIBs such as high capacity and low voltage. However, their practical application is restricted by severe volume changes and mechanical degradation upon lithium alloying and de-alloying processes. In this term polyethylene oxide (PEO) based flexible thin polymer electrolyte could be a promising solution. A combination of nanoparticulate and thin film structure can provide significant mechanical stability of the system and mitigate the volume change limitations.

In this work, ceramic and polymer solid state electrolytes were prepared and deposited on the surface of Si and SiC thin film anodes by drop and dip coating, electropolymerization, and magnetron spattering.

Physical properties of the electrodes were characterized by Raman spectroscopy, X-ray diffraction, atomic force microscopy, scanning/transmission electron microscopies and impedance spectroscopy. Further, the electrochemical properties of the cell with these anodes were evaluated in all solid-state thin film battery.

Acknowledgements
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Advances in Aqueous Zinc Air Batteries

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Introduction

Zinc air batteries have been used as primary batteries with high specific energy and energy density of 400 Wh kg^{-1} and 1200 Wh L^{-1}. To use them as secondary systems, durability of both zinc and air electrodes should be enhanced. Activities to improve zinc and air electrodes in Research & development Initiative for Scientific Innovation of New Generation batteries (RISING) project are presented

Zinc electrode analysis and improvement

Advanced analysis was applied to the historical problems of the zinc electrode such as dendrite growth and shape change [1]. *Operando* X-ray diffraction (XRD) showed that metallic zinc appeared soon after reduction started whereas it took time until ZnO peaks appeared, suggesting that the oxidized zinc species has low crystallinity or is soluble in the electrolyte before it is precipitated as ZnO [2].

Operando X-ray fluorescence (XRF) imaging was employed to find that the zinc species formed during discharging is dissolved into the electrolyte in the vicinity of the zinc electrode, even if the electrolyte is preliminarily saturated with ZnO, implying supersaturation of the zinc species [3]. Such dissolved zinc species can induce undesirable morphology change during cycling to cause deterioration.

Shape change behavior of ZnO composite electrodes was examined using XRD mapping of metallic zinc and ZnO. Metallic zinc was formed on the periphery of the electrode on reduction whereas ZnO growth was observed in the center on oxidation, which is typical of shape change. This strongly suggests zinc transfer through the electrolyte and therefore suppression of the zinc species dissolution is a key to prohibit the morphology changes such as shape change and dendrite formation.

Transfer of soluble $Zn(OH)_4^{2-}$ formed by electrochemical reaction (1) can be suppressed by moving the equilibrium in chemical reaction (2) to the right-hand side if the water activity is decreased. We show that water activity control of the alkaline electrolyte by adding hydrophilic organic compounds [4] is effective for restricting the morphology changes and enhancing the cyclability.

$$Zn + 4OH^- = Zn(OH)_4^{2-} + 2e^- \qquad (1)$$

$$Zn(OH)_4^{2-} = ZnO + H_2O + 2OH^- \qquad (2)$$

Air electrode with high activity and durability

Highly active and durable air electrodes are essential for secondary zinc-air batteries [5]. New types of catalysts including layered perovskite $LaSr_3Fe_3O_{10}$ [6,7], defect perovskite $La(Ca)Mn(Ni)O_{3-\delta}$ [8] and brownmillerite Ca_2FeCoO_5 [9] are proposed to enhance the activity. Higher catalytic activity results in lower overpotential and hence better durability of the air electrode. Catalysts with mesoporous structures are also promising for better durability [10]. The importance of catalyst substrate stability is demonstrate using antimony-substituted tin oxide substrate [11].

Acknowledgment

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Lithium Sulfur Battery - Effects of Binders and Barrier Layers on the Performance and Fading of the Cell

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Lithium/sulfur battery has many attractive properties and is a promising candidate for many applications. In addition to high theoretical energy density (about 2600 Wh/kg), it is made of relatively cheap and non-poisonous materials. Thus, it attracts researcher's attention many years ago (1, 2). However, although much research has been done and many papers have been published, the processes responsible for capacity fading are not well understood. In addition to its attractive properties it has several disadvantages, which includes self-discharge, short cycle life and too low coulombic efficiency. These may be caused by the low electronic conductivity of sulfur and its final discharge products, expansion of the cathode upon lithiation, and the solubility of sulfur and of lithium polysulfides in battery electrolytes. Capacity fading on cycling may result from at least four processes: increase of SEI thickness and resistance, loss of cathode capacity (precipitation of sulfur species outside the cathode), agglomeration and thickening of core-shell sulfur species and increase in cell impedance as a result of reduction of the electrolyte. We report here a detailed analysis of the electrochemical behavior of Li_2S-based cathodes, comprising five different binders and four types of barrier layers during prolonged cycling. We have found that both the type of the cathode binder and the type of the polysulfide barrier layer affect the performance and the fading rate of the battery (3). An optimized combination of a binder and a barrier layer yield initial capacity of 1400 mAh/gS, over 99.5% coulombic efficiency and close to 1000 cycles. Analysis of the impedance spectra of the cells shows that SEI resistance (R_{SEI}), cathode charge transfer resistance (R_{CT}) and lithium diffusion constant (D) are significantly affected by both the binder and the barrier layer. Capacity fading results from the increase of both R_{SEI} and R_{CT} and the decrease of D during prolonged cycling. D decreases due to several processes including: partial blocking of the cathode surface, the precipitation of electrolyte reduction products on the anode (as a secondary SEI) and into the separator.

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Formation of Solid Electrolyte Interphases on Silicon Electrodes

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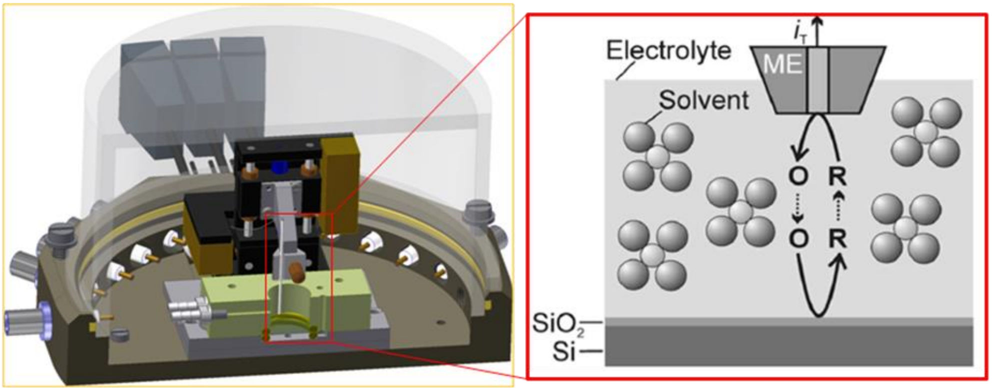
Silicon is considered as one of the promising alternatives to graphite as negative electrode material in lithium-ion batteries. The electron transfer at Si was characterized using the feedback mode of scanning electrochemical microscopy (SECM) and 2,5-di-*tert*-butyl-1,4-dimethoxybenzene as redox mediator. Approach curves and images demonstrate that the electron transfer rate constants at pristine Si are relatively small due to the native SiO_2 surface layer. In addition, the electron transfer rate constants show local variations because of the heterogeneous coverage of SiO_2 [1].



After removal of the SiO_2 surface layer by an HF treatment, the surface shows high positive feedback currents indicative of the absence of a solid electrolyte interphase (SEI). The formation of the SEI could be studied in situ by scanning the potential of the Si electrodes in intervals from the open circuit value to 0.5 V vs. $Li|Li^+$ [2]. The scan was periodically interrupted to record approach curves for the characterization of the interfacial kinetics at intermediate stages of SEI formation. This is an interesting aspect because the formation of the SEI depends on the reductions of electrolyte components.

Upon initiation of the alloying of Li into Si, the integrity of the SEI is challenged due to the strong volume expansion upon lithiation of Si. By intermittent recording of the linear sweep voltammograms with slow scan rates (10 µV/s) the voltammetric features can be directly correlated to the build-up of the SEI if an effect on the interfacial kinetics is evident from the SECM approach curves.

SECM imaging in the feedback mode provides also an impression on the homogenity of the surface layers at different phases of their formation.

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Magnesium Sulfur Batteries

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Demands in energy storage require a significant improvement in the energy density of battery systems. Therefore innovative systems with a substantially higher specific energy and improved cycle life have to be developed.

The combination of Magnesium and Sulfur in a galvanic element addresses several advantages, such as natural abundance, operational safety and a high volumetric capacity.

However the research so far was hindered because a stable electrolyte for Mg-S-Batteries was missing [1]. Muldoon et. al. developed a stable and reversibly working non-nucleophilic electrolyte based on a recrystallized Mg^{2+} salt complex $[Mg(\mu\text{-}Cl)_3(THF)_6][HMDSAlCl_3]$ (HMDS=hexamethyldisilazid) [2]. This crystalline electrolyte salt though could only be obtained in THF, revealing a disadvantageous overcharging and fast capacity fading [2]. A breakthrough in Mg/S battery performance was obtained by Fichtner et. al. They at first synthesized a one-step routine between $[(HMDS)_2Mg]$=magnesium bis(hexamethyldisilazid) and $AlCl_3$in different ethers, enhancing solvent choice and possibility of neglecting aforementioned disadvantages [3]. Furthermore a magnesium-anode enhances safety of Mg-S-battery, due to the missing tendency of dendrite formation [4]. Safety as well as capacity and scalability of fabrication of a battery are important factors to assess market opportunities of these secondary cells. Therefore we are focusing on a cell design that is "easy-to-fabricate" with a realistic material loading. Based on the multiannual experience in the development of lithium-sulfur batteries, we extend our activities to the field of magnesium sulfur-battery-development.

In a first attempt S-C-cathodes with Sulfur content of 50 wt.% and 70 wt.% were evaluated with a 1.2 M Mg^{2+}-salt electrolyte dissolved in a mixture of 2:1 by volume of bis(2-methoxyethyl) ether and an ionic liquid. The influence of the cathode composition was minimal at this early stage of development. Both types of batteries showed a similar discharge capacity of 600 mAh/g(Sulfur) in the first cycle. Furthermore different approaches for a working Mg-graphite composite-anode are presented. Such composite-anodes were prepared via die-pressing and could only be obtained in specific composition. The obtained charge-discharge profiles showed remarkably well defined plateaus, which have not been obtained elsewhere, jet. (see Figure 1).

The preparation routine of the composite-anode was found to have the highest impact on the obtained performance.

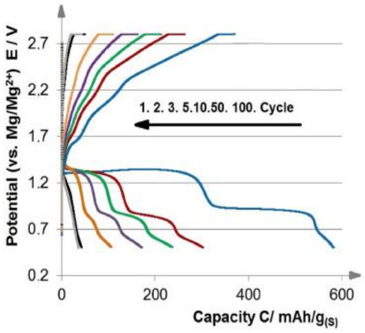

Figure 1: charge-discharge profiles of a 50wt.% sulfur in S-C cathode with a sulfur loading 1mg/cm² and 250μL electrolyte at a C/10-rate with a 75 MPa die pressed Mg-graphite anode

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The richness of V_2O_5 polymorphs as superior cathode materials for sodium insertion

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Due to the cost and low availability of Li sources, Na-ion batteries (SIBs) are attracting considerable interest as tomorrow's world batteries. Compared to LIBs, the number and performance of electrode materials for SIBs are limited but progress in Na intercalation grows very rapidly [1]. Layered materials with Van der Waals interlayer spacing constitute ideal frameworks for intercalation reactions of guest cationic species from which high discharge-charge rate and minimum structural distortions can be expected. While orthorhombic V_2O_5 was identified in the 70's as a promising cathode material for secondary Li batteries [2], it is only very recently that Na insertion was addressed in the α-V_2O_5 phase at room temperature [3].

An alternative way to identify new attractive stable V_2O_5 polymorph consists in considering the chemical removal of metallic species from vanadium pentoxide bronzes $M_xV_2O_5$. Such approach allows to benefit from the availability of new types of structure with various original stackings for the layers (single, puckered, double layered…) combined with a low amount of metallic species thus optimizing the possible specific capacity. This strategy has been successfully applied to obtain the ε'- and γ'-V_2O_5 polymorphs [4,5]. These polymorphs were synthesized from the chemical removal of Cu or Li from the 3D ε-$Cu_{0.9}V_2O_5$ and γ-LiV_2O_5 bronzes respectively, by means of strong oxidizing agents without changing their structure. The ε'-polymorph was reported to reversibly accommodate up to 1.8 Li ions in the 4V-1V potential range [4] whereas electrochemical behavior of γ'-V_2O_5 was shown to explain the enhancement of the cell potential of Li//V_2O_5 [5]. However, in spite of large interlayer distances, the interesting capability of such material for sodium insertion has not yet been investigated.

In this talk, a special emphasis will be given to the newly obtained electrochemical properties at room temperature of α-, ε'- and γ'-V_2O_5 polymorphs as sodium intercalation compound. The structural peculiarities of each phase (single layered α- , 2D double layered ε'-, distorted single layered γ'-) will be discussed and we will demonstrate how they govern their electrochemical properties. Promising data, with large capacities (from 100 to 200 mAh.g^{-1}, see **figure 1**) and an excellent cycle life will allow us to identify new high performance V_2O_5-type materials for use as electrodes in sodium-ion batteries.

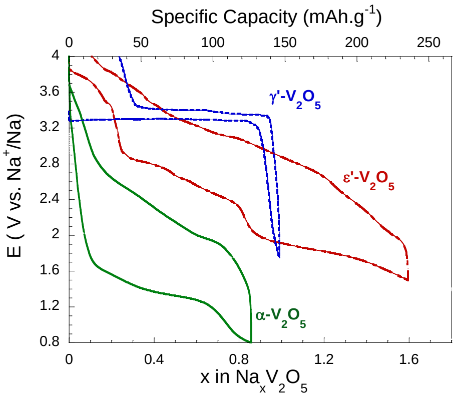

Figure 1. Typical galvanostatic discharge-charge curves at RT of α-, ε'- and γ'- V_2O_5 in a 1M $NaClO_4$/PC electrolyte. C/10 rate.

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Strategies to improve performance of Li/O_2 batteries

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Energy storage is the keyword of global sustainable policies. In this contest, new battery systems of high efficiency and specific energy are required.

Lithium-Air batteries are considered as one of the next generation batteries, due their very high specific energy. In these systems, the lightest electrode components are indeed used to deliver theoretically energy 2-3 times higher than the present Li-ion available values.

The main issues still to be addressed for the development of high performance Li/O_2 (air) batteries are the low cycling efficiency and low cycle life and slow discharge kinetics.

The discharge product, lithium peroxide (Li_2O_2) which is formed on the cathode surface is an insulator that affects battery capacity and causes high overpotential during recharge and, thus, low recharge efficiency [1].

Electrolyte choice is crucial and could drive the Li_2O_2 formation mechanism in a way that mitigates electrode passivation. Specifically, stabilizing the superoxide ion ($O_2^{\cdot -}$) in the electrolyte promotes Li_2O_2 formation in solution which is beneficial for battery discharge capacity and efficiency [2].

Glyme-based solvent-in-salt (SIS) electrolytes have been recently proposed for $Li-O_2$ batteries. These media feature glyme-Li^+ complexes that improve the electrochemical stability of the electrolyte and stabilize superoxide ion with a positive effect on cathode passivation [3].

Moreover, the use of semi-solid inks in replace of solid electrodes has been demonstrated to be effective for a better battery rate response of the $Li-O_2$ system. We have already demonstrated a new battery concept that operates with a flowable catholyte, based on conductive carbon particles dispersed in O_2-saturated non-aqueous electrolyte [4]. ORR takes place on the solid phase of the catholyte, i.e. the carbon particles, limiting the cathode surface passivation, enhancing the $Li-O_2$ battery energy and dramatically delaying the battery cell death. Such approach enabled areal capacity of 180 mAh cm^{-2}, energy of 500 mWh cm^{-2} and current of 4 mA cm^{-2}.

Here we discuss about two strategies to improve semi-solid $Li-O_2$ battery cycling performance. Specifically, we report on i) the use of superconcentrated electrolytes based on tetraethylene glycol dimethyl ether (TEGDME) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and on ii) the optimized carbon composition of the semisolid catholyte which permits to achieve the exceptional high specific energy of 1 kWh kg^{-1} [5].

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Quantification on Traces of Li_2MnO_3 in Li-rich Manganese Spinel by Electron Paramagnetic Resonance (EPR) and its Consequence on the Stoichiometry of $Li_{1+x}Mn_{2-x}O_{4-d}$

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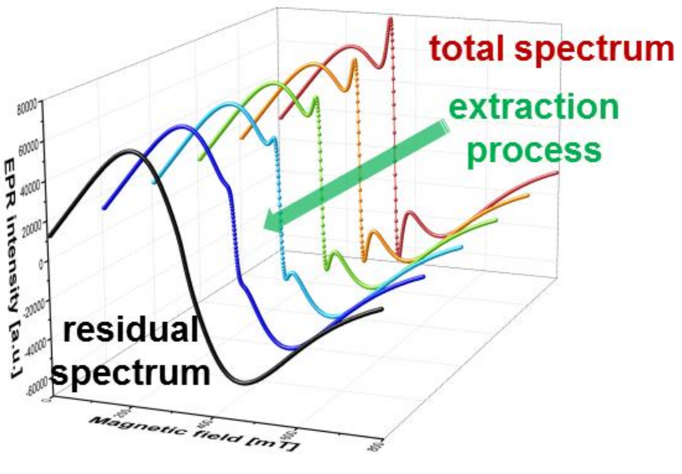
Li_2MnO_3 may be formed as a secondary phase in small quantities during synthesis of lithium manganese spinel materials. The studied samples are synthesized via solid-state route with different lithium contents under several calcination temperatures and annealing processes. A consequence of the existing Li_2MnO_3 is the impact on the exact stoichiometry of the lithium manganese spinel. Besides, the variation of oxygen non-stoichiometry is accompanied by the change of Li_2MnO_3 quantity. When Li_2MnO_3 exists in trace amount in synthesized lithium manganese spinel, detection by XRD is difficult. However, it can be easily monitored by Electron Paramagnetic Resonance (EPR) spectroscopy due to the significantly different EPR spectra between manganese spinel and layered Li_2MnO_3.

Combining the simulation of Li_2MnO_3 partial EPR spectrum and a calibration experiment from pure phased Li_2MnO_3 reference samples, the mass-fractions of Li_2MnO_3 in synthesized lithium manganese spinel materials are quantified. According to the quantification of Li_2MnO_3 mass-fractions and based on the defect model of Li substitution on *16d* sites, the exact value of x in $Li_{1+x}Mn_{2-x}O_{4-d}$ is determined. The impact of Li_2MnO_3 mass-fraction on the stoichiometry of $Li_{1+x}Mn_{2-x}O_{4-d}$ cannot be neglected even when Li_2MnO_3 is less than 1 wt%.

Benefiting from the excellent sensitivity of EPR spectroscopy, both the formation of Li_2MnO_3 from the calcination process and its disappearance after tempering treatment have been tracked quantitatively. On the other hand, the EPR linewidth for lithium-rich manganese spinel materials shows a direct correlation with the ratio between Mn^{4+} and Mn^{3+} in $Li_{1+x}Mn_{2-x}O_{4-d}$.



Schematic description of EPR quantification on Li_2MnO_3
The total spectrum contains both the signal from lithium manganese spinel and Li_2MnO_3. After extracting the simulated partial spectrum of Li_2MnO_3, the residual spectrum is presented for pure phased lithium manganese spinel.

In-Operando Characterization of Structural and Chemical Changes in Layered Oxide Cathodes

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Rechargeable Li ion batteries power most of today's portable electronics due to their high energy density compared to other battery technologies. However, new fields of application for rechargeable Li ion batteries, such as the electrification of transportation, will continue to require improved energy/power density, cost, life time, and safety. Lithium-rich layered metal oxide materials (abbreviated LRM, with composition x $Li_2MnO_3 \cdot (1-x)\ LiMO_2$) have attracted significant attention as potential lithium-ion battery cathode materials due to their high gravimetric capacities and reasonable rate capability.

Dow Chemical R&D has investigated LRM cathode materials for commercial applications and, as part of the materials development, conducted fundamental structural studies on material properties and reactions. High resolution x-ray diffraction and electron microscopy has demonstrated that LRM materials have regions with more monoclinic or rhombohedral symmetry, consistent with previous studies[1,2] and as expected from local compositions that are more similar to Li_2MnO_3 or $LiMO_2$. This heterogeneity persists within single layered oxide particles. Insights into the reaction mechanism of LRM cathodes were obtained through a combination of electrochemical profile analysis, in-operando XRD, and in-operando XAS. Multiple methods were used to acquire data from the same pouch cell batteries at different states of charge, which enabled correlation between different datatypes. Multiple processes were resolved within the first 'activation' cycle, including the decomposition of the Li_2MnO_3 phase and intra-lattice oxide charge storage.[3] Over multiple charge/discharge cycles, LRM cathodes sustained significant and reversible disordering between the metal oxide planes, a reversible change in the local environment of nickel ions, and a slow but irreversible drift in the average crystalline unit cell. In contrast, in-operando measurements on a lithium-stoichiometric metal oxide cathode material (NMC) observed reversible disordering of the metal oxide planes on the first and subsequent cycles.

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Passivation of the Silicon-Graphite negative electrode during Aging of Lithium-ion Full Cells

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Layered oxide positive electrodes, such as $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM), and graphite or silicon- graphite negative electrodes in a lithium-ion battery (LIB) undergo a series of complex structural and compositional changes during electrochemical cycling. These changes have a direct influence on cell performance. The multifold enhancement in energy densities of LIBs using Si-containing negative electrodes is offset by the limited stability at the electrode-electrolyte interface. Mechanical stresses, associated with large volume changes during lithiation and delithiation of silicon, cause disruptions and continuous degradation of the solid electrolyte interphase (SEI) layer; furthermore, particle cracking can lead to exposure of new surfaces to the electrolyte. Electrolyte reduction at these newly-exposed surfaces during subsequent cycling traps additional lithium ions and contributes to irreversible performance loss.

In this presentation we will discuss differences in lithium-ion cell performance loss during calendar and cycle life aging. Our cells contained $Li_{1.03}(Ni_{0.5}Co_{0.2}Mn0_{.3})_{0.97}O_2$ (NCM523) as an active material in the positive electrode, and graphite (Gr) or a graphite-15 wt% silicon (Si-Gr) blend as an active material in the negative electrode. The electrolyte was 1.2 M $LiPF_6$ in (3:7 w/w) ethylene carbonate (EC)/ethyl methyl carbonate (EMC) with 10 wt% fluoroethylene carbonate (FEC). Our tests were conducted in two-electrode (2032-type) coin cells or in multi-electrode cells containing Li and/or Li-Sn reference electrodes (REs). Cells cycled in the 3-4.1 V voltage range (cycle-life ageing) showed 46% capacity loss at the end of 100 cycles. In comparison, cells held at 4.1 V for the same time period (calendar-life ageing) showed 11% capacity loss. The differences in capacity loss are related to volume change in the Si-Gr electrode, which is substantial during cycling and minimal during the calendar-life test. The 11% loss for the Si-Gr cells is higher than the <5% loss observed for Gr cells, which suggests that the SEI layer does not fully passivate the silicon particle surfaces. The reasons for this lack of complete passivation are being explored with a suite of physicochemical diagnostic techniques which include Scanning Electron Microscopy, X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy. The information obtained is essential for the design of enhanced SEI layers, which is necessary to achieve stable long-term cycling and extend cell life.

Calendar-life aging tests were also conducted at full cell voltages of 2.0, 2.5, 3.0, and 3.9 V. Cell capacity retention during these calendar-life aging tests showed a dependence on electrode composition and electrode potentials. For example, at a full cell voltage of 2.0 V, the Si-Gr electrode potential is >1.5 V vs. Li/Li^+, which increases the likelihood of SEI degradation (and gas generation). Information of this nature is needed to determine optimal voltage cycling windows and will be discussed during the meeting.

Investigation of SEI Formation on Lithium Metal Anodes

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The Li plating/stripping performance of Cu||$LiFePO_4$ cells has been investigated for carbonate solutions containing three different lithium salts, $LiPF_6$, $LiBF_4$ or LiBOB. The coulombic efficiencies for these cells are higher in the early cycles, but drop gradually during cycling. The capacity retention and efficiency of the cells is best with LiBOB, followed by $LiBF_4$, while $LiPF_6$ provides the poorest performance. The differences are likely due to changes to the solid electrolyte interphase (SEI) on the surface of the lithium metal electrodes. Ex-situ analysis of the electrodes has been conducted via a combination of XPS and FT-IR to develop a better understanding of the role of the SEI in cycling performance.

Polypyrrole-assistant Oxygen Electrocatalysis on Perovskite Oxides

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Nitrogen-containing electrocatalysts such as metal-nitrogen-carbon (M-N-C) composites and nitrogen-doped carbons are known to exhibit high activities for oxygen reduction reaction (ORR). Even if the mechanism by which nitrogen improve the activities is not completely understood, strong electronic interaction between nitrogen and active sites has been found in these composites. Herein, we demonstrate a case in which nitrogen improves electroactivity, but in the absence of strong interaction with other components. The overpotentials of ORR and oxygen evolution reaction (OER) on perovskite oxide catalysts were significantly reduced simply by mixing the catalyst particles with polypyrrole/carbon composites (pPy/C). Any strong interactions between pPy (a nitrogen-containing compound) and active sites of the catalysts were not confirmed. A scenario based on the sequential role allocation between pPy and the oxide catalysts for ORR was proposed: (1) molecular oxygen is incorporated into pPy as a form of superoxide ($pPy^+O_2^-$); (2) the superoxide is transferred to the active sites of perovskite catalysts; and (3) the superoxide is completely reduced along 4e ORR process.

Unraveling the Ageing Phenomena in NCM Based Cells

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With the emergence of new applications such as electric vehicles, lithium-ion batteries (LIBs) have been attracting increasing attention with a growing focus on high energy density. Among various novel materials, lithium-rich nickel cobalt manganese oxides [$Li_{1+x}(Ni_aCo_bMn_{1-a-b})_{1-x}O_2$, LR-NCM] are considered to be one of the most promising cathode materials for the next generation LIBs due to their high specific charge (~250 mAh/g), good thermal stability, and projected low cost. However, the practical application of LR-NCM is still impeded by the pronounced performance fading resulting both from the instability of the material itself and the unstable electrode-electrolyte interface. In the literature, performance decay is often addressed on the material level. However, the presence of various components in a cell and their possible interactions make LIB a complex system. Therefore, a thorough understanding of the relative importance and the underlying mechanisms of different ageing phenomena on the cell level is essential.

In this contribution, the ageing behavior of $Li_{1.17}(Ni_{0.22}Co_{0.12}Mn_{0.66})_{0.83}O_2$ (HE-NCM) is discussed by comparing its long-term cycling stability to that of conventional lithium-nickel-cobalt-manganese oxides (NCM), in both half-cell and full-cell configurations. The relative importance of material- and interface-related degradation processes in the respective systems is discussed. It was found that interfacial stability determines the performance of NCM half-cells and HE-NCM full-cells. While the specific-charge retention of the former is affected by the formation of a thick layer of electrolyte-decomposition products on the surface of the cathode, the interface instability of the latter causes the excessive lithium consumption on the surface of the anode, indicating very different interface degradation processes.

The interactions at electrode-electrolyte interface are not only defined by the active materials but also by the electrolyte stability in the corresponding potential windows. A direct link between the formation of alkoxides at the anode and the accumulation of electrolyte-decomposition products on the surface of NCM cathodes was established. This finding highlights the importance of anode passivation, preventing further electrolyte reduction.

Transport of electrolyte oxidation products from the cathode to the anode at high cut-off potentials was confirmed to be the cause of the excessive lithium consumption at the anode surface in HE-NCM full-cells. To provide a direct proof of this transport process, a novel method based on isotope labelling and time-of-flight secondary ion mass spectrometry was developed to distinguish the electrolyte-decomposition products formed by direct electrolyte reduction from those transported from the cathode. This method can be further applied for elucidation of the detailed mechanism of the interfacial processes, which can lead to novel solutions for stabilizing the electrode-electrolyte interface in high-potential systems. Besides, in contrast to the common belief that transition metal dissolution accelerates the formation of lithium-consuming solid electrolyte interphase, it was found that there is no direct correlation between the two.

This work is the first step into the understanding of complex ageing phenomena in LIBs. The clear reciprocal influence between the cathode and anode identified in this work underlines the importance of studying LIB chemistries in relevant environments, e.g. in a full-cell. It is clear from this work that holistic approach pursuing the knowledge both on the material and cell levels can lead to a deeper understanding of complex battery chemistry and to further advances in the field of rechargeable batteries.

Inkjet Printing of catalyst gradients for bi-functional catalyst layers for the ORR and OER

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Inkjet printing has gained much attention in recent years in research and development as versatile digital and mask-less fabrication technique to print functional materials[1]. Picoliter sized droplets can be deposited with high precision and reproducibility on various substrates showing micrometer resolution of the created features. Key advantages are the possibility to design and execute the accurate fabrication of patterns with defined geometry and composition. Inkjet printers with parallel printheads enable multilayer printing and the fabrication of gradient materials. In the field of electrochemical energy conversion this technology can be applied for the fabrication of mono- and bi-functional catalyst layers for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER)[2]. Catalyst layers (CLs) are generally composed of the catalyst particles supported on electron conducting materials and an ionomer/ion conducting phase forming microporous networks. The deposition on a membrane results in so-called catalyst coated membranes (CCMs). State-of-the-art catalysts are normally selective and stable for just one of the two reactions, either for the OER or ORR, while they suffer from the opposing reaction. Owing to the asymmetry of the reactions, different catalyst loadings are required and the corrosion of the support material, usually carbon black, plays a major role. Hence, for systems switching between the OER and ORR, such as unitized regenerative fuel cells that are generally not very efficient, it is necessary to find one bi-functional catalyst material, usually a metal or metal oxide alloy, or to mix two selective, but stable catalyst materials forming a bi-functional catalyst layer[3]. The design of such bi-functional catalyst layers requires precise and accurate material deposition technologies.

In this contribution we describe the utilization of inkjet printing to fabricate bi-functional catalyst layers with two inks containing each either Ir/C or Pt/C. The two inks were each composed of precisely adjusted ratios of the catalyst material, ionomer and stabilizing agents and quasi-simultaneously printed from two parallel printheads. Special care needs to be taken for the right ink viscosity, surface tension, density, particle size and printhead characteristics in order to achieve stable printing[4].

We demonstrate the possibility of printing catalyst material gradients in 2D and 3D by adjusting the ink deposition ratios of the two inks. Furthermore, by changing the droplet density or by printing an ionomer from a third printhead, we discuss the possibility of creating structural gradients such as porosity and also proton conductivity. By building up a catalyst layer in a layer-by-layer fashion and analyzing stepwise the catalyst layer properties in terms catalytic activity, stability, conductivity and mass-transport represents an interesting approach of designing and analyzing functional 3D layers by using digital printing.

Knowing the stability issues of the used catalyst materials for long term operations, these known materials were however ideal to demonstrate the feasibility of inkjet printing and analyzing the final CL structures in terms of spectroscopy, microscopy and electrochemistry (e.g. voltammetry, EIS and SECM). This printing concept can be employed for a broad range of other catalyst materials and offer great opportunities for digital catalyst layer fabrications with future perspectives.

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Structure-Activity Descriptors for Transition Metal Sulfides Reactivity for Oxygen Reduction Reaction

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To maximize catalytic activity, Sabatier-type activity plots have been used to determine optimal adsorption, but these do not provide direct relationships for catalyst structure that optimizes activity[1]. The discovery of new electrocatalysts can be accelerated through structure-activity relationships. Such a relationship allows the problem to be defined as finding optimal local environment that maximizes activity. Recently, structure-activity relationships have been developed for metal surfaces[1], and in this work, we extend this approach to obtain a structure-energy-activity relationship for transition-metal sulfides. Transition metal sulfides represent an attractive class of materials for ORR[2]. Their rich phase diagram allows tunability of activity. We employ density functional theory (DFT) using BEEF-vdW exchange correlation functional to study oxygen-reduction thermodynamics on the stable phases of transition metal sulfides: nickel, cobalt, molybdenum, ruthenium, titanium sulfides.

We illustrate the findings using nickel sulfides as an example case. From DFT calculations, we show that there exists scaling between adsorption free energies of OOH* and OH*, which leads to a volcano relationship between the limiting potential and the free energy of OH adsorption, the chosen descriptor. A more relevant quantity plotted is the expected limiting potential (U_{EL}) that was proposed recently[3] and represents the expectation value of limiting potential from a large number of experiments. A trend that is observed across the nickel sulfide phases and that provides a direction for moving towards optimal binding strength is that higher nickel stoichiometry weakens OH* binding, which can be rationalized based on the strong covalent nature of the Ni-S bond. The expected-activity volcano suggests that the Ni_3S_4, NiS_2 and NiS phases exhibit high ORR activity. We explore to identify a structure-activity descriptor based on the coordination numbers of nickel and sulfur atoms. Based on preliminary data, we construct the simplest possible model given by $\Delta G_{OH} = \alpha_{Ni} CN_{N(Ni)} + \alpha_S CN_{N(S)}$, and a least-squares approach to obtain the structure-energy descriptor: $G_{OH} = 0.29(CN_{N(S)} + 0.07 CN_{N(Ni)})$, which has a promisingly low mean absolute error. This relation implies that the strong covalent Ni-S bonding leads to a large weakening of OH* adsorption than the weak Ni-Ni metallic bonding. Therefore, to a first approximation, a simple counting of neighboring atoms around the surface site can be used to identify candidate catalysts. The challenge of finding active ORR catalysts can now be recast in terms of finding sites with the optimal local environment. In this case, our preliminary analysis suggests that having 3 nearest-shell sulfur atoms leads to optimal OH-adsorption weakening for high activity. We observe that all the active surface sites of various Ni-S phases possess this local environment, which shows that the simple descriptor identified is robust.

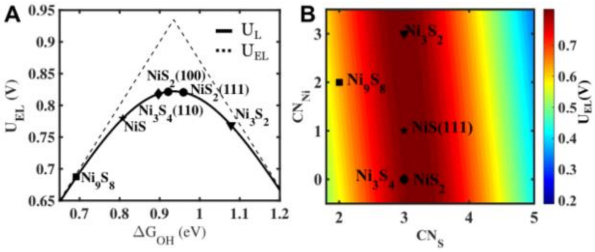

Figure 1: Preliminary results on Ni-S A) Activity volcano showing the expected limiting potential as a function of the DFT-calculated ΔG_{OH}. B) Contour plot of the expected limiting potential as a function of the local environment. The markers are plotted based on the local coordination around the active site for each of the stable nickel sulfide phases.

Identification of structure-energy-activity descriptors for large classes of compounds allows for rapid identification of candidates and robust quantification of activity under reaction conditions. We will report on possible structure-energy-activity descriptors for transition metal sulfides considered. From the set of descriptors, the trends in the two coefficients α_M and α_S can be used to formulate a generalized structure-activity descriptor for all transition-metal sulfides. These coefficients are expected to strongly depend on metal-metal and sulfur-metal bonding characteristics. This approach will allow exploring sulfides as candidate materials for a variety of electrochemical reactions.

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Isotope Effects on the Electrochemical Reduction of CO_2 on a Polycrystalline Copper Electrode

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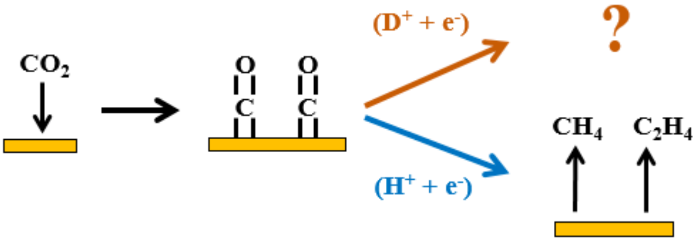
The electrocatalytic reduction of carbon dioxide has attracted the interest of electrochemists and inorganic chemists for decades as a key reaction in facilitating a sustainable low-temperature redox cycle for energy storage and conversion.[1] Ever since Hori made his landmark discovery in 1985 that copper has the unique ability to electrochemically reduce CO_2 to hydrocarbons such as methane and ethylene with good faradaic efficiencies in comparison to other catalysts,[2] substantial effort has been invested to understand the special reactivity of copper for this reaction.[3] In recent years, numerous research articles on electrochemical CO_2 reduction have focused on the determination of the reaction mechanism, both experimental[4] and theoretical,[5,6] as more mechanistic insight is expected to lead to better, tailor-made catalytic systems. On Cu(111), the reduction of CO, a key intermediate in the reduction of CO_2 to hydrocarbons, to both methane and ethylene was observed to take place simultaneously. On the other hand, on Cu(100) a second pathway is observed that forms ethylene at lower potentials without methane formation, especially at high (alkaline) pH. This finding has triggered a lot of debate on the origin of C-C bond formation and proposing a definite mechanism for the formation of methane and ethylene has remained challenging.

For other electrocatalytic reactions, such as the hydrogen evolution reaction and the oxygen evolution reaction, isotope effect studies have proven a valuable tool in gaining further mechanistic understanding. However, no such study has yet been performed for electrochemical CO_2 reduction. As it is known that the reduction of CO_2 towards methane is pH dependent, suggesting a rate determining step in which proton transfer is involved, and the reduction of CO_2 towards ethylene is pH independent, suggesting a rate determining step without proton transfer, we studied the electrochemical reduction of CO_2 in both H_2O and D_2O using state of the art flow cells. Here we will show that although the same product distribution is observed for CO_2 reduction in H_2O and D_2O, the Faraday efficiencies towards hydrocarbon products varies significantly.

Furthermore, we have studied the isotope distributions (both D/H and $^{13}C/^{12}C$) of the hydrocarbons formed during CO_2 reduction in ultrapure water using sensitive GC-MS techniques. We will show that the D/H ratio of methane and ethylene are significantly different to each other. We will discuss the implementations of our findings in the light of proposed mechanisms for electrochemical CO_2 reduction and we will compare the D/H ratio of hydrocarbons formed from the reduction of possible intermediates, such as formaldehyde, to the D/H ratio of hydrocarbons formed in CO_2 reduction in an effort to validate if these are actual intermediates in CO_2 reduction.



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Electrospun ceramic nanofibers as catalyst support materials – let's get practical

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Electrospinning nanofibers into sheets presents a scalable method for producing catalyst support materials used in membrane electrode assemblies (MEAs) for proton exchange fuel cells (PEMFCs). Electrospinning is a robust, simple and cost effective method to produce nanofibers in micro-sized sheets which can be post treated and used in applications ranging from energy production to water purification. Electrospun ceramic nanofibers are of topical interest in PEMFCs owing to their possible ability to increase the durability of platinum (Pt) catalysts due to their unique mechanical properties, thermal stability, corrosion resistance as well as their strong metal support interaction with Pt. In the current study, Tungsten carbide materials were synthesized, characterized and electrochemically evaluated. These materials showed great potential for inclusion in advanced MEA studies. Challenges presented during the manufacturing, evaluation and characterization of electrospun ceramic sheets, are often not published in literature. Some practical experiences and lessons learned from this study are also shared.

Tungsten carbide (WC) has excellent thermal stability, is acid resistant and has a platinum-like electron structure (Zhou et al., 2011). WC nanofibers were spun and calcinated from a polyvinylpyrrolidone (PVP) matrix. These WC fibers, however, oxidize in PEMFC conditions to WO_3, reducing the conductivity of the support material. Various doping agents and alloys with WC were considered to increase the overall lifetime of the nanofibers in the support material, including titanium/titanium carbide, niobium and cobalt. The aim was to increase the electron transfer between Pt and the support, by further shifting the d-band center on the surface Pt and increase the strong metal support interaction between Pt and WC (Ho et al., 2011). The alloys and doped materials were characterized using TEM, SEM and XRD. The WC based materials were coated with the Pt catalyst and their electrocatalytic properties were determined using voltammetric methods and a rotating disk electrode. The durability of the individual materials was determined from the cyclic loss in electrochemical surface area (ECSA) and compared to that of commercial Pt/C.

Practical challenges experienced when producing electrospun microsheets for electrochemical testing and for MEA manufacturing are also discussed. Handling of thin micro-sized sheets of electrospun nanofibers was very challenging and post treatments were minimized. Platinum deposition methods also had to be optimized to match the most favorable method with the limitations of the materials. Due to the polymer matrix required for spinning, the presence of residual carbon required deeper consideration. Using TEM electron energy loss spectroscopy it was established that selected nanofibers were encapsulated with an amorphous carbon layer, and that the deposited platinum nanoparticles were distributed on carbon and not the ceramic composite. Fixing of the microsheets onto carbon electrodes for electrochemical evaluation was done using innovative pastes which wouldn't compromise accurate electrochemical characterization. Direct comparison of microsheets with that of particulate catalyst supports is not possible with conventional rotating disk electrode voltammetry, due to diffusion layer thickness, porosity, diffusion limitation and various material resistance variations. In the current study, the most accurate comparisons with Pt/C were made via the percentage loss of ECSA during cycling.

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Characterizing PEM Water Electrolysis with X-ray Computed Tomography

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Proton exchange membrane water electrolysis (PEMWE) is a clean process enabling efficient electricity storage in chemical form. Due to low ohmic resistance of the PEM the electrolyzers can operate at high current densities resulting in smaller-size stacks compared to alkaline technology[1]. Use of high-loading PGM catalysts for catalyst coated membranes and titanium-based porous transport layers (PTLs) as anode supports are costly. Optimizing the structure of the PTLs by varying through-thickness porosity and improving contact between PTL and CCM is one of the active research areas. To probe these interfaces, as well, as characterize two-phase flow of water and oxygen in anode it is critical to develop in-situ diagnostic tools. We have previously shown use of X-ray computed tomography (CT) to characterize morphology and water transport in gas diffusion layers for polymer electrolyte fuel cells[2-4] and this technique is applicable to PEMWE, although porous materials in PEM electrolyzers have lower X-ray transmission compared to carbon-based materials in fuel-cells, making the measurements more challenging.

In this work we use X-ray computed tomography (CT) to characterize morphology of commercially-available titanium PTLs and correlate morphology to water distribution and two-phase flow behavior. Titanium mesh cloth and titanium frit are compared. The morphological results are input into two-phase, two-dimensional cross-section electrolyzer model for data interpretation and parameters optimization. In-operando X-ray CT cell with a single 1 x 1 mm serpentine channel and active area of 1 cm^2 is used to observe two-phase flow transport, and water permeation into the cathode under constant current density conditions. We will also show an ex-situ X-ray CT corrosion study of carbon-based gas diffusion layers, where morphology change before and after constant potential of 1.5 – 2 V operation at various time intervals will be presented.

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Novel insights into mechanical degradation of reinforced fuel cell membranes using 3D *in situ* structural characterization

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Perfluorosulfonic acid (PFSA) ionomer membranes in fuel cells are susceptible to operational mechanical stresses resulting in fatigue and/or creep driven failure that compromises their durability and lifetime. Fatigue based mechanical degradation is a result of multiple wet/dry humidity cycles that causes micro crack initiation/propagation within the membrane **[1]**. This could lead to gradual increase in gas crossover and ultimately to fuel cell failure. Membranes with non-conductive mechanical reinforcements have been developed to decelerate mechanical degradation, which has shown to improve their durability. Nevertheless, membrane damage development remains a critical failure mode and the fundamental understanding of mechanical membrane degradation is a subject of ongoing research. Two-dimensional scanning electron microscopy (SEM) based studies have typically been used to characterize the degradation-induced structural changes in fuel cell membranes. SEM imaging is inherently destructive which inhibits any tracking of structural changes over time and therefore, membrane degradation evolution studies have been limited to *ex situ* analysis at various stages of degradation. In a recent work, laboratory-based X-ray computed tomography (XCT) was introduced as an advanced alternative imaging technique, which enabled a non-destructive and three-dimensional (3D) failure analysis of fuel cell membranes, revealing novel insights on membrane failure **[2]**. The key objective of the present work is to extend this XCT-based 3D failure analysis approach to an *in situ* investigation of pure mechanical membrane degradation by utilizing a custom designed fixture. This X-ray transparent fixture houses a 9 mm x 4 mm fuel cell MEA fabricated with a reinforced membrane and is subjected to wet/dry cycling producing a pure mechanical fatigue type membrane degradation **[3]**. This novel *in situ* workflow allows for a 3D tracking of the structural/morphological evolution of identical membrane locations as a function of wet/dry cycling time, thus enabling novel failure characterization opportunities.

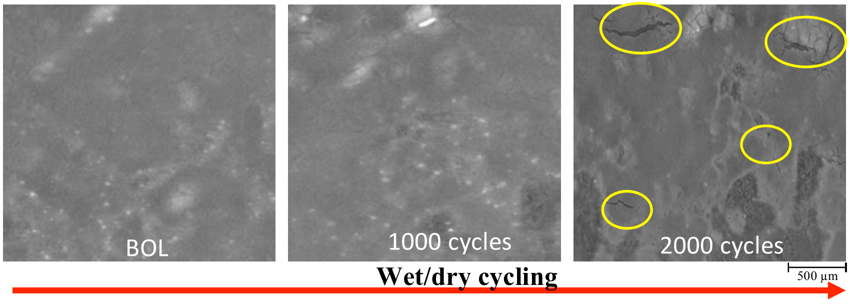

Figure 1: Planar views of the identical locations of membrane inside an MEA, illustrating gradual crack development during wet/dry cycling procedure.

No through-thickness membrane crack is detected up to 1000 wet/dry cycles but sizeable crack development is seen to have occurred during 1000-2000 cycles. Crack distribution and growth within the reinforced membrane are examined from various perspectives by simultaneously studying the 2D planar and cross-sectional views afforded by the 3D nature of imaging. A clear interaction between catalyst layer defects (cracks and delamination) with membrane cracks is observed. Additionally, the reinforcement layer is found to restrict the through thickness growth of membrane cracks at several locations. Overall, the size and density of membrane crack formation at similar cycling stages is found to considerably reduce with the use of reinforced membrane when compared to non-reinforced membrane. Furthermore, a detailed insight to understand the degradation mechanisms between reinforced and non-reinforced membranes is carried out.

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Relaxation Impedance and Identification of Oxygen Reduction Reaction Mechanism in HT-PEMFCs by Simulating AC Impedance Spectra

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High Temperature Polymer Electrolyte Membrane Fuel Cells, (HT-PEMFCs), are one of the most promising alternatives of clean power production by converting chemical energy to electrical energy. Even though the operating principles of an HT-PEMFC are understood, the overall system's behavior is determined by a number of strongly coupled processes, each proceeding at a different rate. In a HT-PEMFC the elusive multistep Oxygen Reduction Reaction, (ORR), taking place at the cathodic electrode takes a major fraction of the open circuit potential. Thus, in order to optimize fuel cell performance by minimizing ORR power losses an in depth understanding of the various processes and their interactions is necessary. One of the most powerful electrochemical characterization methods is the Electrochemical Impedance Spectroscopy technique, (EIS). It is a very powerful and sensitive in situ technique that has the ability to separate potential losses corresponding to different processes which proceed at different rates, (have different timescales), [1]. Unfortunately the behavior of many electrochemical processes, such as Oxygen adsorption relaxation phenomena [2], **Error! Reference source not found.**, and the effect they have on the performance of the fuel cell is very difficult to deduce from experimental spectra. In this study a 1-D dynamic mathematical model has been developed in order to simulate AC impedance spectra under various operational conditions and a Monte Carlo type algorithm was used to estimate the values of the respective kinetic constants by simultaneously fitting multiple AC Spectra. The model incorporates a three-step mechanism for the ORR as well as a detailed macroscopic description of mass and charge transfer across the various parts of the Membrane Electrode Assembly, (MEA). By decoupling the various processes of the simulated AC impedance spectra, information was successfully extracted on the various kinetic and equilibrium constants related with the interaction of the reacting gases in the catalytic layer and the electrochemical interface.

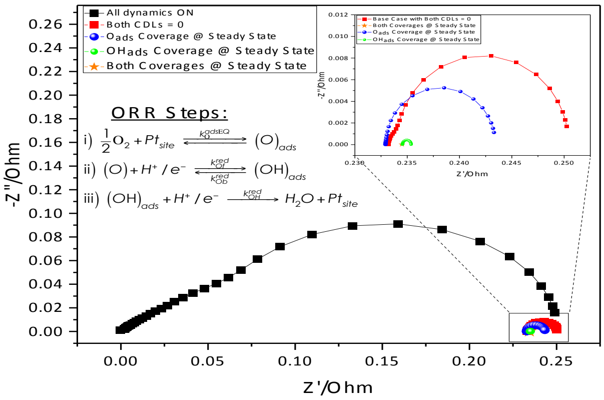

Fig. 1.Typical HT-PEMFC impedance spectrum with all dynamics ON, (black). Inset: Low frequency relaxation impedance due to ORR's intermediate species coverage oscillation when double layer capacitances were set to zero.

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Fundamental Study of OER Electrocatalytic Activity of $La_{1-x}Ca_x(TM)O_3$ Prepared by Atmospheric Plasma Method

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The electrochemical water splitting is a viable strategy for energy storage from intermittent renewable sources such as solar or wind energy. However, the sluggish kinetics of the oxygen evolution reaction (OER) limits the efficiency of the process and hinders its large-scale deployment. While noble metal oxides (RuO_2, IrO_2, etc.) are highly efficient OER catalysts, they are expensive and show poor long-term stability. Recent reports suggest that some transition-metal (TM) oxides, including perovskites of the ABO_3-type, can provide high OER efficiency and good stability. Understanding key factors responsible for the OER performance can enable a rational design of inexpensive highly-efficient OER electrocatalysts. Several structure-related parameters have been suggested to play a significant role, including the oxygen-TM bond covalency and the location and occupancy of the hybridized states between oxygen 2*p* and TM 3*d* orbitals. Fundamental properties of the TM ions, such as the number of *d*-electrons or electronegativity seem also be important. In fact, the OER activity has been correlated with the number of 3*d*-electrons for some perovskite oxides [1]. Recent theoretical studies have also suggested the importance of the TM valency [2] and position of the oxygen 2*p* state [3].

In a current work, we report a study of the OER efficiency for a class of $La_{1-x}Ca_x(TM)O_3$ electrocatalyst. These materials are prepared using atmospherics plasma oxidation method [4], where rapid oxidation and fast cooling offers excellent metastable phase formation and easy synthesis of homogenous, alloyed oxides. With alloy approach, ions can be incorporated at various concentrations at active sites, allowing for precise control of the structure and properties. In particular, perovskites with different TM valance can be prepared by partial ($0 < x < 1$) substitution of La with Ca. This can cause the change of the O vacancy concentration as well as the charge carrier concentration in the TM 3*d*-band and produce mixed valence state allowing for tuning of the band structure via electronic and electron-lattice correlation effects. The OER activity in these samples will be tested using cyclic voltammetry and galvanostatic measurements and overpotential will be measured as a function material composition. Simultaneous materials characterization will be conducted using variety of techniques, including XRD, EDX, XPS and TEM and the structural and energy band parameters will be correlated with the OER activity. Theoretical modeling based on DFT calculation will also be employed to explain experimental data.

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Stabilization of Ultrathin (Hydroxy)oxide Films on Transition Metal Substrates for Electrocatalysis

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Design of cost-effective electrocatalysts with simultaneously enhanced stability and activity is of paramount importance for the next generation of energy conversion systems, including fuel cells and electrolyzers, but remains a grant challenge. In this talk, we use DFT calculations and electrochemical surface science measurements to obtain atomic-level insights into ultrathin (hydroxy)oxide films on transition metal substrates, which exhibit highly flexible properties for electrocatalytic applications. The formation of these supported films can lead to structures with stabilities exceeding what is suggested by traditional bulk Pourbaix thermodynamics, including stoichiometries that do not exist in bulk and properties that are tunable by controlling the voltage, film composition, and substrate identity. Using nickel (hydroxy)oxide/Pt(111) as an example, we show that three-phase boundaries formed at the edges of these stabilized films enhance activity toward hydrogen evolution through a bifunctional effect. We will further show how to apply above understanding to design real-world nanocatalysts with improved performance.

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Alkaline Water Electrolyzers With Base Metal Catalysts Showing 1 A/cm^2 At 1.75 V

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Summary. Alkaline water electrolyzers with base metal catalysts and Sustainion™ membranes show 1A/cm^2 at 1.75 V in 1 M KOH at 80 °C.

Abstract.

This paper will describe the performance of Dioxide Materials' new Sustainion™ membranes in alkaline water electrolyzers with base metal catalysts. Figure 1 shows the conductivity of the membranes. Notice that the conductivity is a factor of 2-4 higher than the closest competitor. the conductivity is stable for thousands of hours at 60 °C in 1 M KOH.

Dioxide Materials has done testing of the membranes in Alkaline water electrolyzers. Figure 2 shows a run at 60 °C in 1 M KOH using commercial nanoparticles from Sigma Aldrich as catalysts. We observe stable performance for 1000 hour with a average voltage loss of only 10 µV/hr.

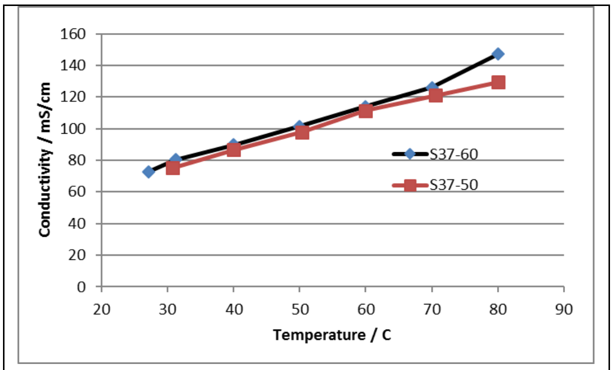

Figure 1 The measured conductivity of Dioxide Materials' Sustainion™ membranes in 1 M KOH

Figure 3 shows a short run done with an optimized catalyst. This catalyst shows 1A/cm^2 at 1.75 V.

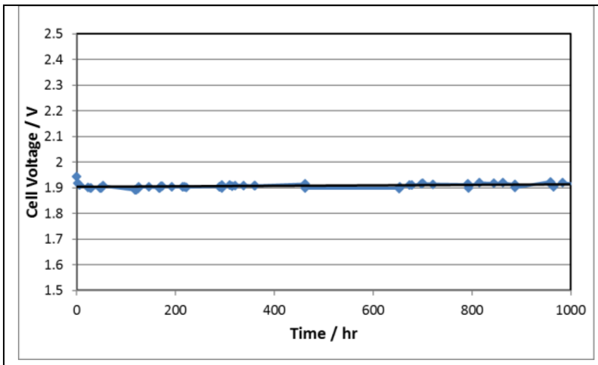

Figure 2 The stability of an electrolyzer with $NiFeO_4$ anode catalysts and NiFeCo cathode catalysts at 60 °C and 1 M KOH. In this case, the current was maintained at 1 A/cm² and the voltage to maintain the current was measured as a function of time

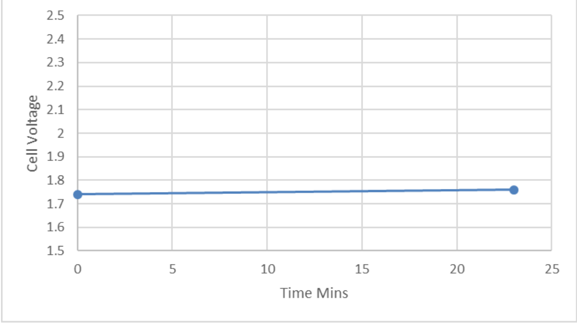

Figure 3 A short run with an improved catalyst at 80 °C and 1 M KOH. In this case, the current was maintained at 1 A/cm² and the voltage to maintain the current was measured as a function of time

Modified NiO/GDC cermets as possible cathode electrocatalysts for H_2O electrolysis & H_2O/CO_2 co-electrolysis processes in SOECs

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H_2O electrolysis constitutes a promising method for the production of pure-H_2 and O_2 by using electrical energy. One characteristic and recent application of this technology is electrolysis at high temperatures, by using Solid Oxide Electrolysis Cells (SOECs). Specifically, the electrical energy that is required for the high temperature (600-1000 °C) H_2O electrolysis process, is much lower than the energy required at low temperatures (<100 °C), which as a result yields significantly higher efficiency and performance in the former case [1]. Although this technological application has considerable advantages, it confronts many problems that prevent the widespread use and commercialization. One of the most important is the deactivation of the fuel electrodes (H_2O/H_2), which is usually ascribed to nickel re-oxidation and/or agglomeration during H_2O electrolysis, or/and carbon deposition during H_2O/CO_2 co-electrolysis [2]. Another disadvantage is the degradation/delamination of the oxygen electrodes. Consequently, recent research activities focus on the development and investigation of new, tolerant fuel (H_2O/H_2) and air electrodes. The aim of this work is the development and study of ceramo-metallic electrocatalysts/electrodes, which are based on commercial NiO/GDC powder (Marion Technologies). This powder is modified with chemical methods by the addition of Ba, Au or/and Mo. The Au or/and Mo modified electro-catalysts have been extensively studied, from our research group, as electrodes in Solid Oxide Fuel Cells (SOFCs) applications [3,4] and their use in SOECs, as H_2/H_2O electrodes (cathodes), is also very interesting. Furthermore, the modification with Ba aims to the protection of the Ni properties, towards the potential limitation of fast re-oxidation or/and agglomeration. All cermets were investigated through physicochemical characterization with the methods of BET, XRD, XPS, TGA-MS, H_2-TPR, O_2-TPO, including specific redox stability measurements under various H_2O-H_2 feed conditions. The powders were also used for the preparation of appropriate paste, which was deposited on solid YSZ electrolytes with the method of screen printing. The prepared/calcined electrodes were kinetically studied, in the form of half cells, for their catalytic activity for the Reverse Water Gas Shift Reaction in the temperature range of 800-900 °C with simultaneous analysis of products/reactants using gas chromatography. Electrocatalytic measurements with Electrochemical Impedance Spectra (EIS) analysis were also performed in single solid oxide cells, within the same temperature range, under H_2O electrolysis conditions by applying different pH_2O/pH_2 ratios.

Acknowledgments.

The research leading to these results has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under the project SElySOs with Grant Agreement No: 671481. This Joint Undertaking receives support from the European Union's Horizon 2020 Research and Innovation Programme and Greece, Germany, Czech Republic, France, and Norway.

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Highly and atomically dispersed Pt based catalysts – Tuning the electrocatalytic activity

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Polymer Electrolyte Membrane Fuel Cells, PEMFCs constitute a clean energy power source and an attractive candidate for many applications, due to their versatility, high efficiency and constructive simplicity[1]. In these systems, Pt based electrocatalysts have proven to be the most active and stable materials for both the anodic and cathodic electrode of the cell. However, high amounts of the expensive Pt catalyst are required at the cathode, due to the slow kinetics of the oxygen reduction reaction that determines the fuel cell efficiency, as well as at the anode when the gas feed is not pure hydrogen. Developing catalysts that would result in a serious reduction in the Pt loads at the electrodes, constitutes an effective strategy for the commercialization of PEMFCs[2].

The (electro)catalysts for many energy applications consist of expensive metals dispersed on solid supports. The performance and stability of the electrocatalysts strongly depend on the physicochemical characteristics of the materials, such as their surface area, their crystalline structure, size and shape of the particles and the interactions with the support. When the dispersion of the metal is high, there are many active metal atoms on a surface. Reducing the size to small metal particles or even atoms could significantly increase both the active surface and the catalyst activity through diversification or strengthening of the metal-support interactions[3]. However, it is very difficult to achieve high and/or atomic dispersion, as well as to maintain the morphology under realistic reaction conditions, since the small particles/atoms tend to agglomerate.

In this work, the preparation of a series of Pt catalysts took place. The deposition of the metal was realized through the reduction of metal precursor salts in a solution. Oxidized and covalently functionalized with pyridine groups[4] carbon nanotubes were used as the substrate. High and in cases atomic dispersion was achieved in the presence of the pyridine groups, denoting the formation of a Pt-N compounds/complexes. Thorough physicochemical characterization of the materials took place, in order to extensively study the effect of the substrate and Pt loading on the final properties like the shape and size of the crystallites, the morphology of the catalyst and the oxidation state of Pt. Additionally, the correlation between these properties and the electrochemical performance showed that it is possible to tune the dispersion and chemical state of platinum in order to enhance its electrocatalytic activity toward the oxygen reduction reaction.

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PGM-free Hydrogen Evolution and Oxidation Electrocatalysts for AEM Electrodes

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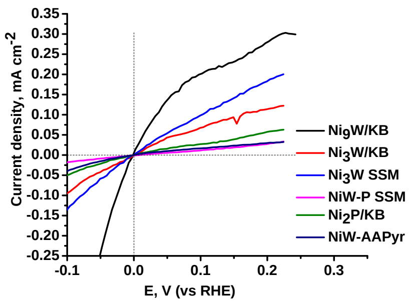
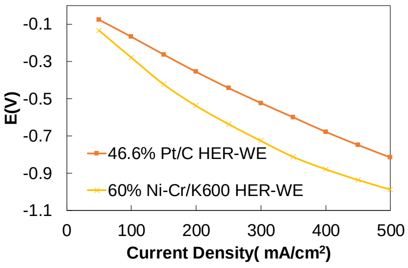
Anion Exchange Membrane Fuel Cells (AEMFCs) are fast developing alternative to Proton Exchange Fuel Cell (PEMFC) technology. A main advantage of this technology is the possibility of replacing PGM catalysts from both anode and cathode and therefore reducing the costs. For example, PGM-free oxygen reduction reaction (ORR) catalysts can outperform Pt/C in terms of their intrinsic activity [1] while several PGM-free electrocatalysts have demonstrated superior fuel oxidation performance[2]. In AEM electrolysis both Hydrogen [3] and Oxygen Evolution[4] PGM-free catalysts have been demonstrated. In the present work we focus on making novel Nickel-based Hydrogen Evolution (HER) and Oxidation (HOR) reaction catalysts, using alloying and mixed and low-coverage complementary metal oxides to fine tune surface-electrochemical interactions and reactions. While the goal of the work is to create bifunctional HER/HOR PGM-free catalysts the current efforts are focused on making the most active nickel-based HER or HOR catalysts. The catalysts will later be matched and hopefully bifunctional catalysts can be produced. (ARPA-E OPEN DE-AR0000688)

A series of nickel-based catalysts were synthesized to create mixed Nickel-alloys and oxides that promote the activation of water and hydroxyl groups on the catalysts. A range of wet-chemical routes was used to produce carbon-supported NiCr, NiW, NiZn, as well as Ni-Nitride and phosphide. The materials were characterized physical parameters such as crystal phase, size, and surface chemistry using XRD, XPS, and Raman Spectroscopy. These materials were evaluated in the reactions of HER/HOR in alkaline media by rotating disk electrode (RDE) method as well as MEA. In RDE for example the peak power current density of NiW/KB in HOR at 0.2V (vs RHE) achieved 0.3 mA cm^{-2}, which is one of the highest values for PGM-free materials. MEAs structures for NiW are still being optimized. NiCr/C on the other hand has already demonstrated excellent MEA performance, with improved catalysts being developed.



1M KOH saturated with H_2, 1600 RPM, 25 °C 0.2 mg_{NiW}/ $cm^{2,}$.



H_2 pumping: AS-4/A-201, 60°C, 300 sccm H_2/N_2 3mg/cm^2_{Pt} , 4mg/$cm^2_{NiCr.}$

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Engineered Carbons Supports (ECSs) for Cathode Oxygen Reduction Reaction Electrocatalysts

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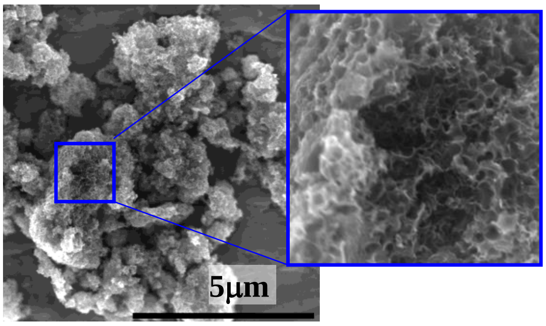
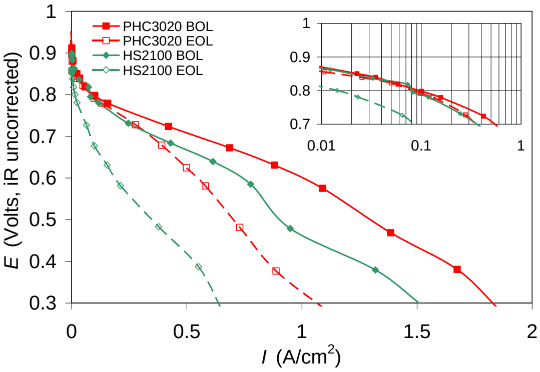
In the development of PEMFC fuel cells main attention is mainly devoted to the "active" portion of the catalysts system, the precious metal nanoparticles. While this approach has led to great improvement in specific activity, existing catalysts are still not meeting the combination of performance and cost necessary for the commercialization of PEMFC.

A key limitation to catalysts today arises from reliance on carbon blacks (CBs) supports that is a matrix for the precious metal catalyst nanoparticles, but which corrode under certain operating conditions. Carbon support modifications that rely on "top-down" graphitization of CB's have so far improved resistance to carbon corrosion, but at the cost of reduced stabilization of precious metal dissolution.

Pajarito Powder developed a "bottom-up" approach where Engineered Carbon Supports (ECSs) are made from organic precursors that yield graphitic materials with controllable morphology and increased stability to corrosion. This method based on technologies licensed from the University of New Mexico [1-3], Northeastern University, and Los Alamos National Laboratory allows manufacture of carbonaceous powders with high level of graphitization with reasonably high yields. The final chemical structure (doping with heteroatoms), morphology (pore size and modality) and surface area can be precisely controlled by selection of organic molecules and types of sacrificial supports.

Pt/C catalysts made using these Engineered Carbon Supports maintain performance under carbon corrosion test protocols and thus demonstrate their utility in achieving the performance/price balance needed for commercializing PEMFCs. The catalyst characteristics and performance, as well as economics of this approach will be presented and discussed. In addition, preliminary results in synthesis and performance testing of hybrid catalysts made using platinum metal group-free (PGM-free) oxygen reduction reaction (ORR) catalysts made by proprietary VariPore® platform with or without Pt nanoparticles added will be presented.





MEA details and testing conditions:
XL Membrane, 45wt% 1100 EW Nafion, 29BC GDL
Cathode: 0.1mg$_{Pt}$/cm^2
Anode: 0.05mg$_{Pt}$/cm^2 HS2100
100% RH, 1.5H$_2$: 2.5Air, 26psig

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Structure sensitivity of Cu electrodes in an alkaline environment?

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Cu electrodes have been the subject of increased interest over the past few decades. The potential application are diverse: from catalysts for CO_2, CO[1] and nitrate reduction[2] to nuclear waste storage canisters[3]. The initial anodic oxidation of Cu electrodes has been studied in detail.[4] However, only a handful of experiments have been devoted to the structural changes that occur at negative potentials, where H_2 evolution, CO_2 and CO reduction take place.

In this work we have investigated single crystal and polycrystalline Cu electrodes prepared by several *common* and *uncommon* experimental approaches. These include mechanical polishing, anodic oxidation in phosphoric acid, *i.e.*, electropolishing, and anodic oxidation in alkaline electrolytes. We compare these with electrodes prepared under ultra high vacuum (UHV) conditions, which are transferred directly to the electrochemical cell; this latter, *uncommon*, approach should, in principle result in more ordered and well-defined surfaces. The more common approaches lead to the formation of a passivating Cu-oxide film on the Cu surface with a thickness of several nm; the oxide would have to be removed under electrochemical conditions and presumably leads to irreversible structural changes. An additional benefit of the UHV approach is that it allows for the application of a huge variety of surface sensitive techniques to be employed before and after the electrochemical measurements.[5,6]

The electrochemical properties of the Cu electrodes in this work were investigated in 0.1 M KOH. Depending on the pre-treatment of the electrodes we can show that different redox features are observed in the potential region between hydrogen and oxygen evolution. Notably, the different pre-treatments also lead to a shift in hydrogen evolution by almost 250 mV. We will show that this shift cannot solely be explained by differences in surface area of the electrodes. With the combined UHV-EC set-up, STM measurements under UHV conditions were performed to determine surface structures and XPS measurements were performed to determine the oxygen content or different oxide compositions in the surface, near surface and the bulk, in both cases before and after the electrochemical investigations. We correlate these changes to the electrochemical phenomena mentioned above. In particular, the distinct electrochemical response of the UHV-prepared electrodes leads us to re-interpret earlier experiments on electropolished Cu single crystals.

Finally, we will discuss the relevance of these findings with respect to the electrocatalytic properties of Cu reported in the literature, especially with respect to CO and CO_2 reduction, which are performed in alkaline or weakly alkaline solutions.

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Approaching 2 W/cm^2 AEMFCs through Electrode Engineering and Controlling the Cell Water Content and Balance

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In recent years, advances in alkaline exchange membrane fuel cells (AEMFCs) with anion exchange membrane (AEM) solid polymer electrolytes have gained traction due to their distinct – and potentially game-changing – advantages over proton exchange membrane fuel cells. However, AEMs and AEMFCs are at a significantly less mature stage in their developmental than PEMFCs. This talk will focus on several fundamental and engineering advances that we have made recently that have enabled our team to create AEMFCs that are able to achieve up to 1.9 W/cm^2 peak power (> 2 W/cm^2 iR-corrected) and 100's of hours of stable operation, bringing AEMFCs much closer to the incumbent PEMFC technology.

In this study, we will discuss the influence of the membrane, ionomer and gas diffusion layer as well as the flow rate and dew points of the anode and cathode gases on AEMFC performance. Using a hydrophilic gas diffusion layer without a microporous layer increases membrane hydration, but also increases the possibility for flooding. Manipulating the dew points led to the counter-intuitive discovery that the cell performs better with the humidity higher at the anode than the cathode, despite water generation and electro-osmotic drag towards that electrode. In fact, removing too much water from the anode caused instability in the cell, while increasing the water at the anode decreased the membrane resistivity. Water back diffusion from the anode to the cathode likely plays an important role in membrane hydration and hydroxide transport through the membrane. We also find that high gas feed flow rate also increases cell performance, not by increasing the availability of reactants, but by improving water management. Finally, we will also discuss the behavior of the AEM and AEI powders in the presence of air both with and without CO_2.

Hydroxide Exchange Membrane Fuel Cells and Electrolyzers: From Materials to Devices

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Hydroxide exchange membrane fuel cells/electrolyzers (HEMFCs/HEMELs) can work with platinum group metal-free (PGM-free) catalysts and thus are potentially more economical than proton exchange membrane fuel cells/electrolyzers (PEMFCs/PEMELs). In this presentation I will present our recent work on the development of PGM-free hydrogen oxidation/evolution (HOR/HER) catalysts and oxygen reduction/evolution (ORR/OER) catalysts. I will also discussion the performance targets for membranes and catalysts for HEMFCs for automotive applications. I may also cover our recent work on a new class of HEMs that are highly ionically conductive, chemically stable, and mechanically robust.

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Engendering Reversibility to Hydrogen Evolution and Oxidation Reaction at High PH Environments

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Enabling reversibility to seemingly facile electrode processes such as HOR/HER are a challenge when subject to high pH. These clearly form technical barriers towards their application in hydrogen based energy storage devices such as in Hydrogen-Bromine batteries. While hydrogen oxidation under acidic conditions involves rapid kinetics, the same process under alkaline electrolyte conditions is known to be a very sluggish process with orders of magnitude lower kinetic activity and the concomitant need for a higher loading of precious metal catalysts. The real advantage of alkaline electrolytes is their ability to enable the use of non-precious fuel cell electrocatalysts as opposed to the corrosive acidic conditions where highly precious metals are unavoidable. The sluggish kinetics of hydrogen oxidation at high pH conditions seriously undermines this major advantage of alkaline electrolyte thereby necessitating the use of precious metal catalysts. *In this presentation, we undertake a fundamental mechanistic approach to unravel the causes of sluggishness of hydrogen oxidation reaction in alkaline electrolyte. We also delineate reaction mechanistic and catalysis parameters that are to design the next-generation of non-precious electrocatalysts for hydrogen oxidation*, and other related processes. This is achieved by unifying the principles of electrochemistry, surface science and coordination chemistry to comprehensively expound the scientific theory behind the *modus-operandi* of alkaline electrocatalysis.

This presentation is *not* only of interest to the fuel cell research community, but to the larger audience interested in the fields of catalysis, surface science, nanotechnology, and materials science for the following reasons:

1) For the first time, we unravel a non-Sabatier type catalysis principle involving a complex interplay between specifically- and quasi-specifically adsorbed reaction intermediates in the reaction layer. This is opposed to the conventional catalysis models that largely emphasize the importance of adsorption energies of the reaction intermediates on reaction pathways
2) We initiate a new trend that focuses on elucidating electrochemical reaction mechanisms as opposed to plethora of studies that focus on reaction kinetics and pathways. While reaction kinetics and pathways are easily accessible in catalysis studies, we have employed a combination of electrochemical and spectroscopic studies along with a series of thought experiments to unravel very profound catalytic reaction mechanisms that are largely unknown so far.
3) The findings from our work related to electrochemical charge transfer are expected to be applicable to other complex catalytic processes as well.

Oscillations of cell voltage and oxygen partial pressures of PEFC analyzed by using optical probes

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Reaction distributions inside polymer electrolyte fuel cells (PEFCs) are inhomogeneous, which is a major cause of the cell performance loss and the catalyst degradation. In order to mitigate the problems, understanding the reaction distributions inside a PEFC is important. Our group has been visualizing the 2D oxygen partial pressure ($p(O_2)$) on the surfaces of the gas diffusion layers (GDLs) of PEFCs during the power generation.[1-3] Recently, we developed a new apparatus that enables to measure the 3D distribution of $p(O_2)$ inside the GDL.[4]

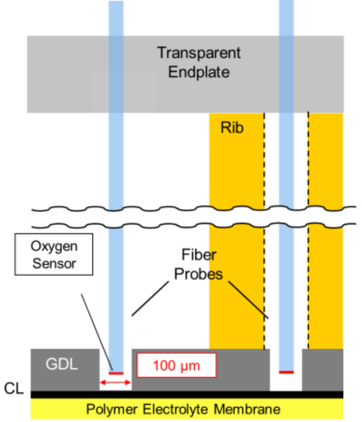

Fig. 1 Schematic representation of $p(O_2)$ measurement inside GDL using fiber probes

The PEFC was equipped with ten straight channels, 30 mm in length and 1 mm in width. The area of the catalyst layer was 20 mm x 20 mm. GDL without a microporous layer (MPL) (SGL, 28BA) was used. In order to measure $p(O_2)$ inside the GDL, we created 100-µm holes through the GDL. In the holes, we inserted multiple glass-fiber probes, 50 µm in diameter (Fig. 1). As an oxygen sensor, a luminescent dye compound, [tetrakis(pentafluorophenyl)porphyrinato]platinum was used, which absorbs blue lights and emits 650-nm red light; the emission intensity lowers as $p(O_2)$ increases. This dye film was coated on the apex of each probe (Fig. 1). The excitation light was introduced into each probe, and the emission from the dye film returned through the same probe, which was then captured by a CCD camera. Prior to the power generation, the calibration curves were obtained under the humidified mixed gases of O_2 and N_2 at each probe. The cell was operated at 60 °C with humidified air and H_2 at 60% RH. The emission intensities were converted to $p(O_2)$ by using the calibration curves.

Fig. 2 shows the cell voltage (black line) and $p(O_2)$ (filled and open red squares under the flow channel and the rib, respectively. See the inset in Fig. 2) using a GDL without an MPL. The apexes of the probes were located 10 µm from the catalyst-layer surface. Cell voltage oscillated at the period of ca. 4 s and with the amplitude of ca. 0.03 V at the constant current density of 0.6 A cm^{-2}. $p(O_2)$ measured at different positions and depths of the GDL oscillated at the same period and phase of those of the cell voltage. The $p(O_2)$ oscillation became larger toward the outlet. The oscillation mechanism will be discussed at the poster.

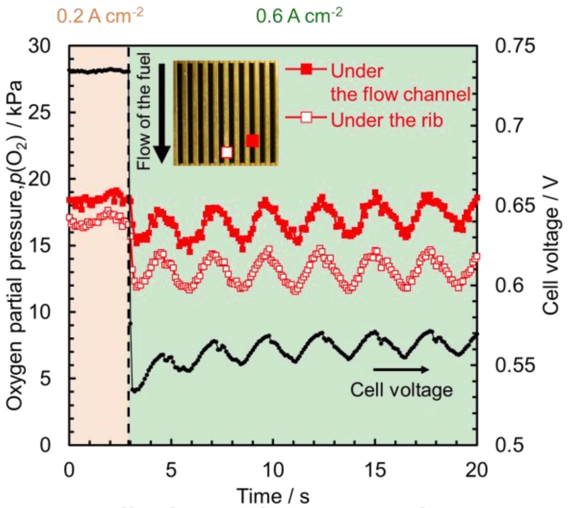

Fig. 2 Cell voltage and oxygen partial pressures inside GDL without MPL.

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A Practical Fuel Cell Membrane based on an Heteropoly Acid Functionalized Perfluorinated Polymer for Hotter and Drier Operation

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There is still a need for membranes that operate in proton exchange membrane (PEM) fuel cells at hotter and drier conditions than can be achieved with current materials, >100°C and <50%RH. One approach pursued by us and independently others is the use of inorganic super acids, such as the heteropoly acids (HPAs). HPAs are a sub group of the large class of metal oxygen clusters known as polyoxometalates in which a central heteroatom is surrounded by a number of W or Mo oxygen octahedra. For proton conductivity it is desirable that a strong negative charge be delocalized across the whole anion so that the proton will be as dissociated as possible. This limits the choice of HPA to the spherical tungsten based Keggin anion with as light as possible a heteroatom. This limit is reached with Si as the P based HPA is known to decompose in the presence of peroxide and the electron deficient nature of B renders the spherical Keggin anion unstable. Many fundamental studies have been undertaken on solid state HPA systems. These studies indicated that despite the original report in the early 80's that HPA had the highest proton conductivity reported at that time, that when dry there proton conductivity was disappointingly low at moderate temperatures.

Our approach is to make monomers from HPA and immobilize the HPA by polymerization into hybrid systems. In order to functionalize the Keggin anion one W oxygen octahedra is removed and a Si or P based organic functionality introduced that may be a monomer or a tether to a functionalized polymer backbone. Our first generation materials based on divinyl functionalized HPA and acrylate chemistry produced films with impressive conductivities, >100 mS cm^{-1} T >80°C and 50% RH. This model system contained ester linkages that we think would be hydrolysed under the harsh conditions of fuel cell operation and so we attached HPA via di-phosphonate linkages to perfluorinated polymers. Very recently we have fully perfected this chemistry and can now produce large area thin, 10 μm, high loaded HPA films for fuel cell cell operation. Not only do the materials have very low ASRs, <0.02 Ω cm^2, under all operating conditions (except freeze), but there is very little cross-over of H_2 and O_2. The materials also survive the DOE mechanical and chemical stability tests. The chemical stability is proof a theory; published by us using PFSA/HPA composite films, the HPA moieties decompose peroxy radicals. The measured water flux is also superior to PFSA materials allowing back diffusion of water during fuel cell operation. Unfortunately, we do not yet have a suitable ionomer for the electrodes to operate in a hot and dry environment and so fuel cell data using PFSA ionomers will be presented under more standard operating conditions.

This work is sponsored by DOE EERE and ARPA-E.

Insights into Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER) for Nitrogen-doped Carbon Nanostructures (CN_x) in Acidic Electrolyte

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Nitrogen-doped carbon nanostructures (CNx) are considered as promising alternatives to Pt-based catalysts for oxygen reduction reaction[1]. However, the nature of ORR active sites for CNx catalysts continues to be debated in literature. These catalysts do not get poisoned upon exposure to CO [2], CN^- [2] and H_2S [3] making techniques such as Mössbauer spectroscopy or X-ray Absorption Spectroscopy (XAS) widely used to understand the nature of ORR active sites in metal-centered ORR electrocatalysts of little use and increasing the challenge of identifying and quantifying the active sites in CN_x catalysts further.

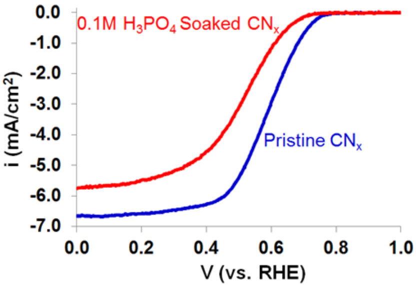

Figure 1. Polarization curves of CN_x catalyst before and after soaking in 0.1 M H_3PO_4

We have, for the first time, demonstrated a poison probe to reveal active sites in CN_x catalysts. Our results show that electrocatalytic activity of CN_x catalysts decreases significantly after phosphate anions adsorb on the CN_x catalyst surface. The H_3PO_4-soaked CNx sample exhibited significantly lower onset potential, half-wave potential and specific kinetic current (iK) than the pristine CN_x sample that was not exposed to H_3PO_4. The presence of $H_2PO_4^-$ species on the H_3PO_4-soaked CN_x sample was also conformed using characterization experiments. To gain insights into whether the loss in activity was due to loss of site density or intrinsic activity of each site, we soaked CN_x in various concentrations of H_3PO_4 and computed pyridinic-N site density using XPS. The loss in ORR activity was found to be linearly correlated with that in pyridinic-N sites (Figure 2). The results support two possible active site models namely i) pyridinic-N sites and ii) C atoms next to pyridinic-N. The former would be rendered inactive by protonation whereas the latter by a site blocking effect of phosphate ions which would also stabilize the pyridinic-NH sites [4].

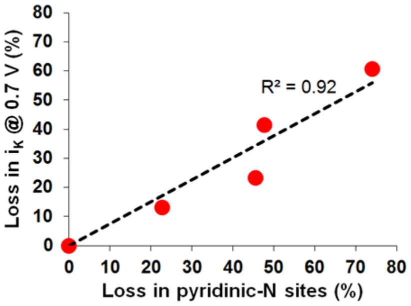

Figure 2. Correlation between the loss in ORR activity and that in pyridinic-N site density as a result of H_3PO_4 exposure

We also establish that CN_x catalysts are efficient bifunctional electrocatalysts for ORR and OER in acidic media. They exhibit significantly lower total overpotential requirements for the two reactions compared to state of the art precious metal-based catalysts namely Pt/C (for ORR) and Ir/C (for OER). To shed light into the nature of ORR and OER active sites in these CN_x materials, we synthesized these CNx materials at different pyrolysis temperatures. This allowed us to control the distribution of the nitrogen functionalities on the surface. This distribution as measured by X-ray Photoelectron Spectroscopy (XPS) was then combined with electrochemical measurements. Our results demonstrate the pyridinic-N species on the edge of a carbon plane and with a lone pair of electrons to correlate with both ORR and OER activity. Additionally, the combined overpotential decreased as the pyridinic-N content increased.

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Implementing Structural Disorder as a Promising Direction to Improve the Stability of PtNi/C Nanoparticles

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Due to strain and ligand effects, the simultaneous presence of concave and convex surfaces and their highly-defective nanostructure (atomic vacancies, grain boundaries), hollow Pt-rich/C electrocatalysts have proven to enhance remarkably the oxygen reduction reaction (ORR) kinetics. However, a technologically-relevant proton-exchange membrane fuel cell (PEMFC) cathode catalyst should be able to maintain its initial catalytic activity on the long-term. This is hardly feasible on nanocatalysts based on platinum alloyed with transition metals (PtM alloys, M being a transition metal) or M-rich core@Pt-rich shell nanoparticles due to the dissolution of the transition metal in the harsh operating conditions of a PEMFC cathode but the question remains open for nanocatalysts in which catalytic activity is not solely due to alloying effects. Herein, the ORR activity of solid or hollow PtNi/C nanoparticles with identical chemical composition but different fine nanostructure was evaluated before and after accelerated stress tests (ASTs) under simulated PEMFC operating conditions (5,000 potential cycles between 0.6 and 1.0 V *vs.* RHE at T = 80°C). Independently on the nanostructure, the combined physical, chemical and electrochemical results show that the losses in ORR activity are related to weakening of strain and ligand effects associated with the dissolution of Ni atoms. However, the catalytic advantage of hollow over solid PtNi/C nanoparticles was maintained during the ASTs. Hence, implementing structural disorder in PEMFC cathode electrocatalysts represents a promising direction to improve sustainably the ORR kinetics.

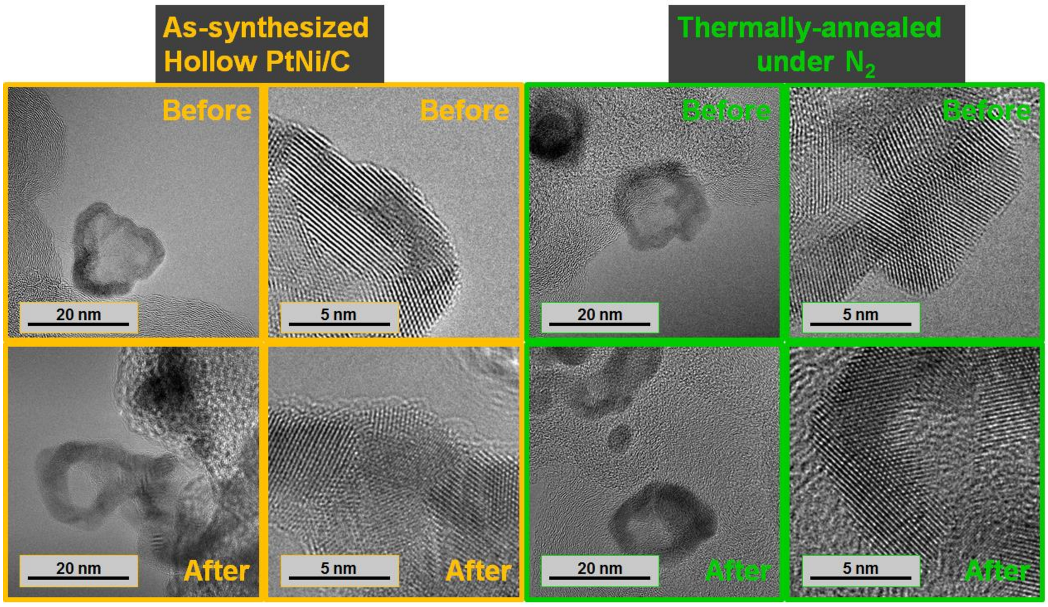

Figure 1: Representative HR-TEM images of the hollow PtNi/C nanostructures (fresh and N_2 -annealed PtNi/C) before and after an accelerated stress test composed of 5,000 cycles between 0.6 and 1.0 V vs. RHE at T = 80 °C

In-situ X-ray Diffraction of Hydrogen Fuel Cell Cathodes

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The ongoing commercialization of PEM hydrogen fuel cells has increasingly demanded lower precious metal catalyst loadings. A better understanding of platinum nanoparticle degradation mechanisms and electrochemistry will be essential in preserving fuel cell performance over increased device lifetimes. In-situ synchrotron x-ray diffraction/scattering is a powerful tool for characterizing commercial catalyst layers in an electrochemical cell[1-2]. Recent advances in hardware (x-ray flux, focus, energy resolution and detectors) presently allow time-resolved scattering measurements and diffractive imaging[3] without compromising electrochemical experiments. New cell designs[4] greatly improve the ease and flexibility of measuring membrane electrode assemblies under environmental conditions and Pt loadings relevant for fuel cell operation and degradation.

The structural effects and kinetics of platinum electrochemistry on nanoparticles can be directly probed using diffraction. The evolution of nanoparticle strain, atomic ordering, oxidation, and dissolution are monitored in the presence of adsorbing molecular species under potential control. Strategies to understand and mitigate the effects of x-ray induced beam damage are discussed.

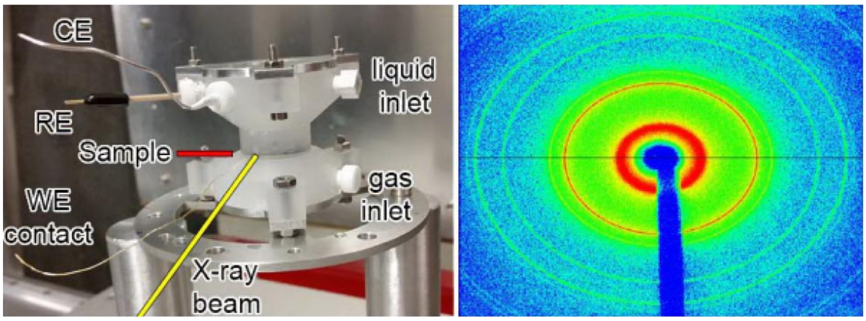

Figure 1. X-ray transparent half-cell suitable for high-energy x-ray diffraction of membrane electrode assemblies (left). X-ray powder diffractogram obtained from fuel cell cathode during oxygen reduction reaction (right).

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Iodine-stabilized PtCo/C as Highly Stable and Active Electrocatalyst for Oxygen Reduction Reaction

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Proton-exchange membrane fuel cells are expected to be one major clean energy source among others to replace fossil fuel in the future. However, they are still not ready to be commercialized on a large scale mainly due to insufficient activity of the oxygen reduction reaction (ORR) on the cathode. At present, supported Pt-based alloy nanomaterials are considered among the most efficient catalysts for ORR.[1] Pt alloyed with early transition metals, such as Fe, Co, Ni and Cu can effectively enhance the ORR activity, durability and lower the Pt usage therefore the cost.[2] However, the durability of supported Pt alloy is still a challenging issue owing to the rapid loss of non-noble metal leaching under detrimental corrosive ORR conditions.[3] Herein, we show an enhancement in both ORR activity and stability on carbon-supported PtCo nanoparticles by modifying surface with iodine. Iodine-stabilized PtCo/C (PtCo/C(I)) nanomaterial was synthesized through a facile in situ reduction method in the absence of surfactants and templates and followed by acid treatment. Cyclic voltammetries of PtCo/C(I), PtCo/C, Ptek PtCo/C and JM Pt/C were shown in Figure 1(a)(c)(e)(g), and the corresponding anodic polarization curves were shown in Figure 1(b)(d)(f)(h). Compared with the commercial JM Pt/C and Ptek PtCo/C catalysts, the specific activity (SA) of PtCo/C(I) is 3 and 1.1 times bigger and the mass activity (MA) is 2.2 and 1.3 times greater, respectively. Significantly, PtCo/C(I) with the stable iodine on the surface possessed much better SA and MA than PtCo/C without iodine.

The iodine-modification-caused enhancement in ORR activity and stability was evidenced by the better performance of PtCo/C with iodine on the surface compared with that without iodine, and further proved by the modification of iodine on commercial PtCo/C. Energy dispersive spectroscopy (EDS) results after accelerated durability tests (ADTs) showed that iodine could stabilize the PtCo nanoparticles by hindering the Co leaching, which was also confirmed by the iodine modification on commercial Ptek PtCo/C.

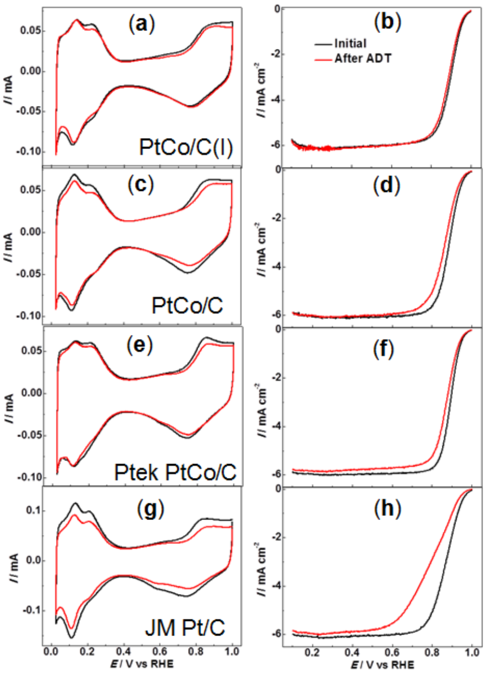

Fig.1 CVs before and after ADT on (**a**) PtCo/C(I), (**c**) PtCo/C, (**e**) Ptek PtCo/C and (**g**) JM Pt/C in O_2-saturated 0.1 M $HClO_4$ at a scan rate of 20 mV s^{-1} and rotation rate of 1600 rpm. ORR polarization curves before and after ADT on (**b**) PtCo/C(I), (**d**) PtCo/C, (**f**) Ptek PtCo/C and (**h**) JM Pt/C in Ar-saturated 0.1 M $HClO_4$ at a scan rate of 50 mV s^{-1}.

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Ternary Alloy Nanoparticles for Polymer Electrolyte Fuel Cell Electrocatalysis

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The commercialisation of Polymer Electrolyte Fuel Cells has been hampered by the high cost of platinum metal. Platinum is currently the most commonly employed catalyst for the oxygen reduction and hydrogen oxidation reactions essential to the operation of these cells due to its high activity and durability. Core@Shell nanoparticles with thin layers of platinum deposited on cores composed of cheaper materials have offered an attractive route towards the reduction of overall loading of platinum, with the retention of active catalyst surface area[1]. Additionally, a range of ternary alloy catalysts have been prepared, and have shown improvements in activity and durability as compared to commercially available standards[2,3].

Cognisance of these prior developments has shaped the approach taken in our own work. Ternary RuSePt nanoparticles have been prepared with core@shell-like surface segregation of platinum, and we intend to demonstrate that the incorporation of selenium protects the ruthenium 'core' from degradative oxidation, enhancing catalyst lifetime. Ternary alloy nanoparticles have thus been synthesised by hot injection of the precursors in oleylamine, and have been characterised using a range of imaging, spectroscopic and diffraction techniques. Controlled formation of well dispersed ternary alloy RuSePt nanoparticles has been confirmed using high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS), (Figure 1). The nanocatalysts were tested electrochemically using a combination of ex-situ rotating disk electrode experiments and in-situ fuel cell testing to establish their catalytic activity and, importantly, demonstrate their enhanced durability.

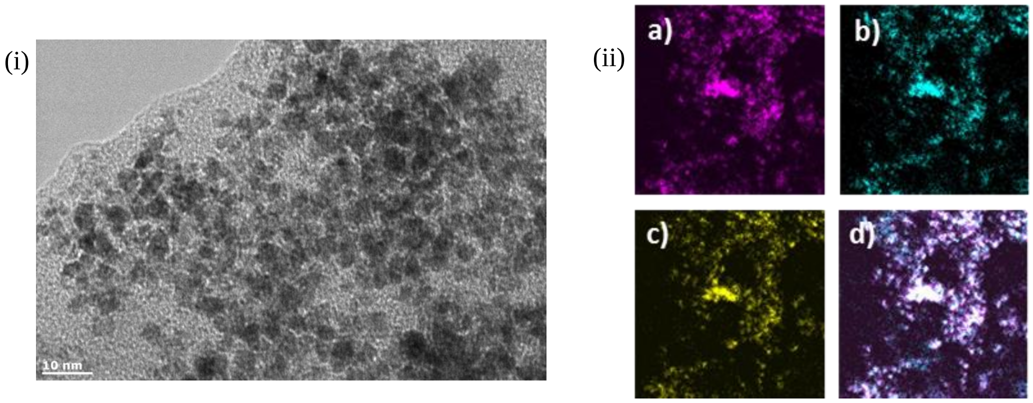

Figure 1. HAADF-STEM image (i) and EDS elemental maps (ii) of as prepared RuSePt particles and supported RuSePt/C, respectively. EDS maps show a) Ru, b) Se, c) Pt and d) an overlay of a), b) and c).

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Structure-to-Property Relationships in PGM-free Catalysts: Integrating DFT and Spectroscopic Approaches

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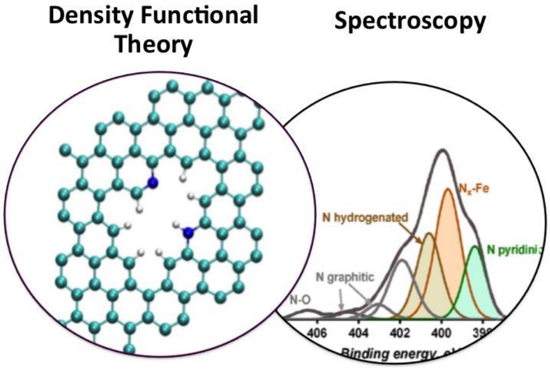
Development of active and durable platinum group metal-free (PGM-free) electrocatalysts based on metal-nitrogen-carbon (M-N-C) materials system critically depends on an understanding of different defect sites/moieties and the ways they participate in the oxygen reduction reaction (ORR). The structure-to-property relationships in these materials are usually established through correlations of observed electrocatalytic activity with spectroscopic methods such as X-ray photoelectron (XPS), X-ray absorption (XAS) and Mössbauer spectroscopy. This is a challenging task that has recently become more feasible by coupling improved spectroscopic techniques with first principles calculations to more accurately interpret the spectroscopic features.

We have recently shown how Density Functional Theory (DFT) calculations of core level binding energy shifts for well-defined defects of the PGM-free catalysts can facilitate the interpretation of XPS measurements.[1] Previous calculations include core level binding energies of graphitic N as well as N-coordinated to Fe and Co in different $M{-}N_x$ motifs/moieties.[2-3] A combination of N 1s XPS and first principles calculations of nitrogen-containing model electrocatalysts[4-5] was further used to elucidate the nature of the nitrogen defects that contribute to the binding energy range of the N 1s XPS spectra above 400 eV. The results confirm that the peak positioned at 400.7 eV in the N 1s XPS spectra of PGM-free catalysts, which is typically assigned to *pyrrolic nitrogen*, contains contributions from other hydrogenated nitrogen-containing moieties such as *hydrogenated pyridinic* functionalities.[5] Hydrogenation and protonation of different nitrogen-containing defects play a major role in ORR activity of the PGM-free catalysts across different pH ranges.

This paper will place a particular emphasis on identifying the separate role of nitrogen- and Fe-N-containing *in-plane* and *edge defects*. Significant variations in the calculated N 1s binding energies show that the chemical groups, which are present on the graphene edges and in the vicinity of Fe-N or N-defects, have a substantial impact on the charge distribution at these sites and can, therefore, influence their reactivity and selectivity.

We will demonstrate how DFT can be used to calculate Mössbauer ^{57}Fe quadrupole splitting in different Fe-containing benchmark materials and $Fe-N_x$ defects in M-N-C catalysts. The quadrupole splitting, which arises from the non-spherical nuclear charge distribution in the I=3/2 excited state in the presence of an electric field gradient at the ^{57}Fe nucleus, was evaluated from the DFT calculated electric field gradient tensor at the Fe nucleus. The results illustrate how combining DFT/Mössbauer approach predicts spectra of moieties that are not found as stable molecules and facilitate establishing key structure-to-property relationships in PGM-free catalysts.



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Effects of Geometry on Cyclable Membraneless Flow Battery Design

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Flow batteries are considered an attractive and flexible technology to help meet the increasing demand for grid-scale energy storage, but they remain expensive.[1] Membraneless electrochemical system architectures have been proposed in order to reduce high costs associated with ion exchange membranes.[2,3] However, while membraneless fuel cells have received considerable scholarly attention resulting in large improvements in power density, relatively little attention has been given to cyclable membraneless flow batteries.[4] A critical question that remains unresolved is whether and how a flow battery without an ion exchange membrane can sufficiently prevent the loss of active material from one electrolyte stream to the adjacent stream, in order to allow a reasonably high coulombic efficiency during cycling. This work considers several flow cell architectures and analytically predicts this crossover between streams over a range of Péclet numbers. The results of this analysis indicate that some flow cell geometries will not support cycling, while others may limit crossover enough to allow it. Experiments measuring crossover in a prototype cell based on one of these architectures and using the hydrogen-bromine chemistry will be used to validate the analysis. These results will be used to determine the best operating conditions for future experiments testing the membraneless flow battery's ability to cycle efficiently.

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Synthesis and Mechanistic Study of Pt-based Tri-metal Catalysts for the Ethanol Oxidation Reaction

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Renewable energy is a field that has been looking for different fuels and systems to meet the ever-increasing energy needs of current society. As of 2014, approximately 85% of global energy usage is through the use of nonrenewable resources.[1]Among several potential sources of clean energy, ethanol is a strong candidate for further research. Ethanol has a high energy density, is a nontoxic liquid, easy to store, easy to transport, and is renewable through the carbon cycle.[2] What makes the commercialization of ethanol fuel cells difficult is ethanol's slow and incomplete oxidation to CO_2, even with some of the best electrocatalysts that have been reported.[3,4] In our research, we have synthesized a ternary PtNiCu electrocatalyst through a one-pot hydrothermal synthesis. From initial studies, PtNiCu shows interesting results by having one of the lowest onset potentials for the ethanol oxidation reaction (EOR) as presented in Figure 1. From IR and NMR studies, we also see a preference for PtNiCu to form CO_2 compared to previously reported catalysts. In this presentation, we will discuss these results in the context of our current mechanistic understanding toward designing better electrocatalysts that will have higher activity in oxidizing ethanol to CO_2 at low potentials.

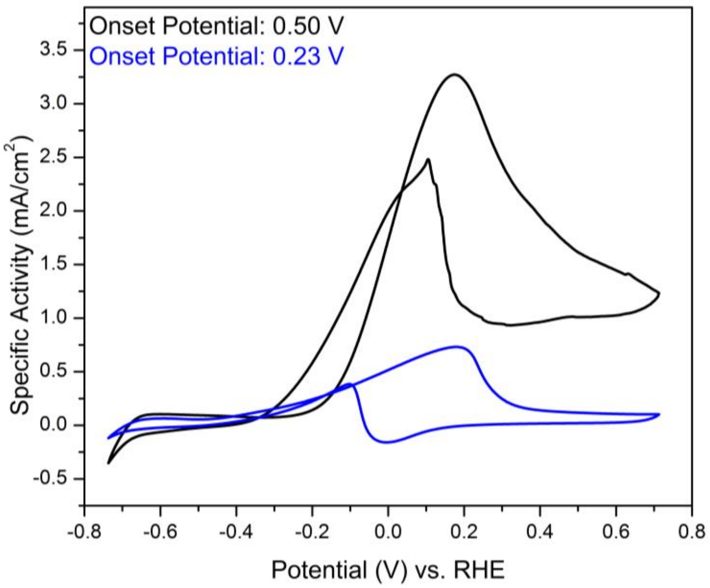

Figure 1. The cyclic voltammograms of ethanol electro-oxidation in 0.1 M NaOH + 0.5 M ethanol on a representative PtNiCu sample (blue) vs. a commercial carbon-supported Pt sample (black). The onset potential of the former (0.23V) is much lower than that of the latter (0.50V), indicating a much higher activity.

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Analysis of proton transport in ionomer/carbon layers using hydrogen pump technique

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To meet 2020 DOE target of 0.125 mg/cm^2 of Platinum (Pt) loading for polymer electrolyte fuel cells (PEFCs') there is a need to reduce Pt use at the cathode. Optimizing electrode morphology with a more uniform ionomer film distributions is a key to reduce oxygen transport resistance at these low Pt loadings[1]. Furthermore, to reduce proton transport resistance in the electrodes higher effective conductivity is desired, which scales with ionomer volume fraction divided by tortuosity. The challenge to electrode optimization is partially due to lower thin film ionic conductivity in the electrode compared to bulk ionic conductivity. This phenomenon is attributed to confinement effects and weak ionomer phase separation. [2]

Ionic conductivity of the PEFC electrodes depends on the ionomer distribution and also on the presence of condensed water to aid in proton transport to electrocatalyst in ionomer-free regions. With the aid of hydrogen pump experiments, we have measured ionic conductivity of the pseudo-catalyst layer (without Pt) made of Vulcan XC-72 carbon and 825 EW 3M ionomer with the range of ionomer to carbon (I/C) ratios of 0.6 – 1.4. These carbon layers were inserted as interlayers between two membranes within the standard PEFC set-up, as previously reported by Iden et al[3]. To extrapolate interfacial and membrane resistances experiments were performed on stacked 2, 4, 6 and 10 carbon layers. In the experiments hydrogen gas is fed into anode and cathode at flow rates of 1 LPM at 80°C, 50%-120% RH and voltage range of 0V to -0.4 V. Polarization curves were plotted and the resistivities were extrapolated from the linear portion of the graph using Ohm's law. As shown by Figure 1 linear trend was observed for the ionic resistivity as a function of carbon electrodes thickness with increasing resistance at lower RH.

After subtracting contact and membrane resistivities (at zero y intercept) effective resistivity for the carbon layers was plotted as a function of RH and compared to the measurements of Nafion 212 membrane. Using the effective ionic conductivity of the carbon layer, ionomer tortuosity can be determined by knowing the ionomer conductivity in the electrode reported in literature. We compare the calculated ionomer tortuosity with that obtained by ionomer mapping from nano X-ray computed tomography.

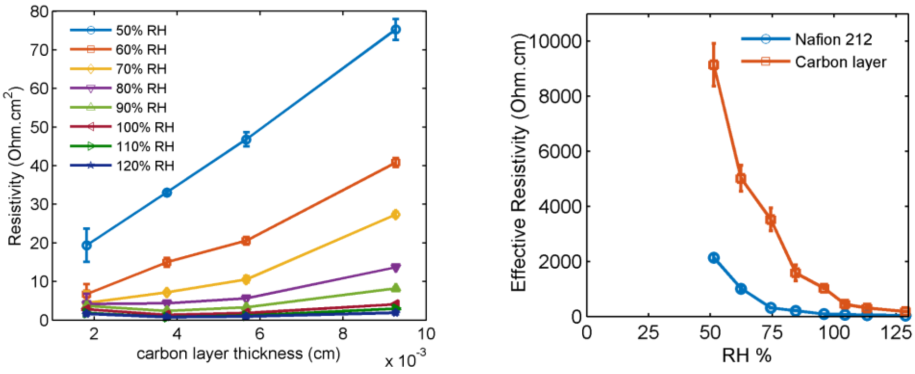

Figure 1: a) Plot of resistivity vs carbon electrode thickness for I/C=1.0 for various RH% b) Plot of effective resistivity per unit thickness of carbon electrode vs RH%.

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Graphitic nitrogen-doped electrodes as model catalysts for oxygen reduction reaction

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Nitrogen substitution and functionalization of carbon materials can be used to modulate the electronic properties, the morphology and the surface chemistry of carbon materials. Nitrogenated carbons have showed catalytic activity for the oxygen reduction reaction (ORR), resulting in a potential alternative for the substitution of precious metal catalysts in energy applications, such as metal-air batteries and fuel cells [1, 2]. Nitrogenated carbons typically contain a mix of nitrogen species thus making it difficult to relate an electrochemical response to individual active sites. Pyridinic- and graphitic-N have been proposed as nitrogen species responsible of the catalytic activity [3, 4], however, the preparation of model electrodes with exclusively pyridinic-N or exclusively graphitic-N is necessary to test mechanistic hypotheses on the role of these specific groups.

Herein, we report the synthesis, characterization and electrochemical testing of model carbon materials with graphitic-N sites exclusively. Amorphous nitrogenated carbon films were prepared using a combination of physical deposition and thermally-driven reactions yielding nitrogenated carbon materials with smooth topography, excellent electrical contact and homogeneous graphitic-N site presentation. These materials were used to study the effect of these specific sites on the ORR activity. Graphitic-N sites were found to improve the onset potential by up to 140 mV with respect to the corresponding undoped materials. Also, a mixed 2e/4e mechanism was evident from rotating ring disk electrode (RRDE) measurements. Despite the high activity observed, graphitic-N sites were found to undergo extremely fast degradation under ORR conditions. We will discuss in-situ electrochemical and ex-situ spectroscopic methods that probe the degradation process. In light of our findings, we propose a strategy to quantify the effect of graphitic nitrogen sites present in a carbon matrix on the electrode activity.

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Stability of binary metallic ceramics in the HER reaction – feasible HER electrocatalysts in acidic medium?

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Fundamental understanding of the behavior of non-noble based materials towards the hydrogen evolution reaction (HER) is crucial for the successful implementation into practical devices. During electrolysis, cost-efficient materials that can withstand the harsh operational conditions (pH, electrode potential, etc.) are crucial, and only a few materials have proven to accept this challenge. To date, binary metallic ceramics (BMC) with distinct properties and high surface area such as phosphides[1-3], sulfides[4-6], carbides[7,8] or oxides[9] have been reported as highly active, cost-efficient candidates to replace low abundant and expensive precious group metals for the HER.[10,11] Unlike platinum, which has been shown to be stable when no transient oxide formation/reduction is involved, the intermittent power input condition may indeed affect the durability of the aforementioned materials. Here, we study a range of reported non-noble HER catalysts from different compositions, including metal carbides, sulfides, phosphides, their base metals and their native oxides and elaborate on their stability and degradation behavior. Explanations of their stability (thermodynamically and kinetically) are discussed, challenges for the application in real devices are analyzed, and measures how to circumvent dissolution are suggested.

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Reduced Graphene Oxide Modified Ni Foam as an Efficient Hydrogen Evolution Electrode

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Alkaline water electrolysis represents promising way of the conversion of the electrical energy into the chemical energy of hydrogen bond. It is industrially well-established technology, which was, however, originally designed with main focus on durability and robustness rather than on the efficiency and flexibility. Besides the fact that alkaline water electrolysis is well known technology, it offers additional advantages over the alternative polymer electrolyte (PEM) water electrolysis. Possibility to use non-platinum metals as the catalysts for hydrogen (HER)/oxygen (OER) evolution reaction belongs to the crucial ones. Ni is the typical representative of the catalyst with the high catalytic activity for both HER/OER and excellent resistance to operational conditions of the alkaline water electrolysis. However, formation of the hydride layer on the Ni subsurface may hinder its electrocatalytic activity towards HER. To prevent this phenomenon, surface of the Ni electrode can be modified by the layer which will make desorption of the hydrogen easier allowing thus to maintain the subsurface of Ni free of hydrides and long-term active.

Graphene has attracted a lot of attention from 2004 when it was discovered by Geim and Novoselov. It is defined as a planar hexagonal ring containing a sp^2 hybridised carbon atom with a two dimensional (2D) honeycomb lattice. Over the years, graphene-supported metal nanoparticles have attracted a great deal of attention and it was found that graphene acts as an active support in these systems. For example, for hydrogen storage, graphene enhances the performance of the composite material through H spillover, enabling further tuning of its properties by the introduction of defects and/or dopants. In HER catalysis, the same process is of immense importance. It enables cleaning of the catalyst surface due to the transfer of discharged H to the active support where it recombines to H_2, allowing the reaction to proceed faster [1].

The objective of the present study is to prepare nickel foam electrode modified by reduced graphene oxide (RGO) and to test its activity for the HER in alkaline water electrolysis with anion selective polymer membrane.

To achieve this aim, graphene oxide was prepared by chemical oxidation of graphite using H_2SO_4, H_3PO_4 and $KMnO_4$ with consequent ultrasonic exfoliation. Prepared RGO was deposited on the surface of Ni foam electrophoretically from colloid dispersion of graphene oxide powder in a mixture of the isopropyl alcohol and potassium hydroxide. The prepared layers were tested by means of FTIR, Raman spectroscopy, XPS, SEM, EDX and TEM as well as electrochemically (cyclic and linear sweep voltammetry) and under the conditions of the alkaline water electrolysis in a laboratory single cell alkaline water electrolyzer.

The results indicate that RGO modified Ni foam electrode represents promising cathode for alkaline water electrolysis due to the spillover effect of the RGO which prevents formation of the hydride subsurface layer.

Acknowledgement

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Transition Metal and Nitrogen Codoped Carbide-Derived Carbon Catalysts for Oxygen Reduction Reaction in Alkaline DMFC

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The oxygen reduction reaction (ORR) plays a great role in developing a sustainable energy economy for the future. However, due to the sluggish kinetics of the ORR platinum-based catalysts are mainly used to make it viable in energy-conversion devices such as fuel cells. In recent years, a new class of efficient catalysts for the ORR has emerged, which incorporate nitrogen-coordinated metal species ($M-N_x$) and/or metal particles covered by graphitic nitrogen-doped carbon layers, which both have been shown to be active towards ORR. In this work, we propose a method to use a carbide-derived carbon (CDC) material, which is then doped with nitrogen and transition metals as an ORR electrocatalyst (M-N-CDC). The use of a CDC with defined porosity as a starting material allows for control of porosity of the final catalyst, which has been shown to be crucial in increasing the ORR activity [1]. The CDC material is doped by pyrolysis in the presence of dicyandiamide and either $FeCl_3$ or $CoCl_2$ using a previously optimized procedure [2,3]. By examining the materials using various physical and electrochemical techniques such as SEM, XPS, N_2 physisorption and RDE we reveal the origins for the ORR activity of these catalysts. In alkaline conditions the catalysts perform superbly, with both Co- and Fe-containing catalysts rivaling the activity of commercial 60 wt.% Pt/C. The BET analysis showed that the pores with a width between 1 and 1.5 nm contained $M-N_x$ active sites, which we propose to be the reason for increased ORR activity, otherwise the catalysts retain their highly microporous nature during the doping procedure, which has been proven to be beneficial for ORR electrocatalysis. XPS and SEM-EDX investigation also confirmed the successful doping of the catalysts. The materials were then tested in alkaline direct methanol fuel cell, where they show performance comparable to 60% Pt/C, with the Fe-based catalyst surpassing even that.

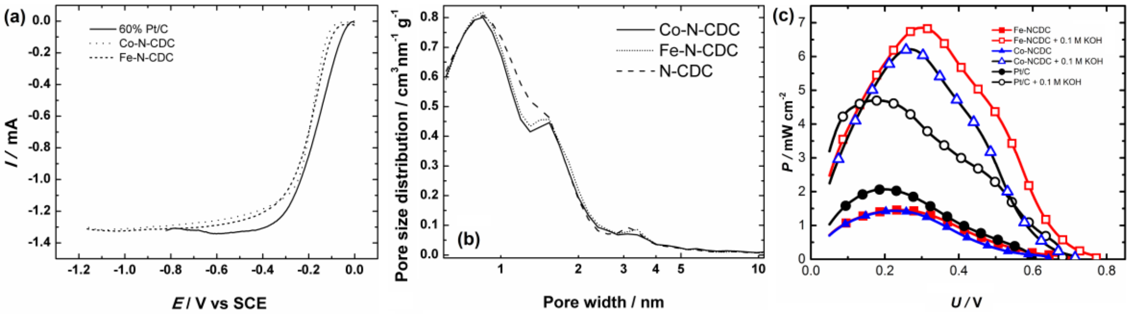

Figure. (a) Comparative RDE results for ORR on M-N-CDC and 60 wt.% Pt/C catalysts in O_2 -saturated 0.1 M KOH at 1900 rpm, (b) pore size distribution for M-N-CDC and N-CDC catalysts, (c) power density curves for the M-N-CDC catalysts and Pt/C with and without the addition of 0.1 M KOH.

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3D Printed Solid Oxide Electrolysers

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Deployment of renewable electrical power systems is increasing rapidly worldwide, driven by decarbonisation needs. Electrolytically-generated fuels may replace conventional sources in applications such as H_2 for transport and CH_4 for heat, produced by (co-) electrolysis of H_2O and H_2O / CO_2, respectively. High-temperature solid oxide electrolysers [1] are potentially attractive options to synthesize these fuels, due to their fast kinetics and high efficiencies, without requiring precious metal catalysts. Normally, they incorporate oxide ion-conducting metal oxide electrolyte(s), such as yttria-stabilized zirconia (YSZ, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$). During electrolysis, H_2O and / or CO_2 are (co-)reduced, typically at porous Ni-YSZ composite cathodes; oxide ions are injected into the electrolyte and are oxidized at composite anodes, such as lanthanum strontium manganite (LSM, $La_{0.8}Sr_{0.2}MnO_3$)-YSZ. Hence, the reactions for H_2O splitting are:

Ni-YSZ Cathode:
$$H_2O(g) + 2e^{-}(Ni) \rightarrow H_2(g) + O^{2-}(YSZ) \tag{1}$$

LSM-YSZ Anode:
$$2O^{2-}(YSZ) \rightarrow O_2(g) + 4e^{-}(LSM) \tag{2}$$

During long-term electrolysis of both H_2O and CO_2, severe anode degradation occurs, believed to occur due to evolution of O_2 (g) into non-percolating pores, causing anode fracture, deactivating reaction sites [2]. Fabrication of anodes with reproducible microstructures by 3D printing [3] is a prospective solution.

Results will be reported of 3D inkjet printing of YSZ-LSM (700-850 °C) and gadolinium-doped ceria electrolyte (CGO) (500-600 °C) with CGO-lanthanum strontium cobalt ferrite (LSCF, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$) anodes of solid oxide electrolysers, together with their electrochemical performance (Figure 1a). Increasing specific surface areas, e.g. by pillar arrays (Figure 1b) results in spatial distributions of potential and current densities, modelling of which was used to predict local (Figure 1b) and reactor-scale (Figure 1a) performances and to select reproducible geometries to be printed. Examples of such simulations will be presented.

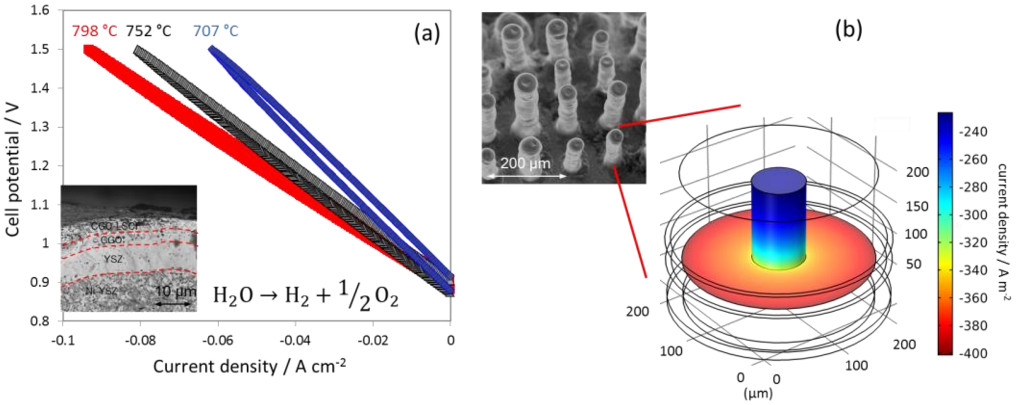

Figure 1. (a) Potential difference (U) – current density (j) – temperature (T) data for H_2O electrolysis with H_2O|Ni-YSZ|YSZ|CGO|CGO-LSCF|O_2, 3D printed except for the Ni-YSZ substrate; (b) predicted (electrolysis) current density distribution with height of a single 3D printed pillar cathode, of the array shown in the photomicrograph [3].

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Interpretation of measurements of potential of zero total charge at electrocatalysts for low-temperature fuel cells

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The potential of zero total charge (PZTC) at an electrode is defined as the potential at which a change in the electrode surface area is not accompanied by a flow of charge to the electrode [O. A. Petrii, *Russ. J. Electrochem.* **49** (5) (2013) 401–422]. In practice the PZTC for electrocatalysts such as platinum is approximated by finding the potential at which there is no flow of charge to the electrode during displacement of adsorbates at the catalyst surface by CO, which may more appropriately be termed the potential of zero displacement charge.

The PZTC is interesting in the context of electrocatalysis since, being related to the bonding of adsorbates at the electrodes, it is a quantity also related to the activity of the electrocatalyst. The adsorbates being displaced in the measurements do not have to be the same as those involved in the electrocatalytic reaction being studied owing to scaling relations between the binding energies of different adsorbates, established by density-functional theory (DFT) calculations [G. A. Tritsaris, J. Rossmeisl, *J. Phys. Chem. C* **116** (22) (2012) 11980–11986]. The PZTC has thus been used to interpret the oxidation reduction reaction (ORR) and oxidation of CO [K. J. J. Mayrhofer, B. B. Blizanac, M. Arenz, V. R. Stamenkovic, P. N. Ross, N. M. Markovíc, *J. Phys. Chem. B* **109** (30) (2005) 14433–14440], and has been correlated to the density of steps vicinal to Pt(111) basal plane surfaces [J. M. Feliu, E. Herrero, V. Climent, *Electrocatalytic Properties of Stepped Surfaces*, in E. Santos and W. Schmickler (Eds.) Catalysis in Electrochemistry, John Wiley & Sons, Hoboken, New Jersey, 2011, Ch. 4, pp. 127 – 163].

In this work we compare the catalytic activity of Ru@Pt core-shell catalysts for the ORR, oxidation of dissolved CO, and the methanol oxidation reaction (MOR) to that of Pt and RuPt catalysts, and show that the PZTC for these catalysts is correlated to their activity for these reactions. We employ DFT-based scaling relations from the literature to relate the PZTC to binding energies for intermediates involved in the different reactions, and show that measurements of the PZTC can be used to infer the rate-determining step as well as trends in the onset potential. The correlations successfully explains the increase in onset potential for both the ORR and the MOR, i.e Pt > Ru@Pt > PtRu.

Development of Group 4 and 5 Oxide-Based Cathodes for PEFCs

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Polymer electrolyte fuel cells are expected for the residential and transportable applications, especially for the automobile use, due to their high power density and low operating temperature. In order to commercialize the fuel cell vehicles widely, the development of a non-noble metal cathode is strongly required. We think that new non-noble metal cathodes should have both high stability and high catalytic activity for the oxygen reduction reaction (ORR). In particular, we believe that high stability in the cathode condition is essentially required for the cathode catalyst. Group 4 and 5 metal oxides, which are well known as valve metals, are stable even in acidic and oxidative atmosphere. However, these oxides are generally insulators. In order to create active sites for oxygen reduction reaction, these oxides should be modified by the formation of the oxygen vacancies and/or the substitution of foreign atoms. We have tried to apply group 4 and 5 metal oxide-based compounds to the cathode catalysts. We successfully obtained nano-sized oxide-based particles dispersed on multi-walled carbon nanotubes to increase the ORR current density [1]. In addition, we recently proposed oxide-based compounds as both precious-metal- and carbon-free cathodes to achieve the superior durable cathodes.

Powders of group 4 and 5 metal compounds (metal organic complexes that contain nitrogen) were dispersed on multi-walled carbon nano-tubes (MWCNT) to prepared the precursors. The precursor was heat-treated at 900°C under low partial pressure of oxygen. After the heat treatment, as shown in Fig.1, the compounds changed to nano-sized oxides that contained small amount of carbon and nitrogen. In addition, we revealed that these oxides had some oxygen vacancies that could act as active sites for the ORR. The nano-sized oxides on MWCNTs showed definite ORR activity and could act as cathode catalyst in the single cell [1]. However, carbon materials are easy to be oxidized at high potentials. Therefore, we tried to develop carbon-free oxide-based cathodes to achieve the superior durability.

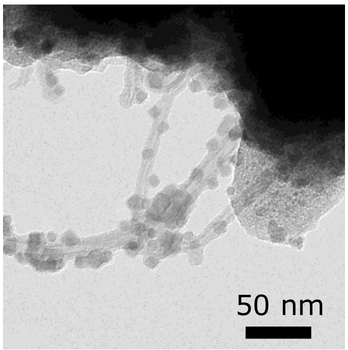

Fig.1 TEM image of zirconium oxide nano-particles on MWCNTs.

We prepared mixture of titanium magneli phase (Ti_4O_7) as electric conductive with niobium-doped TiO_2 ($Ti_xNb_yO_z$) as carbon-free cathodes [2]. The ORR performance of the Ti_4O_7-$Ti_xNb_yO_z$ did not deteriorate during potential cycling from 1.0 to 1.5 V vs. RHE as a start/stop cycle test. Therefore, we successfully demonstrated that the carbon-free oxide-based cathodes had high durability in high potential region. These results indicated that precious-metal-free and carbon-free oxide-based cathodes had great potential as alternative catalysts for platinum.

Acknowledgements

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Tuning Electrocatalysts through Doping

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Electrochemical splitting of water into oxygen and hydrogen is a central process for the generation of renewable energy carriers. Industrially the oxygen evolution reaction (OER) is catalyzed by Dimensionally Anodes (DSA), which consist of a mixture of Ir and Ru oxides embedded into a TiO_2 matrix[1]. These electrodes combine long term stability with a comparably high activity[1]. Driven by the need to find alternatives to scarce and expensive Ir and Ru oxides, the potential of abundant transition metal oxides for water oxidation has been explored[2]. Among the considered materials Mn oxides were found to show a promising activity. A possibility to improve the activity of pure Mn oxides further is mixing with inert or non-inert ions[3]. Depending on the oxide this may change the electrochemical properties either by opening more efficient water oxidation mechanisms[4] or by altering the binding energies of the intermediates[5].

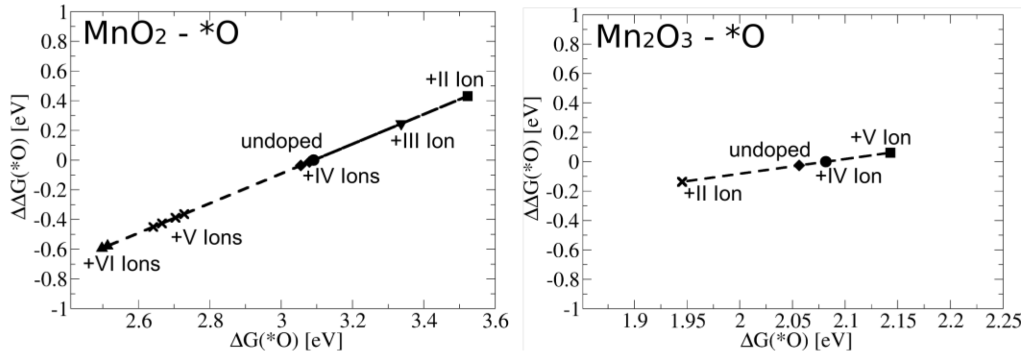

Figure 1: Influence of inert ion doping on MnO_2 (left) and Mn_2O_3 (right).

Inspired by the recent findings suggesting, that inert ions can have a significant influence on the activity of TiO_2[5], we decided to explore the possibility of improving the activity of Mn oxides through doping with inert ions by means of Density Functional Theory (DFT) computations. Our calculations indicate, that doping with different valent inert ions has a strong influence on the activity of β-MnO_2 while it does not affect Mn_2O_3. In Figure 1 the relative changes of the *O binding energies upon doping with inert ions are depicted. In particular the addition of higher valent +V and +VI ions to β-MnO_2 stabilizes the OER intermediates while they are destabilized upon doping with lower valent +II and +III ions. This discovery will be the starting point for a detailed discussion of the factors governing the influence of dopants on Mn oxides. We will present an explanation for the very different behavior observed for the two oxides based on detailed analysis of the electronic structure. The insights gained for Mn oxides will be generalized to other transition metal oxides with relevance to electrocatalysis.

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Oxygen Reduction Reaction on Nitrogen-Doped Graphene Supported Ag Nanoparticles

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In this study three methods were employed to prepare nitrogen-doped graphene supported silver nanoparticles (Ag/NGO). Nitrogen doping of graphene oxide was achieved by pyrolysis of dicyandiamide in the presence of rGO sheets at 800 °C. Silver nanoparticles were synthesized using $NaBH_4$ (Ag/NGO1), glycerol (Ag/NGO2) and ascorbic acid (Ag/NGO3) as reducing agents. The prepared catalysts contained 40 wt% Ag. The materials were characterized by scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy and were electrochemically tested towards oxygen reduction reaction in alkaline solution. The best nanoparticle distribution and smallest Ag particle size was obtained in Ag/NGO1. This catalyst was further studied by STEM and EDS, which affirmed the distribution of silver nanoparticles and showed that the surface of graphene is uniformly doped with nitrogen. The XPS analysis showed the surface nitrogen-to-carbon atomic ratio to be 0.07 and based on Ag-to-carbon ratio, higher degree of particle agglomeration was suggested for Ag/NGO2 and Ag/NGO3.

The electrochemical measurements in alkaline solution revealed that the oxygen reduction reaction on Ag/NGO proceeds via 4-electron pathway to yield water, while on pure support material the number of electrons transferred per oxygen molecule was about 3. The catalyst prepared using glycerol exhibited the highest mass-activity. Adding Ag nanoparticles onto N-doped graphene improved the mass-activity up to 3.5 times. The Tafel plots of Ag/NGO and bulk Ag were parallel to each other with the slope value about -80 mV at low current-densities while the Tafel slope of NGO was about -55 mV. These values suggest that the reaction mechanism is the same for all tested Ag–based catalysts. The results obtained in this study suggest that Ag/NGO is a suitable catalyst for oxygen reduction reaction in anion exchange membrane fuel cells.

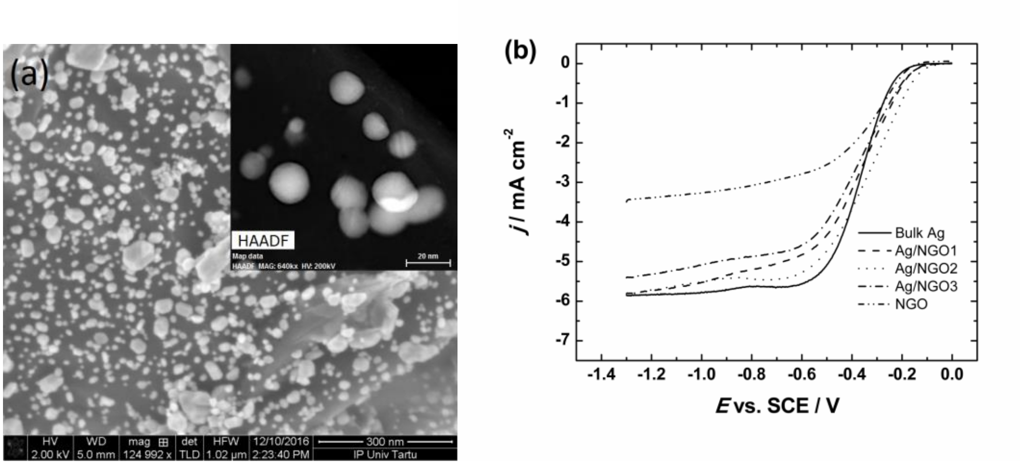

Figure. a) SEM image of Ag/NGO1, inset shows HAADF-TEM micrograph and b) comparison of RDE polarization curves for oxygen reduction in O_2-saturated 0.1 M KOH. ω = 1900 rpm, v = 10 mV s^{-1}.

Insight into the instability of pyrolyzed Fe/N/C catalyst for oxygen reduction reaction

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Pyrolyzed Fe/N/C catalyst is a promising non-precious-metal (NPM) catalyst for oxygen reduction reaction (ORR) in fuel cells. Recently, the ORR activity of Fe/N/C catalyst has been greatly improved, and peak power density of PEMFC with Fe/N/C cathode can reach to about 1 W cm^{-2}. [1] However, the stability of Fe/N/C catalyst is far below the practical requirement. Considerable performance loss can be observed within several tens hours when Fe/N/C-based fuel cells are operated at > 0.50 V.

We found that water flooding and oxidative corrosion are two main reasons for the instability of Fe/N/C catalysts. Most of active sites of Fe/N/C catalysts are located in the micropores. If the micropores are filled with water (so-called micropore water flooding), the rate of O_2 mass transfer will be decreased greatly. We found that surface modification of Fe/N/C catalysts with hydrophobic group, such as trifluoromethylphenyl (Ar-CF_3), can significantly improve the stability, although the catalytic activity decreases (Fig. 1). We further found that introducing the hydrophobic dimethyl silicon oil (DMS) into Fe/N/C catalyst layer to construct triple-phase interface in micropores, Fe/N/C-based direct methanol fuel cell (DMFC) can yield a performance close to that of Pt-based DMFC. [2] As for oxidative corrosion, we observed that corrosive species from ORR (such as H_2O_2 and oxygen-containing radical) and electrochemical oxidation corrosion are two main reasons for the degradation. Electrochemical oxidative corrosion was confirmed by PEMFC test. At the open circuit, when the cathode was fed with wet oxygen for about 10 h at 80 °C, the fuel cell performance will decay significantly; In contrast, when the cathode was fed with wet nitrogen, fuel cell performance changed little. On the one hand, oxygen corrosion can destroy the active sites; on the one hand, oxidation corrosion can increase the amount of oxygen-containing species on catalyst surface, which further worsen the water flooding.

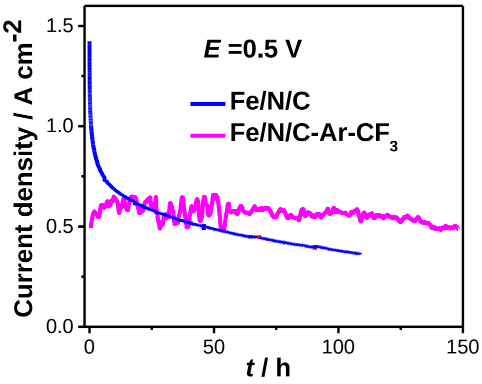

Fig.1 Stability test of Fe/N/C-based PEMFC

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Evaluating several activity enhancement strategies in Pt based nanoparticle catalysts for the oxygen reduction reaction in fuel cells

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Despite its vast possibilities, economical profitability still impedes the widespread implementation of fuel cells and electrolyzers. A major topic within modern electrocatalyst research therefore is the tailoring of nanostructures to enhance the surface specific activity and reduce the mass amount of precious metals. A well-known example is the high Pt loading needed to achieve sufficient reaction rates at the cathode side in PEM fuel cells as a result of the sluggish oxygen reduction reaction (ORR) kinetics.

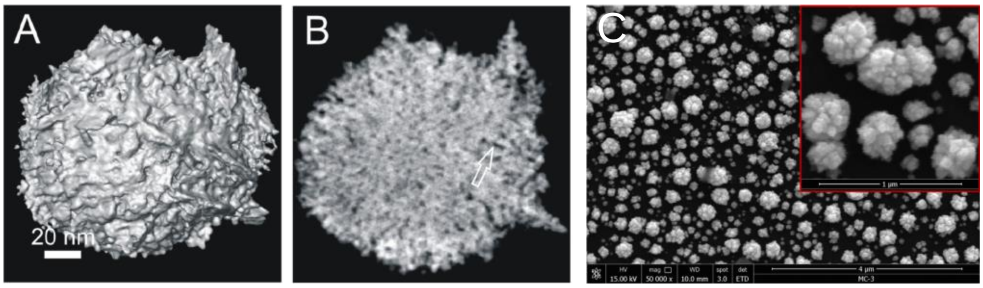

Fig. 1: 3D visualization of a TEM tomography reconstruction (A) and a slice through the 3D data set (B) of an electrodeposited Pt nanostructure. (C) FESEM micrograph of a Pt-Ni catalyst after transmetallation.

In this talk we will give an overview of several recent research projects performed in our research group on Pt based fuel cell catalysts. Some of the most attractive strategies include directing the particle size, tuning metal support interactions, alloying and controlling catalyst morphology.

In a first series of activity enhancement studies, we mainly focused on the particle size and the effect of alloying. Consequently, nanostructured bimetallic catalysts were synthesized by applying multi-step synthesis procedures. Initially, mono-metallic nanoparticles (NP's) of Ni, Cu and Co were obtained through impregnation or electrodeposition methods. [1] Afterwards, the galvanic displacement with a Pt precursor furnished the NP's with a Pt outer shell. The bimetallic electrocatalysts displayed an elevated ORR activity compared to pure Pt and proved to be good candidates as fuel cell catalysts.

In a second series of investigations, we focused on the catalyst's morphology and the relation of this structure to its stability. Existing electrodeposition techniques were further developed to obtain nanostructured Pt particles with pores up to 2 nm and with a strain induced elevated ORR activity. [2] With this straightforward approach practical fuel cell electrocatalyst materials could be prepared. Besides their activity for the ORR, also their long term stability was studied.

To reach these ambitions, a well-considered combination of measurement techniques was applied. Atomic resolution microscopic (SEM, TEM Tomography) and spectroscopic (XRD, XPS) analyses were intertwined with macroscopic electrochemical techniques (CV, LSV, EIS).

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Metal-metalloid alloys in electrocatalysis: Nature of the catalysts under reaction conditions and promotional role of the metalloid elements

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The overriding obstacle to mass production of hydrogen from water as the premium fuel for powering our planet is the frustratingly slow kinetics of the oxygen evolution reaction (OER). Additionally, inadequate understanding of the key barriers of the OER is a hindrance to insightful design of advanced OER catalysts. Metal-metalloid alloys, including transition metal (Co, Fe, Ni) borides, phosphides and silicides, among others, show outstanding activity as dual function H_2 and O_2 evolution electrocatalysts.[1,2] When supported on nickel foam, metal borides and phosphides exhibit exceptionally high OER activity **(Fig. 1**), among the best performance reported for noble-metal free catalysts. However, the structure of the catalysts under reaction conditions, and the role of the metalloid elements (B, P, Si) in promoting their activity is not well understood. In this presentation, in-depth interrogation of the structure of metal-metalloid catalysts, using cobalt and nickel borides and phosphides as model examples, prior to electrochemical activation and under reaction conditions, as well as post-mortem analysis of the catalysts in the aftermath of electrochemical stress will be discussed in detail.

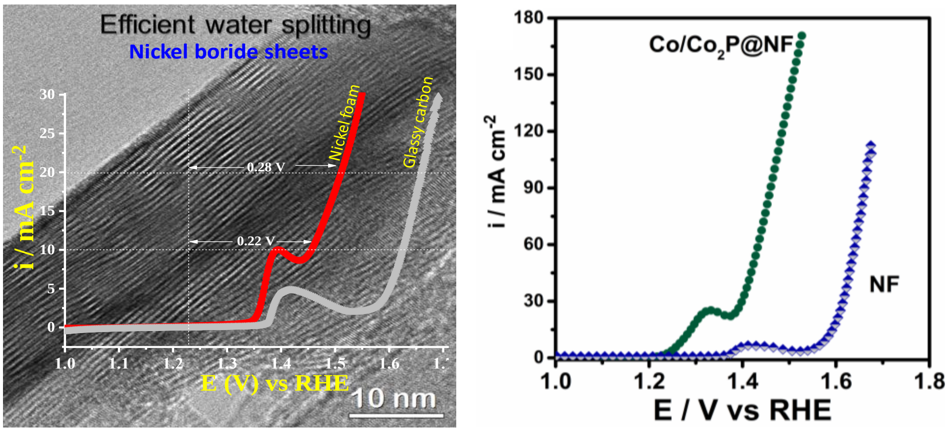

Fig. 1. HRTEM micrograph of a flake of nickel boride showing a layered structure, superimposed with voltammograms showing the OER activity of the catalyst supported on nickel foam and on glassy carbon (Right frame), and OER activity of Co/Co_2P nanoparticles supported on nickel foam.[2]

The metalloid elements modulate the surface electronic structure of the metals through hybridization of the p-orbitals of the metalloid and the metal-d-orbitals, resulting in electron transfer to or from the metal, depending on the nature of the metalloid element. Insights from rigorous electrochemical studies coupled to advanced *operando* spectroscopic investigations, including *operando* X-ray absorption fine structure spectroscopy (XAFS) and *in-situ* Raman spectroscopy, indicate that under OER conditions, metal-metalloid catalysts adopt a metal-metalloid@MOOH (core@shell) structure, which is the active state of the catalyst during O_2 evolution. To underpin the role of the metalloid elements, the discussion will cover the influence of the metalloid elements on intensive catalytic parameters including the activation energy (E_a) and the turnover frequency of the OER, and on the mechanism of the reaction, as well as the nature and dynamics of the transient states of the catalysts prior to oxygen evolution.

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Enhanced Catalytic Conversion of CO_2 and Steam on High-Temperature Co-Electrolysis in Solid Oxide Cells

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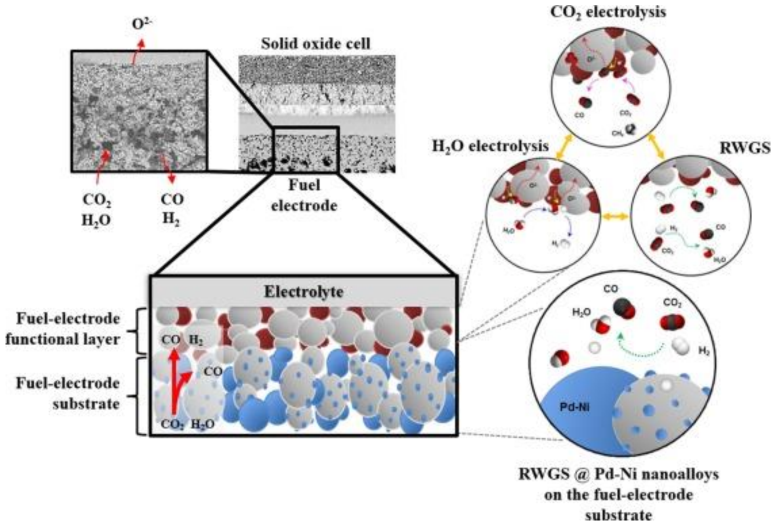
The demand for carbon-neutral technologies has increased over the last two decades because of the negative effects of global warming and climate change caused by excessive carbon dioxide (CO_2) emissions. Various techniques have been studied to develop high-density energy storage and lowering CO_2 emissions in energy and environmental science. To tackle these issues simultaneously, syngas production from high-temperature co-electrolysis of CO_2 and steam mixtures utilizing renewable energy has been proposed. By doing so, renewable electrical energy can be stored in the form of chemical energy, and CO_2 is converted to highly valuable syngas which can be processed further to produce liquid fuels. To make this technology viable, it is imperative to develop a cost-effective and efficient methodology for controlling syngas production given that this system is linked with fluctuating renewable electrical current and CO_2 stream.

In our co-electrolysis research, we seek the development of highly active and selective catalysts employing the quantitative surface analyses, first principles calculations, and the demonstration of robust co-electrolysis operation using a unit cell. First, we investigated the roles of metal catalysts in the high-temperature reverse water-gas shift (RWGS) reaction. We directly observed that the formate group is an intermediate adsorbed species on all highly activated catalysts during the high-temperature RWGS reaction. Second, we show that in-situ nano-alloying noble metals in solid oxide cells can provide such function by using a substantially small amount of expensive noble metals. Catalyzing selectively the reverse water gas shift reaction, this technique enables increasing the CO_2 conversion rate, storing energy more efficiently, and controlling the syngas production rate as well as its quality.

Consequently, these may enhance the syngas productivity and energy storage capacity and provide a capability for adjusting effectively the system to variable renewable electrical energy and CO_2 sources. Also, we believe that our R&D activities lead to the promising technological advances and provide new guidelines in developing the high-temperature CO_2 conversion system.



Synthetic Strategies toward M−N/C Electrocatalysts with Abundant Active Sites for Efficient Oxygen Reduction Reaction

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The development of highly active, durable, and low-cost oxygen reduction reaction (ORR) catalysts is central to making polymer electrolyte fuel cells commercially viable. During the last decade, tremendous recent effort has been devoted to replacing expensive, scarce Pt-based electrocatalysts with non-precious metal catalysts (NPMCs) for the ORR. Among various NPMCs, M−N/C (M=Fe or Co) catalysts have emerged as the most promising ORR catalysts due to their high ORR activities. In this direction, we have endeavored toward the rational design of high-performance M−N/C catalysts and the identification of active species in M−N/C catalysts [1-4].

We have developed a general design strategy based on "silica-protective-layer-assisted" method that can preferentially produce catalytically active Fe−N_x sites towards highly efficient Fe−N/C electrocatalysts [1,2]. This method is applicable to any type of carbon supports as well as Fe and N precursors. One of resulting catalysts, consisting of CNT wrapped with thin porphyrinic carbon layer (CNT/PC), contained relatively high density of Fe−N_x sites, and showed very high ORR activity and remarkable stability in alkaline media. Importantly, the CNT/PC-based cathode demonstrated excellent performances in both alkaline anion exchange membrane fuel cell as well as acidic proton exchange membrane fuel cell.

We have prepared model catalysts toward identifying the active species in M−N/C catalysts [4]. We constructed archetypical hybrid catalysts by the reaction of an organometallic complex, $[Co^{II}(acac)_2]$ (acac=acetylacetonate), with N-doped graphene-based materials at room temperature. In the hybrid structure, the cobalt-containing species is coordinated to heterocyclic groups in N-doped graphene as well as to its parental acac ligands. The hybrid material shows high electrocatalytic activity for the ORR in alkaline media, and superior durability and methanol tolerance to a Pt/C catalyst. Based on the chemical structures and ORR experiments, we could identify a new active species for the ORR: "Co−O_4−N" structure.

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Designing Non-Precious Metal Nanocatalysts for Fuel Cells

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The rapidly increasing energy demand for human activities stimulates the lasting research interests to develop renewable energy alternatives worldwide. The development of low-cost high-performance electrocatalysts for oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) to replace the precious metal-based catalysts would be essential and important for the commercialization of various fuel cell applications.

This presentation will talk about several reasonable ways for designing new non-precious metal nanocatalysts with high electrocatalytic activities and superior stability for ORR and HER. By focusing on the creation and the enrichment of highly active sites for ORR and simultaneously considering the mass transfer and electron transportation, we have developed several efficient metal-free ORR catalysts.[1-3] The further improvement of the performance can be achieved by introducing transition metal or nanostructures into these nanocatalysts.[4-6] Furthermore, understanding the origin of high activity of these electrocatalysts in ORR is also critical for developing efficient non-precious metal catalysts but still challenging. We developed a new highly active Fe-N-C ORR catalyst containing Fe-N_x coordination sites and Fe/Fe_3C nanocrystals, and revealed the origin of its activity by intensively investigating the composition and the structure of the catalyst and their correlations with the electrochemical performance. Based on our experimental and theoretical results, it can be concluded that the high ORR activity in this type of Fe-N-C catalysts should be ascribed to that Fe/Fe_3C nanocrystals boost the activity of Fe-N_x. Last, the presentation will also discuss the design and several examples for highly active HER catalysts.[7-8] These new findings open an avenue for the rational design and bottom-up synthesis of low-cost highly active ORR and HER electrocatalysts.

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Catalysts Supported on Functionalized Carbon Nanotubes for Oxygen Reduction Reaction in PEM/AEM Hybrid Fuel Cells

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Carbon Nanotubes with various of surface functional groups which are carboxyl groups, carbonyl groups, pyridinic-N, pyrrolic-N and graphitic-N are synthesized[1,2]. Two types of catalysts are investigated which are platinum supported on functionalized carbon nanotubes and iron phthalocyanine (FePc) supported on functionalized carbon nanotubes[3,4]. Platinum and iron phthalocyanine are supported on different oxygen and nitrogen doped carbon nanotubes and evaluated in a H_2/O_2 hybrid PEM/AEM fuel cell which exhibit unique advantages of nonplatinum metals as catalysts and enhancing resistance to CO poisoning[5,6]. The existence of oxygen and nitrogen functional groups on the nanotubes is confirmed by XPS. The performance of the catalyst for the oxygen reduction reaction (ORR) is conducted in a hybrid PEM/AEM fuel cell.

The performance of the catalyst for ORR in hybrid fuel cell is found to be affected by the type of the functional groups on the carbon nanotubes. For the platinum catalysts, The platinum supported on both nitrogen and oxygen functionalized carbon nanotubes(Pt/CNTON) and on oxygen functionalized carbon nanotubes (Pt/CNTOX) are more effective in hybrid H_2/O_2 fuel cells compared to the Pt/C, as shown in Figure 1(a). For the FePc catalysts, the iron phthalocyanine supported on axial ligand anchored carbon nanotubes (P-FePc-py-CNT) is found to perform best among the three non-noble catalysts while the iron phthalocyanine supported on nitrogen doped carbon nanotubes (P-FePc-CNTN) is unstable in a hybrid H_2/O_2 fuel cell. The result suggests that adding an axial ligand on the back side of FePc before heat treatment can facilitate oxygen reduction reaction, as shown in Figure 1(b).

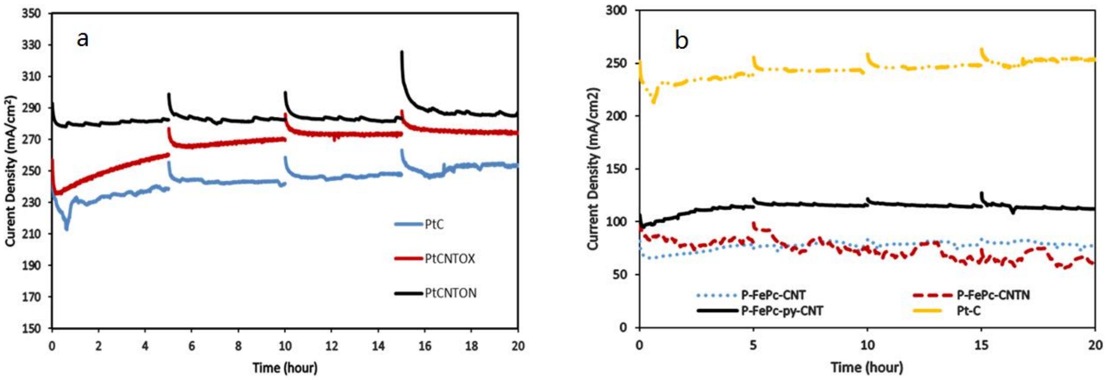

Figure 1. Performance Comparison of a H_2/O_2 hybrid AEM/PEM fuel cell.Stability test in H_2-O_2 hybrid AEM/PEM fuel cell for 20 hours

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Model Electrode Study of Nanosheets with Ru@Pt Core-Shell Structure

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M@Pt core-shell nanoparticles with higher activity towards oxygen reduction reaction (ORR) are promising electrocatalysts for fuel cells. Further reduction in Pt and Pt-group metal usage by increased activity and durability is necessary for voluminous commercialization. We recently succeeded in the synthesis of high surface area nanosheets with a Ru core-Pt shell nanostructure (Ru@Pt-xML(ns)/C, where x is the average thickness of the Pt shell) by surface limited redox replacement method using a monolayer thin Ru nanosheet core supported on carbon black which showed up to 5 times high activity and 2 times enhanced durability compared to practical Pt/C. [1] Analysis revealed that the Pt shell was quite rough (roughness factor=4 for a 3.5ML shell), which we assumed was due to the curved nature of the carbon support. In this study, model electrodes using a flat carbon substrate (glassy carbon) were prepared in an attempt to understand the formation process of the Pt shell on Ru nanosheets by surface limited redox replacement.

A controlled amount of colloidal RuO_2 nanosheet suspension [2] was drop casted onto a polished glassy carbon electrode. RuO_2 nanosheets were transformed into Ru nanosheet (Ru(ns)) by hydrogen reduction in H_2(10%)-N_2(90%) at 200°C. [3] Copper underpotential deposition (Cu-upd) on Ru(ns) was conducted at 300 mV vs RHE in 1 mM $Cu(ClO_4)_2$ + 0.1 M $HClO_4$. Copper was subsequently replaced with Pt at open circuit in a single cell configuration where both Cu^{2+} and Pt^{2+} are present in the electrolyte. [4] This procedure was repeated to control the thickness of the Pt shell. ORR activity was measured in O_2-sat. 0.1 M $HClO_4$ (25°C) by linear sweep voltammetry from 0.05 to 1.2 V vs. RHE at ω = 1600 rpm, ν = 10 mV s^{-1}.

Controlled Cu-upd was conducted on Ru(ns)/GC by varying the upd time (t_{ad}) from 10 to 50 sec at 300 mV vs RHE. The Cu_{ad} oxidation charge increased from t_{ad}=10 to 30 sec and leveled off after 40 sec at 296 μC. The Cu_{ad} oxidation charge for Ru(ns)/GC was 264 μC. These results indicate a near 1:1 deposition of Cu on Ru. Since the Ru nanosheet is one atom thick, a 1:1 deposition means that either Cu is deposited on one side of Ru, or 50% coverage of Cu_{ad} on both sides of Ru. If the Pt deposition was completely flat, the roughness factor should be 1 after consecutive deposition of Pt. In the case of the carbon black support, an increase in roughness factor was observed with increasing x. [1] The roughness factor of Ru@Pt-xML(ns)/GC is constant at 1 for all x, thus it is concluded that a smooth and flat Pt shell is formed on the Ru core. The ORR activity increased with increasing x, and the highest activity was obtained with x=3.5. These results are in good agreement with our earlier studies with porous electrodes.

This work was supported in part by the “Polymer Electrolyte Fuel Cell Program” from the New Energy and Industrial Technology Development Organization (NEDO), Japan.

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In-Situ Examination of Phase-Change-Induced Flow in Gas Diffusion Layers using Micro X-Ray Computed Tomography

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Although fossil fuels are currently the primary energy source on the market, there is significant support behind developing alternative energy technologies. Polymer electrolyte fuel cells (PEFCs) and redox flow batteries (RFBs) are both among the well-known options and utilize porous gas diffusion layers (GDLs). For PEFCs, management of the water byproduct is critical to maintaining performance [1]. Without proper management, liquid water can collect and flood components, including GDLs, and thus prevent reactants from reaching catalyst sites. In order to improve water management, there is a need to better understand the complex relationship between heat transport, mass transport, and GDL structure. As a PEFC operates, the exothermic reaction gives rise to a thermal gradient in the through-thickness direction. This thermal gradient is especially significant in the cathode region of the PEFC; where it gives rise to a gradient in vapor pressure and evaporates some of the liquid water. Because of this, the vapor-pressure gradient induces transport of the water vapor through the GDL from the hot catalyst layer to the cooler gas channels. This phenomenon is called phase-change-induced (PCI) flow and has been shown to be a significant factor in water management for PEFCs [2].

Despite both its importance to water management and previous investigations, PCI flow is still poorly understood compared to other transport mechanisms such as capillary-driven flow. One of the main reasons for this is the difficulty of obtaining *in-situ* measurements and visualizing the evaporating water front. Previously, we reported evaporation rates for water in GDLs under constant temperature conditions [3]. This presentation will discuss the results of an experiment which used micro synchrotron-based x-ray computed tomography (CT) to obtain data regarding water distribution in GDLs subjected to a thermal gradient. We observe higher evaporation rates of water in the GDL at locations that were subjected to higher temperature, as shown by Figure 1a. Furthermore, two evaporative regimes are observed: a slow regime, where water evaporates slowly and redistributes under PCI flow; and a fast regime, where rapid dryout is observed. These results are shown by Figure 1b. We will discuss experiment conditions involving various thermal conditions and GDL materials.

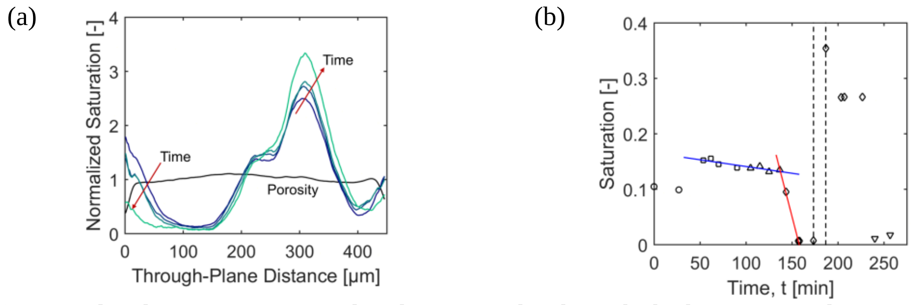

Figure 1. a) Normalized water saturation distribution in the through-thickness GDL direction. The hot surface is at the through-thickness distance of 0 μm. b) Volume-averaged saturation within the GDL as a function of time.

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Active Site of Nitrogen Doped Carbon Graphene Identified by Selectively Chemical Modification

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Nitrogen (N)–doped carbon materials exhibit considerable electrocatalytic activity for the oxygen reduction reaction (ORR), which is essential for several renewable energy systems. Up to now, the ORR active site (or sites) is still unclear, which retards rational design of high-performance catalysts. It has been reported that the catalytic activity of N-doped carbon materials is relevant with the amount of pyridinic N.[1] However, few experimental evidences are provided to reveal the structure of active sites at molecular level, and thus, new approaches are required to identify the catalytic function of different sites on N-doped carbon materials. Here, we reported a novel strategy based on selective modification of pyridinic N on N-doped graphene. Through nucleophilic mechanism, acetyl group can selectively bind to nitrogen atom on pyridinic ring (labelled as NAc-N-graphene); while through radical mechanism, acetyl group can selectively bind to ortho-carbon atom of pyridinic ring (labelled as CAc-N-graphene). The ORR test demonstrated that NAc-N-graphene has an ORR performance similar to the pristine N-graphene, while CAc-N-graphene is completely inactive to ORR (Fig. 1). This result indicates that the ortho-carbon atom of pyridinic ring is the reaction site of N-graphene for ORR.

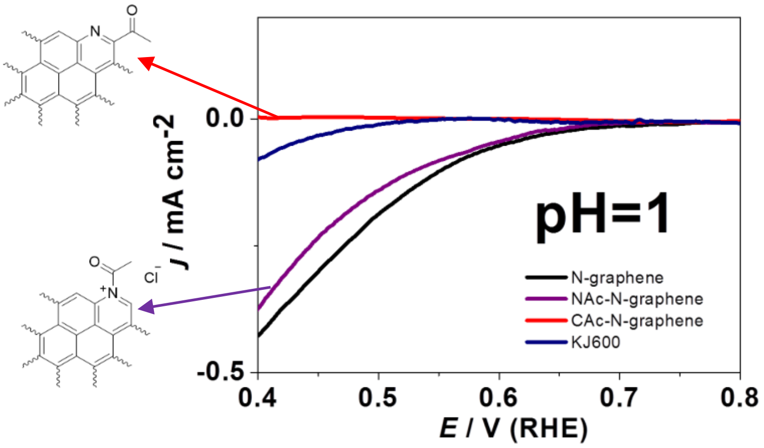

Fig. 1 Polarization curves of N doped graphene (black), N blocked N doped graphene (purple), C blocked N doped graphene and KJ600 in O_2 saturated 0.1M H_2SO_4 solution

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Identification of carbon-encapsulated iron nanoparticles as active species in non-precious metal oxygen reduction catalysts

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The widespread use of fuel cells is currently limited by the lack of efficient and cost-effective catalysts for the oxygen reduction reaction (ORR). Iron- or cobalt-based non-precious metal (NPM) catalysts exhibit promising activity and stability as an alternative to state-of-the-art platinum catalysts for the ORR. There has long been uncertainty as to the active site for ORR in these materials due to the heterogeneity of the as-prepared catalyst. Consequently, the identity of the active species in non-precious metal catalysts remains elusive, impeding the development of new catalysts. By using a purification scheme which removes and then remetallates the active site we substantially reduce this heterogeneity. We demonstrate the reversible deactivation and reactivation of an iron-based non-precious metal oxygen reduction catalyst achieved using high-temperature gas-phase chlorine and hydrogen treatments. The study features the use of a plethora of techniques including Mossbauer, XANES, EXAFS, magnetometry, and vibrational spectroscopy. Our study reveals that protected sites adjacent to iron nanoparticles are responsible for the observed activity and stability of the catalyst. These findings may allow for the design and synthesis of enhanced non-precious metal oxygen reduction catalysts with a higher density of active sites. Kinetic Isotope measurements help to elucidate the mechanism of the ORR in these materials.

Electrochemical Oxygen Reduction Reaction on Earth-abundant Rich Palladium Alloys

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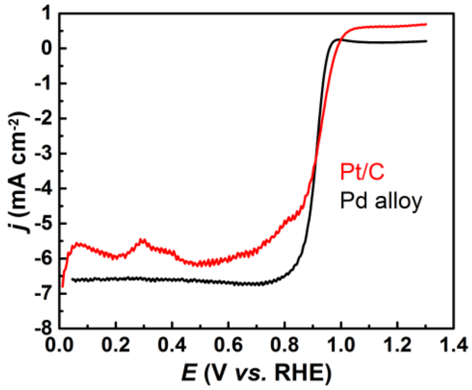

Figure 1. Polarization curves for electrocatalytic ORR using Pt/C (TKK), and Pd alloy nanoparticles consisting of a majority fraction of earth abundant metal supported on a glassy carbon electrode in 0.1 KOH at 1600 rpm rotation rate. The CV is collected at a sweep rate of 20 mV/s and at room temperature.

The conversion of O_2 to H_2O is an important fuel cell reaction for the recovery of renewable electricity from chemical fuels.[1] To date, most materials utilized for the oxygen reduction reaction (ORR) consist of noble metal rich alloys of the form Pt_3X, where X is an earth abundant element.[2] Although catalysts of this type have been demonstrated to exhibit high activity for ORR, the 75% Pt loading translates to a relatively modest decrease in the use of Pt. Pd alloy catalysts have been proposed as an alternative to Pt and Pt alloy catalysts; however lower catalytic performance relative to Pt has prevented these materials from attracting considerable attention.[3] Recently, we have found that earth abundant metal rich Pd alloys can match or outperform Pt for ORR in alkaline media (Figure 1). Pd alloys are promising candidates for replacing Pt in low-temperature fuel cells because 1) Pd is ~1/3 the cost of Pt,[3] 2) earth-abundant metal rich Pd alloys (< 50% Pd) significantly reduce the amount of noble metal usage. Here, we demonstrate that earth abundant rich alloys of Pd are viable alternatives to Pt for ORR, and structure-property relationships will be discussed.

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Overcoming the instability of nanoparticle based catalyst films in alkaline electrolysers by self-assembling and self-healing films

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Large-scale energy storage will play an essential role in the transition from fossil fuel-based to renewable energy due to the intermittency of the energy supply by wind or the sun. Storage of surplus electrical energy in the form of chemical bonds, especially hydrogen, is an attractive solution to level out fluctuations in energy. Electrochemical water splitting is a promising method for the conversion of electrical energy into hydrogen. The overpotential that is necessary to drive the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) at cathode and anode, respectively, makes the use of efficient electrocatalyts necessary. Therefore, enormous efforts are currently devoted to the development of highly active catalysts for both reactions. A substantially high amount of newly developed catalysts is present as nanopowder materials leading to a notorious challenge with respect to engineering of stable electrodes using nanopowder catalysts.

In this work, we present an innovative approach for attaining very stable catalytic films with self-healing capability based on in-situ self-assembly of catalyst nanoparticles during active electrolysis. In this approach, the catalyst nanoparticles are directly added to the electrolyte forming a suspension that is pumped through a running electrolyser cell. Nanoparticles with negatively charged surfaces adsorb onto the anode, while those with positively charged surfaces adhere to the cathode governed by electrostatic forces. Importantly, self-assembled catalyst films possess self-healing properties as long as a sufficient amount of the catalyst particles are present in the electrolyte (Figure 1).

We also demonstrate the proof-of-concept using a non-zero gap alkaline electrolyser using NiFe LDH and Ni_xB catalyst nanopowders, for anode and cathode, respectively. Steady cell voltages were maintained for at least three weeks during continuous electrolysis at 50-100 mA cm^{-2}, which is attributed to very stable catalytic films with self-healing behaviour. Choosing more active catalyst nanoparticles further allows to reduce the necessary cell voltage to drive the electrochemical water splitting at high current densities.

This ground-breaking concept will enable the implementation of novel active catalyst nanoparticles for electrochemical water splitting, and make use of the full potential of the high activity of nanoparticles.

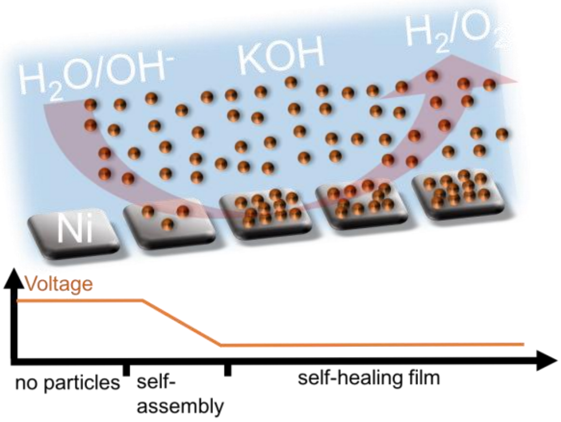

Figure 1. Schematic representation of the different stages during the formation of a self-assembled catalyst film and the corresponding cell voltage.

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Effect of Reduced Pt Loading on Spatial PEMFC Performance under SO_2 Poisoning

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Next generation of proton exchange membrane fuel cells (PEMFCs) requires a substantial reduction in the cost of their production, which can be achieved through economy of scales and by decreasing of platinum content at electrodes. Currently, significant progress has been made in reducing cathode Pt loading from 0.4 to 0.2 mg_{pt} cm^{-2} [1]. Most fuel cells operate with air as an abundant and free of charge oxidant. However, the ambient air typically contains impurities originated from natural and anthropogenic emission sources which have an adverse impact on the performance of high-loaded Pt PEMFC [2]. Due to the current trend in reduction of Pt loading, it is very important to understand environmental adaptability and tolerance of low-loaded fuel cells to the main air impurities and establish air quality requirements. In this work spatial performances of high- and low-loaded Pt PEMFCs exposed to SO_2 were compared and studied using segmented cell system at different operating conditions.

A segmented cell and data acquisition system were operated with commercially available 100 cm^2 membrane/electrode assemblies (MEAs). Pt content was 0.4 mg_{Pt} cm^{-2} for anode and cathode for high-loaded samples, while low-loaded MEAs have 0.1 mg_{Pt} cm^{-2} for both electrodes. The dry contaminant was injected into the humidified cathode air stream. The poisoning proceeded until the cell voltage reached a steady value, after that the contaminant injection was stopped to evaluate the cell recovery in air. MEAs were analyzed by SEM, TEM, XPS and electrochemical methods.

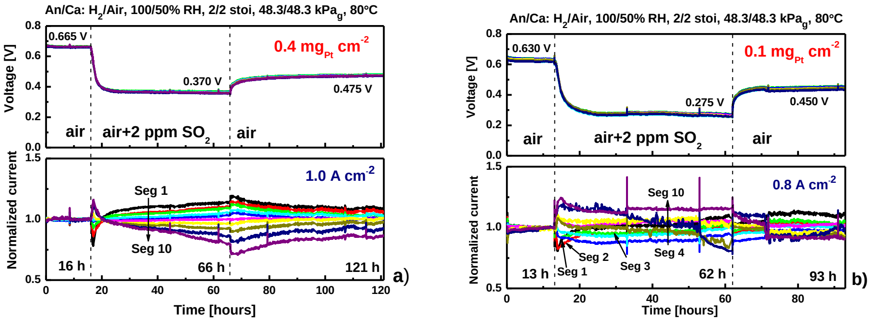

Fig. 1. Voltage and normalized current density for each segment for PEMFCs: a) 0.4 mg_{Pt} cm^{-2} and b) 0.1 mg_{Pt} cm^{-2}.

Fig. 1 shows the voltage response and normalized current density for each segment vs. experiment time for high- and low-loaded PEMFCs operated under the constant current. The injection of 2 ppm SO_2 significantly decreased the voltage during a transition period that lasted ~6-7 h eventually reaching a steady state. The performance loss was ~0.30 and ~0.35 V for 0.4 and 0.1 mg_{Pt} cm^{-2} MEAs respectively. The voltage decrease was accompanied by a significant change in the current density distribution which undergoes several steps. Recovery was only partial and took ~4 h, the cell voltage reached 0.475 and 0.45 V instead of initial performance of 0.665 and 0.63 V for high- and low-loaded MEAs, respectively. Chemisorption of SO_2 at intermediate potentials (0.5-0.7 V) results in the formation of mixture Sulphur containing species as well as zero-valent sulfur (confirmed by XPS) and leads to a decrease in the ECA [3, 4]. Moreover, the S^0 can be oxidized only at high potential (> 1.0 V) which explains the observed partial recovery of the cell. Details of the spatial performance of high- and low-loaded fuel cells, results of electrochemical impedance spectroscopy and SO_2 poisoning mechanism will be presented and discussed.

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Cu@Pd/C and Cu@Pt/C electrocatalysts used as anode for the electrooxidation of crude glycerol as waste from biodiesel in a nanofluidic fuel cell

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Glycerol is the primary by-product of the transesterification of vegetable oils in the presence of acidic or alkaline catalysts during biodiesel production. It Is estimated that per 1 kg of biodiesel produced is obtained 0.1 kg of crude glycerol that is the 10%wt of all over products [1].The resulting residue is a source of crude glycerol, but due to the presence of contaminants it is difficult to use without purification [2]. A large proportion of impurities in unreacted crude methanol of glycerol and soaps formed during the transesterification reaction [3]. Just Brazil, in 2010, was produced 2.397.272 m^3 of biodiesel [4], that generated a high amount of crude glycerol and in consequence, making a new problems related with their finale use and storage. In order to give a solution for this problem, crude glycerol was employed as fuel in an air-breathing membraneless nanofluidic fuel cell operated at room temperature under alkaline conditions. Cu@Pt/C and Cu@Pd/C were synthesized via a chemical reduction method and used as anode electrocatalysts [5, 6]. During the electrooxidation of the crude glycerol in the membraneless nanofluidic fuel cell, the performance of the open circuit voltage (OCV) and the maximum of the power density suggest that the Cu@Pt/C and Cu@Pd/C electrocatalysts exhibit a selective behavior due to that the shape of the polarization curves are similar when were used crude glycerol and analytical grade glycerol as fuels [5]. It is important to mention that the crude glycerol was supplied without purification from the fuel cell.

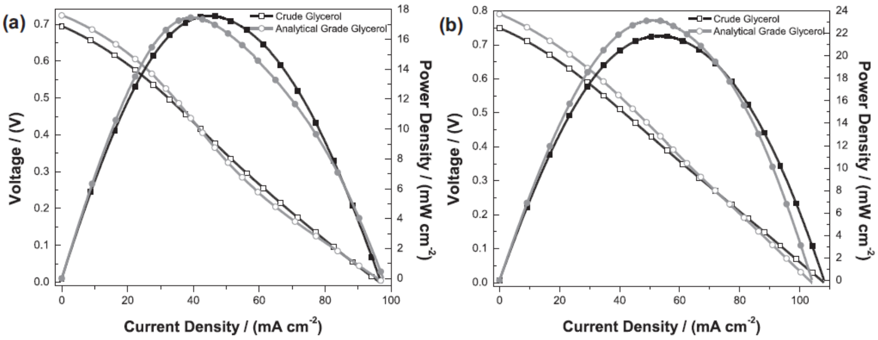

Fig. 1.- Polarization curves for the oxidation of crude glycerol and analytical grade glycerol using a) Cu@Pd/C and b) Cu@Pt/C as anode

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Mass-Selected NiFe(OOH) Nanoparticles for Oxygen Evolution

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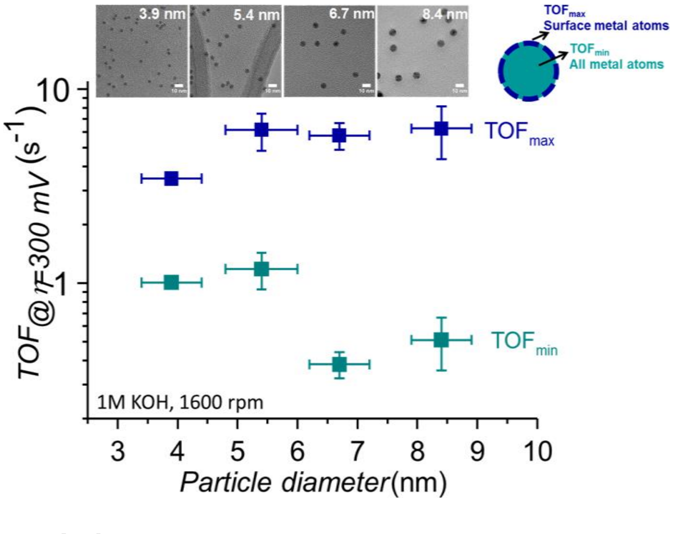
The increase of greenhouse gasses associated with the use of fossil fuels for energy production is one of the main contributors to climate change. Solar and wind technologies hold the potential to mitigate CO_2 emissions. However, their intermittent nature poses a challenge to their increased implementation. The electrochemical synthesis of fuels is the ideal mean of storing electrical energy produced into chemical form. Hydrogen is of particular interest because it can be synthetized from electrolysis of water with minimal efficiency losses. However, the sluggish kinetic of the anodic reaction, oxygen evolution, limits the process efficiency.

Nickel and iron-based oxides and hydroxides are amongst the most active non-precious catalysts for the oxygen evolution reaction in alkaline media. The origin of their intrinsic activity is currently under intense debate. [1-3]. For example, the role of particle size effects and lattice oxygen are not completely clear. In order to develop better materials, it is imperative to gain further understanding of the factors controlling the intrinsic activity and stability of oxygen evolution catalysts. To this end, in our current study, we investigated well-defined model systems of NiFe nanoparticles We previously used the same approach to elucidate oxygen evolution in acid on RuOx catalysts [4].

A wide range of techniques was used to characterize our model system: X-ray Photoelectron Spectroscopy, Ion Scattering Spectroscopy, X-ray diffraction, Secondary Electron Microscopy and Transmission Electron Microscopy. We tested the catalysts for oxygen evolution in 1 M KOH using a rotating disk electrode setup. The turn over frequency (TOF) reported is among the highest in alkaline. According to our study, the particle size and distance of nearest neighbor impact the catalytic activity. The stability against dissolution was also studied using inductively coupled plasma mass spectrocopy.



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Beyond Alloying Effects: Microstrain-Induced Modification of Catalytic Sites Reactivity on Various PtNi/C Nanostructures: Application to the Oxygen Reduction and Alcohool Oxidation Reactions

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The electrical performance of a Proton Exchange Membrane Fuel Cell (PEMFC) is limited by the sluggish oxygen reduction reaction (ORR) kinetics. Thereby, the high platinum content needed at the cathodic catalytic layer to compensate for these slow kinetics creates a major cost barrier for massive commercialization of PEMFC systems. Due to the strain and ligand effects, alloyed PtM/C or M-rich core@Pt-rich shell catalysts (where M is an early or late transition metal) have demonstrated tremendous ORR catalytic improvements compared to pure Pt/C. In this study, we synthetized and characterized nanometre-sized PtNi/C electrocatalysts with low Ni content (~15 at. %) but different nanostructures and different structural disorder: solid, hollow, core-shell or "sea sponge" PtNi/C nanoalloys. These nanostructures were characterized by transmission and scanning-transmission electron microscopy, X-ray energy dispersive spectroscopy, Synchrotron wide-angle X-ray scattering, atomic absorption spectroscopy and electrochemical techniques. Their electrocatalytic activities for the ORR were determined, and structure-activity relationships established. The results showed that (i) the compression of the Pt lattice by 15 at. % Ni provides mild ORR activity enhancement compared to pure Pt/C, (ii) polycrystalline porous hollow nanoparticle feature dramatically enhanced ORR catalytic activity, (iii) the enhancement in ORR catalytic activity can be endorsed to the presence of grain boundaries as show two independent parameters: the microstrain determined from WAXS, and the average CO_{ads} electrooxidation potential (μ_1^{CO}) determined from CO_{ads} stripping measurements. Our experimental work, combined with density functional theory (DFT) indicate that structural defects such as grain boundaries and atomic vacancies result in the formation of surface domains of various Pt lattice parameter distributions and thus enhanced electrocatalytic performance for electroreduction (ORR) and electrooxidation (CO_{ads} stripping experiments, methanol or ethanol electrooxidation) reactions.

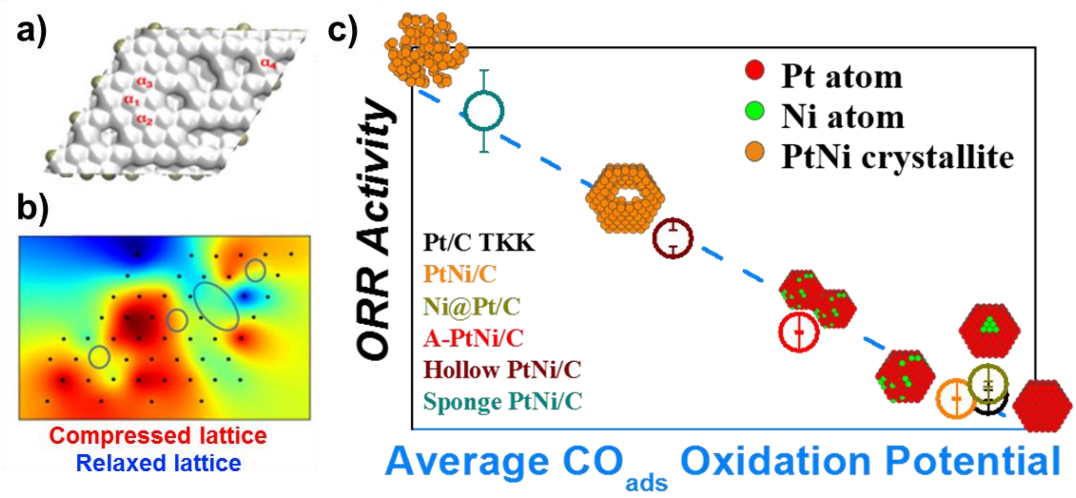

Figure 1: (a) Top view of a 5-layer Pt(111) slab containing 20 % of atomic vacancies randomly introduced after relaxation, (b), predictive map of the inner deformation of the surface and (c) experimental relationship between ORR specific activity *vs.* CO_{ads} oxidation potential for various PtNi/C nanostructures.

On the Influence of Anion Adsorption on the oxygen reduction activity of Non-Precious Metal Catalysts

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Non-precious Metal Catalysts (NPMCs) are currently being investigated as feasible alternatives to platinum for the oxygen reduction reaction (ORR) in fuel cells. However, many aspects are still not fully understood concerning the active sites of the NPMCs. Furthermore, NPMCs suffer from many of the same limitations as Pt-based catalysts (Pt/C) when it comes to degradation in acidic environment and problems with anion adsorption.

In this study, we are focusing on the effect of different electrolytes towards the measured ORR activity of NPMCs. Through experiments conducted in RDE half-cell measurements, thin-films of Fe-based NPMCs are investigated in different conventional electrolyte solutions. These experiments provide information that point towards a different pattern of anion adsorption than what is reported for Pt/C based catalysts. We find that phosphoric acid anions are not inhibiting the ORR in a similar manner on NPMCs as compared to Pt/C. The experimental results are supported by computational modelling of NPMC and Pt surfaces in different acidic environments.

The study can not only help to understand the effect of anion adsorption on NPMCs and the characteristic of the active sites of these important catalysts, it is also of practical importance as high temperature proton exchange membrane fuel cells (HTPEMFCs) employ a phosphoric acid based electrolyte.

Developing Porous Graphene Foam Catalyst for PEM Fuel Cell

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Electrocatalyst that are used in heterogeneous electrochemical systems require 3-phase contact with gas and liquid present. If graphene with high thermal and electrical conductivities can be produced in 3D form, it will help achieving fast charge transfer, high gas/liquid permeability leading to high conversion, stability and long catalyst life. Polymer electrolyte membrane fuel cells are potential target in need of stable and low cost catalyst. Graphene has been utilized for this purpose, but commonly processed with chemical approaches through graphite layer separation. CVD process is not user friendly to produce graphene for heterogeneous electrocatalytic applications.

CVD process was utilized to grow graphene on metal foam structures that were processed at 900-1000 °C. Ar, N_2, H_2, CH_4 were used as carrier gases at varying flow rates. Following growth of porous graphene foam structures, base metal support was etched away. Final component was assembled into a membrane electrode assembly (MEA) after a series of functionalization (Fig. 1). PEM fuel cell testing was performed at different operating conditions under different assembly scenarios (commercial cathode/graphene anode; commercial anode/graphene cathode; graphene cathode/graphene anode, etc.). Figure 2 shows results for porous graphene on the anode side without any Pt catalyst. Response of the cell was recorded under oxygen and air flow and this was compared to a single cell with anode and cathode both coated with 0,4 mg/cm^2 Pt.

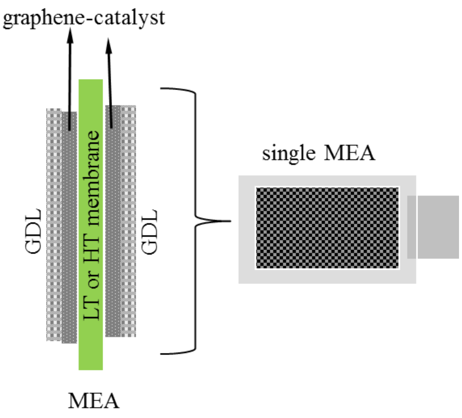

Figure 1. Schematic of graphene integration into MEA

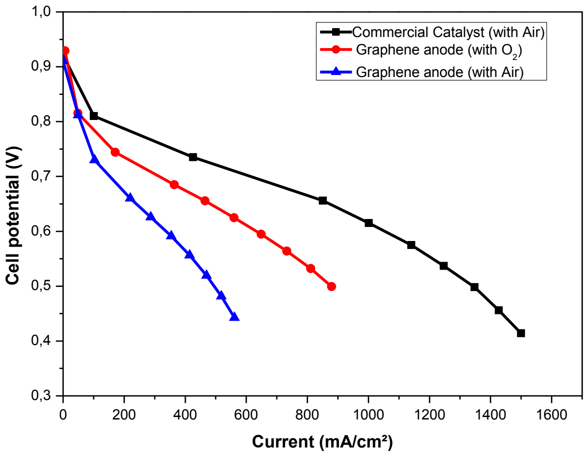

Figure 2. PEM single cell testing with 0,4 mg/cm2 Pt catalyst on the cathode and porous graphene on the anode.

Mass transfer properties and catalytic performance of newly developed materials will be discussed in detail along with doping effect (nitrogen, boron) on graphene formation and fuel cell performance.

Electrochemical Flow Cell/ICP-OES Setup for Investigations of the Oxygen Evolution Reaction

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In order to design stable OER catalysts for water splitting devices, the first step is to define a consistent methodology for robust catalyst investigations. Additionally an experimental setup is necessary, where both stability and activity can be studied using the same set of parameters and with a distinct focus on stability [1].

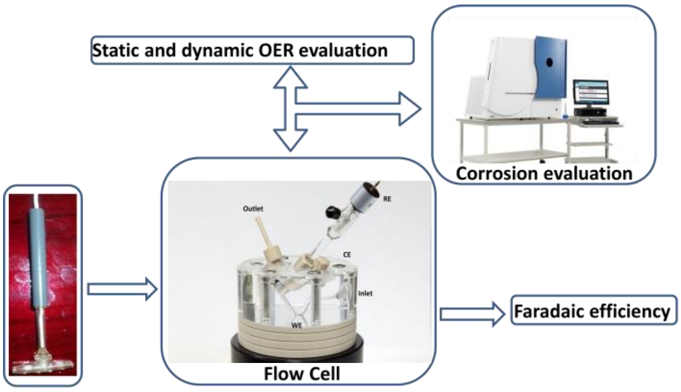

Fig. 1 Flow cell design and analytical techniques for performance and corrosion evaluation of OER catalysts.

For this reason, in this work we investigate promising OER catalysts while focusing on catalyst stability, using a standardized protocol for all measurements. We utilize a specialized setup for monitoring the corrosion profiles of metal oxide catalysts during static polarization. For this purpose, we combine an electrochemical flow cell (EFC) with an oxygen sensor and an Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) for the simultaneous investigation of the catalyst activity, deactivation, and faradaic efficiency (Fig. 1). We tested various catalysts, with IrO_2 and $NiCoO_2$ used as benchmark materials in acidic and alkaline environment [2]. Catalyst specific performance markers are used to compare the catalysts in spider graph plots (Fig. 2).

With this approach we are able to separate different origins of deactivation as, for instance, catalyst corrosion, deactivation by surface changes, and variations in the faradaic efficiency.

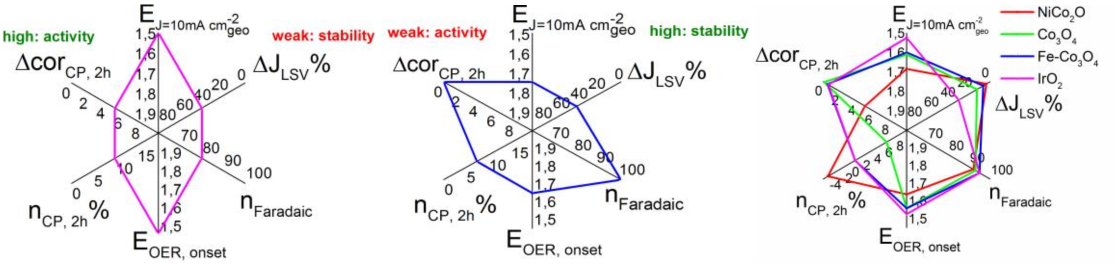

Fig. 2 OER catalyst comparison via spider graph plots of activity and stability-specific markers. Idealistic examples for a) a highly active but less stable catalyst and b) vice versa; c) comparison of different catalysts.

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Is the Rotating Disk Electrode a Suitable Tool for the Evaluation of Catalysts for the Oxygen Evolution Reaction?

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The generation of hydrogen by electrolysis of water is one of the key technologies in sustainable energy scenarios [1]. The limiting factor for an economically feasible application is the kinetically sluggish oxygen evolution reaction (OER) at the anode [2]. As it is less-well understood than its cathodic counterpart, and mostly relies on pricey noble-metal-based catalysts, a tremendous amount of current research focuses on the evaluation of alternative OER catalysts.

Most commonly, a rotating disk electrode (RDE, [3]) is utilized to evaluate novel catalysts. Though the technique does not require complex instrumentation, some care has to be taken when using RDE to compare electrocatalytic performances. Obviously, changes in the experimental parameters such as scan rate, potential range, or rotation speed will have an influence on the results. It is, hence, not straightforward to compare RDE measurements that have been conducted following different protocols. Although some standardization attempts exist [4], there is no widely accepted protocol that would allow for an easy comparison of literature data.

Here we will present our efforts to establish a standardized electrochemical measurement protocol for the characterization of OER catalysts within a multi-partner project. The protocol probes both the activity and, most important, stability of catalysts. In an effort to enable good comparability, all project partners were equipped with identical setups and used identical protocols and chemicals for the characterization of a nickel cobalt oxide-based benchmark catalyst. While it is possible to get a reasonable reproducibility within one laboratory, the comparison of different laboratories and users still reveals a considerable spread of results. This shows that even with the same equipment and protocol, reported literature values cannot be compared straightforwardly.

Hence, an argument is developed that RDE in isolation cannot serve as comprehensive technique for catalyst evaluation. Rather, RDE has to be complemented by additional analysis, which should include structural analysis before and after operation and in-situ analysis where possible. We will present our results and concepts concerning thorough catalyst evaluation including the influence of binders in RDE experiments, in-situ Raman experiments, and scanning electron microscopy.

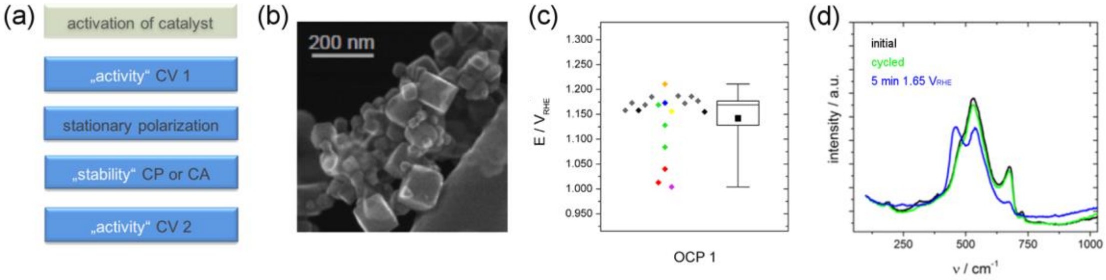

Figure 1: (a) simplified electrochemical standard procedure, (b) SEM of $NiCoO_2$ reference material, (c) variations in OCP of a $NiCoO_2$ standard electrode, (d) catalyst dynamics as probed by Raman spectroscopy

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Nanoporous Pt Networks merge High Specific Activity with High Dispersion

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Standard fuel cell catalysts consist of Pt-based nanoparticles supported on carbon (Pt/C). We demonstrate a new concept using nanoporous Pt-Co networks as catalytic system. In a proton exchange membrane fuel cell (PEMFC) the catalyst is situated in a three-phase boundary between H^+ or OH^-, water and a gaseous reactand. Therefore, the catalyst layers have not only to catalyze the reaction. It also must be optimized for mass transfer of the reactant and proton conductivity, especially under fuel cell operating conditions at 0.6 V. Recent findings show that increasing the activity at 0.9 V_{RHE} is not always followed by increased activity in fuel cell relevant potentials[1]. By optimizing the catalyst layer for high current conditions mass transport is becoming the most important part [2]. In the new ultrathin and porous concept - Pt-Co is supportless and stabilized by itself – high mass transport is ensured. No carbon is necessary, which is also beneficial for the lifetime in PEMFCs [3].

Nanoporous Pt-Co (npPt) networks were synthesized by alternated sputtering of Pt and a base metal in a dual magnetron physical vapor deposition process followed by post-leaching of the base metal. The remaining Pt network was characterized for oxygen reduction activity in 0.1 M $HClO_4$. Specific activity of npPt is reaching the one for Pt-Co thin-films and dispersion is comparable and even higher as for Pt/C catalysts. Combining specific activity and dispersion, nanoporous Pt networks exceed the mass activity of recently explored Pt-Ni nanoframes [4]. Electronic structure, chemical composition, crystallinity, pore size and network dimensions were investigated with several techniques as EXAFS, SAXS, XRD, XPS, TEM and SEM. Nanoporous Pt and Pt/C were benchmarked in a gas diffusion electrode setup which gives information about mass transport processes occurring at fuel cell relevant potentials.

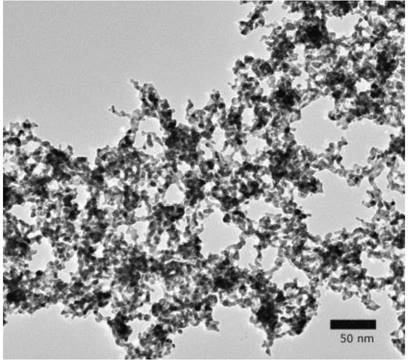

Figure 1: Transmission Electron Micrograph of Nanoporous Pt network

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Insights into the Promotional Effects of Carbon Nano-Onion Support Towards Glycerol Oxidation Reaction at Pd@MnO_2 Electrocatalyst

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Electrocatalyst-Supports play critical roles in the performance of fuel cells. It is well-recognized that the performance of a fuel cell electrocatalyst is intrinsically linked to its support [1]. An ideal support for an electrocatalyst should possess such features as good electrical conductivity, large surface area, good interaction with the electrocatalyst, good corrosion resistance, high stability in fuel cell environments, to mention a few.

Alkaline direct alcohol fuel cells (ADAFCs) have continued to be recognized as viable power sources for consumer and portable electronics compared to the hydrogen-fed fuel cells [1]. The key advantages of alcohols is they are liquids with high volumetric and gravimetric energy densities, and easy to transport. One of the most important polyhydric alcohols that have been recognised as a viable fuel is the glycerol (Gly) due to its bio-renewability, low toxicity, high boiling point and high energy density. Glycerol is less volatile than methanol and so can be easily transportable.

Carbon nano-onion (also known as onion-like carbon (OLC)) is a fullerene-like material with unique physico-chemical properties (e.g., nanostructure, high conductivity, high curvature and surface energy) [2] that have motivated researchers to investigate its possible application in several nanoscale engineering and technologies such as supercapacitors [3,4]. In this presentation, we will discuss our recent findings on the application of Pd@MnO_2 nanocatlyst, obtained via microwave-assisted synthesis, on OLC for the Gly oxidation reaction (GlyOR) in alkaline medium [5]. From our electrochemical measurements, we show that OLC, in contrast to the state-of-the-art Vulcan carbon, strongly promotes the electrocatalytic properties of Pd and Pd@MnO_2 for GlyOR in alkaline medium. To our pleasant surprise, the presence of OLC allowed for the generation of an ultrahigh current density for the GlyOR at Pd@MnO2 compared to when Vulcan carbon was used. We attribute these insightful findings to the synergy from the ternary nanohybrid (Pd@MnO_2/OLC) promoted by the unique intrinsic physico-chemistry of the OLC.

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Tin Dioxide Coated Carbon Materials for Extended Lifetime of Cathodic Electrocatalysts for PEMFC

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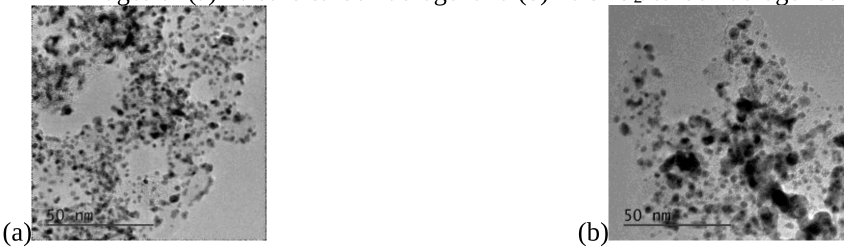
Proton Exchange Membrane Fuel Cells (PEMFC) are energy converters which can be used for automotive, stationary or nomad applications. This system is already used in niche markets. Nevertheless, some drawbacks, such as insufficient durability, need to be overcome to increase the market deployment. This insufficient durability is strongly linked to the corrosion of the carbon support in the cathode electrocatalyst [1]. The carbon corrosion leads to a local collapse of the support and a loss of catalyst which both dramatically reduce the fuel cell performances.

In this work, a coating of tin dioxide nanoparticles was deposited [2] on the surface of carbonaceous materials to create a composite that combines the electric conductivity of carbon with the stability of tin dioxide in fuel cell working conditions. The coating was optimized by increasing the tin dioxide precursor-carbon surface interaction and by adapting the quantity of the tin dioxide precursor to the specific surface area of the carbons. Different carbon materials with different organizations, morphologies and surface chemicals were evaluated: nanotubes, carbon blacks and carbon aerogel (CA). Organized (graphitic) carbons are more resistant to oxidation than amorphous ones [3], whereas carbon supports featuring high specific surface areas favors the dispersion of large amounts of catalyst nanoparticles per unit volume [4]. Bare carbon materials and tin dioxide/carbon composites were physically and chemically characterized by means of XRD, SEM, TEM, EDX, nitrogen sorption, TGA and electric conductivity.

Platinum nanoparticles (targeted platinum loading = 40 wt. %) were deposited on the bare carbons and on tin dioxide /carbon composites (TEM images for a CA support are shown at Fig.1). The catalytic activity of these electrocatalysts towards the oxygen reduction reaction was determined by linear sweep voltammetry (rotating disk electrode technique) at 25°C. Their stability is characterized by accelerated stress tests: load charge ($0.6 < E < 1.0$ V *vs* RHE) and start-up/shutdown ($1.0 < E < 1.5$ V *vs* RHE) protocols, conducted at $T = 80$°C in a four-electrode cell [5]. The electrochemical results depend on the nature of the carbon support (graphitized or not) and on the quality of the tin dioxide coating.

Fig.1 TEM images of (a) Pt-bare carbon aerogel and (b) Pt-SnO_2/carbon aerogel composite



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Controlling the Morphology, Activity and Durability of PtNi Porous Hollow Nanoparticles through the Nature of their Carbon Support

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Porous hollow PtNi/C nanoparticles (NPs) are extremely promising cathode electrocatalysts for proton exchange membrane fuel cells. Their defective structure – *i.e.* high microstrain, huge disparities in generalized coordination number – results in the presence of extremely active sites for the oxygen reduction reaction [1–4]. Moreover, their porous architecture increases the electrochemically active surface and, thus, their mass activity [5]. Controlling the density of structural defects of the surface, as the external and inner diameter of the NPs, is then essential. Here, we discuss the impact of the nature of the carbon support on the NPs morphological and electrochemical properties (see. **Figure 1**), as well as on their stability during ageing (500 cycles between 1.0 and 1.5 V vs. RHE at *T* = 353 K).

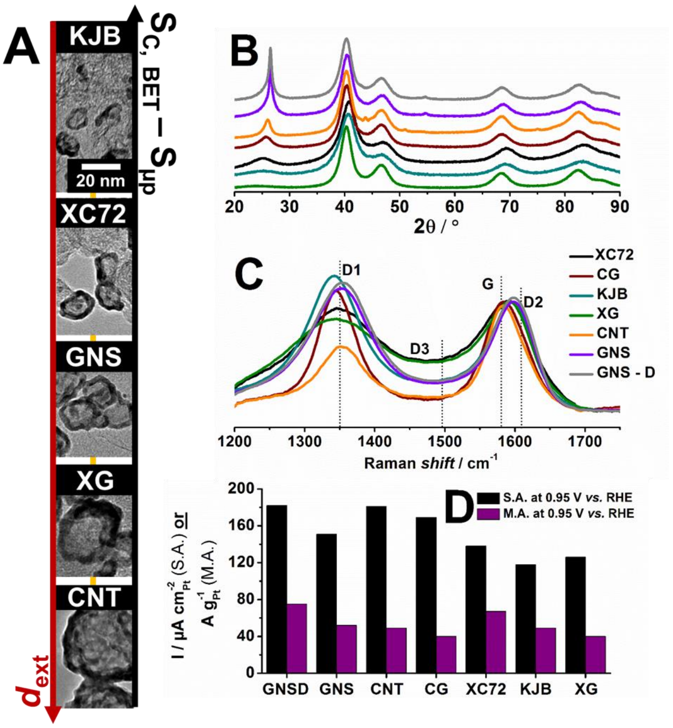

Figure 1: Morphological, structural and electrocatalytic properties of porous hollow PtNi nanoparticles synthesized on different carbon supports: Vulcan XC72 (XC72), Ketjenblack 600 JD (KJB 600), graphitized carbon (CG), Carbon Xerogel (XG), Carbon Nanotubes (CNT), Graphene Nanosheets (GNS and GNS – D, after an acid treatment). **(A)** TEM micrographs of the carbon-supported PtNi NPs, **(B)** XRD and **(C)** Raman patterns of the hollow porous PtNi/C NPs. **(D)** Specific (µA cm^{-2}_{Pt}) and mass (A g^{-1}_{Pt}) activity for the ORR.

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Incorporation of active impurities in nickel oxide leading to an improved activity for oxygen evolution reaction

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Abstract:

Nickel hydroxide $Ni(OH)_2$ and nickel oxide NiO electrodes are known as active electrocatalysts for the oxygen evolution reaction (OER) in alkaline media[1;2]. $Ni(OH)_2$, which in this work was synthesized via precipitation, can be converted to NiO by a simple heat treatment in air, where above a treatment temperature of 300°C NiO is formed. In this presentation, we will investigate the influence of heat treatment temperature on structure and activity using electrochemical and spectroscopic methods. As shown in Figure 1, the heat treatment temperature has a strong influence on electrocatalytic activity. At moderate treatment temperatures, a strong decrease in activity is observed, however at a temperature of 900 °C, NiO is demonstrating enhanced activity towards OER, although not as high as $Ni(OH)_2$. Structural investigations with Raman microscopy and XRD measurements show the formation of non-stoichiometric Ni_xO_y (y>x), an oxide where nickel is probably partly present in higher oxidation states. Non-stoichiometric Ni_xO_y seems to offer a large number of active sites due to electronic imbalances that are mostly of the same kind as in $Ni(OH)_2$, as concluded from cyclic voltammetry experiments by a similar behavior with applied potential. Raman spectroscopy experiments in dependence of the applied potential at the Ni_xO_y will reveal more specific information about structural changes during the oxidation process. Furthermore, a slight expansion of the unit cell of NiO at these high temperatures seems to optimize bond strength and binding energies of OER intermediates and hence activity of the reaction. Obviously, heat treatment leads to the formation of active sites transforming an inactive material to an improved catalyst for OER.

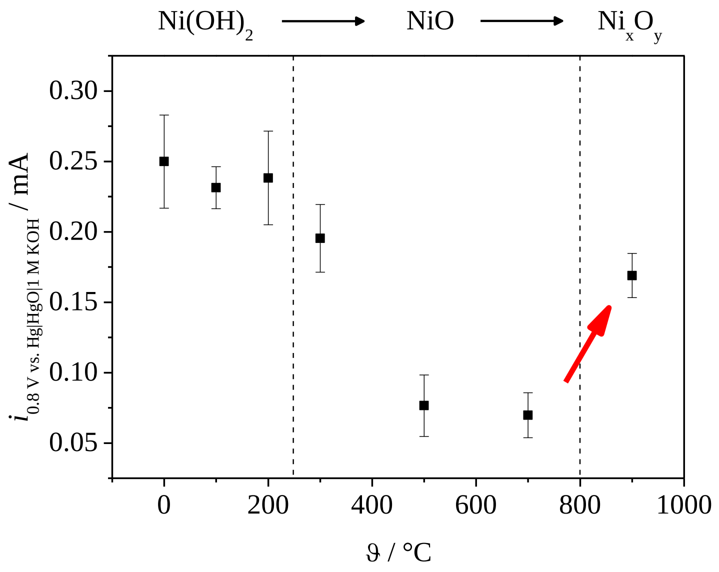

Figure 1: Activity (at 0.8 V vs. Hg|HgO|1 M KOH reference electrode) of nickel hydroxide heat treated at different temperatures and drop-coated onto glassy carbon electrodes (Ø 4 mm, 88 µg cm^{-2}) as obtained via linear sweep voltammetry in N_2 purged 0.1 M KOH solution with a scan rate of 1 mV s^{-1} from 0.0 to 0.8 V.

Literature:

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Study on Degradation of Solid Oxide Cells during Electrolysis and Co-Electrolysis Operation

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High temperature steam and co-electrolysis have a high potential for the efficient production of hydrogen or syngas as energy carriers for a sustainable energy supply. For a further development of this promising technology, development work on materials and cells as well as extensive operational experience is still needed. A main objective is to develop highly efficient and long-term stable cells and stacks using novel electrode materials and to improve the degradation behavior by elucidating the relevant degradation mechanisms.

In this paper we report a systematic investigation under relevant operating conditions such as temperature, fuel gas composition and current density on the long-term behavior of solid oxide cells. A special test bench allowing the electrochemical characterization of four cells simultaneously has been established. This arrangement allows for variation of one distinct operating parameter while keeping other parameters strictly constant. Fuel electrode and metal supported cells containing perovskite-type air electrodes fabricated by ceramic processing and sintering techniques have been electrochemically characterized in electrolysis and co-electrolysis operating mode by monitoring I-V curves and electrochemical impedance spectra. A series of measurements over at least 1000 hours each in the temperature range of 750-850 °C with different fuel gas compositions including different steam-to-carbon ratios and different current densities between 0 and 1.5 A/cm^2 has been performed in steam electrolysis and co-electrolysis operating mode. The progress of degradation was monitored in-operando approximately every 150 h by impedance spectroscopy measurements. Post-test investigations have been conducted to link the changes in electrochemical behavior with the microstructural changes and to correlate them with operational parameters. Results of electrochemical cell characterization performed at different operational conditions in electrolysis and co-electrolysis mode as well as on degradation phenomena observed are presented. Underlying mechanisms based on different electrochemical processes will be discussed.

A Novel RRDE Theory to Correct Quasi-Four Electron Oxygen Reduction over Fe/N/C Cathode Catalysts

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Understanding the kinetics of the oxygen reduction reaction (ORR) for fuel cell applications is quite important but difficult because the four-electron pathway is often overestimated by including a quasi-four electron pathway that consists of the formation and reduction of H_2O_2. To solve this problem, here we demonstrate a novel analysis method with experimental data over a Pt-free Fe/N/C cathode catalyst[1]. In this study, H_2O_2 voltammetry was conducted separately to evaluate the rate constant of the H_2O_2 reduction, k_3, more accurately, and the obtained data were combinatorally analyzed with those from the ORR experiments. First, mathematical modification of the conventional Damjanovic approach was performed as a modified Damjanovic approach, based on newly derived equations (1)-(3). And then the effect of the catalyst loading density was carefully studied by utilizing a novel reaction model (Fig. 1) with consideration of the quasi-four-electron pathway to avoid overestimation of the four-electron pathway kinetic parameters. Fig. 2a shows the reaction currents evaluated with the modified Damjanovic approach for a 120 μg cm^{-2} of a Fe/N/C catalyst prepared from polyimide nano-particles, resulting the overestimation of I_1. Fig 2a shows the reaction currents after the correction utilizing the model shown in Fig 1b. The contribution of I_2 and I_3 clearly increases by utilizing the newly proposed model.

$$I_1' = I_\mathrm{D} - \sqrt{\left(\frac{I_\mathrm{R}}{N}\right)^2 \left(1 + \frac{4k_3}{Z_2\omega^{\frac{1}{2}}}\right)} \qquad (1)$$

$$I_2' = \frac{1}{2}\left(\frac{I_\mathrm{R}}{N} + \sqrt{\left(\frac{I_\mathrm{R}}{N}\right)^2 \left(1 + \frac{4k_3}{Z_2\omega^{\frac{1}{2}}}\right)}\right) \qquad (2)$$

$$I_3' = \frac{1}{2}\left(-\frac{I_\mathrm{r}}{N} + \sqrt{\left(\frac{I_\mathrm{R}}{N}\right)^2 \left(1 + \frac{4k_3}{Z_2\omega^{\frac{1}{2}}}\right)}\right) \qquad (3)$$

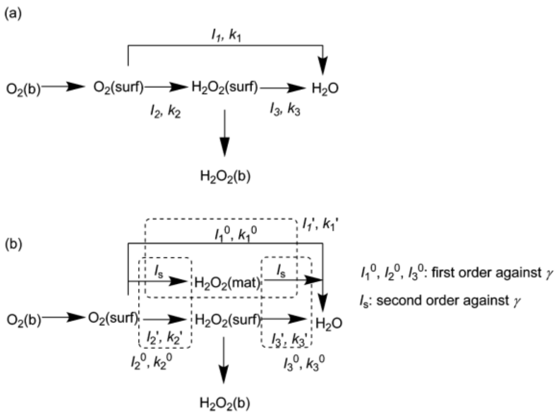

Figure 1. (a) Damjanovic and (b) newly proposed model.

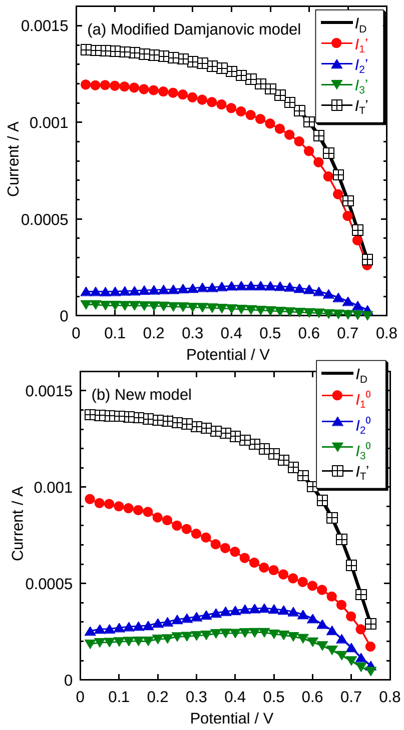

Figure 2. Reaction currents analyzed with (a) modified Damjanovic model and (b) new model.

Acknowledgements

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Pt and PtCo Alloy Catalysts Supported on SnO_2 with Fused-Aggregate Network Structure for PEFC Cathodes

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Under polymer electrolyte fuel cell (PEFC) operating conditions of low pH, high humidity and high potential, the carbon support has an intrinsic thermodynamic instability and degrades to carbon dioxide by oxidation. Non-carbon support materials that do not degrade in the high potential region will be required for high durability fuel cell vehicles (FCVs) for commercial use. Based on these viewpoints, we succeeded in the synthesis of Nb and Ta-doped SnO_2 (Nb-SnO_2, Ta-SnO_2) supports with similar microstructure as carbon black (CB), by use of the flame oxide synthesis method.[1-4] The oxide crystallites obtained (size, 10-20 nm; specific surface area, 40-100 m^2/g) were partially sintered with nearest neighbor particles and constructed a fused-aggregate network structure. The development of both necking between particles and increased volume of primary pores (diameter < 30 nm) accompanied the change of microstructure from a closed-packed aggregate type to a chain-like aggregate one, which led to an improvement of the electrical conductivity on these SnO_2 supports. The durability during an accelerated durability test of startup/shutdown cycles (0.9-1.3V, 30 s) showed that the Pt catalyst supported on Nb and Ta-doped SnO_2 (Pt/Nb-SnO_2, Pt/Ta-SnO_2) had much higher durability than that of commercial Pt catalyst supported on carbon black (Pt/CB, Tanaka Kikinzoku Co.) and Pt catalyst supported on graphitized carbon black (Pt/GCB, Tanaka Kikinzoku Co.). We also succeeded in the synthesis of PtCo alloy catalysts supported on Ta-SnO_2 ($Pt_{100-x}Co_x$/Ta-SnO_2). The PtCo alloy catalysts were ca. 3 nm in diameter and highly dispersed on these SnO_2 supports, with high durability under acidic conditions. The mass activity and kinetically controlled current density for ORR at 0.85 V of $Pt_{100-x}Co_x$/Ta-SnO_2 increased with increasing Co content (x). The highest ORR activity at $Pt_{75}Co_{25}$/Ta-SnO_2 was confirmed to be over 2.5 times larger than that of commercial Pt/CB by use of a rotating disk electrode (RDE) evaluations. The durability during an accelerated durability test of load cycles (0.6-1.0V, 3 s) was also much higher than that of commercial PtCo/GCB. We concluded that $Pt_{100-x}Co_x$/Ta-SnO_2 was the preferred catalyst, with high ORR activity and high durability under the startup/shutdown and load cycle conditions.

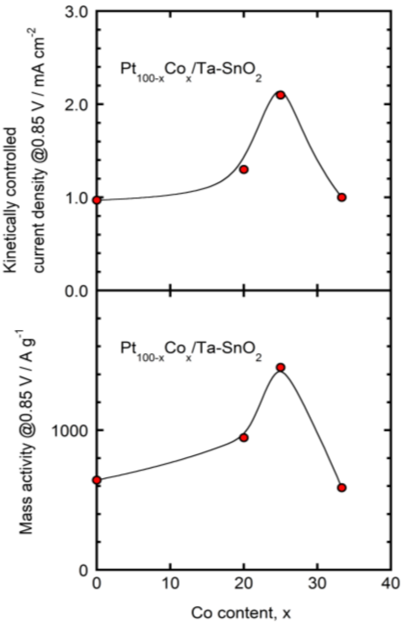

Fig. 1 Kinetically controlled current density and mass activity at 0.85 V for ORR activity at $Pt_{100-x}Co_x$/Ta-SnO_2.

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In Operando X-ray Based Structural Investigation of NiFe and CoFe Layered Double Hydroxide during the Oxygen Evolution Reaction

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Water electrolysis utilizes electricity to produce hydrogen from water, a process which is particular interesting for storing excess energy from renewable energy sources. In this technology, hydrogen is evolved at the cathode and oxygen at the anode. The kinetics of the oxygen evolution reaction (OER) are particularly sluggish, motivating the development of highly active and stable electrocatalysts. In alkaline electrolytes, NiFe based (oxy)hydroxides have been identified among the most active catalysts.[1] Their crystal structure is known as layered double hydroxide (LDH) and is composed of layers of edge sharing metal oxygen octahedra that are intercalated with water molecules and charge balancing anions (Figure 1, insert).[2] The incorporation of Fe^{3+} ions in $Ni(OH)_2$ layers is considered to be responsible for the formation of this structure and its activity enhancement.[3] Similarly, incorporation of Fe^{3+} into $Co(OH)_2$ leads to CoFe LDH. This catalyst has also superior OER activity respect to Fe-free $Co(OH)_2$.[4] Identification of the OER active structure is important for designing more active catalysts and there are evidences that the OER active structure of LDH catalysts during OER is different than the one of the as prepared materials.[3] Oxidative deprotonation and the electrocatalytic reaction might lead to structural differences that are only observable with *in operando* or *in situ* methods.

In this presentation we will discuss the results of an *in operando* X-ray absorption spectroscopy and diffraction study on crystalline NiFe and CoFe LDH nanostructured catalysts. We identified the structure of the catalytically silent and active catalyst state and observed that for both catalysts the interlayer distance contracts under operating conditions to a similar value (figure 1). Our results show structural modifications under operating conditions which correlate with the electrochemical activity in alkaline electrolyte. Thus they provide new insights into the structure of the active catalysts state which will help to understand the processes under catalytic conditions.

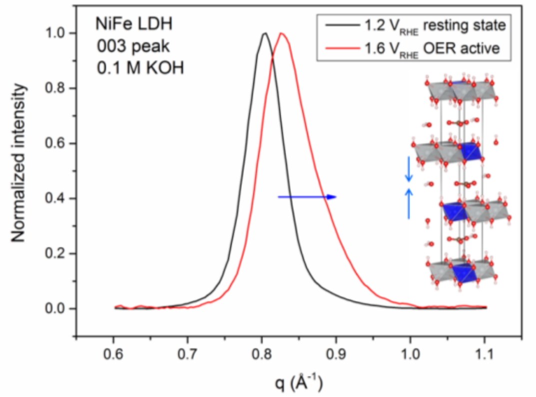

Figure 1. Shift of the (003) diffraction peak associated to the interlayer distance for NiFe LDH catalysts between the resting state (black) and OER active state (red) (unpublished). 3D structural model of the as prepared NiFe LDH with intercalated water and carbonate ions shown in the insert.

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An X-Ray Absorption Look into the Structure of Iron and Cobalt Based Electrocatalysts for PEM Fuel Cells

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Earth-abundant metal-nitrogen-carbon electrocatalysts designed for low temperature fuel cells, metal-air batteries and electrolyzers are the most promising candidates as alternatives to high-cost Pt catalysts. Heat-treated Me-N-C (Me=Fe, Co) catalysts, synthesized from the pyrolysis of elemental precursors, reinforced the commitment in finding a viable alternative to the platinum-based rivals, as they demonstrated to efficiently catalyze the cathodic oxygen reduction reaction (ORR) in fuel cells.[1,2]

In spite of recent progresses in terms of catalytic activity, the exact structure of the active FeN_xC_y or CoN_xC_y moieties formed at high temperature has remained elusive for two main reasons. First, the non-crystallographic ordering of the metal atoms in pyrolyzed Me-N-C catalysts and the low density of active sites. Second, the simultaneous presence in the vast majority of pyrolyzed catalysts of ORR-active sites along with ORR-inactive or less active phases (reduced metal, metal-carbide, nitride or oxide) has prevented recording the spectroscopic fingerprint of the active sites.

A cornerstone of the present study is the synthesis of active Me-N-C catalysts that are entirely free of metal-based particles. This allowed us recording the spectroscopic response of the metal-based moieties atomically dispersed in graphene sheets. A powerful combination of Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near-Edge Spectroscopy (XANES) allowed us to decipher the active sites' nature. In particular, the XANES analysis, involving the optimization of several model structures to fit the experimental spectrum, revealed a porphyrinic-like arrangement of N and C atoms around the central Fe ion (Figure 1).[3] This result contrasts with the pyridinic nitrogen structure often assumed till now. As for Fe-N-C, the porphyrin-like CoN_4C_{12} moiety is found to be the most probable structure, but other defective moieties with lower coordination number are also viable candidates. Furthermore, *operando* XANES spectroscopy performed in the ORR potential region shows a distinct behavior of CoN_xC_y and FeN_xC_y moieties, highlighting differences in the way how such sites catalyze the ORR.

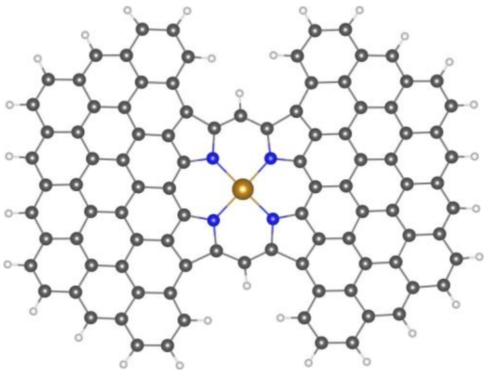

Figure 1 Porphyrinic-like model found to be the underlying architecture in Fe-N-C and Co-N-C catalysts.

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PGM free Electrocatalyst based on Fe-N$_x$ modified Mesoporous Carbon prepared from Biosources for ORR

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The physical amount of platinum existing on the Earth is barely enough to cover the world demand in the next forty years for fuel cell vehicles. Furthermore, the high cost and the low durability of platinum-based catalysts are serious obstacles to the large-scale commercialization of PEMFCs. Nitrogen doped mesoporous carbons are emerging as a new class of Pt free materials for ORR.[1,2] In particular, it was observed that doped carbons containing small amount of transition metals, such as Fe or Co, can catalyse the O_2 reduction to H_2O at overpotentials comparable to that of the most active Pt catalyst.[3]

In this paper, nitrogen doped mesoporous carbons containing small amount of Fe and/or Co (M@N-MC,) were prepared from several types of low cost carbon source polysaccharides. The synthesis consists in the formation of a hydrogel embedding an iron or cobalt metalorganic complex, which should assure an optimal Fe dispersion before pyrolysis and an optimal porosity network after pyrolysis. After the freeze-drying of the gel, the material is subjected to a first thermal treatment to obtain a crude product, which is further activated at high temperature. XPS analysis reveals the presence of various forms of iron oxides and a distinct peak due to the Fe−N$_x$ bond at 708.6 eV (Fig. 1a). Beside Fe-N$_x$ not visible from TEM analysis, iron is present as core shell NPs with iron oxide core and carbon shell.

The catalytic performances of catalyst ink prepared from M@N-MC were investigated by cyclic voltammetry and by rotating ring-disk electrode in 0.1 M $HClO_4$ attesting that O_2 is reduced following an almost 4e$^-$ pathway at very positive potentials (0.8 V vs RHE) (Fig. 1b).

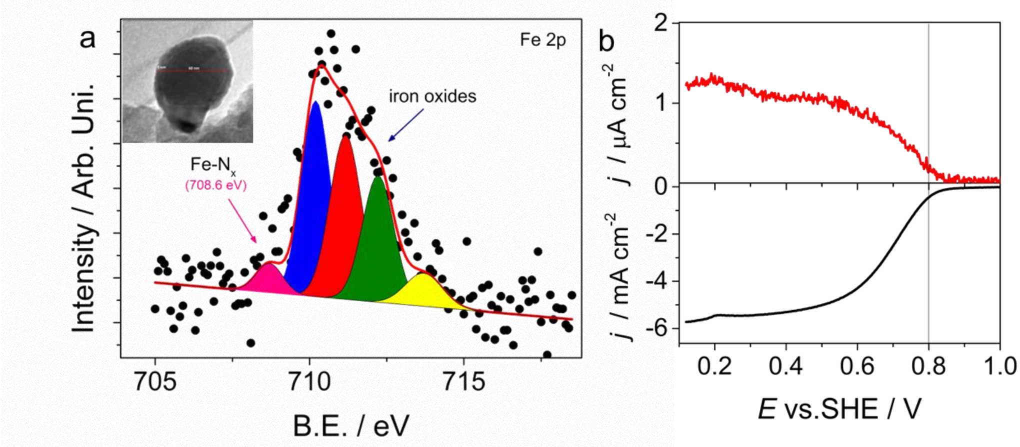

Figure 1. (a) Fe 2p XPS detailed study and deconvolution signals, and Fe NP TEM image (b) Example of RRDE measurement on Fe@N-MC in 0.1 M $HClO_4$ at 1600 rpm and ν = 5 mV/s.

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Hexagonal Close-Packed Platinum-Nickel Alloy Nanostructures and their Superior Activity towards Hydrogen Evolution Reaction

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Noble metal materials have enormous applications in many important fields.[1] The discovery of new crystal phases of noble metal materials provides an opportunity for achieving novel functionalities due to different atomic arrangements and electronic structures of allomorphs, and thus is an important approach for new materials/catalysts development.[2] However, the regulation of crystal phases is extremely difficult. Only a few meta-stable phases of noble metal based nanocrystals (NCs) were reported so far, and most of them are achieved in harsh conditions (such as high temperatures and high pressures) or with specific template.[2] Herein, we report a successful synthesis of hexagonal close-packed (*hcp*) Pt-Ni alloy nano-multipods in a mild solvothermal condition. Compared with the face-centred cubic (*fcc*) structure (thermodynamic stable state), the unexpected *hcp* Pt-Ni alloy nanostructure exhibits superior catalytic property towards hydrogen evolution reaction in alkaline electrolyte. The overpotential is only 65 mV *vs* reversible hydrogen electrode (RHE) at a current density of 10 mA·cm^{-2}, and the mass current density reaches 3.03 mA·μgPt^{-1} at -70 mV *vs* RHE, which is 6.5 and 2.0 times higher than those of commercial Pt/C and the *fcc* counterpart, respectively. In addition, the activation energy of the *hcp* Pt-Ni excavated multipods was measured to be 17.8 kJ·mol^{-1}, which was smaller than that of *fcc* counterpart (27.5 kJ·mol^{-1}) and the commercial Pt/C (32.0 kJ·mol^{-1}). The results indicate that the intrinsic activity of the *hcp* Pt-Ni excavated multipods for HER is better than those of the *fcc* counterpart and the commercial Pt/C in a basic medium. The enhanced HER activity of the *hcp* Pt-Ni excavated nano-multipods can be due to the allomorph effect of the Pt-Ni alloy.

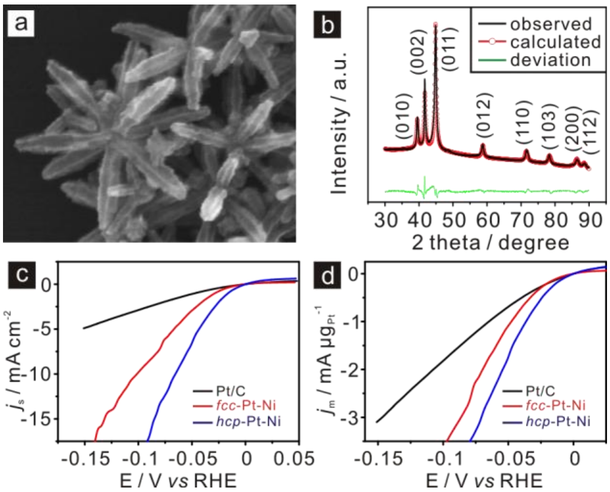

Figure 1. (a) SEM image (b) XRD pattern of the *hcp* Pt-Ni nano-multipods. (c)-(d) HER polarization curves of three catalysts (*hcp* Pt-Ni nano-multipods, fcc Pt-Ni and Pt/C, respectively) in 0.1 M KOH normalized by (c) ECSA and (d) mass of Pt. Scanning rate: 10 mV·s^{-1}; rotation rate: 1600 rpm; temperature: 293K.

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Mechanistic Insight into Alkaline Oxygen Reduction Reaction over Nitrogen bearing Carbon Spheres

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A modern solution to the ever-increasing energy demand is air breathing electrodes underlying the principle of oxygen reduction reaction (ORR). A step ahead either in efficient ORR electrocatalysis or in understanding the mechanism involved is equivalent to advancing towards resolving crisis in energy production (like in fuel cells) as well as storage (like in batteries). The present study is directed towards analyzing the path followed for complete conversion of oxygen to water in alkaline media by anisotropicaly designed nitrogen bearing carbon spheres (NCS) as catalyst. The NCS catalyst was synthesized using soft-template methodology without the need of post-synthetic template removal and resulted in a total nitrogen content of just 2.6% yielding promising ORR activity. The carbon atoms located in close proximity to the anisotropic N-atom had relatively positive charge compared to the other carbons and were found to be the active sites for adsorbing the incoming oxygen to perform electroreduction as suggested by density functional theory calculations. Mechanistic insight was achieved by an in-depth microelectrochemical assay employing pulsed chronoamperometric sample generation-tip collection (SG-TC) mode to detect the transitional H_2O_2 species which on one hand precisely determines the ORR onset (found to be 0.985 *V vs.* RHE) and on the other, details the ongoing mechanism due to its fast and localized screening ability. These outcomes were further supported by performing rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) measurements whose rigorous analysis yielded a high oxygen reduction rate constant of 4.6×10^{-4} cm/s and confirmed the involvement of H_2O_2 species with its further reduction to water at high reduction potentials also supported from theoretical considerations. Besides this, the electrocatalytic activity was also imaged with high resolution for the first time by scanning electrochemical microscopy (SECM) in highly alkaline media depicting the homogeneously distributed active sites throughout the catalyst. Therefore, the employed NCS catalyst was found to be kinetically efficient and sturdy for reducing O_2 in highly alkaline media towards becoming a promising ORR catalyst in low temperature fuel cells.

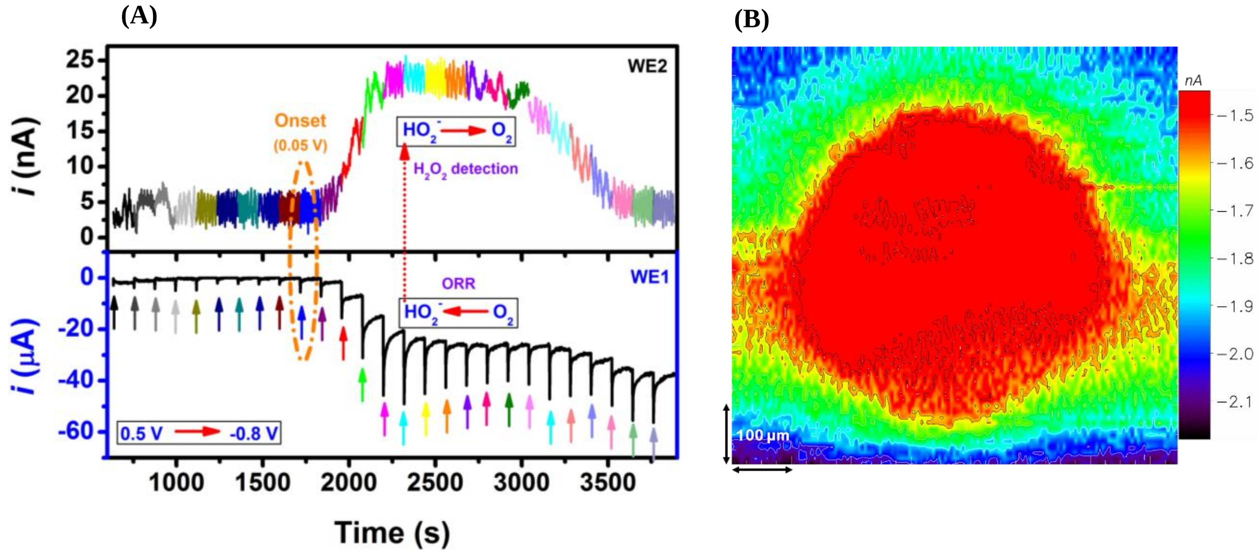

Figure. (A) Chronoamperometric SG-TC measurement of reaction occurring at the Pt ultramicroelectrode (WE2; held at 0.5 *V*) in response to the application of potential pulse profile at the NCS sample (from 0.5 to -0.8 *V*) over NCS spot (WE1) to reduce oxygen in 1 M NaOH and (B) SECM imaging performed in redox-competition mode for the NCS spot *vs.* Pt ultramicroelectrode. CE: Pt coil; RE: Hg/HgO/1M NaOH

Distribution of Current Lines in Catalytic Layers of PEM Water Electrolyzers

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ABSTRACT

The concept of Proton Exchange Membrane (PEM) cell was initially developed for fuel cells [1], and later extended to water electrolysis (PEM-WE). PEM-WE is considered as a key technology for the production of hydrogen of electrolytic grade. Main applications are (i) H_2 as chemical for miscellaneous end-uses in the industry sector; (ii) H_2 as an energy vector for land, sea and air mobility; and (iii) H_2 as an energy vector for large scale energy storage (power-to-gas). In conventional PEM-WE technology, proton-conducting membranes made of perfluorosulfonated polymers are used as solid electrolyte and cell separator. Platinum group metals (PGMs) are used as electrocatalysts because of their high electrochemical activity towards the two half-cell reactions and their appropriate chemical stability. Unsupported or carbon-supported platinum nanoparticles are used at the cathode for the hydrogen evolution reaction (HER) and unsupported iridium dioxide particles are used at the anode for oxygen evolution reaction (OER). Modern PEM-WE cells are efficient and very compact. Operation at current densities of several A.cm^{-2} is common good practice, not only in laboratory-cells but also in MW-scale commercial systems. However, the kWh-to-H_2 efficiency is a critical parameter that still requires optimization. This can be achieved by improving the chemical composition of electrocatalysts, but also the micro-structure of catalytic layers and the cell design. In PEM-WE cells, porous current collectors (usually made of millimeter-thick plates of sintered titanium particles, with open porosity for gas collection) are pressed against micrometer-thick catalytic layers. The distance between contact points varies with porosity and can be 10-50 μm apart (Fig. 1). Despite the HER and OER overvoltages, and the membrane resistance, that tend to homogenize current lines within catalytic layers, there are local-scale current distribution heterogeneities. Resulting local thermal gradients that can induce specific ageing processes (e.g. via local differential swelling or hot spot formation) do exist, a situation that needs correction. In addition, the overall cell efficiency can be negatively impacted because of the higher cell resistance. The situation can be even worth when catalytic layers thinner than average are used to minimize PGM contents [2,3]. The purpose of this communication is to report on a coupled numerical/experimental analysis of current lines distribution (both primary and secondary) in PEM water electrolysis cells (Fig. 2). The impact of the porosity of current collectors on the electrochemical efficiency of electrolysis cells has been determined (Fig. 3). It is shown that current lines are heterogeneously distributed. The efficiency of the water splitting process is affected and a variety of ageing processes than tend to reduce the lifetime and long-term electrochemical performance of the cells are induced.

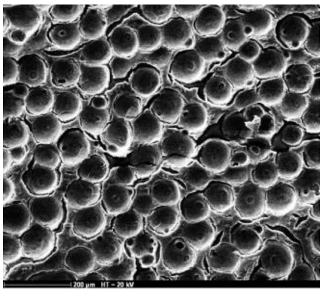

Fig.1. top SEM view of PEM-WE O_2-catalytic layer.

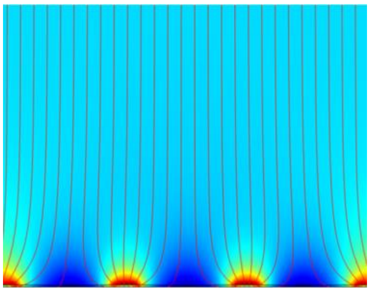

Fig. 2. 2-D calculated current line distribution in a PEM-WE cell.

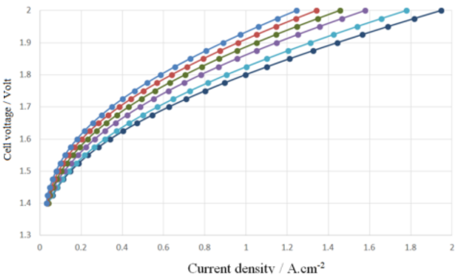

Fig.3. calculated U-j curves for collectors of different porosity.

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A Carbon-Support-free Titanium Oxynitride Catalyst with Improved Activity for Oxygen Reduction Reaction in Acidic Media

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Most non platinum-group-metal (PGM) catalysts for polymer electrolyte fuel cell cathodes have hitherto been iron(cobalt)/nitrogen/carbon [Fe(Co)/N/C] composites owing to the high activity [1]. However, the stability remained insufficient and recent studies revealed the instability was mainly due to the slow oxidation of carbon-supports [2]. Group IV or V metal oxides, another class of non-PGM catalysts, are free from carbon oxidation whereas they have attracted less number of researchers in the fuel cell community. One of the reasons is the difficulty in evaluating the ORR activity due to the insulating nature of oxides, which resulted in the use of instable carbon-supports [3]. We therefore recently synthesized carbon-support-free titanium oxynitride catalysts [4]. By simply changing the supports from previously used carbon black [5] to hydrothermally synthesized Ti_4O_7, the catalyst displayed the highest activity among carbon-support-free oxide catalysts whereas further improvement in activity was still necessary to be comparable to that of Fe/N/C and platinum catalysts.

In this study, two factors were revealed to significantly enhance the activity. The one is to optimize the solvent in the precursor dispersion and the other is to utilize second pyrolysis under NH_3 gas as shown in the top and bottom panel of Fig. 1, respectively. The half-cell test results and surface analyses with Raman and X-ray photoelectron spectroscopy revealed that activity increased with increasing nitrogen doping level on the surface TiO_2, agree well with our previous reports [4,5]. By optimizing the NH_3 pyrolysis temperature, nitrogen-doped TiO_2 catalyst exhibited only 0.06 V higher overpotential compared with commercial carbon-supported platinum in 0.1 mol dm^{-3} H_2SO_4 solution for the first time.

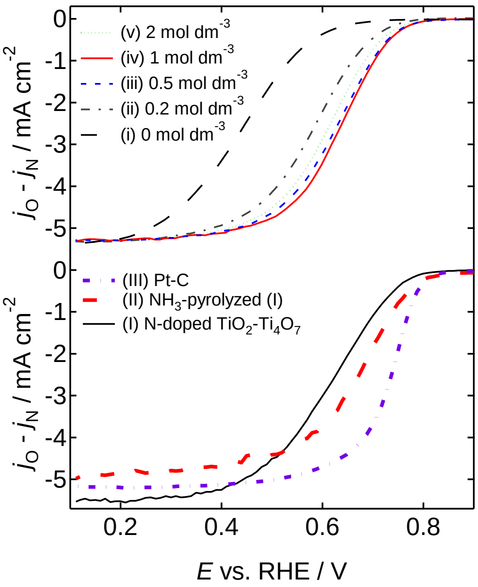

Fig. 1. Rotating disk electrode voltammograms of (top) support-free N-doped TiO_2 synthesized from TiF_4 with five HCl concentrations after optimizing the N_2-pyrolysis temperature and (bottom) (I) N-doped TiO_2–Ti_4O_7 synthesized under conditions identical to those of (iv), (II) NH_3-pyrolyzed (I) at 700 °C, and (III) commercial Pt-C. The optimized N_2-pyrolysis temperature for (i), (ii)–(iv) and (v) were 950, 850 and 900 °C, respectively. The scans were performed in N_2 and O_2 atmospheres, with the rotation speed of 1500 rpm at a scan rate of 5 mV s^{-1} in 0.1 mol dm^{-3} H_2SO_4 solution.

Acknowledgements
This work was partially supported by a Grant-in-Aid for Scientific Research (C) (26420132) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) in Japan; a research grant from the Nippon Sheet Glass Foundation for Materials Science and Engineering; a research grant, KJ-2539, from the Kato Foundation for Promotion of Science in Japan; a research grant from Nippon Life Insurance Foundation and a research grant from Yashima Environment Technology Foundation. The X-ray photoelectron spectra were acquired with the support by Nanotechnology Platform from the MEXT in Japan.

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Durability of unsupported Pt-Ni Aerogel Cathodes in Polymer Electrolyte Fuel Cells

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State-of-the-art polymer electrolyte fuel cells (PEFCs) require large amounts of carbon-supported platinum nanoparticle (Pt/C) catalysts (up to 0.4 mg_{Pt}/cm^2_{MEA}) to account for the large overpotential of the cathodic oxygen reduction reaction (ORR) [1]. To reduce these excessive Pt-loadings and thus PEFC costs, the catalysts' ORR activity and stability must be enhanced; e.g. by alloying platinum with other metals like Ni, Cu, Co [2] and by replacing or completely removing the carbon support that suffers from significant corrosion during the normal operation of PEFCs [3].

To mitigate these activity and stability challenges, unsupported bimetallic Pt-Ni aerogels (see Figure 1) consisting of interconnected nanochains (~ 30 m^2_{ECSA}/g_{Pt}) were synthesized [4]. These materials meet the US Department of Energy ORR activity target for 2017 of 440 A/g_{Pt} at 0.9 V_{RHE} [5] when tested in liquid half cells. Considering that many promising catalysts have not demonstrated the outstanding performance expected from liquid half cells tests in the actual PEFC, performing the latter experiments is crucial to evaluate new materials from an application point of view [6]. Thus, Pt-Ni aerogels were processed into membrane electrode assemblies (MEAs) and characterized in a differential PEFC [7].

In this contribution, we will report on the MEA optimization process for unsupported Pt-Ni aerogel ORR catalysts and compare cell performance and durability (start-stop cycles, load cycles) to a conventional Pt/C benchmark (see Figure 1). The catalyst layers were investigated by focused ion beam - scanning electron microscopy (FIB-SEM) and transmission electron microscopy (TEM), pointing at the great impact of the catalyst layer structure and pore size distribution on the PEFC performance, and providing insights into the dominant degradation mechanisms during durability tests.

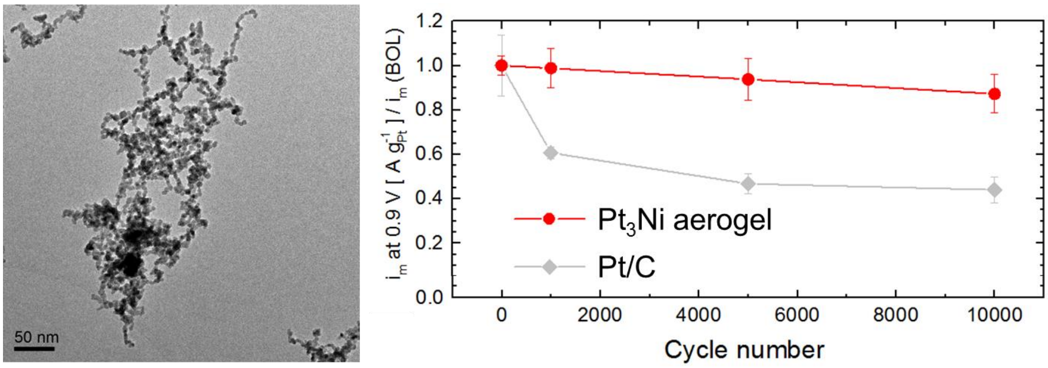

Figure 1. TEM image of Pt_3Ni aerogel (left) and mass activity evolution for start-stop cycle durability test between 1.0 and 1.5 V (right).

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Selective Oxygen Evolution Reaction in Seawater Electrolyzers by using NiFe-LDH as Highly Efficient Catalyst Material

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In times of energy revolution, renewable energy saving plays an ever-increasing role. Commonly used water electrolysis for hydrogen production requires precleaned or easily available freshwater sources. The direct use of seawater could promote sustainable energy technology in areas of scarce fresh water but easily accessible seawater. To realize a seawater electrolyzer, a selective Oxygen evolution reaction (OER) catalyst that simultaneously suppresses the Chlorine evolution reaction (ClER) is required.

Based on a seawater electrolysis design criterion[1], highly crystalline Nickel Iron layered double hydroxides (NiFe-LDH) was identified and prepared to be tested in a membrane based electrolyzer using anion exchange membranes. The crystallinity was confirmed by using X-ray diffraction (XRD) and elemental composition by using inductively coupled plasma -optical emission spectrometry (ICP-OES). The catalyst materials were tested in artificial seawater (0.5 M NaCl) and different KOH concentrations. A current drop was determined when adding NaCl to the electrolyte, while increasing the KOH concentration counteracted the loss in current density. To explore this effect, the anion exchange membranes (AEM) were further investigated regarding their Ion conductivity at different KOH and NaCl concentrations using a four-electrode set-up. Long-term stabilities were further tested galvanostatically and as load alternating day/night measurements. After reapplying seawater splitting potential, a strong "recovery effect" was discovered that could help increase overall activity and efficiency.

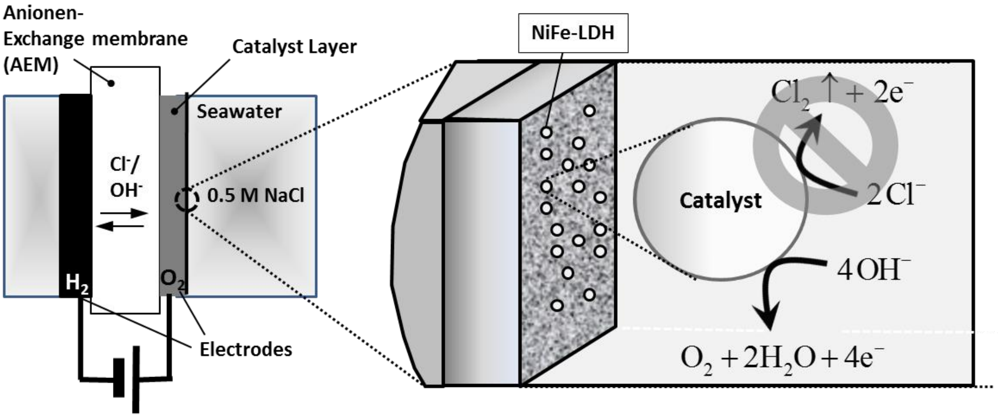

Figure 1:Simplified model of membrane based alkaline seawater electrolyzer and the corresponding anode reactions

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Tailoring the pore structure of cathodes for improving the steam electrolysis performance of solid oxide electrolysis cells

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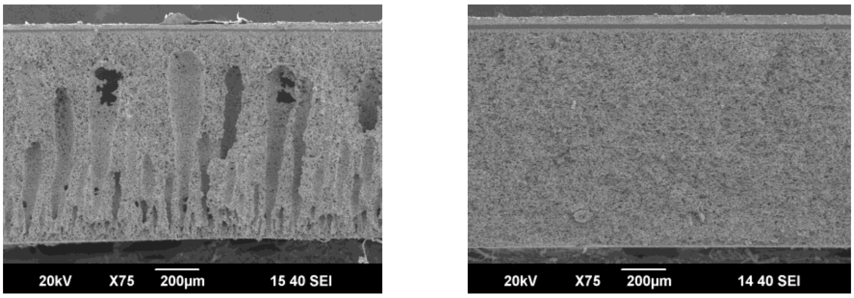
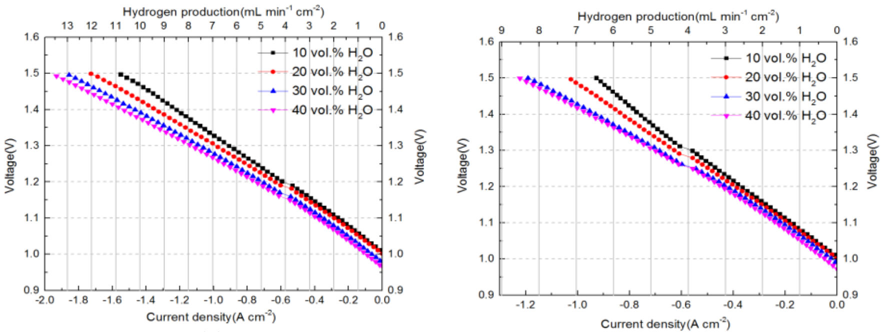
This study was aimed to improve the steam electrolysis performance by optimizing the pore structure of cathodes in solid oxide electrolysis cells (SOEC). Two planar NiO–yttria-stabilized zirconia (YSZ) cathodes were prepared by the phase-inversion and conventional tape casting method, respectively. The two cathodes had a similar thickness of ~900 µm, but exhibited distinctly different pore structure (Fig. 1). One contained finger-like straight open large pores which were created via the phase inversion mechanism, while the other contained randomly distributed pores which were created using graphite as pore former. The two cathodes were used as supports to fabricate solid oxide electrolysis cells (SOECs) comprising a 12 µm thick YSZ electrolyte layer and a 22 µm thick YSZ-$La_{0.8}Sr_{0.2})_{0.95}MnO_{3-x}$ anode. The steam electrolysis performance of the two cells was measured at 750°C at various steam concentrations. The cell with a cathode prepared by the phase-inversion method showed a high current density of 1.14 A cm^{-2} and a high H_2 production rate of 7.94 mL $cm^{-2}min^{-1}$ at 1.3 V and 40 vol. % humidity, while the cell with a cathode prepared by conventional method only 0.72 A cm^{-2} and 5.0 mL $cm^{-2}min^{-1}$ (Fig. 2). The much better electrolysis performance for the former cell is attributed to the presence of large straight open pores in the cathode allowing fast gas phase transport and thus exhibiting weak concentration polarization. It is concluded that the phase inversion tape casting is a simple and effective method for preparation of cathode-supported SOECs with desired pore structure.



(a) (b)

Fig.1 Cross-sectional SEM images of SOECs with cathodes prepared by (a) the phase-inversion and (b) the conventional tape casting method.



(a) (b)

Fig.2 Current-voltage curves of planar SOECs with cathodes prepared by (a) the phase-inversion, (b) conventional casting method. Testing temperature: 750°C.

Acknowledgment

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$NaBH_4$ concentration effects on the borohydride oxidation reaction (BOR) efficiency and mechanism at gold and platinum electrodes

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The borohydride electrooxidation reaction (BOR) has been under extensive focus in the last decade, because it is the anode reaction of direct borohydride fuel cells, devices that could positively compete with H_2-fed PEMFC for the powering of portable electrical devices. However, the theoretical promises of the BOR (theoretically possible *ca.* 0.4 V below the oxidation potential of hydrogen) are not experimentally validated yet: no practical electrode material is capable to oxidize the BH_4^- anion at low potential without significant hindrance of the hydrogen evolution reaction (HER, *i.e.* cathodic decomposition of water) [1]. Besides, a clear blur exists regarding the real faradaic efficiency of the BOR: for example, the number of electrons exchanged per BH_4^- anions has been found to vary between *ca.* 2 and 8 for Pt electrodes (see Refs. [2,3] for details) and many studies still consider Au as a potential DBFC anode catalyst. This uncertainty clearly originates from a lack of fundamental understanding of the BOR, in particular with regards to the influence of the experimental conditions on the reaction.

To go beyond these uncertainties, the present contribution experimentally surveys the BOR for varying concentrations of $NaBH_4$ (5, 50 and 500 mM) relevant to earlier model studies but also real DBFC tests. By coupling electrochemistry (rotating (ring-)disk electrode) to differential electrochemical mass-spectrometry (DEMS – Figure 1), it is shown that Pt remains more faradaic efficient than Au at any concentration of $NaBH_4$, at least below 0.4 V *vs.* RHE, the region of interest for DBFC. From these experimental findings, the BOR model from Ref. [4] is refined; it takes into account the HER as a (near-unavoidable) parasitic reaction but also poisoning issues with adsorbed BOR intermediates.

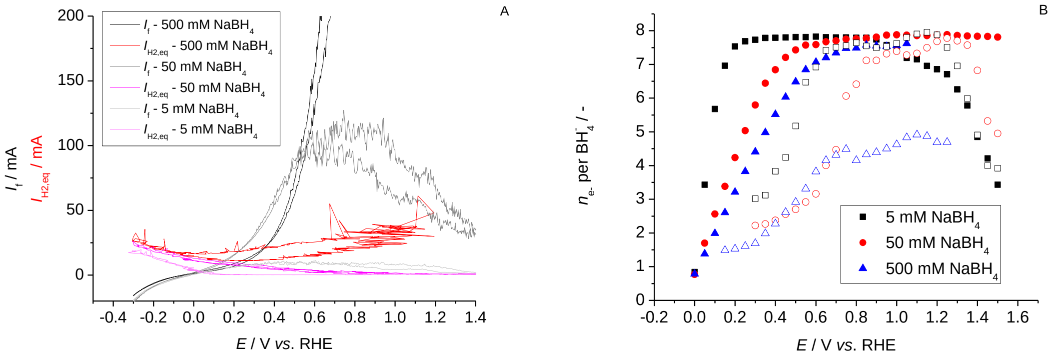

Figure 1: (A) IR-corrected faradaic BOR current and equivalent H_2 DEMS current monitored on Pt electrodes for different concentrations of $NaBH_4$. (B) Corresponding number of electrons exchanged per BH_4^- (plain symbols) compared with those monitored for an Au electrode in similar conditions (open symbols).

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Stabilization of Iron-Based Electrocatalysts for the Oxygen Reduction Reaction by Ultra-Low Amounts of Platinum

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Platinum has long been the state-of-the-art catalyst for the oxygen reduction reaction (ORR) in low-temperature fuel cells (FCs). More recently, N-doped carbon materials with embedded Fe- or Co-active sites have challenged Pt-based catalysts. With their low cost and high abundance, higher loadings can compensate for their lower activities.[1–3] However, they still lack sufficient stability under typical operating conditions.[4–6] One source of degradation can be oxygen radicals, originating from H_2O_2 as a side product of the reaction, which can significantly harm the catalyst and the FC-membrane.[7]

Here, ultra-low amounts of Pt (0.5 - 2 wt%) are deposited onto a well-characterized Fe-N-C material, prepared from phenanthroline, Fe^{II}-acetate, and the metal organic framework ZIF-8.[8] The resulting hybrid catalyst is intended not only to have an increased overall activity, but also to show better long time stability than the base Fe-N-C catalyst, for instance via peroxide scavenging by the added Pt.

Surprisingly, the Pt addition did not influence the activity, neither in the rotating disc electrode (RDE) nor in a single FC test station. What seemed initially as an unsuccessful attempt revealed its key capability during the stability measurement: In contrast to the Fe-N-C catalyst, the hybrid material with only 1 wt% Pt could fully sustain the current density at 0.5 V for 50 h (Figure 1). Even more important, the activity was also retained at potentials above 0.6 V, which is the technologically relevant potential range.

From electrochemical results as well as X-ray analytics, it can be assumed that initially Pt is in an inactive state for the ORR. Interestingly, several post-mortem investigations indicate that this is unchanged even after the stability measurement. At the same time, Mößbauer spectroscopy shows that the total Fe-content in the hybrid material remains constant during operation. In conclusion, the present Pt-species prevent the degradation of the Fe-active sites without influencing the ORR itself, which shows a unique decoupling of activity and stability in the hybrid catalyst.

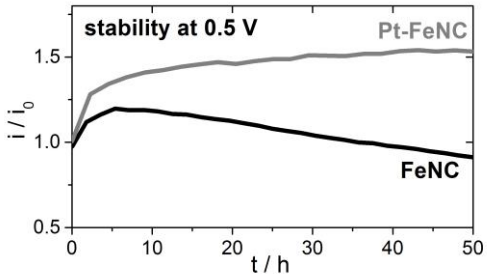

Figure 1 Chronoamperometric measurement over 50 h at 0.5 V in a single fuel cell test station (H_2/O_2, p_{rel}= 1 bar, T= 80 °C)

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Fluorine-Free Pt Nanocomposites for Three-Phase Interfaces in Fuel Cell Electrodes

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The first generation of proton exchange membrane fuel cells uses costly and unsafe perfluorinated sulfonic acid polymers (PFSAs) as membranes and as ionomers impregnating electrodes to achieve the three-phase boundaries. PFSAs imply paramount issues for large-scale manufacture, use, commercialization, and recycling. Alternative non-fluorinated polymers should allow obtaining not only membranes but also adequate ionomer suspensions in convenient solvents for preparing efficient catalytic layers, which has not yet been achieved. Here, we propose a universal solution consisting of the transposition of the three-phase boundary at the molecular level by grafting directly at the surface of carbon-supported Pt nanoparticles a non-fluorinated proton-conducting polymer combining the catalytic activity of the former and the transport properties of the latter. The length of the polystyrenesulfonate polymer chain (as a model polymer) and the number of polymer feet per platinum nanoparticles have been optimized in order to achieve the highest active surface area and activity as possible. It was shown that low grafting density and high degree of polymerization gave the best configuration. The great potency of such nanocomposites as cathode catalysts for PEMFC was evidenced not only in a standard three-electrode cell but also under real working conditions in a single hydrogen/oxygen fuel cell, where higher activity and stability were obtained with a nanocomposite material in comparison to those with a classical Pt/C + Nafion electrode.

3D-porous carbon nanofibers as promising support for platinum catalyst to enhance oxygen reduction reaction in fuel cells

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The major challenges faced by proton exchange membrane (PEM) fuel cells are high cost and insufficient durability, which are largely hindering their commercialization proceedings. These two major challenges are closely related to the Pt-based catalysts for cathode oxygen reduction reaction (ORR) due to the sluggish ORR kinetics at PEM fuel cell cathode. In the effort to reduce the cost and improve the performance of Pt-based ORR catalysts, tremendous efforts have been made through strategies of material selection, shape/size/structure controls and the fabrication of carbonaceous support, where the nanotubes, nanofibers and nanorods, etc. are at the forefront of potential in the design and preparation of Pt-based catalysts support. In this article, we report the promising initial performances of a 3D-structured PCNFs prepared by a facile electrospinning mediated pre-oxidation/carbonization procedure, which were then employed as the support to deposit platinum via an ethylene glycol reduction method. Benefiting from the aforementioned characteristics, the resulting Pt/PCNFs performs quite ORR activity, stability and fuel cell power density which are much superior to a conventional platinum catalyst with carbon black as the support (JM20), as show in Fig. 1. The special morphology of PCNFs support may lead to the following conclusions: (1) PCNFs could make Pt nanoparticles a uniform deposition and distribution, leading to more exposure of the active sites; (2) the loose 3D-channels of the catalyst layer induced by PCNFs could reduce mass transfer resistance significantly, thus increase local Pt catalyst utilization; and (3) the catalyst layer consisting of Pt/PCNFs could act as microporous layer so that water drainage can be improved to prevent the electrode from flooding. Thus 3D-porous carbon nanofibers show promising support for platinum catalyst to enhance ORR in fuel cells.

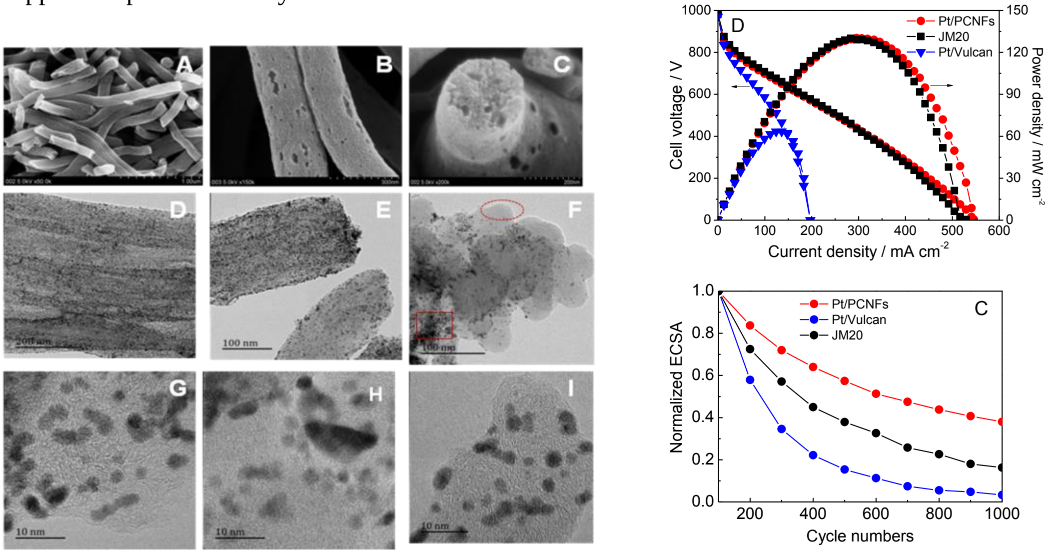

Fig. 1 (A), (B), (C) FE-SEM images of PCNFs support; (D), (E), (G) HR-TEM images of Pt/PCNFs; (F), (H) HR-TEM images of Pt/Vulcan; (I) HR-TEM image of JM20. (M) Single cell performance at 25°C; (N) the normalized ECSA curves

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Cobalt hexacyanoferrate supported on Sb-SnO_2 a promising non-noble anode catalyst for PEM water electrolyzers

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Polymer Electrolyte Membrane Water Electrolysis (PEMWE) is an appealing electrolysis technology with fast response, production of electrochemically-pressurized H_2 and low footprint. However, its current high cost could limit its widespread application in the future. Its operating conditions (acidic medium and high electrochemical anode potential) strongly limit the choice of materials that may be used, especially as Oxygen Evolution Reaction (OER) catalysts. Unsupported IrO_2 prevails as the anode catalyst in PEMWE but iridium is the rarest metal in Earth's crust with a production < 9 tons a year (1).

While Prussian-blue type coordination polymers are a well-known class of materials with interesting photocatalytic and electrochemical properties, such coordination polymers have only recently been demonstrated to be efficient catalysts for the OER (2). Among them, cobalt hexacyanoferrate (CoHFe) has hitherto shown the highest OER activity in neutral and acidic electrolyte (3) and, remarkable for precious-metal-free materials, has displayed strong stability in acidic medium down to pH 1 (4). However, CoHFe has not yet been integrated in a Membrane Electrode Assembly and tested in a PEMWE device. In doing so, a major drawback of CoHFe, and Prussian Blue analogues in general, is their low electronic conductivity. Hence, such catalysts need to be properly interfaced with an electron-conductive support that also tolerates the anode operating conditions of PEMWE. While the preparation of composites of CoHFe or Prussian blue analogues deposited on carbon allotropes has previously been investigated, carbon allotropes are unsuitable for PEMWE due to high rates of electrochemical carbon corrosion above 1.2 V *vs*. RHE, especially at temperatures above 60°C.

We will report on the interfacing of CoHFe nanoparticles with a conductive oxide that withstands the PEMWE anode conditions, namely antimony-doped tin oxide (ATO). The latter has recently been investigated as a corrosion-resistant support for platinum particles at the cathode of PEM fuel cells (5) and also as a stable support for IrO_2 at the anode of PEM electrolyzers. CoHFe nanoparticles were prepared by a modified literature protocol, involving the addition of 0.03 M $K_3Fe(CN)_6$ in formamide to 0.02 M $Co(NO_3)_2$ in formamide, forming a dispersion of CoHFe nanoparticles. ATO tubes were prepared by electrospinning $SbCl_3$, $SnCl_2$ and polyvinylpyrrolidone followed by calcination, as previously reported by us (6). The effect of weight content of CoHFe on ATO was investigated and the composite catalysts were characterized for OER in liquid electrolyte and in PEMWE. The CoHFe-ATO composite catalyst shows promising activity and stability in PEMWE operating conditions (80°C, Nafion® polymer electrolyte). The electrochemical response is stable during short stability tests up to 1.9 V, while the limited decay at 2 V and larger decay at 2.2 V is due to the instability of ATO at such high potentials.

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Anode Catalyst Layer Contributing to the Overall Impedance of Polymer Electrolyte Membrane Electrolysis Cells during Water Electrolysis – A Hypothesis

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Polymer electrolyte membrane electrolysis cells (PEMECs) for water electrolysis have been investigated with electrochemical impedance spectroscopy during operation at ambient pressure and at various operating conditions including current densities from 0.35 to 1 A/cm^2 and temperatures from 53 to 69 ˚C. Two interconnected processes dependent on current density and with summit frequencies around 0.4 and 100 Hz, are causing a large part of the overall impedance of the cells as can be seen in figure 1. The impedance measurements are complemented by iV-characteristics and cyclic voltammetry of the PEMEC. The iV-characteristics are linear at current densities above 0.16 A/cm^2 and cyclic voltammograms obtained at 61 ˚C are similar to those reported for iridium oxide in sulphuric acid (Papaderakis et al. 2015). In this presentation a hypothesis suggesting the anode catalyst layer to cause a large part of the overall PEMEC impedance will be presented. It is explained how this may account for findings from the three different electrochemical methods.

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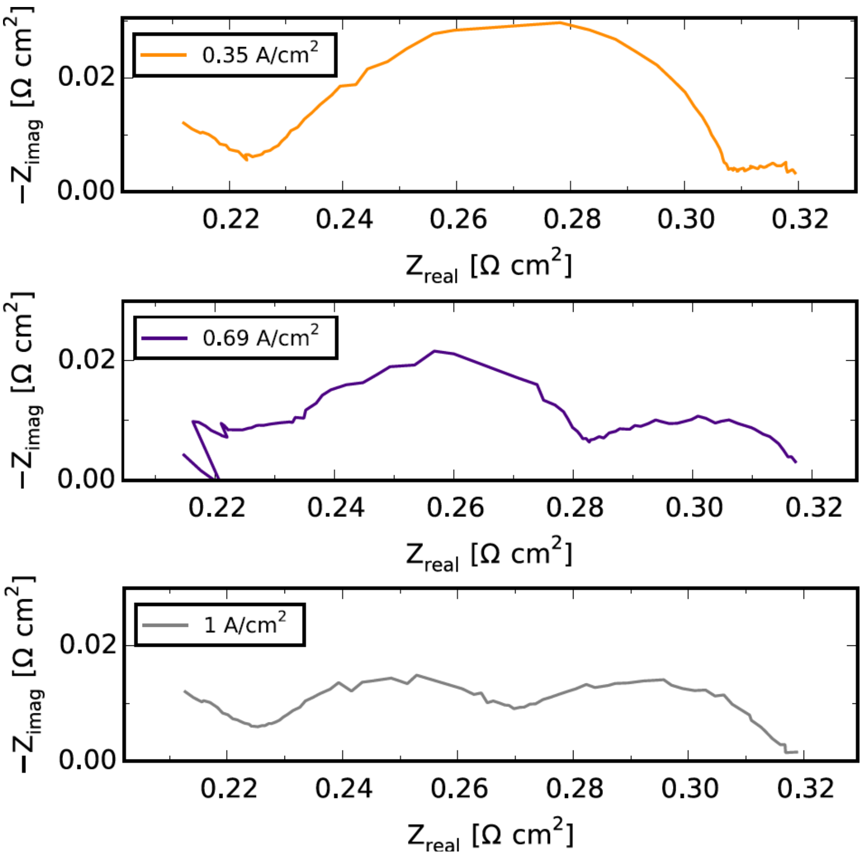

Figure 1. Electrochemical impedance data represented in Nyquist plots obtained on a PEMEC at current densities of 0.35 A/cm^2 (upper graph), 0.69 A/cm^2 (middle graph) and 1 A/cm^2 (lower graph) during water electrolysis at ambient pressure and 61 ˚C.

Improvement of Cell Performance in Low-Pt-Loading PEFC Cathode Catalyst Layers with Pt/Ta-SnO_2 Prepared by the Electrospray Method

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To reduce the Pt loadings in cathode catalysts for polymer electrolyte fuel cells, we focused on the catalyst material and catalyst-layer (CL) fabrication method, and prepared low Pt loading CLs with Pt/Ta-SnO_2 by the electrospray (ES) method [1] (Fig. 1). Two CLs were prepared by the ES method with different mass ratios of ionomer binder to support material (I/S), I/S = 0.7 and 0.2, and are compared to that prepared by the pulse-swirl-spray (PSS) method. Both ES CLs have higher porosity than that for the PSS CL, and have improved ionomer coverage and increased electrochemically active surface area (ECA) and mass activity at 0.85 V. In particular, that for the ES with I/S = 0.2 has high porosity and remarkably increased cell performance. The improvement obtained by use of the ES method can be explained on the basis that the coverage and uniformity of ionomer are increased due to the small droplet size. The performance of the ES cells is high, particularly under high backpressure conditions, because of the improved transport of both O_2 and protons. (Fig. 2) [2]

This work was supported by funds for the "Superlative, Stable, and Scalable Performance Fuel Cell" (S-Per-FC) project from the New Energy and Industrial Technology Development Organization (NEDO) of Japan. We are also grateful to Dr. Kazuyuki Tada and Mr. Kenji Ikeda from Fuji Xerox Co., Ltd. for helpful advice in electrospray method and to Dr. Ryo Koda from Panasonic Corporation for analyses by FIB-SEM.

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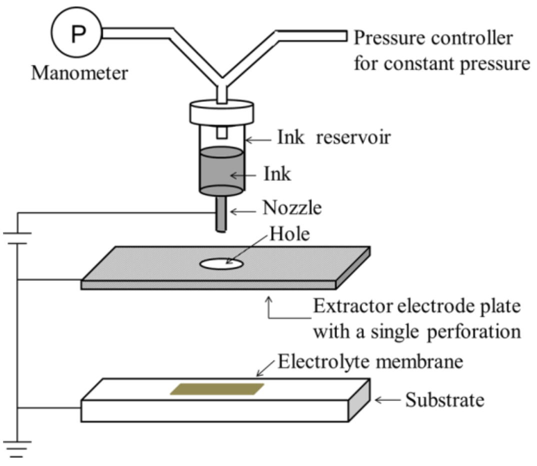

Fig.1 Schematic drawing of the ES process.

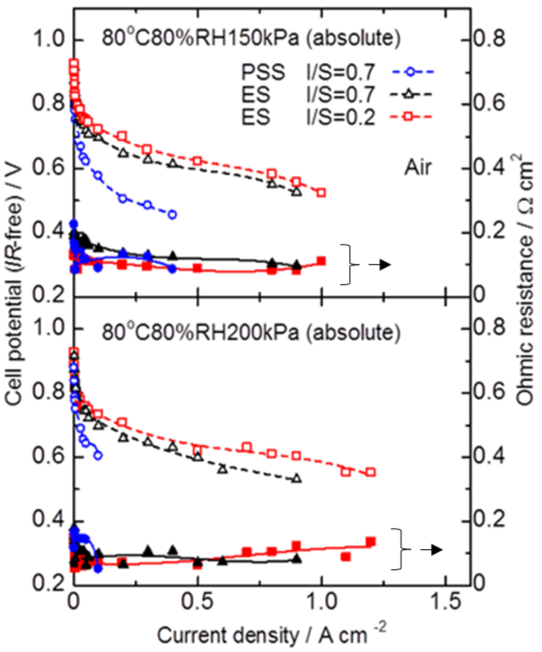

Fig.2 *IR*-free polarization curves, Ohmic resistances for PSS I/S = 0.7, ES I/S = 0.7 and ES I/S = 0.2 at 80 ºC, 80% RH, air/H_2, back pressure 150 kPa (absolute) and 200 kPa (absolute). The Pt loading amounts of the cathode CLs were confirmed to be 0.048 mg cm^{-2} (PSS I/S = 0.7), 0.048 mg cm^{-2} (ES I/S = 0.7) and 0.054 mg cm^{-2} (ES I/S = 0.29).

Electrode optimization and practical application of microbial fuel cells

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Microbial fuel cells (MFCs), promising for converting biomass energy into electricity, have attracted much research attention. In a typical MFC, exoelectrogens accumulate at the anode, degrading organic matters into small molecules and electrons. Electrons travel through the external circuit to the cathode where electron acceptors would be reduced, to form a complete circuit. Despite the emerging research enthusiasm in this field, challenges still remain including the material optimization and practical applications. Firstly, anode is an important element to accommodate the exoelectrogens, and should possess superior conductivity, space bio-compatibility and fast kinetics, meanwhile low cost and good stability. Exploration of such ideal anode materials is necessary. Secondly, oxygen is commonly used as a commonly used electron acceptor at the cathode because of its low cost, sustainability and abundant reserve, however the kinetics of oxygen reduction reaction is very slow while Pt/C catalyst is commonly applied to accelerate the kinetics. Exploration of highly efficient and stable meanwhile cost-effective catalysts is a must. Thirdly, MFCs provide low power output because of its intrinsic properties, and how to make best use of it would be a challenge.

Herein, we present our recent work on optimizing MFC anodes by utilizing natural protein to produce nitrogen-enriched pseudographitic anode with tunable flexibility, developing noble metal-free catalysts for oxygen reduction reaction for MFC cathode. In addition, we have also take advantage of the feasibility of using wastewater as the MFC anode fuel to develop a BOD sensor, to monitor wastewater quality with a short response time, which would promote MFCs into practical applications.

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Design and comparison different power management systems for mobile APU based on PEM fuel cell

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Modern rescue and military units require for their efficient work numerous electronic devices. Their number is rapidly growing in time. Whereas in fifties of the 20th century the typical equipment consisted of an electric lamp, in the 21st century it was extended *e.g.* by walkie-talkie, GPS, night-glasses and other electronic devices. Although energy consumption of these devices dramatically decreased within the last decades, demands on their performance is continuously growing. For all of them cut-off of the energy supply, or providing mobile, long-lasting and reliable energy supply for outdoor activities, represents an important issue. Typical long-time consumption of police/fire brigade mobile base with necessary equipment comprises 100-200 W of base load and up to 300 W of peak consumption. PEM fuel cell stack based mobile APU represents promising solution of this problem. Its main advantages are high flexibility and efficiency, high process intensity, instantaneous refueling and absence of moving parts, the last aspect being a reason of fuel cell silent operation. This fact is very important especially for medicine and military applications. Products of reactions taking place in the PEM fuel cells are electric energy, heat and water exclusively. This fact allows application of this technology also in areas sensitive to exhalations.

All above-mentioned devices represent dynamic loads. It is in contradiction to the preferable PEM fuel cell operation regime. This is reason, why power management is necessary for its efficient operation. This problem can be accomplished by utilizing correspondingly sized accumulators connected to the fuel cell stack. Li-ion accumulators represent suitable option to solve this task. It is due to their low weight and high charging/discharging currents. Main drawbacks consist in decrease of these currents by the low temperature, typically bellow 10 °C. At the temperature bellow 0 °C it is not possible to charge them. APU weight should not exceed 15 kg limit. It represent upper weight limit of the entire system. This limit excludes lead accumulators and super charge ion battery. Peroxide radicals are generated during operation on electrodes. These radicals can attack membrane and catalyst support. Elegant solution of this problem represents short-circuiting of the fuel cell for couple of milliseconds. These short-lasting shortcuts can be problematic for connected devices and represent a problem for balancers in standard acu-packs. Promising solutions and an alternative option represents utilization of supercapacitors. It is because they are able to switch fast between charging and discharging mode and to operate under high current load in a broad area of temperatures. Their main disadvantages consist in lower energy/weight ratio and higher spontaneous discharging current when compared to accumulators.

Target of this work is to propose different configurations and parameters of APU power management individual components. They have subsequently been tested with respect to minimizing variation in APU voltage with changing load. Selection of power management components was limited due to the requirement of limited weight of the system. In this study two typical APU applications were considered: (i) charger of accumulator of mobile base, wan, guard boats or medical centers and (ii) fully autonomous APU system. In the first case APU consists only of PEM fuel cell stack, supercapacitor with low capacitance and accumulator with low capacity. Accumulator was necessary only for starting the system up. In the second case the system has to be able to operate in an island regime. The best ratio between desired stability and weight of the APU were determined for system consisting of PEM fuel cell, supercapacitor with small capacitance and accumulator able to work with high currents.

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Graphene and Graphene Oxide in low temperature fuel cells for enhanced performance.

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The barrier and electrical properties of graphene and graphene oxide have been well documented with significant discussion around their efficacy as additives in low temperature PEM fuel cells. Graphene oxide has been demonstrated to be an ionic conductor but impermeable to dry gases and electrons. Graphene is an excellent in-plane electronic conductor but impermeable to all species apart from protons through the plane.

Here we will describe the work carried out at Manchester University incorporating Graphene, Reduced Graphene Oxide (RGO) and Graphene Oxide into PEM fuel cell Membrane Electrode Assemblies (MEA's).

Reduced Graphene Oxide and boron and nitrogen doped RGO has been added to/replaced the carbon in the microporous layer adjacent to the cathode catalyst and provides enhanced fuel cell performance (up to 84% improvement in power density) due to greater electrical conductivity.

Graphene Oxide (GO) has been added to the Nafion binding layer in a Direct Methanol Fuel Cell (DMFC) providing additional tortuosity and hence reduced methanol permeability, the optimisation of the GO loading has led to superior performance(up to 50% improvement in power density) when compared to a standard DMFC.

The addition of CVD graphene and hBN into the MEA has demonstrated no change in proton conductivity but lower fuel permeability, supporting the hypothesis of CVD graphene as a proton conductor and again increasing the power density achievable (30% in the initial experiment) by a DMFC.

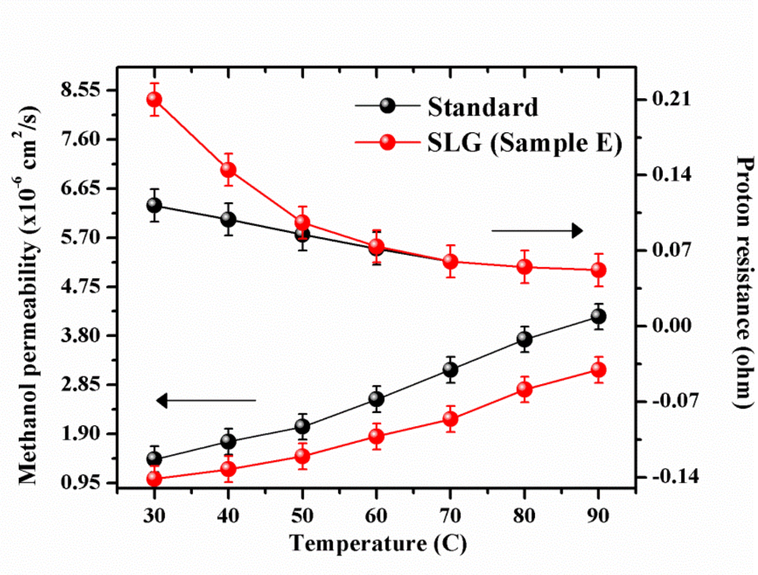

Figure 1. Methanol permeability and proton resistance values obtained at different temperatures for the MEA with standard and SLG.

R_2MnRuO_7 (R = Dy, Ho, and Er) Pyrochlore Oxides as Bifunctional Oxygen Electrocatalysts

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Electrochemical energy storage/conversion systems are becoming more appealing as a solution to the depletion of fossil fuels. However, the kinetic limitations to the rate of oxygen-based electrochemical reactions (ORR/OER) hamper the efficiency of these devices.[1] The development of more efficient and stable materials is a critical step for the final introduction of these devices in the market. Platinum-based catalysts and IrO_2 remain as benchmark materials for the ORR and OER, respectively, in acidic and alkaline environments,[2] but significant efforts have also been focused on earth-abundant and low-cost materials.[3] A growing number of publications on the electrocatalytic properties of Mn-based oxides have emerged in recent years,[4] proposing composition-activity relationships which may appear somewhat contradictive. Our recent work has demonstrated that changes in the redox state of the B-site at Mn based perovskites are directly linked to their activity towards ORR, providing the clearest indication that oxygen bond breaking requires changes of oxidation states within a range close to the reversible oxygen potential.[5]

In this work, we have synthetized a series of Ru-Mn pyrochlore oxides of the general formula R_2RuMnO_7 (R = Ho, Dy, Er) via a wet chemistry procedure, providing a detailed analysis of the bulk and surface structure employing X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS). For the first time, the activity of these materials as bifunctional oxygen electrocatalysts is evaluated (figure 1), which is comparable to recently reported values.[6] Normalization of the ORR activity by surface active site, reveals that the R_2RuMnO_7 pyrochlore oxides show at least twice the activity of $LaMnO_3$.[5] It will be experimentally shown that the of Mn/Ru–O bonds affect the ORR and OER activities. Moreover, we shall follow the interatomic distance changes of Mn–O bonds us using in situ X-ray absorption spectroscopy (XAS) to investigate the structural stabilities of the pyrochlore catalysts during electrocatalysis.

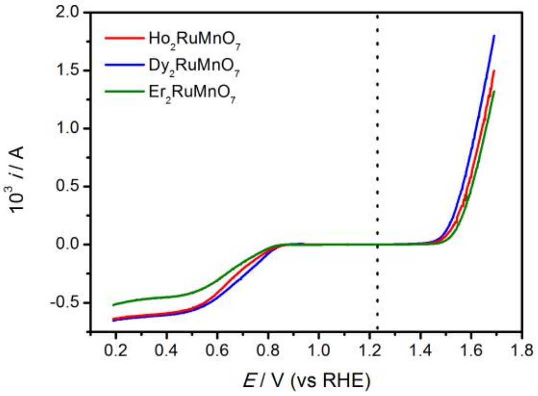

Figure 1. RDE responses of the various R_2RuMnO_7 (R = Ho, Dy, Er) nanoparticles supported on a thin mesoporous carbon layer at 1600 rpm in O_2-saturated 0.1 M KOH at 0.010 V s^{-1}.

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Fabrication of nitrogen doped mesoporous carbon@$NiCo_2S_4$ arrays on nickel foam as an advanced charge storage material

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Generally, material properties such as high surface area, pore size distribution, variable oxidation states and good electronic conductivity are the basis for charge storage application of certain carbons, polymers, metal oxides and sulfides. Recently, transition metal sulfides, $NiCo_2S_4$ in particular, are in the forefront as electrode materials for energy storage devices. But the cyclic performance of metal sulfides is inadequate for charge storage applications. Hence it is important to improve the cyclic stability of $NiCo_2S_4$ by designing composite materials with carbons or active metal oxides as components. In this work, we have fabricated $NiCo_2S_4$ and $NiCo_2S_4$@NMC (nitrogen doped mesoporous carbon) heterostructures on nickel foam employing hydrothermal method. This method allows us to directly obtain binder free electrodes for supercapacitor applications. The electrode composite materials are characterized by XRD, BET, Raman spectroscopy, SEM, HRTEM, and XPS. The electrochemical activity of these materials is investigated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and impedance spectroscopy (EIS). The $NiCo_2S_4$@NMC composite shows unique architecture with higher surface area (42 $m^2\ g^{-1}$) and better conductivity compared to $NiCo_2S_4$ (11 $m^2\ g^{-1}$). This composite material also shows highest capacitance value of 2017 F g^{-1} at 3 A g^{-1} compared to $NiCo_2S_4$ and $NiCo_2S_4$-graphene electrodes reported in the literature. It has excellent cyclic stability, retaining 90% capacitance after 5000 cycles. The excellent performance of this composite material is attributed to the easy accessibility of the space between the NMC sheets and $NiCo_2S_4$ to electrolyte ions through electro-activation process, which makes it as an advanced energy storage material.

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Low-temperature aqueous carbon/carbon electrochemical capacitor

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In the recent years, remarkable attention was focused on the new environmentally friendly electrochemical capacitors, especially for the devices containing aqueous electrolytes. Such electrolytes are characterized by high conductivity, low price and they are easy to prepare and handle. Unfortunately, among all these advantages of water based solutions, one major problem of freezing temperature has to be mentioned. To overcome this drawback, there is a need to look for new improved electrolyte formulations.

In order to undertake this challenge, new solvents composed of water with organic additive were prepared. Differential Scanning Calorimetry (DSC) experiments performed for electrolytes and for carbon electrodes soaked in electrolytic solutions shown that organic additive allowed to decrease the freezing point until -40°C. Moreover, it is worth to mention that the microporous character of activated carbon electrodes has the remarkable impact on the freezing point of electrolyte used.

The electrochemical performance of the systems containing new electrolyte composition was tested in temperatures ranging from 40°C to -40°C and no difference in performance was observed. The stability of the electrolyte in high temperature was evaluated by floating method. Moreover, three-electrode cell experiments demonstrated two simultaneous redox reactions occurring in this system: the reduction of nitrates was observed and confirmed by *in-situ* Raman spectroscopy on the negative electrode while the presence of organic additive activated the beneficial redox response of carbon functional groups on the positive electrode.

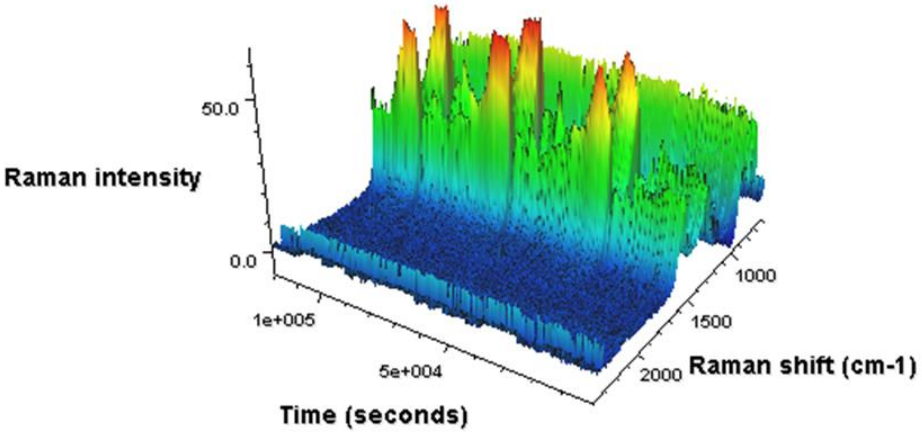

Figure 1 In situ Raman spectra of carbon cloth ACC 507-20 in 1M KNO_3, scanning speed 0.1 mV s^{-1}

P3MT/VACNT/Al Nanocomposites Electrodes With High Capacitance For Supercapacitor

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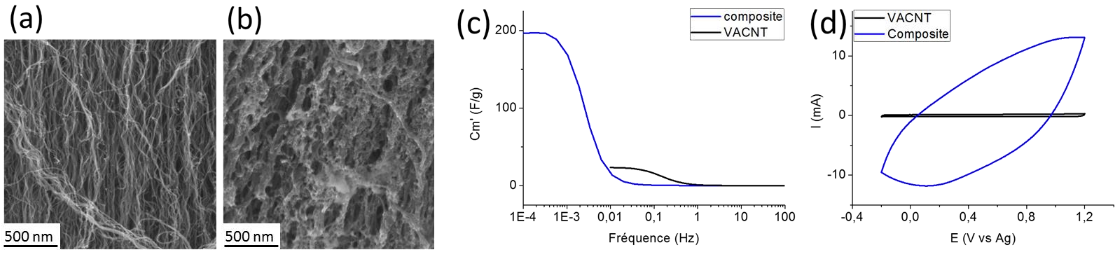
Supercapacitors are desirable for applications requiring high power densities. Among the various types of supercapacitors, electrochemical ones based on electronically conducting polymers (ECP) as electrode material are particularly interesting because of their high capacitance (1). However, their energy densities and their electrochemical stability are still limited (2,3). In order to improve the capacitance and the energy density of such pseudo-capacitive supercapacitors, our strategy consists in making nanocomposite electrodes of poly-3-methylthiophene (P3MT) in ionic liquid media deposited onto the surface of nanostructured electrodes composed of very dense carpet of vertically aligned carbon nanotubes (10^{11} – 10^{12} CNT/cm^2) on an aluminum collector (VACNT/Al).

In this study, different electropolymerizations methods (cyclic voltammetry, galvanostatic, potentiostatic, pulsed methods (3,4)) were used to optimized the deposition and the storage properties of P3MT. Nanocomposites with weight ratios of P3MT/(P3MT+CNT) ranging from 5 to 90% were obtained and characterized by electrochemistry (CV and EIS) and microscopy (figure (a,b)).

The results demonstrate a conformal deposition of polymer increasing the electrodes' capacitance from 32 mF/cm^2 before polymerization to up to 1300 mF/cm^2 after polymerization (figure (c,d)).

Finally, stability tests of electrodes and coin cells assemblies were studied and their performances will be presented.



SEM figures of: (a) VACNT (b) composite ;(c) Real capacitance and (d) CV: VACNT (black line), composite (blue line)

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Self-charging Microbial Desalination Cells: New Class of Power Generating and Water Desalination Devices

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For the first time, the electrodes (anode and cathode) of a microbial desalination cell (MDC) were used as negative and positive electrodes of an internal supercapacitor.

The system is based on three chambers physically separated by polymeric membranes. High surface area carbon brush is used as anode electrode and inserted into the first chamber with an empty volume of 33mL filled with a solution of 50%wt of activated sludge and 0.1M potassium phosphate buffer respectively. The anode chamber is separated from a desalination chamber containing salty water (30gL^{-1} NaCl) through a cation exchange membrane (CEM). Desalination chamber has an empty volume of 11mL. The last chamber is the cathode chamber that is separated from the previous chamber through an anion exchange membrane (AEM). The cathode has an air-breathing configuration based on a mixture of activated carbon, carbon black, and PTFE with the addition of Fe-AAPyr (2mgcm^{-2}) as catalyst.

Anaerobic conditions are achieved in the anode chamber due to the microorganisms that consumes oxygen. The anode electrode is then negatively self-polarized. Aerobic conditions instead are established at the cathode due to the air-breathing configuration that guarantees the presence of oxygen. These conditions actually push the potential towards high values. The red-ox reactions happening to the two electrodes, self-charged anode and cathode electrodes that actually act as negative and positive electrode of an internal supercapacitor. Therefore, the negative electrode is attracting counter ions (Na^+) from the solution though the CEM, and similarly, the positive electrode is attracting negative ions (Cl^-). Electrodes are then discharged releasing the counter ions in the solution and producing high current/power pulses. The electrodes are then self-recharged without the utilization of external power source.

Discharges/self-recharges cycles for a total duration of 44 hours were performed with t_{pulse} of 1 s at 2.9 Am^{-2} followed by a rest 20 sec. Electrochemical data, solution conductivity and pH were recorded along the experiments. The solution conductivity of the desalination chamber halved within 24 hours with an initial value of 49 mScm^{-1} and a final value of roughly 25 mScm^{-1}. The solution conductivity value then stabilized at roughly 20 mScm^{-1} after 44 h. The pH of the three chambers did not vary along the experimentation remaining within a range between 7 and 8.

Highest maximum power of 1.8 Wm^{-2} was recorded and this results which was mainly affected by cathode semi-cell impedance. An additional capacitive electrode (AdE) was added into the cathode chamber to overcome the cathode ohmic losses. Cathode ohmic drop was reduced and therefore higher maximum power density was reached. With AdE, maximum power density was 3 Wm^{-2}.

Differently than electrodialysis or capacitive deionization, supercapacitive MDC is capable of doing electrostatic discharges and self-recharged supercapacitor in acqueous media without the addition of external power sources.

Tailoring the Electrode/Electrolyte Interface to Improve the Energy Density of Graphene Based Lithium-ion Capacitor

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Lithium ion capacitor(LIC) is a type of electrochemical energy storage device that can combine the power property of a supercapacitor and the energy property of a lithium ion battery simultaneously[1]. Therefore, it is a kind of very promising device nowadays. The actived carbon is often used as the cathode and the graphite or lithium titanate works as the anode[2]. Recently, graphene is introduced into the actived carbon cathode due to its excellent electronic conductivity and large specific surface area. Therefore, graphene can work as conducting additive to decrease the ohmic resistance of the actived carbon electrode laminate. And more importantly, it can also provide capacitance behavior to further enhance the energy density property of the whole LIC device. Although many experimental results involving LIC with graphene are reported in literature[3-5], the detail understanding of electrode/electrolyte interface in graphene based LIC is very limited.

In this work, the role of graphene in LIC is investigated in detail theoretically and experimentally. Firstly, the quantum capacitance of graphene with different defect and surface chemistry is calculated when it is used as positive electrode in LIC. The results shows that the defected structure and doped atoms have very different effect on the quantum capacitance due to the energy gap in density of states(DOS). Then, the electrolyte behavior near the electrode interface is modeled using classical molecular dynamics method. At the same time, the interaction between graphene and anions, solvent molecular in the electrolyte is also discussed. Some specific adsorption processes between the anions and graphene are believed to enhance the interface capacitance. Finally, the electrode/electrolyte interface is tailored accordingly to enhance the capacitance behavior of graphene. The results from this work will help to further develop high energy graphene based LIC.

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Synthesis of High Specific Surface Area Mesoporous Carbon Nanospheres and Their Electrochemical Performance

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To improve the energy density of supercapacitors, carbon material in organic electrolyte with higher operating voltage have received great attention due to the great improvement of their energy density and wider range of working temperature. The application of NH_3 as chemical activation agent is a common method of activation in carbon material because of the ability to construct porous structure, bring high specific surface area and porosity, and enlarge pores at the same time.

In this study, Alginic acid (AA) was used as a precursor to prepare carbon nanospheres via hydrothermal reaction. In the control of the concentration of AA solution, form and the diameter of carbon nanosphere are adjusted to make the shape of nanosphere intact and its diameter dispersity in control. Finally, the nanosphere is observed to own a diameter around 400~500 nm, distributing on both shape and diameter uniformly. Through activation by NH_3, the mesoporous carbon nanosphere with high specific surface area was obtained, with specific area of 1805 m^2/g, total pore volume of 1.50 cm^3/g, among which mesoporous specific surface area of 958 m^2/g, mesoporous pore volume of 1.14 cm^3/g (76%).

Our composites show several superior properties, including good electron transport, rapid ion penetration and higher conductivity when used as supercapacitor electrode materials in organic electrolyte. Electrochemical measurements show that mesoporous carbon nanosphere has high capacitance and high capacity retention. In organic electrolyte 1M $LiPF_6$ (EC:DMC:EMC=1:1:1) the electrodes obtained can reach a specific capacitance value of 110 F/g under current density of 0.1 A/g, and remains 70% of its capacity under a high current density of 20 A/g.

In situ NMR Study of Ion Transfer during The Charge/Discharge Of Supercapacitors

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The foreseen energy crisis and the evolution towards an all-electric devices society calls for ever improving energy storage systems. Among them, supercapacitors (Electrochemical Double Layer Capacitors) are powerful devices with extremely long cycle life and the ability to be charged and discharged within a few seconds. The actual challenge for the development of supercapacitors on a larger scale is to increase the stored energy density. The full understanding of the molecular processes which contribute to the charging mechanism is essential to overcome the current limits.

Nuclear Magnetic Resonance (NMR) spectroscopy is sensitive to the local environment of atoms. This technique was proved to be extremely powerful for the study of supercapacitors [1,2]. *In situ* measurements are essential to follow in real time the dynamics of ions in the supercapacitors. As NMR is a bulk technique, conventional spectroscopy suffers from the overlap of the signals of the ions in both electrodes of the supercapacitor. We combine NMR spectroscopy and NMR imaging (MRI) to separate the signals of ions in each electrode, using an electrochemical cell designed especially for NMR measurements [3], similar to Swagelok cells used in laboratories for electrochemical testing.

Electrodes are prepared by spreading a paste of nanopopous activated carbon powder (85%) mixed with a PTFE binder (10%) and carbon black (5%). The electrolyte is tetraethylammonium (TEA^+)-tetrafluoroborate (BF_4^-) in deuterated acetonitrile. Cells were first conditioned (charge/discharge cycles with progressive potential increase). We follow the evolution of the cations by ^1H NMR and anions by ^{19}F NMR in each electrode with *in situ* Chemical Shift Imaging and short echo times. The measurements are performed on OCV before charging, at full charge (holding the voltage at 2.5 V) and after one charge and discharge (holding the voltage at 0 V). We will present the influence of conditioning on distribution and mobility of the cations and anions, as observed *in situ* on each electrode of the supercapacitor.

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Ferrocenated Ionic Liquids and their Polymers for Energy Storage

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- **Electroactive ionic liquids** are obtained by linking ferrocenyl moiety to imidazolium or triflimide structures
- Their electrochemistry is studied either as a **liquid phase** or as a solid as **poly(redox ionic liquid)**
- Charge transfer with ferrocenyl moieties is applicable in **energy storage devices**

Redox-active electrolyte supercapacitors (RESC) are obtained by dissolving electroactive species in the electrolyte as a mean to increase the energy density of carbon-based capacitors. RESCs are most often using aqueous electrolytes due to a higher solubility of redox molecules in water compared to organic solvents. For the same reason, ionic liquids (ILs) have not been extensively studied as electrolyte in RESCs despite the fact that they could present the advantage of an increased maximum operating voltage. So far, a compromise must be done between fast transport and high solubility of the redox molecule (obtained in aqueous electrolytes) and a high cell voltage (obtained with organic solvents and ionic liquids). RESCs may benefit from the development of electroactive electrolytes specifically formulated for this purpose, and which should *i)* allow high concentrations in redox species, *ii)* present a high maximum voltage, and *iii)* include a self-discharge suppression mechanism. This work demonstrates that electroactive ionic liquids, in which a redox moiety is covalently linked to one of the ions, may be used to meet these challenges. Electroactive ILs were obtained by modifying the common ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [EMIm][NTf_2], with ferrocene. The ferrocene redox unit was linked either to the cation ([FcEIm][NTf_2]) or the anion ([EMIm][FcNTf]) (Fig. 1). Alternatively, ferrocene was used to modifiy vinyl-imidazole which, after isolation and purification, was polymerized. The structure of the poly(redox ionic liquid), poly(RIL) is presented in Fig. 2.

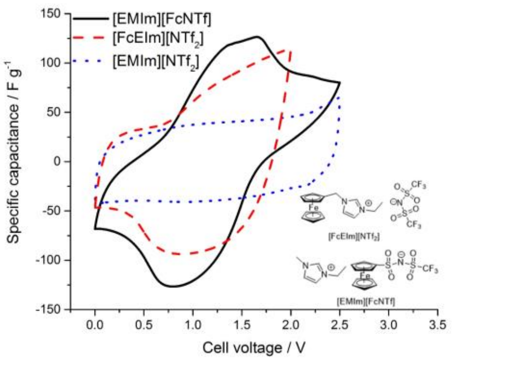

Fig. 1. CV of cells with 80 wt.% of the ionic liquid in acetonitrile obtained at a scan rate of 10 mV s^{-1} at a temperature of 25°C.

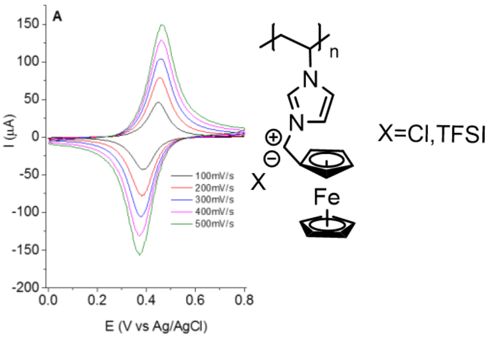

Fig. 2. CV of the poly(redox ionic liquid) film on GCE in 1 M $NaClO_4$. Structure of the poly(RIL)

The electrochemical response of both solid and liquid redox IL systems was studied by cyclic voltammetry (curves in Fig. 1 and 2, respectively). Both systems show a reversible redox couple from the oxidation and reduction of the ferrocenyl unit on the IL but the electron transfer in the liquid system (80 %wt. of redox IL in acetonitrile) is hindered by the slow diffusion in highly viscous media. The redox polymer on the other hand provided a very fast and reversible exchange. We will demonstrate that the redox polymer behaves similarly as poly(vinylferrocene) and that each redox center is independent from the other. The IL moiety favors the solubility of the poly(RIL) so it can easily be casted from solution. The reversibility of the poly(RIL) film in aqueous solution is strong dependant on the anion used in the electrolyte and follows the Hofmeister series. The use of both types of electroactive ionic liquids as redox species in supercapacitors will be compared to highlight the advantages and limitations of each.

Overcoming Challenges Associated With Obtaining Accurate Impedance of Large EDLCs

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As electrochemical impedance spectroscopy (EIS) becomes more widely used it is increasingly coming up against systems where the accuracy of the resulting spectrum is likely to be limited by the system making the measurement. Large electrochemical double layer capacitors (EDLCs) are some of the lowest impedance devices that are regularly interrogated by EIS and are more likely to yield EIS spectra that include system artifacts and offsets. Here we look at how to determine system limits and use that knowledge to obtain accurate EIS for these challenging systems. This starts with detailing the attention to detail needed during setup so that trustworthy results can be achieved. The system contributions to impedance at low frequencies arising from, e.g. common mode rejection ratio (CMRR) and high frequencies from mutual inductance in the cabling will be isolated using low Z surrogates. That data can then be used to determine whether the EIS from a given EDLC is accurate or to correct the spectrum in cases where the system contribution is significant. As a final step, the use of transmission lines to more accurately model EIS spectra will be addressed.

Comparative study of electrolytes based on lithium, sodium or potassium salts dedicated to symmetric or hybrid capacitors.

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Supercapacitor systems are interesting due to their high power storage capability which is widely in demand for many applications like electric vehicles. Carbon–based symmetric capacitors are also attractive due to the diversified morphologies [1] of these materials and their high stability which makes it the most commonly used electrode material for electrochemical double layer capacitors (EDLC). To combine high energy and high power density within a single device, hybridization between EDLC and lithium-ion batteries has been also investigated. Several electrolytes tailored to these electrochemical devices have been studied. Alkali-ion salts (lithium, sodium and potassium) based electrolytes are very interesting due to their properties and it has been already demonstrated that they are very promising for application in supercapacitor [2].

Herein, a comparative study of physico-chemical and electrochemical properties of different electrolytes containing lithium, sodium or potassium salts are presented. The effect of temperature on the transport properties of each mixture was investigated like conductivity, viscosity and density. Conductivities of studied mixtures, relatively interesting, reach 30 mS.cm^{-1} at 20 °C. Besides, performances of these electrolytes were investigated for symmetric or hybrid capacitors applications, using cyclic voltammetry, galvanostatic charge-discharge and impedance measurements. Investigations were performed at 20 °C with activated carbon as electrode material in working symmetric capacitor. For hybrid capacitor, a battery electrode was used as negative electrode (Bat). Finally, efficiency and capacitance of symmetric AC/AC or hybrid Bat/ AC systems were evaluated.

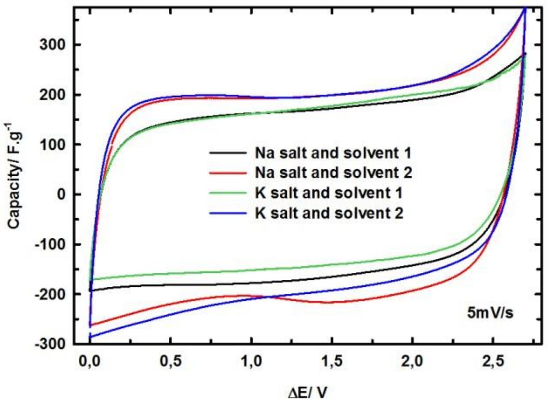

Fig 1 : *Cyclic voltamograms using two electrodes cells with activated carbon in 2 different solvents with sodium or potassium salts at 5 mV.s^{-1}, at 20°C.*

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Effect of Electrolyte Concentration on Aqueous Supercapacitor Performance

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Electrochemical capacitors or supercapacitors have found their niche as a promising solution for fast charging and regenerative energy acquisition. In most of the applications they are used to complement batteries but, owing to their excellent low temperature performance, calendar and cycle life, fast charge-discharges and reliability,[1] they can even replace them in those applications where size and weight are not of primary concern.

The use of aqueous over organic electrolytes has the advantage of providing higher ionic conductivity, and therefore, higher capacitance. However, their typically lower stability potential window, ~1 V vs. ~3 V, limits the energy density of aqueous-based supercapacitors and narrows correspondingly their application spectrum besides being a more affordable, safer and environmentally friendlier alternative. Nevertheless, recent works showed that electrodes made of activated carbon can work in aqueous neutral sulfate salts in a voltage window of about 1.9 V without significant capacitance fading.[2] These results opened up the possibility of using other aqueous neutral electrolytes also in an extended voltage window.

In this work aqueous alkali metal chloride electrolytes were investigated as potential candidates for carbon/carbon supercapacitors. Chloride anions are smaller than sulfates, and thus, they could be coupled with less expensive activated carbons with narrower micropores instead of strongly activated carbons with larger micropores. In order to optimize the cell performance, especially at high current densities, we studied the effect of electrolyte concentration. By using electrolyte concentrations at the maximum conductivity value, i.e. 6M LiCl, 5M NaCl and 2M KCl, we found that cell performance was improved, leading to almost perfectly rectangular-shaped CVs with a nearly negligible resistive contribution (Figure 1). Thus, as distinct from sulfate-based supercapacitors where the maximum electrolyte conductivity did not provide the highest capacitance and the lowest resistance,[2] the optimum cell response follows the maximum electrolyte conductivity in the case of chlorides.[3] Moreover, high-current capacitance retention was also greatly enhanced in supercapacitor cells working at 1.6 V. The resistance of the symmetric cells was also significantly diminished by using the optimum electrolyte concentrations, with remarkable improvements not only in the equivalent series resistance, but also in the distributed resistance. Both high-rate capacitance and lower resistance are beneficial to increase the energy of supercapacitors working at high discharge rates.

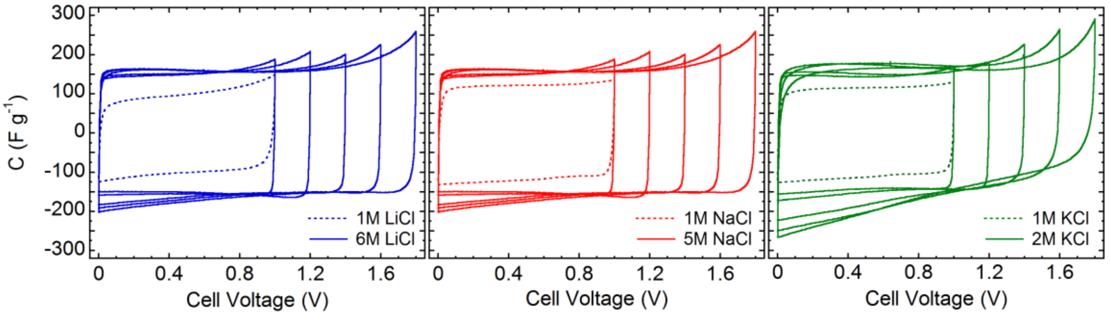

Figure 1. CVs of symmetric supercapacitor cells (at 5 mV s^{-1}) in 1M chloride solutions and 6M LiCl, 5M NaCl and 2M KCl aqueous electrolytes, respectively.

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All solid state on chip interdigitated micro-supercapacitors fabricated on 3D silicon wafer

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In order to enhance the energy density of micro-supercapacitors (MSCs), pseudocapacitive materials such as transition or noble metal oxides (RuO_2, MnO_2,…), nitrides (TiN, VN, RuN..) or conducting polymers can be used as MSC's electrodes [1]. Nevertheless, these pseudocapacitive materials implemented in MSCs do not significantly boost areal energy and power densities compared to superior to carbon based MSCs, mainly due to the limited cell voltage of pseudocapacitive material (1 V in aqueous media) regarding the carbon technology (3 V in organic electrolyte). Moreover, one attractive way to significantly improve the energy densities of MSCs when the footprint area is limited as in miniaturized devices is to improve the surface to volume ratio by developing a high specific area with a 3D scaffold [2]. When thin films are step-conformally deposited on a 3D scaffold exhibiting high area enlargement factor (AEF), the areal capacitance of the 3D MSC is significantly enhanced at least by one order of magnitude compared to the planar one.

In this communication, we will present the fabrication of on-chip all solid state 3D symmetric MSCs with interdigitated electrodes that exhibit high areal energy densities. The MSC are fabricated using compatible CMOS technology. The 3D MSC (footprint area = 4 mm^2) consists in 2 interdigitated electrodes composed of 8 fingers per polarity. Each finger is based on a robust and dense array of 3D microstructures to improve the volume to surface ratio in order to keep a low footprint area. The MnO_2 thin films are deposited on the 3D interdigitated electrodes by pulsed electroplating technique and the thickness of the amorphous MnO_2 thin films is kept at an homogeneous thickness of $\approx$ 500 nm all along the microstructured pillars. 3D MSC tested in aqueous electrolyte [2] exhibits energy and power densities close to 10 $\mu Wh.cm^{-2}$ and 20 $mW.cm^{-2}$ respectively. To increase the cell voltage, ionic liquids were used as electrolyte (EMI TFSI and PYR13 TFSI) [3]. Symmetric MnO_2/MnO_2 MSC has been successfully tested up to a 2 V electrochemical window with good capacitance retention (> 6000 cycles) with similar performance as in aqueous electrolyte.

Finally, ionic liquids were confined in a silica matrix in order to form a solid ionogel [4] with good thermal and mechanical properties as previously experienced in MSCs using carbon [5] or silicon [6] electrodes. Different MnO_2 based MSCs were assembled to form all solid state devices that can be operated in a wide temperature range and which performance compete well with those of already published devices, but with the advantage of an all solid state design preventing leakage, electrolyte evaporation, flammability and compatible with micro-electronic processes.

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Electrochemical Activation of Carbons for High-Voltage Organic Electrical Double-Layer Capacitors

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In this work, soft carbons and few-layer graphene were electrochemically activated for promoting the specific capacitance for the applications of high-voltage organic electrical double-layer capacitors (EDLCs). Soft carbons with variations in the microstructure were provided by CPC Co. Taiwan. The few-layer graphene was grown by the plasma-enhanced chemical vapor deposition (PECVD) method with a microwave plasma torch (MPT) technique to control the quality and thickness of graphene. The manipulation of heteroatom doping on few-layer graphene sheets have been successfully demonstrated to create various functionalities of such a typical two-dimensional (2D) material through the same method. The material characterization includes X-ray diffraction, Raman spectra, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy.

In this work, cyclic voltammetry (CV) is employed to activate the charge storage capacity of both soft carbons and few-layer graphene sheets in the commercial organic electrolyte, 1 M $TEABF_4$ in PC. For soft carbons with the micro-graphite domain structure, potentiodynamic activation in the commercial organic electrolyte, 1 M $TEABF_4$ in PC is very useful for enhancing the specific capacitance although the electrochemical reversibility needs to be improved. On the other hand, soft carbons with the alkali-annealing pretreatment showed the more obvious enhancement in the total specific capacitance in comparison with the untreated ones. From the XRD patterns, the diffraction peak of graphite is shifted by the irreversible electrochemical activation in organic electrolytes, indicating the expansion of graphite layers by the intercalation of ions/solvents.

Graphene sheets of different qualities and thickness were prepared via the variation in the synthesis parameters (e.g., pressure, CVD time, flow rate, etc.). Various few-layer graphene sheets have been potentiodynamically activated by CV between 0 and +2 V as well as between 0 and -3 V (vs. $Ag/AgNO_3$) in 1 M $TEABF_4$/PC. The above two activation processes significantly enhances the specific capacitances of graphene sheets as the positive and negative electrode materials in organic EDLCs with a cell voltage > 3.5 V. Moreover, the effects of thickness and graphene domain size on the activation efficiency are systematically compared. Furthermore, the potential window and cycle number of activation were optimized to achieve the highest specific capacitance with acceptable reversibility. The positive and negative electrode materials after the electrochemical activation at 25 mV/s from 0 to +2 V and from 0 to -3 V for 10 cycles showed the doubled specific capacitance in comparison with the as-prepared ones.

Two-Dimensional (2D) Transition Metal Carbides, Nitrides, and Carbonitrides (MXenes) as Electrode Materials for High-Performance Supercapacitors

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Since their discovery in 2011, the family of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides known as MXenes have received considerable attention for energy storage applications due to their favorable and tunable electronic and physical properties [1,2]. MXenes are ideal candidates for applications requiring materials that can store and deliver large amounts of energy at high rates. MXenes have high specific capacitances due to their redox-active transition metal surfaces and when MXenes are fabricated into binder free, free-standing films they have exceptional electronic conductivity (>5000 S/cm) [3]. MXenes are capable of storing charge in a wide variety of aqueous electrolytes and it has been shown that MXenes are capable of electrochemically intercalating cations of various charges (K^+, Na^+, Mg^{2+}, Al^{3+}) into the interlayer spaces between their 2D nanosheets [4,5]. Furthermore, MXenes are not limited to operating only as electrode materials for aqueous supercapacitors. The reversible intercalation and deintercalation of large cations, such as 1-ethyl-3-methylimidazolium (EMI^+) and tetraethylammonium (TEA^+), into the 2D layers of MXenes has been demonstrated in organic and ionic liquid electrolytes [6,7].

In addition to the intrinsic electrochemical properties of MXenes, the ease with which MXenes can be dispersed in numerous aqueous and organic solvents to form stable, colloidal solutions [8] adds another dimension to the range of electrochemical applications in which MXenes can be used. The ability for MXenes to form functional inks that can readily be printed, spray-coated, or spin coated in any desired pattern enables the creation of MXene thin-film coatings that are ideal for applications that require high-performance, microscale energy storage devices, such as on-chip energy storage or small, portable electronics [9,10].

The ability MXenes have for storing and delivering large amounts of energy at high power densities in numerous electrolytes paired with the versatility with which they can be processed for use as active materials in energy storage devices puts MXenes in a promising position to lead the research and development of the next generation of devices for energy storage and delivery.

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Vertically Aligned Carbon Nanotubes (VACNT) grown on Al current collector for high performances EDLC

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Electrodes materials based on Vertically Aligned Carbon Nanotubes (VACNT) have attracted a great interest for building high performances Electrical Double Layer Capacitors (EDLC). In this work, vertically aligned CNT (VACNT) grown on aluminum substrate by aerosol-assisted CCVD (1,2) is used as electrodes in EDLC systems (Figure 1). The performances of the EDLCs, i.e. gravimetric, areal and volumetric energy, power, and serial resistance are examined as a function of VACNT thickness and density (or CNT diameter) for conventional electrolytes including propylene carbonate (PC), acetonitrile (ACN) based electrolytes and room temperature ionic liquids (RTILs). Further studies and analysis have been also carried out to examine the influence of morphology (TEM and SEM), surface chemistry and defects (Raman and XPS spectroscopy) on EDLCs performances. Furthermore, the aging of the VACNT EDLC has been studied by following the capacitance and the impedance evolution during cycling. In the main we will show that VACNT/Al electrode can be an effective electrode to build high power EDLC devices.

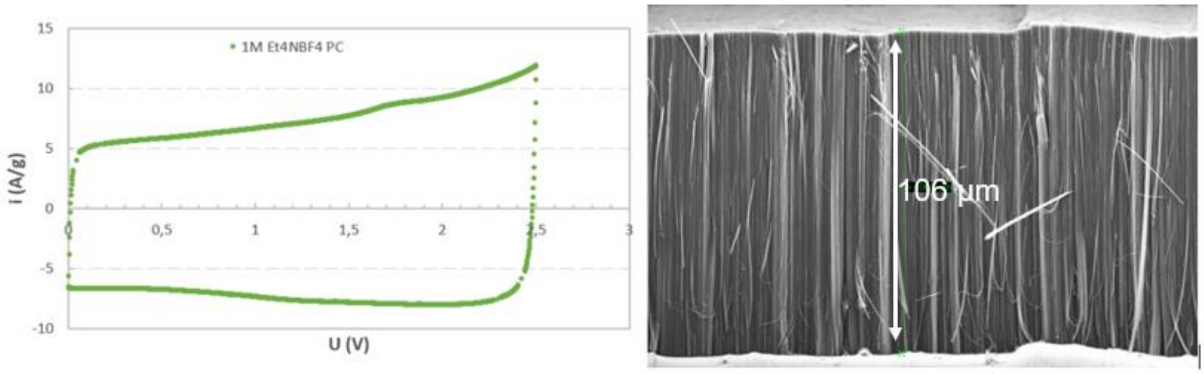

Figure 1 : CV of symmetric VACNT based EDLC at 1V/s using PC/1M Et_4NBF_4 mixture and a cross section view of the VACNT grown on Al collector by CCVD

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MnO2/VACNT nanostructured electrodes for supercapacitors

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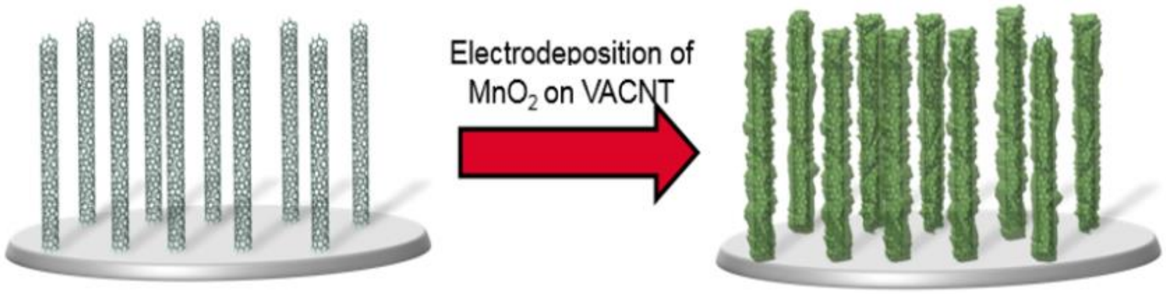
Manganese oxide is one of the most promising oxide for supercapacitor applications due to its low cost, friendly environmental aspect an pseudocapacitive performances[1 2] .The electrochemical performances of MnO_2 are largely dependent on its morphological properties and specific surface area. The association of carbon nanotubes (CNT) with MnO_2 is a well-known way to improve the electronic conductivity and the electrochemical performances of the composite. Nevertheless, the main researches use a chemical way for the preparation of composites and the CNT are usually entangled which limit a fine control of their morphology [3 4].

In this work vertical aligned CNT (VACNT) previously grown on aluminum[5] by aerosol assisted CCVD[,6] have been used as 3D matrix host for the electrodeposition of nanostructured MnO_2. The main objective was to deposit homogeneously MnO_2 inside the entire depth of the films. Classical electrochemical techniques such as cyclic voltammetry, chronopotentiometry or sequenced chronopotentiometry have been used for the electrodeposition. Various parameters have been studied for optimizing the process in order to obtain high performances in term of charge storage and electronic transfer (specific capacitance and impedance performances).

Electrochemical characterizations (cyclic voltammetry, galvanostatic cycling and electrochemical impedance spectroscopy) of the nanocomposites VACNT-MnO_2 have been performed in order to highlight the capacitive and kinetic behavior of the materials. Then SEM, TEM, SEM-EDX, XPS, Raman, and XRD characterization have been carried out in order to examine the morphology, the chemical structure, the localization and the thickness of the manganese oxide layer on the VACNT. Our results clearly showed that a thin and homogeneous oxide film, through a careful control of deposition parameters, successfully cover the thick VACNT substrate. These well-organized nanocomposites have been used as electrodes for both symmetric and asymmetric aqueous supercapacitors and will be described in detail and compared to the literature[7].



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Characterization of Graphene Synthesized with Various Reducing Agents Using Cyclic Voltammetry and Electrochemical Impedance Spectroscopy for Supercapacitor Application

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Graphene and graphene oxide (GO) are intensively studied and find application in many fields, including supercapacitors, due to the extraordinary properties of these materials: good electrical conductivity, excellent electron mobility, and decent mechanical resistance. The supercapacitors are devices combining the properties of capacitors and batteries. Actually, GO is the most often used precursor for the electrodes of graphene-based supercapacitors [1]. The reason for this is not only its suitable structural characteristics but also a low cost. Structural properties of GO depend on its synthesis and reduction. In this work, orthoboric acid without and with additives (glycerol and ascorbic acid) have been applied to reduce GO.

GO was reduced in the melt of H_3BO_3 with the optional addition of glycerol or ascorbic acid. To improve the reduction efficiency, the thermal treatment at 800 ºC was applied after the reduction process. The efficiency of the reduction was analyzed gravimetric and spectroscopic methods. The structural analysis confirms that the thermal heating after the reduction enhances the reduction efficiency. The additives are able to influence the reduction efficiency.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to determine double layer capacitance of the samples obtained after GO reduction. The results showed that reduction conditions are extremely important for the capacitance values. The double layer capacitance obtained from CV is lower after the thermal treatment than that before thermal treatment. EIS gave more precise evaluation of the specific double layer capacitance and it was in the range up to 1 mF cm^{-2} [2]. Most probably it is due to changes of the porosity of the film. Detailed evaluation of the dependence of the double layer capacitance on GO reduction conditions will be discussed in the presentation.

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High voltage carbon/carbon supercapacitors performing down to -40ºC in neutral aqueous electrolytes

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Due to the energy *vs* voltage square dependence, commercially available carbon/carbon supercapacitors (SCs) mostly implement organic electrolytes, e.g., $TEABF_4$ in acetonitrile, enabling reaching voltage values up to 2.7-2.85 V [1-2]. However, the implementation of these electrolytes imposes extensive drying of carbon electrodes and construction in moisture-free atmosphere, resulting in high production costs. Besides, the low flash point of acetonitrile with potential to release harmful gas maybe the cause of safety issues under emergency situations. In this context, the recently demonstrated voltages up to 1.5 V with carbon/carbon SCs in neutral aqueous alkali sulfate electrolytes represent an attractive opportunity to develop safe, eco-friendly and low cost systems [3]. Voltage exceeding the thermodynamic stability of water, e.g., 1.23 V, is owing to a local pH increase in the porosity of the negative activated carbon (AC) electrode, causing important di-hydrogen evolution over-potential [4].

Apart the aforementioned advantages, freezing at relatively high temperature (ca. -5ºC for 1 mol.L^{-1} aqueous alkali solutions) represents an important disadvantage of neutral aqueous electrolytes in comparison to organic ones which can be easily applied down to -40°C. In this work, two novel strategies are proposed to enable the operation of SCs with salt aqueous electrolytes down to -40°C. The first one consists in adding methanol to aqueous Li_2SO_4 in order to lower the freezing temperature [5]. Differential scanning calorimetry (DSC) on a 0.7 mol L^{-1} solution of Li_2SO_4 in water/methanol (7:3) mixture reveals freezing at -51ºC. Three-electrode cell investigations under negative polarization on a carbon electrode in this electrolyte demonstrate almost complete quenching of hydrogen chemisorption at -40ºC (Figure 1a). As a consequence, an AC/AC cell displays the rectangular CV characteristics of an electrical double-layer capacitor at -40°C (Figure 1b). The capacitance determined by galvanostatic cycling up to 1.6 V is 68 F g^{-1} at -40°C against 89 F g^{-1} (per mass of one electrode) at 24°C (Figure 1c). Notwithstanding, due to the low dielectric constant of methanol compared to water, the salt solubility is reduced after the addition of methanol, which results in low conductivity solutions and lower power of SCs. The second strategy enables to solve this issue by implementing an aqueous solution of choline chloride (conc. 5 mol kg^{-1}). As shown in figure 1d, at -40°C, SCs using aqueous choline chloride display square-shape cyclic voltammograms with excellent charge propagation. In addition, owing to the high concentration of the electrolyte, the capacitance values of 126 F g^{-1} and 103 F g^{-1} at 24ºC and -40ºC, respectively (Figure 1c), are much higher than in the case of the former solution containing methanol as anti-freezing agent. During the presentation, the pros and cons of the two strategies will be illustrated by a detailed electrochemical study, and the mechanisms at the electrode/electrolyte interface will be discussed.

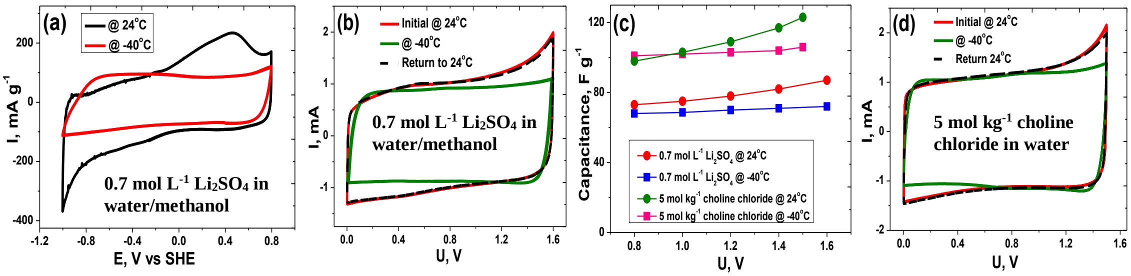

Figure 1. CVs (2 mV s^{-1}) of (a) AC in three-electrode cell and (b) AC/AC cell using 0.7 mol L^{-1} Li_2SO_4 in water/methanol mixture (7:3). (c) capacitance *vs* voltage for SCs using 0.7 mol L^{-1} Li_2SO_4 in water/methanol and 5 mol kg^{-1} aqueous choline chloride, and (d) CVs of an AC/AC cell using 5 mol kg^{-1} aqueous choline chloride.

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Tracking ion intercalation into layered materials on the nanoscale

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In the past decades, electrochemical capacitors (supercapacitors) have drawn considerable attention for applications in portable electronics, grid and transportation systems due to their rapid power delivery and an almost unlimited cycle life. In search for new materials with higher electrochemical performance, two dimensional (2D) transition metal carbides – MXenes, are of particular interest owing to their excellent electrical conductivity and high volumetric capacitance[1][2]. A variety of aqueous cations can be electrochemically intercalated into Ti_3C_2, the most studied MXene to date, resulting in very high volumetric capacitance outperforming a variety of carbons[1]. The mechanism for high capacitance was essentially described as intercalation pseudo-capacitance arising from redox reactions of the Ti atoms. On the other hand, Ti_3C_2 shows intercalation capacitive behavior even at quite high rates, while normally a slow intercalation takes place in layered battery materials.

Similar to graphite or other electrode materials in various electrolytes, MXene electrodes also show a significant change in volume when ions are intercalated. This electro-chemo-mechanical coupling can be used to get unprecedented insight into ion intercalation pathways with lateral resolution of 10's of nm using Scanning Probe Microscopy (SPM) techniques. In this communication, we introduce contact resonance SPM which allows to extract mechanical properties and its changes under electrochemical control when ions are intercalated into MXene[3][4].

Of special interest to boost energy storage is the intercalation of multivalent ions such as Mg^{2+} which suffers from sluggish intercalation and transport kinetics due to its ion size. By combining traditional electrochemical characterization techniques with electrochemical dilatometry and contact resonance atomic force microscopy, the synergetic effects of pre-intercalation of K^+ ions are demonstrated to improve charge storage of multivalent ions, as well as tune mechanical and actuation properties of Ti_3C_2 MXene[4][5]. Our results have important implications for quantitatively understanding the charge storage processes in intercalation compounds and provide a new path for studying the mechanical evolution of energy storage materials.

The experiments and sample preparation in this work were supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. The facilities to perform the experiments were provided by the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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Evidence of pseudocapacitive behavior on $FeWO_4$ by ex-situ, in-situ and operando spectroscopies

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Carbon based electrodes store charge through capacitive processes, but with limitation due to pore size distribution and specific surface area of the porous carbons [1]. Unlike carbon electrodes, pseudocapacitive electrodes can store larger amount of charge thanks to fast and reversible surface redox reactions that confers them a "capacitive like" behavior [2]. Since electron transfers are involved at the surface or subsurface of the pseudocapacitive materials, multiple valency cations are involved in the charge storage mechanism as it was shown for MnO_2 or RuO_2 electrodes. However, to fully understand the electrochemical behavior of pseudocapacitive materials, a deeper understanding of the precise role of their electroactive elements is still required. Up to now, this issue has mainly been addressed by the use of in situ experiments [3] which require long polarization steps at constant potentials that are not compatible with the time frame of electrochemical capacitor operation.

Metal tungstates ($M^{2+}WO_4$) represent an important group of inorganic high-density oxides that were recently proposed as potential electrode for electrochemical capacitors and Li-ion batteries. Nanosized iron tungstate ($FeWO_4$) for example has been synthesized using various methods (polyol-mediated synthesis, hydrothermal synthesis, microwaves synthesis, ultra centrifugation synthesis). The different powders of $FeWO_4$ have been electrochemically tested in aqueous electrolytes, exhibiting a pseudocapacitive behavior over a limited potential window [4]. Subsequently, operando X-ray absorption spectroscopy was used for the first time on such pseudocapacitive electrode at SOLEIL Synchrotron on the ROCK beamline (Rocking Optics for Chemical Kinetics) in order to probe the charge storage mechanism while operating the electrode using potentiodynamic conditions. XAS measurements were performed on $FeWO_4$ electrode at both Fe K-edge and W L3-edge, allowing very accurate determination of the oxidation state evolution of both Fe and W during cycling. Operando XAS enables to evidence the role of Fe^{2+}/Fe^{3+} in charge storage while W^{6+} seem to act as a spectator cation. In this communication, the main results will be presented and the relationship between capacitance and the characteristics of the different $FeWO_4$ powders will be detailed.

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Charge balance of hybrid energy storage system via vanadium and tin redox activities in aqueous solution

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Enhancing the energy storage capacity by use of redox active electrolytes has emerged as a facile strategy to compensate the intrinsically low charge capacity of electric double-layer capacitors (EDLC).[1] Fundamentally, the charge storage mechanism for redox electrolyte aided energy storage systems rely on both Faradaic and non-Faradaic reactions. In general, Faradaic reactions are introduced by the redox activities of the electrolyte, such as vanadium complexes,[2] potassium ferricyanide/ferrocyanide,[3] and iodide containing electrolytes.[4] Non-Faradaic reactions originate from electric double-layer formation within the porous carbon electrodes.[5] With these hybrid features, the redox electrolyte aided hybrid energy storage (REHES) systems can provide a battery-like specific energy over 20 Wh/kg and supercapacitor like specific power over 1 kW/kg as well as cyclic stability over 2,000 cycles.[6]

In this work, the characteristic features of the REHES systems will be presented such as diffusion behavior of redox active electrolytes in porous carbon electrode and influence of the porosity of the carbon. Additionally, we outline the importance of charge balancing considering the choice of redox pairs and cathodic anodic limit. Particularly, we will focus on the REHES system with tin and vanadium redox activities.[2] While introducing a vanadyl and tin sulfate mixture aqueous solution, a significant capacity enhancement (75 Wh/kg) was achieved as enabled by the redox activities of tin and vanadium complexes. Yet, a remaining challenge of this approach is the irreversible formation of tin oxides at the positive electrode which causes the blocking of the pores in the carbon electrode leading to a limited specific power (1.5 kW/kg). In order to prevent unfavorable tin oxide formation at the positive electrode, asymmetric redox electrolytes can be applied with the aid of anion exchange membrane; tin fluoride as catholyte and vanadyl sulfate as anolyte ($SnF_2|VOSO_4$).[7] While the transportation of tin and vanadium complex cations are effectively hindered by the anion exchange membrane, the power performance of the $SnF_2|VOSO_4$ system is significantly enhanced (3.8 kW/kg). The robustness of the system was confirmed by galvanostatic cycle tests over 6,500 cycles (40 days).

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2-methylimidazole-derived Ni-Co Layered Double Hydroxide Nanosheets for Hybrid Supercapacitors

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Supercapacitors (SCs) exhibit high power density, long cycle lifetime, and excellent safety in extreme conditions, which makes them very useful in various applications such as backup power suppliers, hybrid buses, and heavy hybrid trucks.[1] Recently, the research on SCs has been focused on improving the energy storage ability of conventional carbon-based SCs (<10 Wh kg^{-1}) for broader applications.[2]

Layered double hydroxide (LDH) is a type of material which is considered to be desirable for supercapacitors due to its high surface area and feasibility for fast intercalation/de-intercalation of charged ions.[3] Specifically, Ni and Co based LDH (NiCo-LDH) materials have attracted lots of attention due to their high activity. As a battery-type material, the whole crystalline structure of NiCo-LDH is involved in the faradaic charge storage process through intercalation/de-intercalation of electrolyte ions [4], resulting in an extraordinary charge storage capacity. However, these candidates normally suffer from low conductivity and fragile crystalline structure, leading to a limited capacitance, poor rate, and cycling stabilities.

In this work, we fabricate NiCo-LDH directly on a carbon fiber cloth (CFC) as binder-free SC electrodes using 2-methylimidazole as a complex agent. The ultra-thin NiCo-LDH nanosheets are intimately grafted on the CFC forming a 3D porous hierarchical nanostructure. This unique nanostructure enables high exposure of the active sites of the material for efficient charge transfer during the operation of SCs. The absence of binder material in our NiCo-LDH/CFC electrode ensures good electrical properties of the material and efficient kinetics in the charging/discharging process of the device. Owing to these merits, as-prepared NiCo-LDH/CFC electrode exhibits a considerable high capacitance, outstanding cycling stability (61% at 60 A g^{-1}), and long-term cycling duration. The energy density and power density of the material were assessed by assembling a hybrid SC, which achieves a high energy density (59.2 Wh kg^{-1} at a power density of 850 W kg^{-1}) and a large power density (34 kW kg^{-1} at 13.4 Wh kg^{-1}). This highlights the advantage of the new method for the synthesis of high electrochemical performance electrode materials for supercapacitors.

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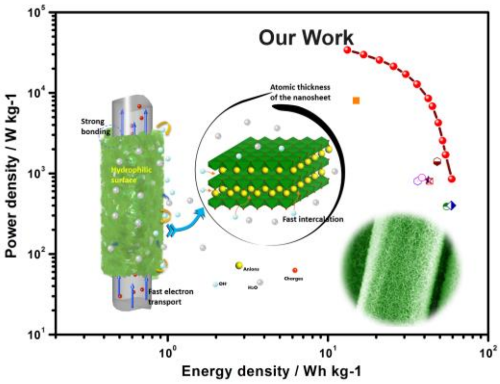

Fig. 1 Schematic illustration of the excellent energy storage ability of as-prepared NiCo-LDH/CFC material

Drying of Non-aqueous-electrolyte Electric Double Layer Capacitors

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Electric Double Layer Capacitors (EDLCs), sometimes referred to by the product names Supercapacitor or Ultracapacitor, have extremely long life primarily because they store charge via physical processes at an electrode-electrolyte interface with no electron transfer. High durability demands use of extremely pure materials so as to minimize chemical side-reactions that could negatively impact operational and cycle life. Water is one such impurity that must be minimized in non-aqueous-electrolyte EDLCs. It typically is reduced to low levels through elevated-temperature drying under vacuum conditions. This paper reports results from our investigation of EDLC drying with a goal of optimizing the process. Drying temperature and drying time were the two factors investigated using a quadratic experimental design. Several responses were measured including capacitance and series resistance stability. The rate of EDLC gas generation was also an examined response.

Twenty seven identical non-aqueous-electrolyte EDLCs were fabricated using facilities in the Case Western Reserve University capacitor prototyping laboratory (see http://energy.case.edu/CECFF). Popular commercial materials were used to fabricate these capacitors including Kuraray YP-50 activated carbon, Showa Denko surface-treated aluminium current collector, NKK cellulose separator, and BASF acetonitrile-solvent electrolyte. Two double-side-coated current collectors with two separators were spiral-wound into EDLC bobbins. **Figure 1** (left) is a photograph of a wound bobbin with two projecting electrical tabs and package piece-parts, which includes a 22-mm-diameter aluminum can and a “snap-in style” header. Shown on the right is a sealed capacitor next to a $0.25 US coin.

Before packaging, bobbins were dried under vacuum in groups of three at one of nine time-temperature conditions (**Figure 2**). For example, nine bobbins were dried at 90 °C, one group of three for 20 hours, one group of three for 70 hours, and one group of three for 120 hours. Each group of bobbins was packaged under dry-box conditions immediately after drying. Electrolyte was added just prior to package sealing.

Capacitors from all nine groups were aged at 65 °C with the continuous application of 2.7 V. Capacitors were periodically cooled to room temperature and characterized for capacitance, series resistance, and package swelling. Weibull life analysis was performed using the aging data with actual and defined failures. Actual failures included 1) electrical shorts or opens, and 2) package rupture due to internal gas generation. Defined failures included 1) a series resistance increase of 100% over the initial value or 2) a 30% loss in capacitance over the initial value. An analytical formula was derived that relates capacitor life to its drying time and its drying temperature and thus allows drying process optimization.

Figure 1: (left) Capacitor package, package header, and wound bobbin. (right) Sealed capacitor next to $0.25 US coin.

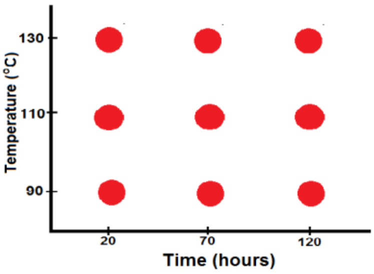

Figure 2: Nine drying conditions used in this non-aqueous electrolyte EDLC drying study. Three capacitors were in each drying group. After bobbin drying and packaging, the 27 capacitors were aged at 65 °C with 2.7 V applied continuously.

Binder free Platinum nanoparticles decorated Graphene-Polyaniline composite for high performance supercapacitor application

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ABSTRACT

Recently, supercapacitors have attracted wide attention as energy storage devices in the scientific community due to high power density, low maintenance cost and longer cyclic life. Conventional supercapacitors use insulating binders with active materials for fabricating working electrode. Use of such binder reduces the electrical conductivity, thus causing energy wastage of supercapacitor. To overcome it, here, we report binder free Platinum (Pt) nanoparticles (NPs) decorated Graphene–Polyaniline (Gr-PANi) composite modified Glassy Carbon Electrode (GCE) for supercapactior application. Gr-PANi composite was prepared by electrochemical polymerization method and Pt decorated Gr-PANi composite was synthesized by electro-deposition of Pt NPs at -0.2V on the surface of Gr-PANi/GCE. FESEM image of Pt decorated Gr-PANi composite revealed nano-fibrous structure of PANi (average diameter of 50-100nm) wherein Pt NPs were found uniformly deposited on the surface of PANi nanofibers. Interconnected network of PANi nanofibers made matrix highly porous, thereby, providing larger surface area for diffusion of electrolyte inside the film. Presence of Pt, Gr and PANi was confirmed by EDS, XRD and Raman scattering. CVs were performed in 1 M H_2SO_4 solution to analyze capacitive behavior of Gr-PANi/GCE and Pt-Gr-PANi/GCE. Integrated area in CV of Pt-Gr-PANi/GCE was larger than that of Gr-PANi/GCE, suggesting its higher specific capacitance. Here, Pt NPs improve the electrical conductivity by enhancing electron transfer between electrode and electrolyte. Pt NPs decorated Gr-PANi composite based supercapacitor exhibited higher specific capacitance of 922.5 F/g than only Gr-PANi modified electrode (525.6 F/g) at same current density (1A/g) which indicates synergistic effect of electrical double-layer capacitance and pseudocapacitance resulting from Gr and PANi respectively and excellent catalytic ability of Pt NPs. When the current density was as high as 5 A/g, 77.2 % of the specific capacitance was maintained which suggests that the Pt NPs decorated Gr-PANi composite based electrode has a better sustainability to higher current and superior rate performance. Specific capacitance obtained at 5 A/g from Pt NPs decorated Gr-PANi composite electrode was 712.2 F/g which is higher than other reported Gr-PANi composite based electrodes like binder-free layered Gr-PANi composite film modified electrode (210 F/g at 5 A/g), microspherical Gr-PANi composite based electrode (475 F/g at 5 A/g). Thus the as-synthesized novel Pt NPs decorated Gr-PANi composite offers simple, promising electrode material for energy storage devices.

Material Category and Sequence Effects of Core-Shell Structures on Morphology and Electrocapacitive Performance of Energy Storage Electrodes

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Synthesizing core-shell structures as the electrocapacitive material is one of the feasible ways to fabricate effective energy storage electrodes. Most of researchers only focus on single core-shell system and optimize the morphology of nanomaterial to enhance the electrochemical performance.[1, 2] In this work, novel prospects are made on core-shell structures. Firstly, based on the same materials for constructing the core-shell structure, effects of the material exchange as the core and shell on the morphology and the electrochemical performance are investigated to understand the core-shell structure in a novel way. Two couples of the materials are used on constructing the core-shell structures, *i.e.*, Ni_xCo_yO nanowires and Ni_xMo_yO nanosheets as well as the Ni_xCo_yO nanosheets and MnO_2 nanosheets. The scanning electron microscopy (SEM) images are shown in **Figure 1**. The well-defined core-shell structures are obtained when Ni_xCo_yO is used as the core, regardless of the morphology of Ni_xCo_yO and the corresponding shell materials. However, the pure nanosheet or nanowire arrays are obtained when Ni_xCo_yO are acted as the shell. It is inferred that the formation of the core-shell structure significantly depends on the size and the intrinsic properties of the materials used as the core and the shell, and the larger size of the material should be used in the core to synthesize the well-defined core-shell structure. Better electrochemical performances are achieved for the core-shell electrodes no matter the morphology is single-component or core-shell type, as compared with those for the single material electrodes. Also, the well-defined core-shell structures using Ni_xCo_yO as the core shows better electrochemical performances among the core-shell electrodes. Secondly, the effect of the material category with the same morphology of the core-shell system on the electrocapacitive performance of the energy-storage electrode is studied. Multiple core-shell systems are made using the same core of the $NiCo_2O_4$ nanosheet and different shell materials, *i.e.*, NiS, NiO, $NiMoO_4$ and MnO_2. The SEM images are shown in **Figure 2**. The electrochemical performance of the energy-storage electrodes based on the core-shell structure is investigated after making the highly similar morphologies for all the core-shell systems. The electrochemical performances are enhanced for the core-shell electrodes as compared with that for the electrode with single $NiCo_2O_4$ nanosheet array, but the $NiCo_2O_4/MnO_2$ core-shell electrode shows reduction on the specific capacitance (C_F) unexpectedly. The highest specific capacitance of 5.23 F/cm^2 is obtained for the $NiCo_2O_4$@NiS-based electrode evaluated by using the galvanic charge/discharge (GC/D) curves at the current density of 5 mA/cm^2, probably due to the better intrinsic property of NiS as the electrocapacitive material other than its morphology superiority since the structure variation is almost excluded in the work.

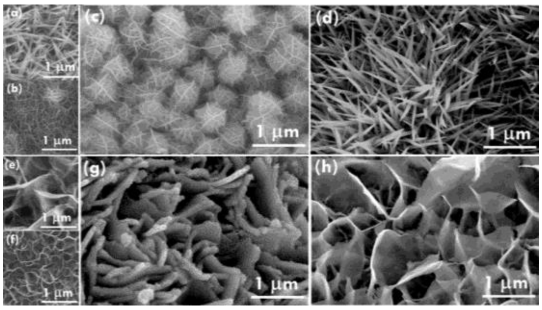

Figure 1 SEM images for (a) Ni_xCo_yO nanowires, (b) Ni_xMo_yO, (c) Ni_xCo_yO@Ni_xMo_yO, (d) Ni_xMo_yO@Ni_xCo_yO, (e) Ni_xCo_yO nanosheets, (f) MnO_2, (g) Ni_xCo_yO@MnO_2, and (h) MnO_2@Ni_xCo_yO nanostructures.

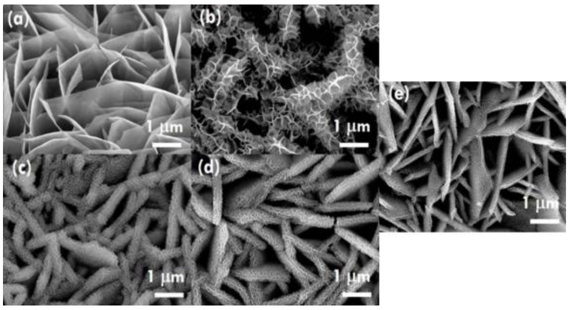

Figure 2 SEM images for (a) $NiCo_2O_4$, (b) $NiCo_2O_4$@NiS, (c) $NiCo_2O_4$@NiO, (d) $NiCo_2O_4$@$NiMoO_4$, and (e) $NiCo_2O_4$@MnO_2 on Ni foam.

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Highly Ordered Mesoporous $MnCo_2O_4$ with Cubic *Iα3d* Symmetry for Electrochemical Energy Storage

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The increasingly serious environmental problems associated with fossil fuels have prompted intense research interest into the development of sustainable and reliable energy storage systems. Among a wide variety of innovative technologies, supercapacitors, as a type of rechargeable energy device, have attracted great attention owing to their high power density, minimal maintenance cost, long life span and fast charge/discharge ability. The outstanding properties of supercapacitors make them important power source components for electric vehicles (including trams and buses), forklifts and other high power portable devices. The supercapacitor typically involves two identical electrodes that store charge in the double layer in the electrolyte adjacent to the electrodes. A variation on the supercapacitor is often described as a "hybrid supercapacitor" where one of the electrodes exhibits more battery-like behaviour and therefore improves the energy density of the device. There is much interest in such hybrid type devices made from inexpensive materials using very highly ion conductive KOH as the electrolyte, carbon as a classical double layer capacitive negative electrode and various transition metal oxide type materials as the positive electrode. Recently, the development of earth abundant transition metal (Ni, Co and Mn etc.) oxide and hydroxide materials has attracted enormous research effort owing to their low environmental impact and theoretically high energy-density capability. Nonetheless, despite recent progress, great challenges still remain for non-noble electrode materials to achieve excellent capacity and stability performance.

In this study, highly ordered cubic *Iα3d* mesoporous $MnCo_2O_4$ with crystalline framework was synthesized through a facile nanocasting method. The obtained mesoporous $MnCo_2O_4$ possesses hierarchical porosity with pore size of about 5 and 17 nm, respectively, and exhibits an enlarged surface area (133 m^2/g) compared to binary mesoporous Co_3O_4 (98.6 m^2/g) and MnO_2 (75.0 m^2/g). Significantly, the hierarchical mesoporous structure of $MnCo_2O_4$ is beneficial for exposing more electroactive sites, improving the charge transfer and facilitating the ion transport. Furthermore, the obtained mesoporous $MnCo_2O_4$ was drop-casted onto a Ni foam scaffold to achieve the $mMnCo_2O_4$ coated NF electrode ($mMnCo_2O_4$/NF), which can be used as positive electrode for a "hybrid supercapacitor". As a consequence, the $mMnCo_2O_4$/NF electrode shows a high charge storage performance of 199 mAh g^{-1} at current density of 1A/g, long cycle stability and excellent rate capacity. This study demonstrates ordered ternary mesoporous materials with controllable porosity have great potential for high-energy-density electrochemical energy storage.

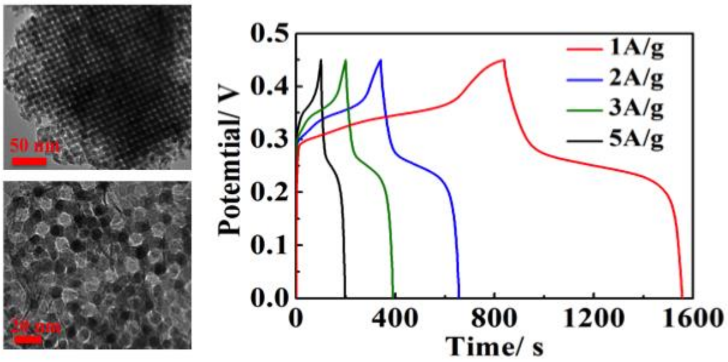

Figure 1. TEM images of ordered mesoporous $MnCo_2O_4$ with two kinds of pore sizes and corresponding charge/discharge voltage profile at various current densities.

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Selective dissolution of metallic glasses and nanocrystalline alloys

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Rapidly quenched binary and multicomponent metallic glasses and nanocrystalline alloys are subjected to chemical and electrochemical selective dissolution. Amorphous alloys of precious metals as well as of transition metals are investigated. To achieve desired micro- and nanoporous structures the dealloying conditions (types and concentrations of the electrolyte, temperature) were optimized. The effect of the electrode potential on the dissolution process is also found to be crucial. For some of the amorphous ribbons (e.g. Zr-based) the etching takes place with constant rate in three dimensions, indicating a surface controlled dissolution process. The etching velocity is found to be very high, as the whole dealloying process proceeds in several minutes. As a result three-dimensional homogeneous microporous structures are obtained. Besides, the evolution of the morphology and microstructure of the nanoporous materials at different stages of dealloying is investigated by SEM and High Resolution Transmission Electron Microscopy (HRTEM) equiped with EDS microanalysis. The resulting ligaments size ranges from tens to hundred nanometers. The changes in the ligament composition and microstructure at different dealloying times are correlated to the alloy copmposition and mechanism of dealloying. Additionally, the microstructure evolution is related to the electrocatalytic activity of porous alloys. The electrocatalytic activity for Hydrogen and Oxygen evolution of the dealloyed ribbons is compared to the as-cast alloys and other known electrocatalytic materials.

Fabrication of nanoporous nickel and its electrochemical application for hydrazine decomposition

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Nanoporous nickel is a new multi-functional porous material with a three-dimensional and bicontinuous nanoporous structure. The development of nanoporous nickel is of vital importance in electroanalysis[1], super capacitor[2], and catalysis[3]. In our research, the precursors of Ni-Al alloy are synthesized on Ni foil via magnetron co-sputtering. and then nanorous Ni samples are prepared by one-step dealloying from Ni-Al precursor alloys in 1M HCl solution. The structure, morphology, composition and electro-catalytic properties of the samples are characterized by SEM, TEM, EDS, XRD, GC, AUTOLAB. The result exhibites that the samples appear an uniform bi-continuous and large area nanoporous structure. The ligaments and pore channels both with a length of nearly 45 nm spread throughout the whole film.

Then we explore the electrochemical performance of the nanoporous nickel for hydrazine decomposition. The result demonstrates that, at a oxidation potential of -0.7 V in 1M NaOH and 0.1M N_2H_4 solution, the effect for hydrazine decomposition of nanoporous nickel possesses better electro-catalytic performance compared to nickel foil. The promotion of the electro-catalytic properties are ascribed to the increase of the superficial area and the active spot. The development of the non-noble metal catalysts will significantly improve the technology for the hydrogen generation and energy story.

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Development of Active Nanoporous Catalysts based on De-alloyed of $Cu_xAu_{(1-x)}$ Alloys

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The commercialization of fuel cells demands for the development of highly active, durable, and cost-effective catalysts that will have broad applications in energy, transport and even security sectors. Most catalysts for such applications contain Pt an element known for its high catalytic activity but unfortunately a most expensive metal.[1,2] Currently one way of reducing the total cost of fuel cell catalyst, is by using an inert conductive support coated by a small amount of Pt-based catalyst. Such a support could be a nanoporous Au (NPG).[1,2] NPG is a very conductive material, and with its open, 3D interconnected porous framework it has a very large surface area than planar Au. Once developed on a C-based support, the NPG can be terminated with Pt or Pt-containing alloys by surface-limited redox replacement (SLRR), and then applied as the catalyst in the key catalytic reactions.[3]

In our previous work, we established an all-electrochemical synthetic approach for a NPG-based catalyst.[3] The fabrication procedure involved $Ag_xAu_{(1-x)}$ alloy electrodeposition followed by selective dissolution of Ag (de-alloying) ultimately generating the desired NPG structure with a thickness of less than 20 nm[4]. NPG Pt-based catalysts made from $Cu_xAu_{(1-x)}$ precursor alloys were studied. The alloys of different size and shape were synthesized through various routes. Generally, the precursor is subjected to de-alloying and the resulting NPG is structurally and morphologically characterized before being functionalized with Pt and then assessed for performance and durability in formic acid oxidation tests[1].

More specifically, $Cu_xAu_{(1-x)}$ bulk alloys, electrodeposited alloys, and chemically synthesized Cu_3Au nanorods (intermetallic and random alloy)[5-7] are subjected to a comparative de-alloying study with emphasis on their parting behavior and resulting structures. The de-alloying curves exhibit quite unique behavior owing to size and structural differences based on their synthetic routes. Pb underpotential deposition (Pb UPD) was used to assess the surface area development of the NPG. SEM and TEM images display the morphology before and after de-alloying. Finally, basic activity and durability tests of the catalytic properties of various Pt-coated de-alloyed structures during formic acid oxidation are presented and discussed as well.

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Dealloying Routes and the Role of Adsorbates on the Structure of Nanoporous Gold

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Nanoporous gold (NPG) is discussed as a promising material for Pt-free alternative (electro-) catalysts[1,2], for high-rate actuation[3] or sensing[4] as well as switchable microfluidics component.[5] Its structure is composed of a continuous network of nanoscale ligaments that are interpenetrated by a continuous pore phase. Bulk-scale NPG is predominantly manufactured by a dealloying process which employs the dissolution of a sacrificial metal from either a Au-Ag, Au-Cu or Au-Al alloy. Besides the alloy and its composition, we show that the dealloying method (potentiostatic or open-circuit corrosion) can significantly influence the geometry of the NPG structure, its composition or the macroscopic sample shrinkage. The sample surface is found to significantly differ from the bulk structure. Different electrolytes within the potentiostatic corrosion induce different chemical conditions so that the rate of Ag dissolution is modified.[6] Under the assumption that the NPG structure forms under simultaneous re-structuring of the remaining solid phase upon the dissolution of the sacrificial metal, we conclude that a faster Ag removal induces a more extensive re-ordering phase. Besides this well-known mechanism, we discuss the influence of anion adsorption on the velocity of the surface re-structuring based on our observations. Anions such as hydroxide, nitrate or perchlorate are found to electro-adsorb on the forming ligament surface and to finally alter their formation rate. Since Ag is further known to aggregate to clusters on the surface[7], we performed X-ray photoelectron spectroscopy (XPS) to differentiate between bulk and surface-located Ag in samples that were dealloyed by different protocols. Contrary to energy-dispersive X-ray spectroscopy (EDX), a quantification of surface Ag is possible. Our results show that depending on the dealloying route, different ratios of surface Ag (by XPS) to bulk Ag (EDX) may result. We conclude from our comparative study that the dealloying route will have a remarkable influence on the later functional properties of NPG especially within the field of catalysis.

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Synthesis of Electrocatalytically Active Copper-Containing Multimetallic Nanostructures

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Multimetallic nanoparticles have attracted considerable interests because the multiple components synergistically improve the catalytic activity for electrochemical reactions. In addition to composition, controlling the morphology of the nanoparticles is possible to further optimize the performance of these nanostructures in their applications. Seeded growth is a robust approach to synthesize bimetallic and multi-metal nanostructures. Different configurations of nanostructures could be controlled by the geometry of the seeds and the growth rate of the secondary components. While numerous studies have shown the success in tailoring the morphology of bimetallic noble metals using the seed-mediated method, applications of this method involving *3d* transition metals are limited. In this talk, a seeded growth of copper-containing, multi-metal nanostructures will be presented. This method involves both the use of noble metal and copper nanoparticles as seeds. By tuning the reaction rate, the deposition of the second metals could site-selectively occur on specific facets of the seeds. Additionally, the diffusion rate of the dissimilar metals increases with increased temperature, thereby dictating the conversion between core-shell/heterostructures and alloy/intermetallics. In situ heating and cooling electron microscopy study on individual nanostructures will also be discussed. These copper-based nanostructures are catalytically active for methanol electro-oxidation. A comparison study of structure and composition effects on the electrocatalytic activities will also be presented. The electron coupling effects on the oxidation states of the different components in the multimetallic nanostructures will be discussed to provide some guideline for rational design of next-generation electrocatalysts.

Dealloying of Alloy Nanoparticles toward Optimization of Electrocatalysis

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Controlled structural remodeling of multimetallic alloy nanoparticles triggered by chemical or electrochemical dealloying allows one to deliberately fine-tailor the compositions, interior architectures, and surface structures of dealloyed nanoparticulate materials, thereby providing a unique pathway toward the optimization of electrocatalysis. Percolation dealloying of macroscopic alloy membranes involves selective leaching of the less-noble elements from the alloy matrices accompanied by structural remodeling of the more noble components, resulting in the formation of nanoporous foams consisting of noble element-rich nanoligaments that are interconnected to form a unique 3D solid-void bicontinuous, sponge-like architecture. The percolation dealloying of metallic alloys has recently been further extended from macroscopic membranes to particulate nanostructures, enabling controlled introduction of nanoscale porosity to metallic nanoparticles that are either free-standing colloids or supported on substrates. The nanoporosity evolution during percolation dealloying is found to be synergistically guided by several intertwining structural rearrangement processes, such as the kinetically controlled leaching of the less noble elements, the thermodynamically driven ligament coarsening, and the framework expansion governed by Kirkendall effects, all of which exhibit profound impact to the activity, durability, and selectivity of the dealloyed nanoelectrocatalysts. We have recently demonstrated that the density of surface active sites, the specific active surface areas, the local surface atomic coordinations, and the surface structural stability of the dealloyed sponge-like nanoelectrocatalysts can all be fine-tuned through deliberate control over the dealloying kinetics. This talk focuses not only on the mechanisms underlying the intriguing structural evolution of alloy nanoparticles during percolation dealloying and galvanic replacement, but also on the structure-composition-property relationships that underpin the electrocatalytic behaviors of the dealloyed noble metal nanoparticles.

Thiols and Crystallographic Cracking of Au Nanomaterials

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During dealloying in acidic electrolytes gold alloys show also a considerable ripening process of the forming ligaments due to a high ad-atom surface diffusion. At the same time the resulting nanoporous structures eventually shrink in volume. Thiol molecules form a strong specific bond on Au surfaces and also easily build up self-assembled monolayers. When a gold alloy surface is modified by thiols the surface diffusion is largely suppressed [1] resulting in an inhibition of the initial dissolution and dealloying corrosion [2]. With the application of a higher dealloying potential a localized mode of dealloying occurs which may lead to cracking of the locally formed nanoporous regions in line with their volume shrinkage [3-5]. The cracks show a pronounced crystallographic morphology leading to clearly distinguishable patterns on different oriented surfaces. The formation of the micrometre-scale cracks offers insights in the dealloying process and the foundation of stability of nanoporous structures.

The initiation of the localized dealloying on thiol-modified Au alloy surfaces occurs at arbitrary sites (Figure 1a). To study the nature of the initial breakdown of the dealloying inhibition and the molecular mechanisms of suppression of dealloying by the organic thiol film the applied film can be modified in a controlled way. One possibility is to use micro-contact printing in combination with different types of molecules in order to create controlled disorder in the protecting film (Figure 1b). This approach enables a better molecular-scale understanding of corrosion inhibition as well as nanostructure formation and stability of nanoporous materials during dealloying.

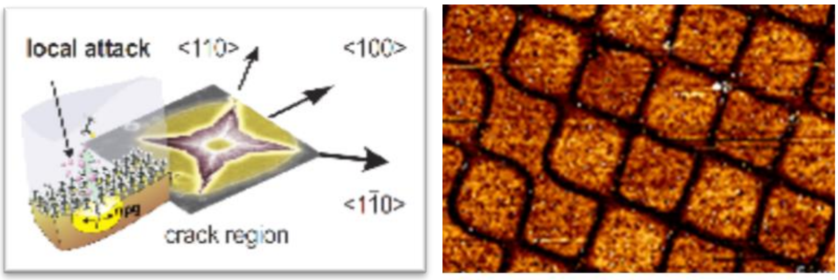

Figure 1 a) Crystallographic cracking [5] on Cu-Au b) A nanostructured thiol film.

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Advanced Characterization and Properties of Dealloyed Layers on AgAu(Pt) Alloys

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Binary and ternary AgAu(Pt) alloys were prepared with a constant (Au + Pt) of 23 at%. The Pt contents were low, 1-3 at% [1]. Atom-probe tomography (APT) was used to make compositional images with near-atomic resolution after growing thin dealloyed layers potentiostatically in perchloric acid solution, and electroplating Cu into the pores for mechanical stability [2]. Plating of Cu into nanoporous metals is an interesting subject in its own right - Lee et al. [3] showed a kind of subpotential curvature-induced deposition within nanoporous Pt. For the first time, in the binary AgAu alloy, nanoligaments were observed whose cores were very close to the precursor alloy composition. This contrasts with the commonly used nitric acid immersion, where Ag leaching out of the ligaments, and their coarsening, occurs after quite short immersion times. Elaborate analyses of the APT data reveal slight aberrations caused by ion trajectory overlap from adjacent regions of different composition, and also new ways to analyze such effects and to determine the greatest errors that could arise at the sub-nm scale. For the ternary alloy precursor, the ligament size is refined and Pt is enriched on the ligament surfaces. The exact geometry of the Pt enrichment is still under investigation, in view of possible aberrations, but appears to be somewhat spotty or particulate at the nm scale.

In parallel with the APT measurements, fragments of dealloyed material have been examined in an environmental TEM capable of heating the samples and introducing hydrogen or oxygen [4]. More detail has been obtained on previously inferred surface enrichment phenomena – typically, oxygen enhances Pt segregation to ligament surfaces and stabilizes the morphology, while hydrogen encourages desegregation of Pt and consequent coarsening [5].

Other ongoing studies involve electrochemical impedance spectroscopy, revealing new phenomena related to ionic conduction in nanosized channels.

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Templated Dewetting-Dealloying of Metals: Designing Photocatalytic Platforms

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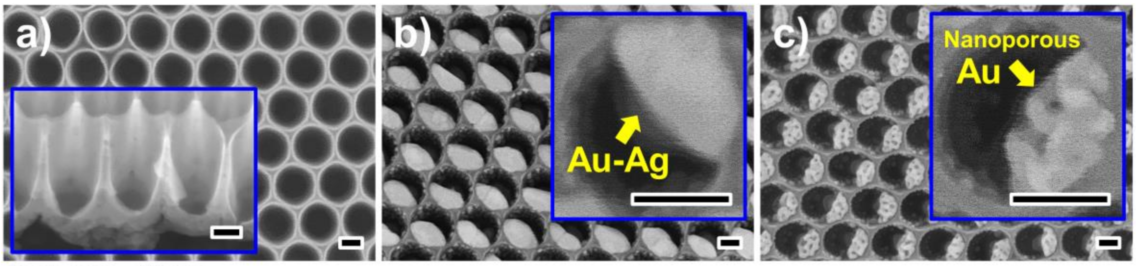
Nanoscale processing tools such as electrochemical anodization,[1] metal dewetting[2] and dealloying[3] can be combined to precisely design photocatalytic platforms for H_2 generation.

We use highly-regular arrays of TiO_2 nanocavities with periodicity and depth of some 100 nm[4] (Fig. a) onto which thin metal films (nominal thickness < 30 nm) are conformally sputter-coated and dewetted, that is, a suitable thermal treatment is carried out that brings about morphological evolution of the metal film into periodically arranged metal particles. The periodicity of the TiO_2 surface is a requirement for templated dewetting and enables self-ordering of the dewetted metal nanoparticles into the TiO_2 nanocavities.[5]



Scale bars = 50 nm

Particularly intriguing features arise from sputter-coated combinations of metals. Depending on the chosen elements, dewetting can lead to alloyed metal nanoparticles of controllable composition (Fig. b). Moreover, when one of the sputtered metals (*e.g.* Ag) is less noble than the other (*e.g.* Au), the alloyed-dewetted structures can be dealloyed, *i.e.*, the more (electro-)chemically active element (Ag) undergoes selective dissolution leaving behind nanoporous noble metal (Au) particles with high specific surface area into the TiO_2 cavities (Fig. c).[6]

These structures combine the intrinsic photocatalytic features of TiO_2 with charge-transfer cocatalytic ability of noble metals,[7] thus providing a versatile platform for photocatalysis.[8–10] We illustrate how self-ordering concepts such as anodization, alloying, dewetting and dealloying can be synergistically interlaced to reach fine control with nanoscopic precision over the resulting metal-TiO_2 structures in order to maximize their photocatalytic efficiency.

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Uniform hierarchical nanoporous Pd by dealloying - synthesis and hydrogen driven actuation performance

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Nanoporous (np-) gold is the model system of choice for many studies of dealloying-made nanoporous metals since the microstructure is particularly uniform and synthesis results highly reproducible. Np-gold is also exceptional since it can be made in the form of mm- or cm-sized monolithic bodies with excellent mechanical integrity and deformability. It would be of interest to establish dealloying protocols for alternative nanoporous metals with comparable qualities. Here, we report a strategy for preparing macroscopic, monolithic and uniform bodies of np-Palladium with excellent mechanical deformability [1]. We use electrochemical dealloying of $Cu_{85}Pd_{15}$ in H_2SO_4. Remarkably – and quite reproducibly – the single step dealloying process leads to a hierarchical network structure with two well-defined ligament sizes. Thermal coarsening leads to more normal structures with ligament sizes that can be established over similar ranges as in np-gold. Thus, the material may indeed provide an alternative to np-gold as a model system for nanoscale structural or functional materials. Our study exemplifies this by exploring actuation through electrochemically controlled hydrogen sorption. The actuation strain reaches amplitudes up to 4.0%, which are stable over for more than 1000 cycles. Furthermore, in view of the macroscopic sample size in all three dimensions, the switching time for actuation is remarkably fast.

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Electroless Deposition of Pb ML – A Prelude to Highly Selective Electroless ALD Process

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The improved understanding of nucleation kinetics has led to various discoveries in which the thin film growth was manipulated to enhance the evolution of atomically flat epitaxial overlayers. Exploiting some of these results has led to invention of several new methods and protocols for electrodeposition where underpotentially deposited (UPD) monolayer is used as a mediator, surfactant or sacrificial template. In this talk we present results demonstrating an electroless ALD process in which an electrolesslly deposited Pb monolayer is used as a reducing agent and sacrificial material in SLRR reaction with noble metal ions such as Pt, Pd, and Ru. The full deposition cycle involves sequential exposure of the substrate to the solution for Pb monolayer deposition and then to solution for SLRR reaction and noble metal deposition. This results in an overall deposition of controlled amount of noble metal which is the function of the areal density of deposited Pb monolayer and stoichiometry of the SLRR reaction. Therefore, the process mimics, to a great extent, the standard ALD cycle where adsorption of the metal precursors and surface catalyzed reaction are replaced by electroless Pb monolayer deposition and SLRR reaction. If the two-step SLRR cycle is repeated an arbitrary number of times, a highly compact, smooth, and conformal noble metal thin film is grown. The deposition process is highly selective to the metal substrates at which Pb forms an UPD monolayer providing an advantage when certain integration requirements are considered. The process is designed for (but not limited to) aqueous solutions with fairly simple and stable chemistry that can be easily scaled up to any size and shape of the substrate surface. Results demonstrating details and underlying phenomena controlling this process will be discussed. In addition, an example of a high quality of Pt, Pd, and Ru films grown on Cu and other substrate will be shown, as well as the applications of this process for metallization of structures relevant to semiconductor device fabrication.

Nanoporous Metals for Energy Applications

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The first part of this talk will summarize recent progress made in integration of nanoporous gold (np-Au) derived nanomaterials into targets for inertial confinement fusion experiments at the National Ignition Facility. Bulk nanoporous gold made by dealloying provides extremely good and simple control over feature size and, if combined with atomic layer deposition, allows fabrication and tooling-free integration of macroscopic ultralow-density foam components with tunable density and composition into inertial confinement fusion targets. The second half of the talk will summarize recent progress made in understanding the catalytic reactivity of np-Au and related materials at Harvard's Energy Frontier Research Center IMASC (Integrated Mesoscale Architectures for Sustainable Catalysis). Unsupported bulk mesoporous dilute alloy catalysts such as nanoporous gold have the potential for major impact on improving the energy- and atom-efficiency of chemical synthesis. The underlying design principle of this class of catalysts is that the more noble majority alloy component provides the desired selectivity while the more reactive minority alloy component (Ag in the case of np-Au) provides the required reaction sites for oxygen or hydrogen dissociation. The reactivity and long-term stability critically depends on the alloy composition and local arrangement of the alloy components. Applying this principle to other nanoporous metals made by dealloying provides an opportunity to design new catalysts.

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Re-evaluation of Au as a core for Pt monolayer oxygen reduction reaction catalyst

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Proton Exchange Membrane Fuel Cells (PEMFCs) are promising solution for ever growing problems associated with fossil fuel availability and related environmental effects. However, high Pt catalyst loading in the cathodes is required due to the sluggishness of the oxygen reduction reaction (ORR) and Pt dissolution under fuel cell operating conditions, causing high cost of PEMFCs. The concept of Pt monolayer (PtML) electrocatalysts [1] offers a possible solution to these problems because it provides ultimate reduction in Pt loading, complete utilization of Pt, and possibility to tune performance of PtML by its interaction with substrate.

We recently showed that PtML shell deposited on Pd or PdAu alloy core has higher activity and stability than pure Pt electrocatalysts [2]. However, due to the incomplete Pt shell, Pd (noble metal) shows some instability under prolonged highly oxidizing conditions that may occur in fuel cell operation. As a non-Pt group metal, Au is a good candidate for the core material since it is stable under the oxidizing conditions of the ORR and it has high natural abundance. However, the lack of interest in the Au@Pt core-shell catalysts can be attributed to two impeding effects on ORR activity, that are, the strong bonding of OH and O to Pt due to the up-shifts of d-band center for Pt on Au core induced mainly by the strain effects [3], and the blocking of active sites of Pt due to the Au segregation onto the Pt surface [2, 4].

We are reporting on two novel Au containing cores for PtML ORR catalysts. The first one is Au core with the low-coordinated surface sites doped by Ti oxide, e.g. vertex and edges, while Pt occupies the surface facets, Ti-Au@Pt [5]. The other one is AuNi core in two different structures: alloy ($AuNi_a$) and core-shell ($AuNi_{cs}$) [6]. All catalysts showed better performance compared to the commercial Pt/C and Au@Pt catalysts. In case of Ti-Au@Pt, higher ORR activity is due to presence of TiO_2 which repulsively interact with Pt-OH thus reducing its coverage and boost ORR activity. TiO_2 is also responsible for enhanced stability of Ti-Au@Pt since it prevents Au atoms from segregating onto the Pt surface and thus can largely retain the electrochemical surface area. In case of AuNi@Pt, improved activity is due to electronic and geometric effects, while better stability is probably due to presence of Ni that modifies segregation properties of Au.

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Nanoporous Metal Electrodes for Fuel Cell Technologies

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Polymer electrolyte membrane fuel cells (PEMFCs) allow ambient condition direct conversion of chemical energies in chemical fuels into electricity, with particular advantages of being highly effective, environment friendly and portable. For those fuel cells using oxygen or air as the oxidant, the oxygen reduction reaction (ORR) occurred on the cathode remains the major obstacle for the commercialization of PEMFCs because of its low kinetics, which in turn results in relatively low catalytic efficiency and high price due to excessive use of precious metals, such as Pt.

Compared with traditional nanoparticulate-type electrocatalysts, dealloyed nanoporous metals (NPMs) possess additional structural advantages when acting as either catalyst supports or active electrodes themselves, such as three-dimensionally interconnected pore/ligament structure, excellent conductivity and structural flexibility. By means of advanced electron microscopy, modeling and electrochemical testing, this talk will start with addressing critical issues in NPMs that determine their apparent electrocatalytic performances, including strain effect, electronic effect and ligand effect. The second part of this talk will discuss the development of NPM-based membrane electrode assemblies (MEAs) for actual implementation in both H_2 and direct liquid fuel cells.

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In situ STM Studies of Electrochemical Alloying/Dealloying of a single atomic layer

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Unraveling alloying and dealloying processes is of prime importance for understanding catalytic or corrosion resistance of alloys. In the present work, we study electrochemical alloying and dealloying of a single atomic layer at the nanometer scale. We use in situ Scanning Tunneling Microscopy (STM) to study electrochemical deposition and dissolution of monolayer films of bimetallic alloys. We will first consider two examples of monolayer alloy films NiAu and NiPd deposited on Au(111) and show how following in–situ the dealloying process allows to quantitatively measure the enhanced "nobleness" of the Ni induced by the presence of Au or Pd. Second, we will compare co–deposition and sequential deposition of NiAg, NiPd and NiAu to explore how the miscibility of these metals influences the final deposit morphology.

The alloy layers were deposited in mixed conditions where the more noble metal is deposited under diffusion conditions and Ni is deposited close to the Ni Nernst potential. For deposits performed sequentially, the Ni was deposited first in kinetic conditions and then the noble metal was deposited in a diffusion limited process. These deposition procedures yield a quasi two dimensional growth for all alloys. The thickness of the films was limited to one atomic layer of less in order to allow studying the morphology without interference of the underlying layers.

In Figure 1, the dissolution of NiPd alloy monolayer is shown. From the cross–correlation between the dissolution potential, the spatially localized preferential dissolution and the local Pd content we could establish a relation between the dissolution potential of Ni atoms as a function of the density of neighboring Pd atoms (Figure 2) [1].

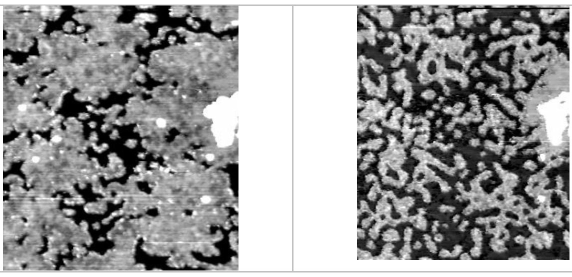

Figure 1: in–situ STM images of $Ni_{51}Pd_{49}$ alloy monolayer dissolution. Image size 60 nm x 70 nm.

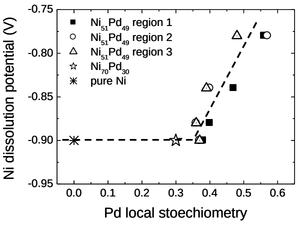

Figure 2: Ni dissolution potential as a function of the local Pd content

Figure 3 presents the surface morphology after depositing Ni monolayer islands followed by Ag, Pd and Au deposition. The detailed analysis of these deposits clearly shows the presence of alloying in the case of Pd and Au and some specific preferential alloying atomic sites [2].

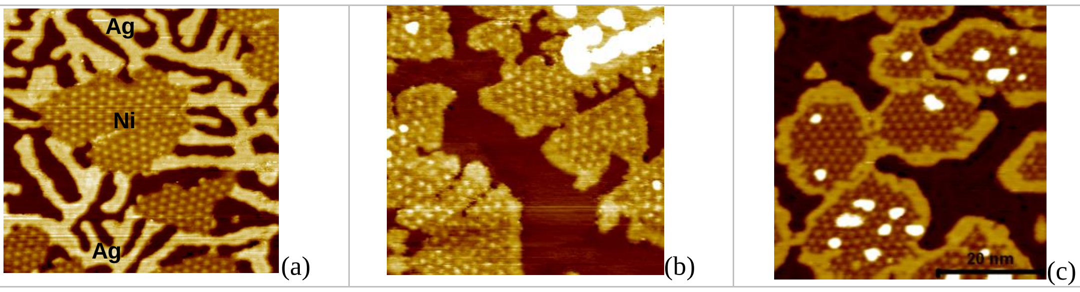

Figure 3: in–situ STM images of Ni islands covered by submonolayer of Ag (a), Pd (b) and Au (c). Image size 50 nm x 50 nm.

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Dealloying of Binary Catalysts in Hydrogen Fuel Cell

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A reduction in the amount of Pt required in proton exchange membrane fuel cell remains a developmental priority. Dealloyed catalysts, PtCo and PtNi in particular, are the leading cathode catalyst candidates due to their high activity for oxygen reduction reaction (ORR) and relatively high stability.[1,2] The term 'dealloyed' is attributed to its method of preparation where alloy nanoparticle precursor with high content of transition metal (e.g. Co) is first prepared, following by an oxidation treatment, either by acid leaching or electrochemical oxidation, in order to remove a majority of the transition metal. Even though the catalyst has experienced extensive oxidative treatment during the catalyst synthesis, the dealloying process continues to evolve under fuel cell operating conditions due to exposure to an acidic environment and high electrode potentials. This results in the catalyst transition metal dissolving into the electrolyte phase. In turn, this causes losses in catalytic activity and subsequent reductions in proton, water and O_2 transport properties of the fuel cell electrodes. In order to operate the fuel cell at its optimum and mitigate performance loss, it is important to understand the dealloying mechanism and how different factors affect the process in the fuel cell.

This talk will outline the current understanding of the dealloying process of PtCo electrodes under both simulated and actual fuel cell operating conditions. Studies are performed to quantify the amount of leached Co and Pt ions during potentiostatic and potentiodynamic conditions in an electrochemical cell with aqueous acid electrolyte. The amount of metal ions that are released into the solution were monitored with on-line ICP-MS in a flow-through electrochemical cell and using ICP on the solution samples that are extracted during the cycling. While the amount of Pt dissolved during voltage cycling is well studied, the impact of potential cycling on Co leaching is not well understood. Initial set of measurements show that the amount of Co leached is a strong function of upper potential limit (UPL) and less impact due to lower potential limits (LPL), however Pt dissolved is strong function of both UPL and LPL. In addition to quantifying leached Pt and Co, changes in the particle characteristics and metal compositions of the particles were also quantified using SAXS. Fundamental models were developed to explain the mechanisms of degradation process under potential cycling. Models show that the leaching process is strongly related to the type and growth of Pt oxides on the catalysts. Mechanistic understanding and quantification of these processes is necessary to optimize the operating procedures of the fuel cells.

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Nanoscale Imaging and Dynamics of Dissolution and Dealloying using Coherent X-rays

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Coherent x-rays are different from ordinary x-rays as a laser is from a flashlight. While ordinary x-rays provide atomic scale ensemble average structures of materials or their interfaces, coherent x-rays are sensitive to nanoscale details of a particular sample such as steps, defects, and strains. In this talk, we will cover the basic concepts of coherent x-ray scattering and recent examples where new information was obtained using coherent x-rays otherwise unavailable.

The crystal truncation rod intensity consists of intensity points sensitive to the average surface electron density in ordinary incoherent x-ray scattering. In coherent x-ray scattering, the single point is, when carefully measured, composed of complex interference patterns, known as x-ray speckles. The speckles are representatives of the detailed structures of the interfaces. In ordinary x-ray diffraction, these details are all lost by the ensemble average. There are two ways to use the speckle patterns to study the electrochemical interfaces: i) in time domain and ii) in real-space imaging. (i) The speckle patterns are sensitive to the nanoscale details of the interface. If the interface structure changes in time, the speckle patterns change. The change can be measured to estimate the dynamic properties of the interface even when the average structures do not appear to change. (ii) The complex speckle patterns can be inverted back to real space images. The measured speckle patterns lack the phase information that is necessary to invert them to images. However, a computer aided oversampling technique makes the inversion possible with iterative processes of simulating the phases.

Examples to discussed in this talk are silver step dynamics[1] and silver dissolution reaction.[2] The silver surfaces have been extensively studied using conventional electrochemical techniques and much is known. Here we measured the applied potential dependent rate of atomic step motion of the Ag(001) surface in weak NaF electrolyte using x-ray photon correlation spectroscopy (XPCS). For applied potentials between hydrogen evolution and oxidation, the surface configuration completely changes on timescales of 10^2–10^4 seconds depending upon the applied potential. (Fig. 1) The potential dependence was modeled with the step line capacitance. The second example is visualizing the silver nanoparticle dissolution. A silver nanoparticle was stepped to a dissolution potential in 0.1 M $HClO_4$ solution and imaged with Bragg coherent diffraction imaging (BCDI). (Fig. 2) A series of images of a silver particle suggest that the dissolution reaction occurs in two distinctive steps. First, there is an incubation period with no apparent dissolution occurs until a dislocation loop is created. Once the dislocation loop is exposed to electrolyte, a rapid dissolution occurs. We will also cover our recent dealloying study.[3]

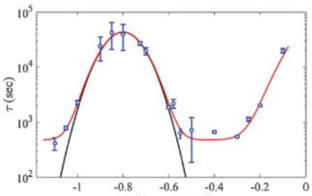

Fig. 1. XPCS results of Ag(001) surface. Decay constant (τ) as a function of applied potential at L=0.2. The solid black line corresponds to only the contribution from step line capacitance, while the red line includes the phenomenological component. For reference, PZC is near −0.8 V where the surface and line capacitances are zero.

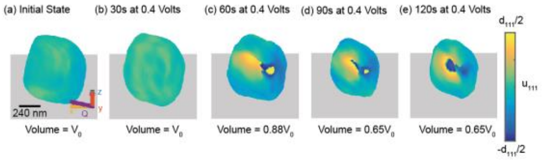

Fig. 2. BCDI of a silver nanoparticle. Dissolution proceeds in two steps: i) creation of dislocations and ii) rapid dissolution at or near the dislocation loop exposed to the acidic electrolyte. (a-b) The particle shape and size does not change during the initial 30 sec in the dissolution overpotential of 0.25 V. (c-d) Significant dissolution occurs after the appearance of a dislocation loop (60 sec) exposed to the electrolyte. (e) Eventual increase of Ag concentration in electrolyte slows further dissolution of the particle (120 sec).

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Surface oxides at nanoporous gold investigated by surface interrogation mode of scanning electrochemical microscopy

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Nanoporous gold (NPG) represents a porous electrode whose understanding lags considerably behind that of smooth electrodes, especially with respect to mass transport behavior inside the pores. Here we are interested in exploiting the large internal surface area (relative to the geometric area) for investigation of surface oxides using the surface interrogation mode of scanning electrochemical microscopy (SI-SECM).[1]

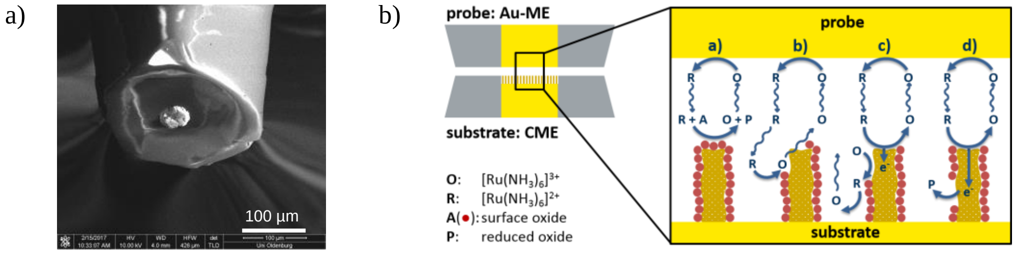

Fig. 1: a) SEM of NPG-CME and b) scheme of proposed titration mechanism

The SI-SECM mode allows for the investigation of adsorbates on a substrate electrode without changing the electrode potential during detection. The power of this technique was first demonstrated for surface oxides and adsorbates on a smooth gold electrode and was further developed since. A probe microelectrode (ME) is positioned above a same-sized substrate ME. First, an adsorbate is formed in a potential step at the substrate ME while the probe electrode is held at open circuit potential (OCP). Secondly, the substrate ME is switched to OCP to preserve the adsorbates. A titrant is generated at the probe ME from a redox mediator which is present in the bulk solution. The oxides are removed from the surface by a chemical reaction and the initial form of the redox mediator is regenerated. Therefore the current at the probe ME is higher than expected for a thin layer cell of the same dimensions. Once the adsorbate is fully consumed, the current drops to the diffusion-controlled current in the thin layer cell. By integration of the current response, the amount of adsorbate can be quantified.

NPG was formed by free corrosion in HNO_3.[2] The material was powdered and filled into a cavity ME[3] of 25 µm diameter and 8 to 25 µm recess (Fig. 1a). This allowed us to test the concept of SI-SECM for catalyst powders of high surface area that are typically used in gas diffusion electrodes. The surface oxides were formed during potential excursion to 0.7 V up to 1.6 V vs. Ag/AgCl. The time needed for fully titrating surface oxides was found to depend *only* on the real surface area of the porous electrode whereas the depth of the cavity had no influence. The calculated amounts were in agreement with values on smooth electrodes. Additionally we observed that the end of titration was indicated by a sudden drop of current as steep as for smooth electrodes. These observations led us to the formulation of a possible titration mechanism in a COMSOL model (Fig. 1b). We believe that analogous to extended conducting surfaces in SECM, a concentration cell is formed along the ligaments (perpendicular to the outer electrode surface). This equilibrates the concentrations inside the porous network almost instantaneously once the passivating oxides are removed. This might explain the absence of mass transport retardation inside the pores. The COMSOL simulations reproduced the experimental curves when assuming different oxide species with inherently different reduction kinetics and passivating properties.

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Mechanism and Kinetics of the Electrocarboxylation of Aromatic Carbonyls in Ionic Liquids

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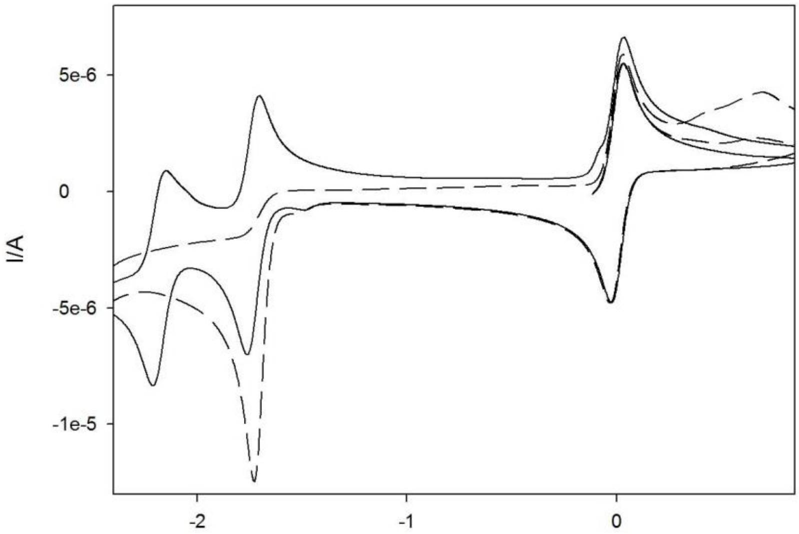
Room temperature ionic liquids have received considerable attention over the past two decades as neoteric solvents for a host of chemical transformations and processes. Being molecular solvent free non-volatile fluids, entirely ionic in composition, and inherently conducting, they are very attractive for many electrochemical applications including for fundamental molecular electrochemical studies and preparative-scale electrochemistry. Although most common RTILs are relatively benign, it known that they can influence chemical and electrochemical reactivity.

The electrochemistry of benzophenones has long been use as a marker for electrochemical reactivity in a range of environments since it is strongly influenced by solvent polarity and proton availability. In this presentation we describe the detailed electrochemistry associated with the electrocarboxylation of a range of benzophenones in butylmethylpyrrolidinium bis-triflimide ionic liquid ([Bmpy][NTf$_2$] and discussed the mechanism and kinetics in terms of the IL environment and the effect of substituents. It will be shown that that mechanism is ECE (or DISP1) and that the rate of the electrocarboxyaltion step is a direct function of the electro-negativity of the substituents as expected from the Hammett relationship.



E vs Fc$^+$/ Fc, 4-Cyanobenzophenone (10 mMol dm^3) in bmpy NTf$_2$, with (dotted line) and without CO$_2$ (solid line) present, at 10 mV/s.

Tin and alloys electrodeposition in choline chloride-based ILs- nucleation studies and surface analysis

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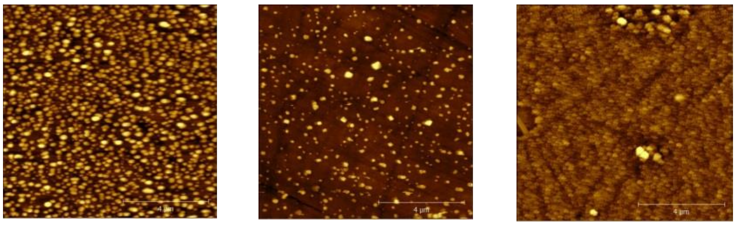
Metal electrodeposition is crucial for a variety of industrial applications, where particularly tin (Sn) has been applied as a coating due to its non-toxicity, ductility and corrosion resistance. [1] Pure Sn coatings have been used to form a protective surface to resist air oxidation in order to enhance corrosion resistance. Bright Sn coatings also provide decorative finishes that can be esthetically pleasing even when exposed to air and moisture. [2] DES have been used for the deposition of a range of metal coatings such as Sn [3] and its alloys (Sn-Zn, Sn-Ni, Sn-In, etc.) [4–6], among many other metals and its alloys. [7,8]
In this work the research was focused on the nucleation studies of Sn for three different DES, ethaline, reline and propeline. Sn, Sn-Ni and Sn-In alloys electrodeposition from solutions of DES at 75ºC were cherecterized by cyclic voltammetry, chronoamperometry and atomic force microscopy (AFM) analysis on a GC electrode. Chronoamperometry and nucleation studies show that Sn electrodeposition on GC surface occurs through an instantaneous process with growth controlled by diffusion.



Ethaline **Propeline** **Reline**

Figure 1. Atomic force microscopy images of the deposits of Sn on a copper electrode obtained from different DES by a chronoamperometric pulse at -1250 mV (vs. silver pseudo reference electrode). Time of the potential pulse of 60 s. T= 75 ºC.

The growth of the deposits was followed by AFM and nature of DES clearly influences the metallic film growth at initial stages. The corrosion resistance of the pure metals and alloys were studied and comparisons between DES and co-deposited metals will be presented and discussed.

Acknowledgments

N.M. Pereira would like to acknowledge FCT – Fundação para a Ciência e a Tecnologia for granting the PhD fellowship SFRH / BD / 89441 / 2012 financed under QREN – POPH – Advanced Training subsidized by the European Union and national MEC funds. The authors also want to thank to NOVTINALBEST project (contract number M-ERA.NET/0009/2012) and to the PEST program PEST-C/QUI/UI0081/2014. CMP and AFS also would like to thank the COST Action CM1206 – EXIL – Exchange on Ionic Liquids.

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Carbon Electrodes in Room Temperature Ionic Liquids – Effect of IL Type, Electrode Microstructure and Surface Chemistry on Capacitance and Electron-Transfer Kinetics

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The properties of room temperature ionic liquids (RTILs) and the structure of the electrified interfaces they form with carbon electrodes has been the subject of both fundamental and applied research, particularly in the field of energy storage devices like supercapacitors. RTILs have great potential to replace conventional organic solvent/electrolyte systems because of their environmentally-benign characteristics (non-volatility, non-toxicity) and excellent thermal and electrochemical stability. The physicochemical properties of RTILs can be flexibly tuned through selection of the component ions. Research is needed to better understand the structure of electrified interfaces formed in these novel media at carbon electrodes of different surface chemistry and microstructure. Traditional models of the electrochemical double layer based on the dilute-solution approximation may not be applicable to RTILs because of the absence of solvent, the high concentration of ions, strong interionic columbic forces, and electrostatic and hydrophobic interactions of charged ions with the electrode surface.

In this presentation, electrochemical investigations of the capacitance of carbon electrodes as a function of potential, the RTIL type, carbon electrode type and surface chemistry will be reported on. 1-alkyl-3-methylimidazolium-based RTILs were studied at boron-doped-diamond and nitrogen-incorporated tetrahedral amorphous carbon thin-film electrodes. Comparison measurements were made using glassy carbon. Cyclic voltammetry and electrochemical impedance spectroscopy were used to measure the electrode capacitance. Additionally, the electrochemical response of ferrocene derivatives in the different RTILs was investigated at these same electrodes. Cyclic voltammetric results will be reported. Heterogeneous electron-transfer rate constants were calculated from ΔE_p-υ trends and verified by digital simulation.

Characterization of Gallium Electrodeposition in PP_{13}TFSI and N_{1114}TFSI Ionic Liquids

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Gallium is a metal widely used in the electronic industry for the semiconductive properties of its alloys like gallium arsenide, or gallium nitride. As minerals rich in gallium are not common on earth, they are not usually used as a primary source for production. Most of the gallium commercialized comes from Bayer liquors which is recovered with different techniques like electrodeposition. Gallium electrodeposition occurs at a potential close to hydrogen evolution in aqueous media limiting the interest of this electrolyte [1]. As ionic liquids possess a wide electrochemical window, they appear very attractive for the electrodeposition of this metal. Some works have already showed the feasibility of gallium electrodeposition in ionic liquids [2, 3].

This work has for objective to improve the understanding of gallium electrodeposition in ionic liquids. Gallium trichloride at low concentration (60 mM) has been selected as source of gallium and was dissolved in TFSI based ionic liquids (PP13TFSI and N1114TFSI) known for their high cathodic stability (down to +1V vs Li^+/Li). Gallium deposition on glassy carbon, titanium and stainless steel have been studied and the deposits characterized by FEG-SEM, EDS, XPS and AFM to determine the composition and size distribution of gallium particles. Then, the nucleation mechanisms have been determined and have been found to depend on the nature of IL as well as substrate. Finally, an EQCM study has allowed to compare the energy efficiency of the electrodeposition in function of the working electrode and ionic liquid used.

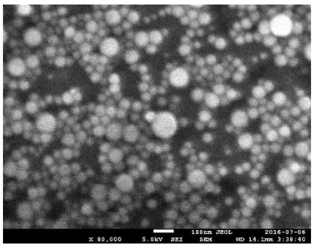

Fig 1: FEG-SEM analysis of gallium deposited on titanium in N1114TFSI

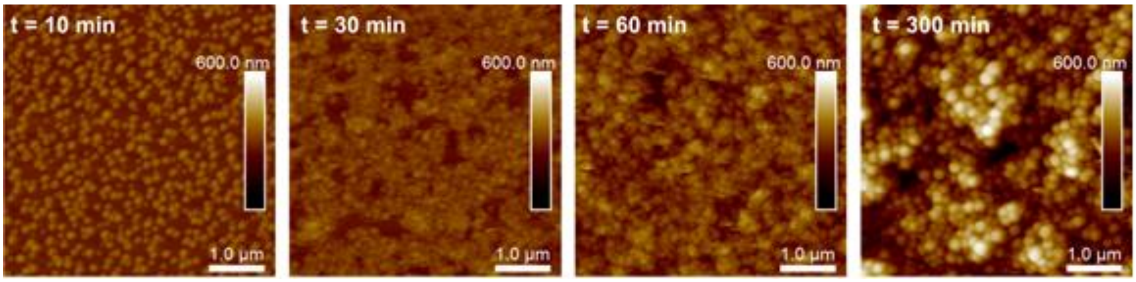

Fig 2: AFM of gallium deposition at -1.8V vs Pt on HOPG electrode in N1114TFSI

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Electrocatalysis on Ionic Liquids: Defining Experimental Conditions

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The use of room temperature ionic liquids (ILs) for electrocatalytic purposes is a relatively new and promising field that emerged in Electrochemistry on the past few years [1-3]. However, to fully understand the role played by the ILs from an electrocatalytic point of view, it is of outstanding importance controlling some critical experimental parameters including water content, temperature and chemical nature of the IL, among others [4]. In the present communication, we evaluate different pre-treatments to minimize the water content on different imidazolium based ILs. However, this initial water content must be also kept under control during the specific electrocatalytic experiments. In this regard, we will show that for relevant electrochemical reactions such as CO_2 electroreduction or even for deoxygenating purposes (through argon bubbling), the use of gas filters is indispensable to control the water content during the experiments. All these experimental conditions will allow the role of the ILs to be better understood.

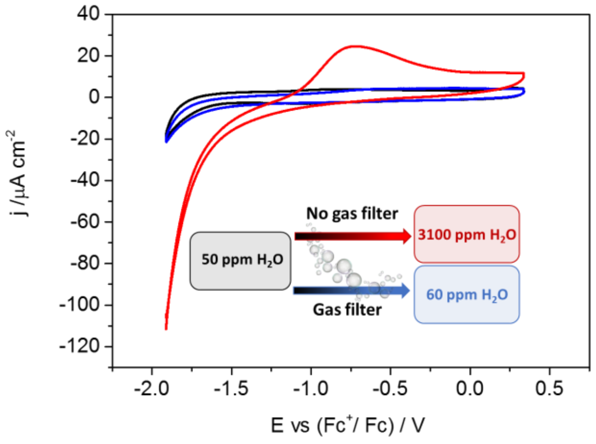

Figure 1. Cyclic voltammetry obtained in 1-Butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) with Pt nanoparticles under different conditions, (black line) Ar saturated (using a H_2O/O_2 gas filter), (blue line) CO_2 saturated (using a H_2O/O_2 gas filter) and (red line) CO_2 saturated (*without* using a H_2O/O_2 gas filter). Scan rate 50 mV/s and all curves referenced against Fc^+/Fc.

Acknowledgements
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Electrochemical Studies of CO_2 Reduction in 1-butyl-3-methylimidazolium chloride

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We present an electrochemical analysis of the effect of CO_2 in 1-butyl-3-imidazolium chloride ionic liquid under an inert Argon atmosphere and ambient atmospheric conditions monitored by a relative humidity sensor. A two-electrode electrochemical setup was used to perform these experiments in an atmosphere controlled glove box with Pt as both the working and counter electrodes. The electrochemical potential window of the studied ionic liquid was measured using cyclic voltammetry by increasing the cathodic potential up to -3.0V vs Pt. CO_2 was bubbled directly into the ionic liquid for 30 mins and 1 hour. The electrochemical response of the system was measured while controlling the potential window of each experiment. These results show a shift in various peaks present in the voltammograms of the pristine ionic liquid when compared to the data after introducing CO_2 into the system which we posit as a change in the chemistry of the ionic liquid. Further studies are necessary to elucidate the makeup of these species and further insights into the electrochemical reduction of the species present in the system.

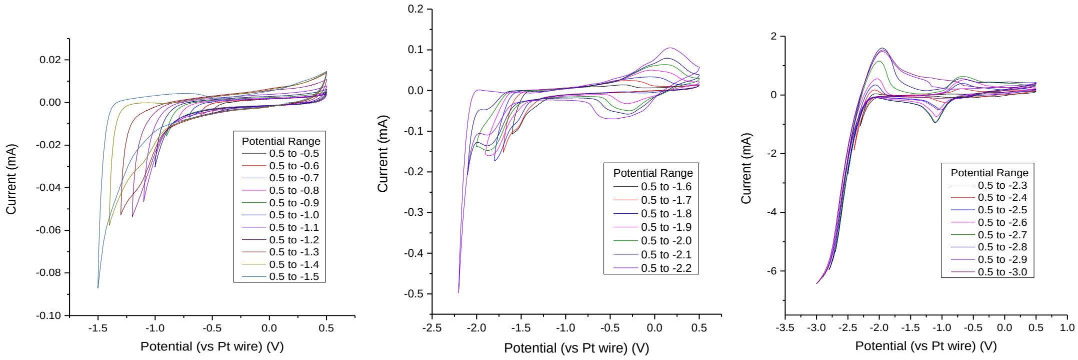

Figure 1: Cyclic voltammetry of [Bmim]Cl at 100mV/s increasing the potential window cathodically by 0.5V vs Pt wire.

Modelling Zinc Batteries with Ionic Liquid Electrolyte

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Rechargeable zinc ion batteries are potential candidates for low-cost and efficient energy storage devices [1]. Zinc is an abundant element which is non-toxic, cheap and environmentally benign. Primary zinc batteries have a long history and are established commercially [2]. However, technical problems associated with zinc ion batteries are yet to be resolved [1]. The key component is the electrolyte because it must be stable over a wide electrochemical window and allow reversible metal deposition.

Ionic liquids are promising candidates for stable battery electrolytes [3]. Their advantages comprise a large electrochemical window (up to 6V), chemical and thermal stability, non-flammability (as safety asset) and low vapor pressure [4]. In particular, ionic liquids minimize dendrite growth during electrodeposition and have high ionic conductivity [4]. Zinc-air batteries with ionic liquids are potentially stable towards moisture as well as carbon dioxide and can support a reversible oxygen electrochemistry.

In this talk, we present a thermodynamically consistent transport theory of zinc batteries based on room temperature ionic liquids. Upon this framework we model a zinc ion secondary battery with a mixture of ionic liquid and water as electrolyte. This setup is described experimentally in Ref. [1]. The battery comprises a zinc anode and a Prussian blue analogue cathode in combination with a choline-acetate-water mixture, [Ch]OAc+30%wt water. [Ch]OAc, is a biodegradable, biocompatible, and inexpensive ionic liquid.

Our focus lies on the systematic derivation of a set of fully coupled transport equations for the ions, charge and heat based on the development of modeling methodologies for lithium-ion batteries [5]. The battery is simulated along one dimension and good agreement with the experimental observations described in Ref. [1] is found.

For the understanding of microscopic structures, we incorporate the hardcore particle nature of the medium into our transport theory. In the vicinity of an electrified interphase, we find a quasi-crystalline structure with crowding and overscreening [6].

This work was supported by the Federal Ministry of Education and Research (BMBF) via the project "Zinc/Air Battery with Advanced Materials for Storage of Renewable Energies and Grid Balancing" (LUZI).

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An Equimolar Ternary Molten Mixture of Crownether–Water–Imide Superacid: A Hydronium Solvate Ionic Liquid with Strong Acidity

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When two or more kinds of substances are mixed, the mixture can show properties different from those of pure substance. We report physicochemical properties of an equimolar ternary mixture of crownether–water–imide superacid, *i.e.* 18-crown-6-ether (18C6), H_2O, and an imide superacid bis(trifluoromethanesulfonyl)amide (HTf_2N; Tf = CF_3SO_2). In this mixture, water exists as hydronium (H_3O^+) ion, 18C6 as a ligand to form [H_3O^+·18C6] complex cation; its counter anion is Tf_2N^- anion, a dissociated species of HTf_2N. Thus, the mixture is an ionic liquid [H_3O^+·18C6]Tf_2N (Fig. 1). We had briefly reported successful synthesis of this ionic liquid which melt below *ca.* 70 °C, according to elemental analysis, IR, and DSC results [1]. Our new results of NMR and Raman measurements confirmed that ionic species of [H_3O^+·18C6] and Tf_2N^- predominantly exist in the mixture. For instance, the ^{1}H NMR spectra at molten state (75 °C, Fig. 2) show only two singlets at 10.85ppm and 3.23ppm. The former is for H_3O^+ and the latter is for CH_2 of 18C6. The peak area ratio was 1:8, in good agreement with the theoretical ratio for H_3O^+ and 18C6, *i.e.* $C_{12}H_{24}O_6$. This means that the mixture can be classified as a solvate ionic liquid [2]. Since previously-reported solvate ionic liquids —equimolar binary molten mixtures of ligand molecules and metal salts— all contain metal ions, [H_3O^+·18C6]Tf_2N is the first example of solvate ionic liquids where nonmetal cations are solvated. Interestingly, an equimolar mixture of H_2O and HTf_2N remain un-ionized in some conditions, suggested both experimentally and theoretically [3,4]. 18C6 is a good hydrogen-bonding acceptor and binds H_3O^+ ion almost selectively due to its cavity size [5]; thus, the combination of 18C6, water, and HTf_2N results in full ionization.

Acidity and proton transfer in ionic liquids are of fundamental interest and may be used as media for new acid-base reactions, including separation, purification and extraction. In nonaqueous or concentrated aqueous media —[18C6·H_3O^+]Tf_2N should belong to the latter—, Hammet's acidity function (H_0) is used to describe a measure of relative acidities. H_0 for an IL is evaluated by indicator method, *i.e.* UV-visible measurements of IL specimens mixed with an indicator. As a result, with 2,4-dinitroaniline ($pK_{a\ aq} = -4.53$) the value of H_0 for molten [H_3O^+·18C6]Tf_2N (75 °C) was estimated as strong as $H_0 = -4.41$. Since the strongest value of H_0 for ILs —evaluated using the indicator method— has been $H_0 = -3.6$ [6,7], our findings marked a new record. Such a strong acidity in [H_3O^+·18C6]Tf_2N should result from the combination of the weak bases 18C6 and H_2O and the strong acid HTf_2N. Since the amount of water is limited, leveling effect of water is absent in [H_3O^+·18C6]Tf_2N.

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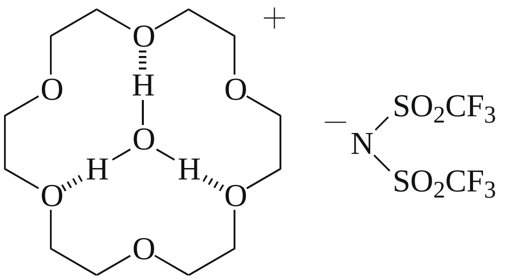

Figure 1. Schematic structure of [H_3O^+·18C6]Tf_2N.

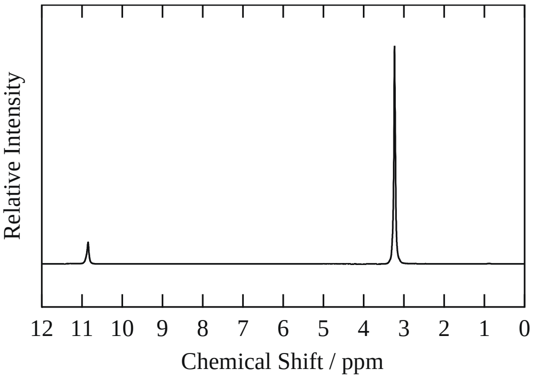

Figure 2. ^{1}H NMR spectrum of [H_3O^+·18C6]Tf_2N obtained at 75 °C.

Ultrasound Supported Electrodeposition of Tantalum

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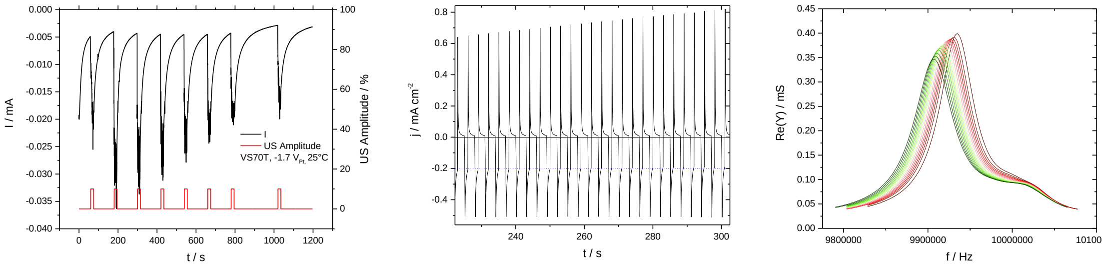
There is a broad range of applications for thin coatings of tantalum, due to its excellent chemical and corrosion resistance, combined with good mechanical properties, and its biocompatibility[1,2]. It is possible to deposit high quality Ta layers from molten salts at very high temperatures[3,4]. However, an electrodeposition method operating at less harsh conditions with a high deposition rate, and the ability to control precisely the layer thickness and quality is desirable. In literature it has been shown that it is possible to deposit Ta layers at rather moderate temperatures from ionic liquids[5]. Furthermore, an enhancement in the layer quality was reached by using pulse plating[6]. However, the layers still are not suitable for technical applications.

In this study, the deposition of tantalum from TaF_5 dissolved in the ionic liquid 1-N-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imid (BMP TFSI) was explored in depth. Instead of the frequently used Pt wire quasi reference electrode a true reference electrode for use in ionic liquids was applied. The main focus was on the influence of the fluid dynamics at different temperatures on the deposition process and the properties of the obtained layers. Known for its extreme enhancement of mass transport in aqueous electrolytes, ultrasound was applied to enhance the deposition rate in the relatively high-viscous ionic liquid. Electrochemical measurements (cyclic and square wave voltammetry, potential step experiments) were complemented by the electrochemical quartz microbalance technique (EQCM). For comparison and validation, experiments with a rotating disc electrode were also carried out. It was found that application of ultrasound significantly enhances cathodic currents (Figure 1a) and frequency changes of the EQCM. Factors contributing to this enhancement (acoustic streaming, cavitation and temperature change) are discussed. Also pulse plating combined with EQCM was applied to mitigate mass transport limitations (Figure 1b and 1c).



a) b) c)

Figure 1. a) Ultrasound supported electrochemical deposition (-1.7 V vs Pt) of Ta from 0.5 M TaF_5 in BMP TFSI, b) pulsed deposition of Ta at room temperature (E_{on}=-1.7V for 1s and E_{off}=-0.9V for 3 s) with c) corresponding change in EQCM admittance signal.

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Oxygen Reduction Mechanism in a Highly Na^+ Concentrated Pyrrolidinium-based Ionic Liquid

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The increasing energy demand requires new energy storage technologies to meet current and also future needs. Metal-O_2 batteries are especially attractive due to their superior specific energy related to the use of a light metallic anode, and the use of oxygen as active materials in the cathode which is not stored within the battery.

Among those chemistries, sodium-oxygen are attracting a great deal of attention due to their high specific energy (e.g. 1605 or 1108 Wh kg^{-1}, depending on the final discharge product)[1] [2] [3] but also their low production cost and the abundance of sodium.[4]

On the other hand, ionic liquids are interesting alternative electrolytes due to their superior electrochemical and thermal stability, which enhances the overall safety of the battery [5]. Reports of the plating and stripping of sodium in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [C_4mpyr][TFSI][6] exemplify their feasibility for secondary sodium batteries.

On the other hand, comprehensive studies regarding the impact of the electrolyte composition on the oxygen reduction mechanism are important in efforts to deliver highly efficient rechargeable sodium-air batteries. Thus, we report the oxygen reduction mechanisms and discharge products in a pyrrolidinium-based ionic liquid in the presence of different Na^+ ion concentrations.

Upon increasing the Na^+ concentration, the oxygen reduction becomes more efficient (e.g. 74%) and the onset potential of the reduction process shifts 0.35 V more positive due to a superior solvation of the superoxide anion ($O_2^{\bullet-}$) by Na^+ [7]. Computational studies were studied to understand the coordination of superoxide anion in the pyrrolidinium-based ionic liquid as a function of Na^+ concentration. Radial distribution function (RDF) showed a significant decrease in the coordination number $O_2^{\bullet-}$ - $[C_4mpyr]^+$ upon Na^+ concentration increase due to the preference of $O_2^{\bullet-}$ - Na^+ coordination as already observed in the electrochemistry experiments.

Finally, charge and discharge experiments were performed using an in-house cell using carbon paper as air cathode leading to an increase in specific capacity with Na^+ concentration. Thus these observations will provide a platform of potential electrolytes for Na-air batteries.

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Ion pairing in ionic liquids

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The use of ionic liquids as electrolytes largely relies on the conductivity of these materials. Some experiments indicate that the association of the ions into ion pairs or larger aggregates is a significant influential factor in the conductivity of these materials, while other experiments directly contradict these findings. In this regard theory can offer a great help, where a detailed molecular level understanding can be obtained on the structure of these electrolytes.

The picture on ion conductivity in ionic liquids can be put in a different perspective, if we consider the substantial charge transfer observed between the ions. Calculating the total charges of the ions in the bulk of generally applied ionic liquids results in values between 0.7-0.91e, showing that the charge transported by the movement of the individual ions is lower than expected. This data can be used directly to revisit the discrepancies between conductivities and ion diffusivities. Introducing a model ion pair into the liquid in a molecular dynamics environment, and changing the charge transfer between the cation and anion within this ion pair showed that the charge transfer itself decreases the level of aggregation, and it is, therefore, counteracting the ion pairing.

The molecular dynamics simulations described above correspond to the bulk phase structure of the liquid. Interfaces of liquids, however, can behave completely different from the bulk, and considering that the applications of ionic liquid electrolytes are often related to surfaces, ion pairing is necessary to investigate also as a surface phenomenon. Through molecular dynamics simulations of the liquid/vacuum interface we found that the bulk and the surface are fundamentally different in terms of ion pairing. Compared to the bulk, the ions at the surface stay together for a longer time, while also diffuse together longer distances. The analysis of the distances of neighboring ions showed that they are generally closer to each other at the surface, supporting the picture of an increased ion pairing at this region.

Thus, as a conclusion of this series of studies, ion pairing in ionic liquids is a rather elusive phenomenon, which is difficult to observe and even define, and which depends on a lot of factors, including the structure of the ionic liquid, charge transfer and the locality. The same factors influence the conductivity of the ionic liquid itself, and therefore designing ionic liquids as electrolytes requires a rather complex understanding of the molecular structure of these materials.

On Electrodeposition of Ruthenium in Room Temperature Ionic Liquids

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Platinum group metals, such as ruthenium, rhodium or palladium, are largely used due to their catalytic activities, which can occur both in their metallic states, and in their oxidized states. Even if their properties are interesting in many industrial applications, such as catalyst materials in fuel cells [1] or as diffusion barriers in the semiconductor industry [2], they are not used in large amounts. The reason for that is their very low availability in the Earth's crust. Therefore, it is very important to use small amounts of these metals, as well as to try to recover them from used parts via electrochemical methods.

This paper presents recent results from authors' labs of ruthenium electrodeposition in air and water stable ionic liquids. Two ionic liquids have been studied, namely 1-butyl-3-methylimidazolium dicyanamide and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide.

Electrochemical quartz crystal microbalance (EQCM) measurements have been performed parallel to the cyclic voltammetry, or galvanostatic and potentiostatic deposition. Thus, one can calculate in situ the deposited mass. Moreover, the stoichiometry of the deposited species was obtained from the EQCM measurements. Thin Ru layers could be obtained at room temperature. The nucleation and growth rate for Ru were facilitated by increasing the temperature of the electrolyte. The morphology and composition of the deposited layers were characterized by scanning electron microscopy with energy dispersive X-ray as well as by atomic force microscopy. We could show that the type of ionic liquid used, as well as the temperature influence drastically the electrodeposition of Ru.

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Electrocatalytic H_2O_2 generation
at
Ionic Liquid|Water Interface

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Biphasic systems with room temperature ionic liquid (RTIL)|water interfaces are important constituents of an increasing number of physicochemical systems including advanced materials [1,2]. There are hundreds examples of modified electrodes with ionic liquids as one of the film components and some of them were applied to O_2 reduction reaction [3-5]. It has to be also mentioned that application of RTIL–water systems in synthesis has been limited so far [6,7].

It has been demonstrated that polarisation control (chemical or electrochemical) of the liquid|liquid interface may provide favourable conditions for chemical reactions generating H_2 or H_2O_2 [8]. In particular H_2O_2 can be obtained from dissolved dioxygen at the interface between water and an organic solvent immiscible with water with a strong electron donor such as decamethylferrocene (DMFc) dissolved in the organic phase [9,10].

Following our preliminary report [11], we will demonstrate that by using the same methodology hydrogen peroxide can be generated at a RTIL|water interface:

$2\ DMFc + O_2 + 2H^+ \rightarrow 2\ DMFc^+ + H_2O_2$

The reported study involves 14 RTILs. The product was detected by: colorimetric substrate depletion, scanning electrochemical microscopy (SECM) and in some cases by optical readout with fluorogenic substrate [12]. The efficiency of reaction depends on the type of RTIL and possible correlations with their properties will be discussed. The experiments with carbon paste electrode with DMFc solution in hydrophobic ionic liquid as a binder [13] demonstrated that electron donor can be regenerated electrochemically. The data will be also compared with obtained with analogous system involving viscous hydrophobic solvent [14].

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Heterogeneous Electron Transfer Kinetics of the $[CeCl_6]^{3-/2-}$ Redox Reaction in Ionic Liquids Based on the Bis(trifluoromethylsulfonyl)imide Anion

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Hydrophobic, highly conductive ionic liquids (ILs) with wide electrochemical windows and large liquidus ranges can be prepared through simple synthetic procedures by combining selected quaternary ammonium cations with bis(trifluoromethylsulfonyl)imide anions (Tf_2N^-). Judicious choice of the organic cations can lead to a family of ILs with very similar chemical properties and widely varying physical and transport properties.[1] Typically these ILs are liquid well below room temperature. For example, one very popular member of this family of low-melting salts, $BuMePyro^+Tf_2N^-$ [$BuMePyro^+$ = 1–butyl-1-methylpyrrolidinium] exhibits a melting point of -18 °C.

A recent electrochemical and spectroscopic investigation of Ce species in this IL that was carried out with the addition of the chloride donor, $BuMePyro^+Cl^-$, indicated that the chemistry of Ce^{4+} and Ce^{3+} is restricted to the octahedral chloride complexes, $[CeCl_6]^{3-}$ and $[CeCl_6]^{2-}$, respectively.[2] Both species are stable on the time scale of voltammetry in this solvent, but the Ce^{4+} species does appear to react slowly with Cl^- in the ionic liquid over long periods of time. Cyclic voltammetry experiments at platinum electrodes involving the $[CeCl_6]^{2-/3-}$ electrode reaction revealed a peak potential separation, ΔE_p, > 100 mV, indicating that this likely outer-sphere reaction is quasireversible at room temperature. The unexpectedly slow kinetics of this heterogeneous reaction and the fact that the viscosity of this family of ILs can be varied over a wide range by choosing different cations to pair with the Tf_2N^- anions presents at ideal opportunity to probe the effects of solvent dielectric relaxation dynamics on the activation step of this reaction by directly examining the dependence of the heterogeneous rate constant, k^0, on the absolute viscosity, η. The prevailing assumption is that k^0 is inversely proportional to η through the nuclear frequency factor, ν_n, and the Debye relaxation time, τ_D. Classical investigations of this phenomenon have been undertaken by Bard and coworkers[3, 4] with the one-electron reduction of $[Fe(CN)_6]^{3-}$ and Cr(III)EDTA in aqueous solutions by varying the concentration of the indifferent solutes, dextrose and sucrose. Studies have also been undertaken in ILs. For example, the kinetics of the $[Fe(Cp)_2]^{+/0}$ reaction was investigated in Lewis basic $EtMeImCl\text{-}AlCl_3$ [$EtMeIm^+$ = 1-ethyl-3-methylimidazolium] by varying the IL composition,[5] which affords considerable variation in the viscosity, and indirectly in $BuMePyro^+Tf_2N^-$ by measuring k^0 as a function of temperature for the $[Fe(CN)_6]^{3-/4-}$, $[Fe(Cp)_2]^{+/0}$, and $[Fe(bpy)_3]^{3+/2+}$ reactions.[6]

This paper describes the results of an investigation of the kinetics of the $[CeCl_6]^{2-/3-}$ electrode reaction in this IL as well as in $Bu_3MeN^+Tf_2N^-$ [Bu_3MeN^+ = tri-(1-butyl)methylammonium], $BuMe_3N^+Tf_2N^-$ [$BuMe_3N^+$ = 1-(1-butyl)trimethylammonium], $BuMeIm^+Tf_2N^-$ [$BuMeIm^+$ = 1-(1-butyl)-3-methylimidazolium], and $EtMeIm^+Tf_2N^-$ by using electrochemical impedance spectroscopy. The experiments were carried out in IL solutions that contained equimolar amounts of $[CeCl_6]^{3-}$ and $[CeCl_6]^{2-}$. The resulting impedance data were fitted to the Randles-Ershler equivalent circuit model to extract k^0. This work shows that k^0 does indeed vary linearly with $1/\eta$ in these ILs. These results also imply that the identity of the cation itself has little influence on the rate of the electrode reaction, at least within this set of similar ILs.

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Electrochemical deposition of reactive metals and their alloys from ionic liquids

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Refractory metals are, as their name states, metals of high stability regarding their chemical, thermal and mechanical properties.[1] Therefore, these metals provide an excellent possibility to protect other metals which are exposed to conditions where properties such as high corrosion and high wear resistance are needed. Aluminum is well known to form a dense, adhering and stable oxide layer which leads to good corrosion resistance. By alloying aluminum with other elements, such as manganese or chromium, those properties can be improved.[2]

Besides common techniques to coat substrate materials like CVD, PVD or dip coating, electrodeposition of refractory metals and aluminum has several advantages such as coating of even and coherent layers on the substrate and the possibility to coat complex geometries.[3]

Unfortunately, those metals cannot be deposited in aqueous media due to their rather negative redox potential. To solve this problem a lot of research has been carried out with molten salts, which have a much wider electrochemical window but require high process temperatures up to 800°C, or metal organic processes, including highly flammable species. This drawback can be avoided by using ionic liquids which have electrochemical windows of 5-6 V and are liquid at room temperature.[4]

The electrodeposition of refractory metals and aluminum from ionic liquids has attracted a lot of attention throughout the past two decades. Nonetheless there are still many obstacles to overcome in order to obtain coherent layers with good adherence which provide high resistance against wear and corrosion. Especially the pretreatment of the substrates plays a decisive role for well adhering layers. Furthermore, the deposition parameters, e.g. temperature, current density and additives, strongly influence the layer morphology and properties. Additionally, the precursor choice is crucial due to the complex reduction mechanism which in the case of electrodeposition of refractory metals from ionic liquids probably consists of multiple electron-transfer steps. This induces the possibility for the formation of stable intermediate species that are incorporated into the layer at higher current densities. This challenge appears especially when metal halides are used as precursors.[5] To solve this problem one approach contains the usage of different non-halide salts as precursor.

This contribution aims at gaining a deeper insight into the individual steps of the process of the electrodeposition and describing the challenges and their causes that hinder the deposition of crack-free and well adhering layers. Several in-situ techniques were used, such as scanning probe microscopy and electrochemical quartz crystal microbalance. Additionally, we applied the rotating ring disc electrode to study the reduction mechanism in detail. Furthermore, anodic etching of the substrates in ionic liquids was used to enhance the adhesion of the layers. With the gained knowledge, we want to deposit crack free and coherent layers of aluminum and its alloys as well as niobium and tantalum on different substrates, such as Au, Cu, Ni and different steels, to provide a cost efficient and easy to handle process for protecting materials which are exposed to extreme conditions.

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Carbon Dioxide Conversion at the metal-RTIL interface

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The Electrochemical Reduction of Carbon dioxide (ERC) to valuable products is a promising strategy for CO_2 remediation. Products such as carbon monoxide, formic acid, oxalate and some hydrogenocarbons are known to be formed depending on the material of the electrode and the use of aqueous or organic electrolytes.

The ERC presents several limitations due to the fact that large overpotentials are needed to reduce the CO_2 molecule. In aqueous media, the Hydrogen Evolution Reaction (HER) is also encountered at potentials at which ERC is observed, decreasing the faradaic efficiency of the CO_2 conversion.
The search of conditions for an efficient electrochemical reduction of carbon dioxide is presently an active topic in electrochemistry. To avoid competition with the hydrogen evolution reaction and to increase the solubility of CO_2, room temperature ionic liquids (RTILs) appear as alternative electrolytes.

Here we report on the influence of the ionic liquid composition on the electrocatalytic performance and selectivity of the CO_2 electroreduction. RTILs composed of a common anion, bis(trifluoromethanesulfonyl)imide ($[NTf_2]^-$), known to solubilize fairly large amounts of CO_2 and different cations such as imidazolium, ammonium and pyrrolidinium have been considered. The electrochemical behavior of CO_2 in these media was studied by voltammetry, while the liquid and gas products formed during electrolysis were analyzed by chromatographic techniques and NMR spectroscopy.

The cathodic stability of the ionic liquids at gold electrodes has a tremendous impact on the CO_2 electroreduction process. In $[BMIm][NTf_2]$, the reduction of the imidazolium cation is concurrent with the reduction of CO_2, decreasing the faradaic efficiency for the formation of CO, but also producing an adduct with CO_2. The reduction of pyrrolidinium and ammonium-based ionic liquids is shifted to more negative potentials and does no longer appear as a competitive reaction.

Owing to its wide accessible potential window, $[BMPyrro][NTf_2]$ is ideally suited to investigate various strategies for the electrochemical use of CO_2. Besides the potential, it is shown that the nature of the electrode (copper or gold), the controlled addition of protons or the presence of electroactive co-reactants have an influence on the generated products and on the overall efficiency of the reduction process.

In Situ Electron Microscope Observation for High Capacity Anodes in Next-Generation IL-Based Li Batteries

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Today, Li-ion battery (LIB) has become an indispensable part of our daily lives. Most electric devices and vehicles employ LIB. Further improvements of the LIB system in terms of charge-discharge capacity, rate capability, and cycling durability are urgently required to satisfy the rapidly evolving customer and large-scale applications. A wide variety of advanced active materials for anode and cathode have been reported. Among them, development of high capacity anodes such as alloy-based materials and metallic Li provide promising choices to boost the practical energy density. High reactivity of these materials towards both electrolyte and air, however, makes an accurate understanding of anode reaction mechanisms difficult.

Based on our experiences on electron microscope techniques with ionic liquids (ILs) [1], we recently designed and fabricated several Li batteries for the *in situ* electron microscope observation. With this, we have succeeded in obtaining the information concerning morphological variation, elemental distribution, composition of solid electrolyte interphase (SEI), etc. at the high capacity anodes during charge-discharge processes [2,3]. Figure 1 depicts the schematic drawings of the typical Li batteries for *in situ* scanning electron microscope (SEM) and transmission electron microscope (TEM) observation. Binder-free Si anode or bare Ni substrate (for Li deposition/dissolution) was used. $LiCoO_2$ electrodes were employed as the cathode. A polyolefin or glass microfiber filter separator was sandwiched between the $LiCoO_2$ cathode and the anode. The IL electrolyte was 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)amide ($[C_2mim][FSA]$) with 0.87 mol L^{-1} lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]) or equimolar mixture of Li[TFSA]–tetraethylene glycol dimethyl ether. In this presentation, we will introduce our recent achievements on the *in situ* SEM and TEM observation of high capacity anode reactions in the IL-based Li batteries.

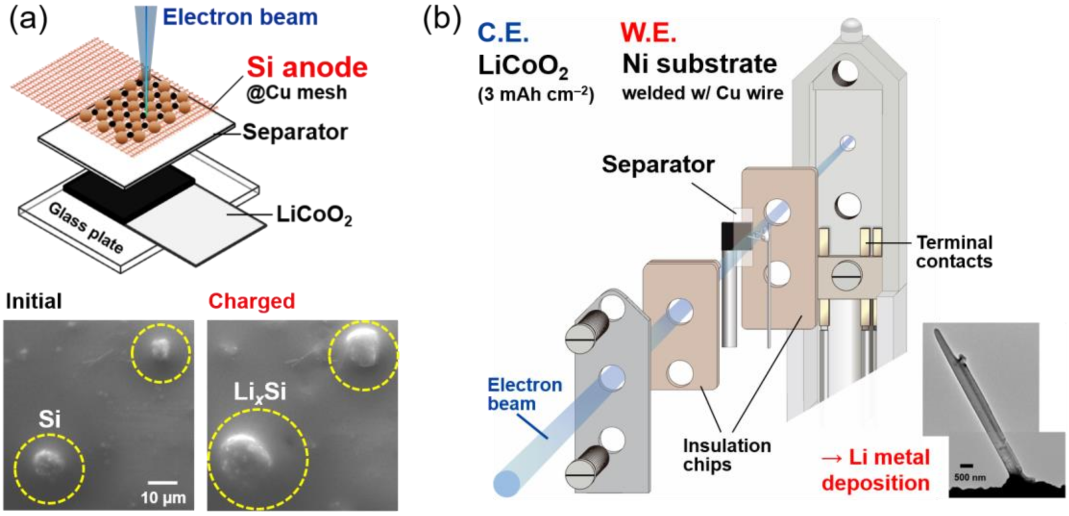

Figure 1. Schematic drawings of typical IL-based Li batteries for *in situ* (a) SEM and (b) TEM observation of the high capacity anodes. Electron microscope images obtained by the usage of the cells were also given under each drawing.

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Nanofibers of Imino-Imidazolium Iodide Grafted Hexafluoropropylene as the Quasi-Solid-State Electrolyte for Dye-Sensitized Solar Cells

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A conventional dye-sensitized solar cell (DSSC) with a liquid electrolyte (LE) suffers from leakage problems, due to sealing imperfection, leading to lower stability of the cell. In view of this, quasi-solid-state electrolyte has attracted great interest, owing to the long-term stability of its DSSC. In this study, an imidazolium cation-functionalized polymeric ionic liquid, designated as imino-imidazolium iodide grafted hexafluoropropylene copolymer (IIG-I), was synthesized by polymerization using poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and 1-butyl imidazole. We intended to combine the advantages of both PVDF-HFP (long-term stability for its DSSC) and 1-butyl imidazole (high-conductivity and non-volatility to the electrolyte) for the pertinent DSSC. The IIG-I was electrospun on an indium tin oxide (ITO) glass, removed, and used in the electrolyte of the DSSC. The fibrous structure of the electrospun IIG-I (average fiber diameter: 80.6 nm) and the spacing among the fibers are seen as advantageous for absorbing the liquid electrolyte uniformly. Owing to this structure and spacing of the IIG-I, ions in the electrolyte are expected to move freely. The DSSC with the so-obtained quasi-solid-state electrolyte has exhibited a power conversion efficiency (η) of 9.26%, while the one with a bare liquid electrolyte (without IIG-I) has shown an η of only 8.63%; the cell with PVDF-HFP has exhibited a rather poor η of 7.27%. The synthesized copolymer was analyzed by Fournier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. Field-emission scanning electron microscopy (FE-SEM) and thermogravimetric analysis (TGA) were used to characterize the membranes of the IIG-I. The electrolytes were studied by transient absorption spectroscopy (TAS), electrochemical impedance spectroscopy (EIS), and linear sweep voltammetry (LSV). The electrospun membrane has not only rendered a higher power conversion efficiency for its DSSC, but also has improved its long-term stability, with reference to these performance parameters of a DSSC with a common liquid electrolyte.

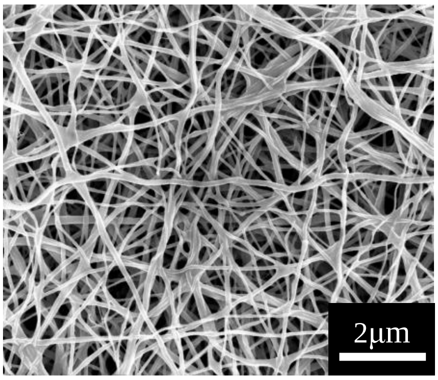

Fig. 1 FE-SEM image of electrospun membrane of IIG-I.

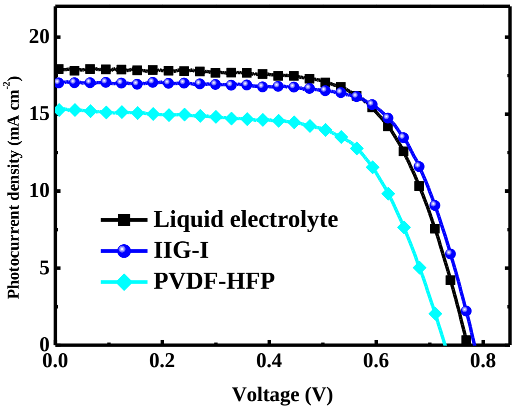

Fig. 2 Photocurrent density-voltage curves of the DSSCs with IIG-I, PVDF-HFP, and the liquid electrolyte, obtained at 100 mW cm^{-2} (AM 1.5G).

Preparation of Al–RE Intermetallic Compound Whisker in LiCl–KCl Melts by Molten Salt Electrolysis

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Abstract:

Mg–based/Al–based alloys are considered to the most promising new energy materials. Nevertheless, the widespread use of magnesium−lithium alloys is limited by the poor mechanical properties of alloy, especially the hardness. Consequently, this work presents a novel and effective method[1] for direct formation of Al−RE (RE=Sm, La) intermetallic compound whiskers in Mg–based/Al–based alloy. The electrochemical behavior of RE(III) on active Mg/Al electrodes in LiCl–KCl melts was investigated by different electrochemical measurements. The Al−RE intermetallic compound whiskers were prepared by galvanostatic electrolysis on active Mg/Al electrode, and Al_4RE phase was identified by XRD. The SEM and TEM with electron diffraction were employed to further investigate the microstructure and crystal structure of Mg–based/Al–based alloy containing whiskers. Fig. 1 illustrated the SEM (a), TEM (b) and electron diffraction (c) images of Mg−Li−Al−La alloy. As shown in Fig. 1a, many needle−like precipitates were formed in Mg–based alloy. The needle−like precipitates were finally determined to be Al–RE intermetallic compound whiskers by TEM (Fig. 1b) with electron diffraction (Fig. 1c). Micro hardness, Young's modulus and corrosion potential of alloy with whiskers were improved in comparison with non–whiskers reinforced alloy.

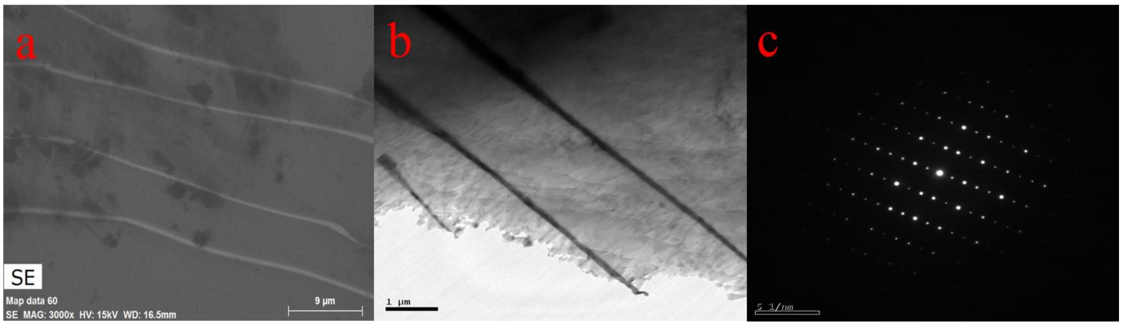

Fig. 1 SEM (a), TEM (b) and electron diffraction (c) images of Mg−Li−Al−La alloy

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Output Characteristics of Al-Cl_2 Cell in EMIC-$AlCl_3$ Ionic Liquid

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We have proposed a cycling process of aluminum using molten salts or ionic liquids [1-3]. In this process, (1) chlorination of aluminum scrap by a chlorination cell reaction is the most important process because the supplied energy can be reduced in the electrowinning process of the $AlCl_3$.(Fig. 1) In this study, we report output characteristics of Al-Cl_2 cell in 1-ethyl-3-methylimidazolium chloride (EMIC)-$AlCl_3$ ionic liquid. The ionic liquid as an electrolyte of the cell is attractive because the electrode reaction of Al progress at relatively low temperatures in the liquid. In this experiment, a lower operation temperature contributes to avoid evaporation of $AlCl_3$ which is produced by the cell reaction in the ionic liquid. The cell characteristics were evaluated by using graphite cathodes with cylindrical and circular cone shape or different density and a pure aluminum anode.

The electrochemical cell (ϕ 50×120 mm) used here is made of Pyrex glass, and the anode of the cell is pure aluminum plate (Nilako, 99.999%), 70×30 mm with the cathode (ϕ□21 mm) made of graphite (Tokai carbon, EE200). The circular cone type graphite cathodes (angle of inclination of the cone from 20 degrees to 60 degrees) are used. Densities of graphite cathode are 2.0, 1.6, 1.4, 1.32 and 1.27 gcm^{-3}. All of the graphite cathodes except for the circular cone parts were covered by PTFE tape. The chlorine gas was introduced to the graphite cathode through a glass tube. To protect from direct contact between the aluminum anode and the chlorine gas, a PTFE plate was set near the chlorine gas outlet. The electrolytic melt was a mixture of EMIC (Merk, 99%) and $AlCl_3$ (Fluka, 99.0%) with a total volume of 200 cm^3 and prepared with a molar ratio of 2 to 1 at room temperature. Chlorine gas (Showa Denko, 99.99%) was introduced into the electrolytic melt, and excess chlorine gas remaining after the cell reaction was absorbed by 1M NaOH solution. The electrodes were connected to a potentiostat (Hokuto Denko, HZ-5000), and the current-voltage relation was measured at a voltage range from the open circuit voltage to 0.5 V with a scan rate of 1.0×10^{-2} Vs^{-1} in the ionic liquid. All experiments were conducted at 313 K, with the thermal management carried out by water cooling and heating from outside of the electrochemical cell.

The open circuit voltage of the Al-Cl_2 cell showed about 2.1 V. In voltammogram measurement, the current density increased in proportion to the angle of the graphite cathode until 40 degrees. When an angle of the graphite cathode exceeded 40 degrees, the current density decreased with increases in the angle of the graphite cathode. In the graphite cathode with different density, current densities from 17 to 23 $mAcm^{-2}$ were obtained in graphite cathode density from 2.0 to 1.27 gcm^{-3} at 0.5 V. In the cell using graphite cathode of 1.27 gcm^{-3}, maximum output was shown. In the graphite cathode of low density, macro pores of different sizes were observed at the surfaces by SEM observation. The macro pores may contribute for improvement of output characteristics because reduction of chlorine gas occurs at around the pores on graphite surface.

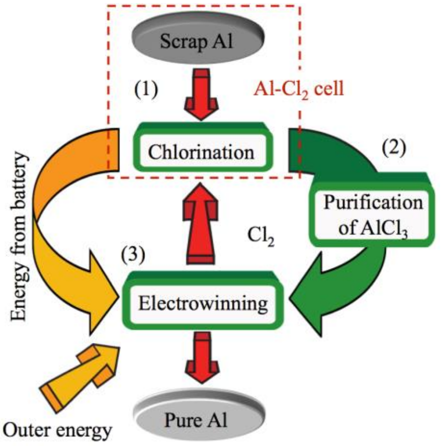

Fig. 1 Flowchart of an electrochemical cycle system for reproduction of pure aluminum from aluminum scrap.

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Coupling of electroleaching/electrodeposition of platinum in ionic liquid melts : application to the recycling of platinum from spent proton exchange membrane fuel cells

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The platinum nanoparticles used as catalyst in Proton Exchange Membrane Fuel Cells (PEMFCs) represent around 46% of the total price of the cell and is one of the limitations for their large scale commercialization. The treatment of spent PEMFC through the recovery of platinum catalyst is a major concern for their development. Usual recovery routes for platinum-containing catalysts are pyro-hydrometallurgical processes, combining a calcination step and an aqua regia treatment, generating fumes and NO_x emission.

An electrochemical recovery route by coupling electrochemical leaching and electrodeposition in ionic liquids (ILs) is proposed here, more environmentally friendly, performed in "soft" temperature conditions and without any gases emission. Imidazolium chloride ILs were selected for their complexing ability against platinum and their good electrochemical stability. They were used either pure or diluted in a low coordinating IL : BMIMTFSI (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide).

The electroleaching of massive platinum was first investigated in several chloride-based ILs. BMIMCl (1-butyl-3-methylimidazolium chloride) appeared to be the best of leaching media tested, as passivation phenomena were observed in other ILs. BMIMCl + BMIMTFSI melts were then tested, containing different BMIMCl amounts. A marked increase of the leaching rate with BMIMCl content was observed up to 0.5 M. For contents higher than 0.5 M, the leaching rate was comparable with the one obtained in pure BMIMCl.

The study of the electrochemical recovery of leached platinum revealed that its electrodeposition is impossible in the electrochemical window of pure BMIMCl, due to its high chloride concentration. On the contrary, platinum electrodeposition was successful in BMIMCl + BMIMTFSI ILs melts for BMIMCl content up to 0.5 M. ILs melts were then successfully used for platinum recovery from fuel cell electrodes. By further modulating the composition of the melt and the electrode potential control mode, it also appeared possible to simultaneously leach and electrodeposit platinum in a single cell process (Figure 1).

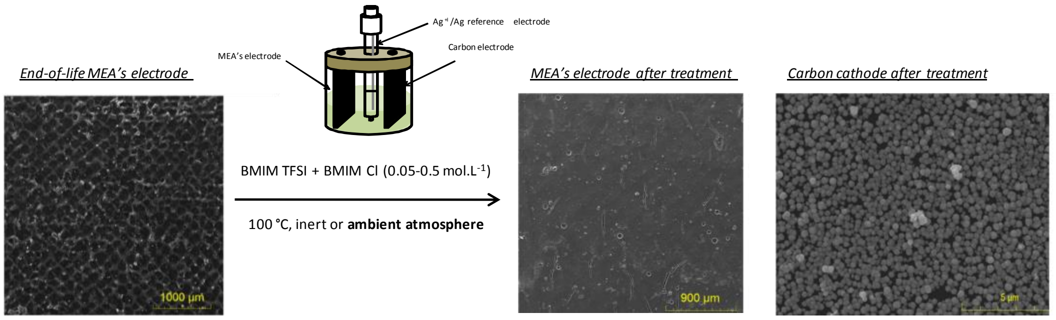

Figure 1 : Single cell process for the electrochemical recovery of platinum from spent proton exchange membrane fuel cells

Simple Electrochemical Preparation of Rare Earth Nanostructured Thin Films in Room Temperature Ionic Liquids

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Rare earth metals and compounds are widely used in magnets, fluorescent lamps, sensors and batteries, etc. Nowadays, electrochemical deposition represents one of the promising synthetic ways for the preparation of rare earth nanomaterials with improved physicochemical properties. However, to investigate the redox transformations of rare earth elements, a suitable electrolyte should exhibit a sufficiently wide electrochemical window. In this context, the use of room temperature ionic liquids (ILs) as electrolytic media looks appropriate [1].

Our research focuses on the immobilization of samarium-based thin films on Indium Tin Oxide-coated glass (ITO) in ILs to obtain interesting materials for new advanced functional devices [2]. First, we have determined the electrochemical stability domain of the bare ITO electrode in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPyrTFSI) by cyclic voltammetry and electrochemical impedance spectroscopy, and the results have been confirmed by XPS analysis. Second, we have studied the electrochemical behavior of $Sm(TFSI)_3$ salt dissolved in BMPyrTFSI. Cyclic voltammetry analysis has shown that the electrochemical reduction of samarium(III) species on ITO electrode is an irreversible diffusion-controlled process. The generated samarium(II) species are soluble, and no formation of samarium-containing deposits has been observed in a wide range of the applied potentials. On the other hand, we have found that even a small addition of water to the anhydrous electrolyte leads to significant changes in the electrochemical response of Sm(III)/Sm(II) redox couple and to the formation of well-adhering films with a nanoporous structure (Fig. 1, left image). These deposits have been fully characterized by a set of physicochemical methods. Chemical analysis (EDS and XPS) has confirmed not only the presence of samarium, but also the inclusion of BMPyrTFSI in trace amounts. The mass of deposited samarium has been determined by ICP-OES.

Our study has revealed that the deposition conditions (applied potential, duration, initial concentration of $Sm(TFSI)_3$ and content of residual water in BMPyrTFSI) have a strong influence on the chemical composition and morphology of the obtained films. In some cases, the reduction of indium(III) and tin(IV) oxides to metallic state has been observed. This process has been accompanied by formation of nanoparticles on the electrode surface (Fig. 1, right image). It should be noted that such material is a potential candidate for nonlinear optics [3].

Electrochemical, spectral and other physicochemical properties of the obtained films are actually under study.

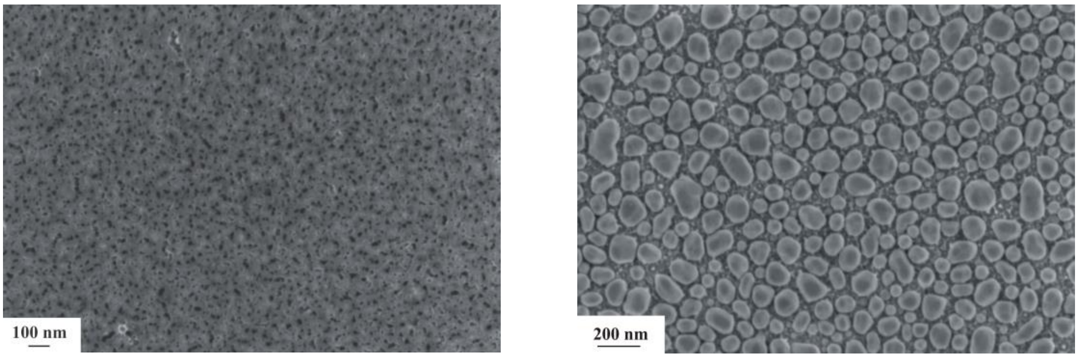

Fig. 1. SEM images of the obtained films on ITO electrode

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Exploring the Oxygen Reduction Reaction in Ionic Liquids to Synthesize Silver Oxides with Unusual Oxidation State

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Oxidizing metal species electrochemically is an alternative and efficient way to tailor-make metal oxides, being possibly even preferred over chemical oxidation for certain practical applications. The main goal of our work is to achieve higher/unusual oxidation states of silver with oxygen (Ag_xO_y) by electrochemical synthesis. The use of ionic liquids (ILs) as electrolyte offers thereby a great opportunity, since their unique electrochemical properties (wide stability window, intrinsic ionic conductivity) stand out compared to conventional organic and aqueous electrolytes.

Our approach is to use an electrochemical cell, similar as reported for Na/O_2 cells [1,2], with a silver metal anode, oxygen supplied at the porous carbon cathode and either [emim][TFSI] or [Pyr13][TFSI] as electrolyte with silver salt (either 0.5 M Ag[TFSI] or Ag[OTf]) for sufficient ion transport.
The intended reaction mechanism is as follows: At the anode, silver ions are stripped from the metal into the IL ($Ag \rightarrow Ag^+ + e^-$) and migrate to the cathode. Here, two reactions can take place, namely the backwards reaction of the anode reaction to plate silver and the reduction of the dissolved oxygen molecule to the superoxide ion, i.e. the oxygen reduction reaction (ORR: $O_2 + e^- \rightarrow O_2^{\bullet -}$). The latter cathode reaction is crucial for the formation of a silver oxide product. In literature, this reaction is expected to take place at approximately –0.98 V vs. Ag/Ag^+ in [emim][TFSI] [3].

For this work, cyclic voltammograms are used to characterize the occurring electrochemical reactions within the aforementioned set-up. SEM images were taken to investigate whether the intended product was deposited in the cathode (see Fig 1, left). Besides, the existence of the superoxide anion will be investigated by ESR measurements.
Exemplary results are shown in Figure 1: In a neat IL, the ORR is evident at around –0.9 V vs. Ag-wire. In presence of silver ions, the reduction of silver ions seems to be favored and thus no silver oxide is formed (Fig. 1).

Based on these results, we will give an outlook on how to enforce the ORR by changing the influence of O_2 pressure/concentration and temperature of the electrochemical synthesis. All in all, we want to show the advantages using electrochemistry in ILs for the synthesis of compounds not accessible through aqueous solutions.

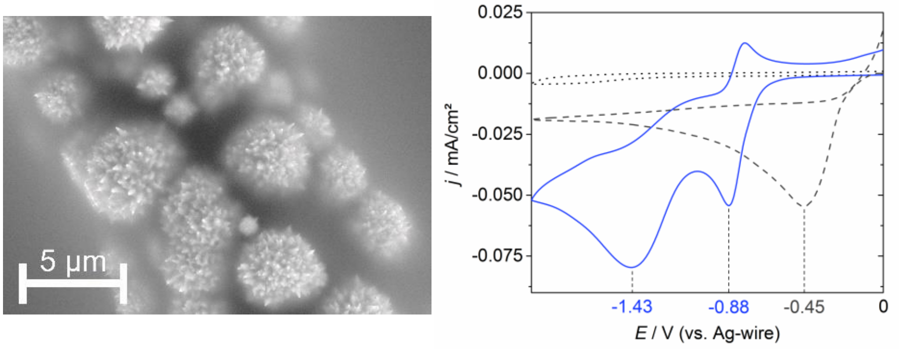

Figure 1: left) SEM image of deposited silver on the porous carbon cathode; right) CV of neat IL ([Pyr13][TFSI]; dotted line), neat IL saturated with O_2 (solid blue line) and IL with O_2 and silver salt (0.5 M Ag[OTf]; dashed black line) at the reduction potential; silver wire as reference, silver sheet anode, glassy carbon cathode, scan rate: 20 mV/s.

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Template-free electrodeposition of 1D Te nanostructures in ionic liquids

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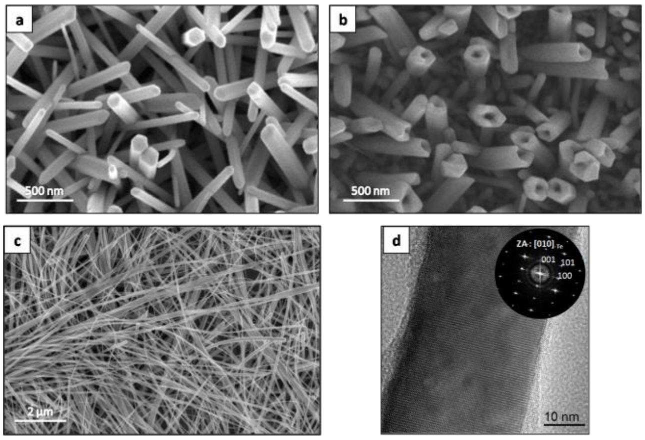
Electrodeposition of nanowires is usually performed in a porous template and involves multiples fabrication steps, like the preparation of the template and its removal. A single step template-free electrodeposition would in some cases be more convenient, for example to synthesize core@shell structures. It has been shown in literature that ionic liquids, in addition to have high electrochemical and thermal stabilities, can act as capping agents allowing the formation of nanostructures without using a template [1].

We will present here the template-free electrodeposition of Te nanostructures in a piperidinium ionic liquid. A systematic study of the influence of synthesis parameters Te(IV) concentration, applied potential, nature of the cation and of the anion of the ionic liquid and the halide content in the electrolyte) was conducted and revealed that the deposits morphology mainly depends on mass transport conditions and Te(IV) speciation. Under diffusional control, nanowires are deposited (Figure a), whereas by applying high overpotential values and then severe mass transport conditions, hollow nanostructures are formed due to a limitation by species supply (Figure b) [2].



The electrolyte composition determines the Te(IV) speciation that also strongly influences the morphology of the nanostructures. Specifically, the addition of a small amount of bromide ions in the electrolyte allows to synthesize 70 µm long hair-like nanowires with a mean diameter of 50 nm (Figure c) [3]. High Resolution Transmission Electron Microscopy analyses show that the nanostructures are single crystalline and grow along the *c*-axis, with a smooth interface and no external surface layer (Figure d).

Examples of core@shell nanostructures that could present interesting properties in the field of thermoelectrics will also be presented, elaborated by electrodeposition of a shell on the Te nanowires.

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Ionic Transport in ionic liquids and poly(ionic liquids) and its lithium mixtures

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This work presents the physicochemical characterization of ionic liquids (ILs) and poly(ionic liquids) (PILs) with different cations, and their mixtures with Li^+. We discuss properties as electrochemical window, density, viscosity and ionic conductivity. We have measured the diffusion coefficient by two different techniques, PGSE-NMR and Li electrodeposition with microelectrodes. In addition, we have calculated the Li^+ transport number by the PGSE-NMR technique and by an electrochemical approach. We use Raman spectroscopy and molecular dynamics simulations to evaluate the short-range structure of the liquids. The results found in this work suggest that these Li^+ mixtures present outstanding have promising potential as electrolytes for lithium batteries.

Lithium-ion batteries are one of the most popular types of batteries, especially for its high charge density and being rechargeable. These batteries are used extensively in portable devices such as cell phones, laptops, digital cameras. Mixtures of aprotic organic solvents and $LiPF_6$ are used in these batteries. However, the flammability of organic solvents and low thermal stability of LiPF6 makes it prohibitive to build lithium-ion batteries using such systems for large devices. ILs have been widely studied due to the unique properties that they display, such as low vapor pressure, non-flammability, thermal stability.

The polarity and hidrophilicity or lipophilicity can be varied through a suitable choice of the anion. The phosphonium ionic liquids, are thermally stable and they are interesting for use in electrochemical systems. With the strongly electron-withdrawing phosphonium groups, the anion is expected to possess several desirable properties, such as resistance to oxidation and weak cation coordination. In the present study, two ionic liquids, triethylpenthylphosphonium bis(trifluoromethanesulfonyl)imide ([P2225][Tf2N]) and (2-methoxyethyl)trimethyl phosphonium bis(trifluoromethanesulfonyl)imide ([P222(2O1)][Tf+N]) were studied. Related to PILS, we have studied the poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide. The results found in this work suggest that these Li^+ mixtures present outstading transport properties. In the case of PILs, they can be used as solid electrolytes or as binders. All liquids are stable till over 400°C and it is observed that adding the lithium salt, there is an increase in the viscosity and density, but surprisingly a slight increase in the ionic conductivity is observed. This result is unusual compared with other ILs derives from other anions and it shows that it is a promising result considering the application as electrolyte for lithium ion batteries.

Studies of molecular motions and interactions in ionic liquids electrolytes by Nuclear Magnetic Resonance

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Key Words: Ionic liquids, lithium, NMR, HOESY, molecular dynamics

In the last couple of decades, ionic liquids have been recognized as potential new electrolytes. Thanks to their unique properties, ILs are currently used for a wide range of applications, for example their conductivity and Li diffusion properties make them very good candidates for applications linked to electrochemistry, such as electrolytes in batteries. However, the molecular interactions and motions in ILs are still not fully understood. The main goal of this research project is to study the molecular dynamics and ionic interactions in a series of Li salt-containing ammonium/phosphonium TFSI and FSI based ionic liquids by NMR, primarily using pulsed field gradient diffusion measurements and T1 measurements but also using the nuclear Overhauser effect (NOE).
Using a special NMR technique called HOESY (Heteronuclear Over Hauser Effect SpectroscopY), we investigating the molecular arrangements between ions by extracting a magnetization transferred through space which, in combination with molecular dynamics simulations, can give a better understanding of ion proximities, arrangement and motions.

Preparation and Characterization of a Rechargeable Battery based on Conductive Polymers and Aluminum in an Ionic Liquid Electrolyte

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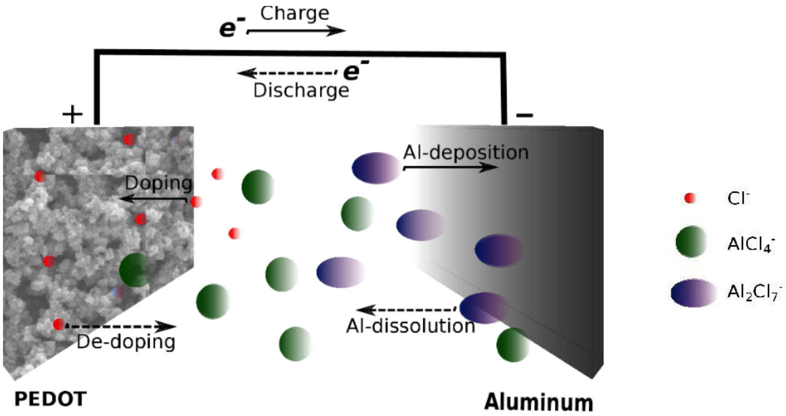
Energy storage devices like rechargeable batteries have currently a minor contribution to the challenges of the energy conversion to sustainability. Nevertheless, the growth of renewable energies will define the energy storage devices as an indispensable element of the power grid [1]. Therefore, it is necessary to overcome the main problems of current high performance batteries like safety, an upper capacity limit and limited raw material resources [2]. This work presents the concept of a non-aqueous rechargeable battery based on aluminum and a conductive polymer as active electrode materials [3] in a chloroaluminate ionic liquid. The work includes the electro-deposition of a conductive polymer as positive electrode and studies of its structure by scanning electron microscopy and doping and de-doping mechanism by quartz crystal microbalance and cyclic voltammetry [4]. Furthermore, the deposition and dissolution of aluminum as negative electrode were investigated by electrochemical and microscopic methods [5]. The performance of the battery was determined in a laboratory-scale cell. Galvanostatic cycling shows an average discharge voltage of 1 V and a specific energy of 84 Wh kg^{-1} referred to the sum of the masses of the polymer and aluminum. Improvements up to 228 Wh kg^{-1} have been achieved by using a porous electrolyte support. Thus the cell proposed here could be a sustainable alternative for high performance storage devices like lithium-ion batteries.



Graphical abstract of the charge and discharge reactions at the positive (PEDOT) and negative (aluminum) electrode of the battery system.

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Modelling the Effects of pH, Temperature, Radiation and Water Volume on the Evolution of Carbon Steel Corrosion

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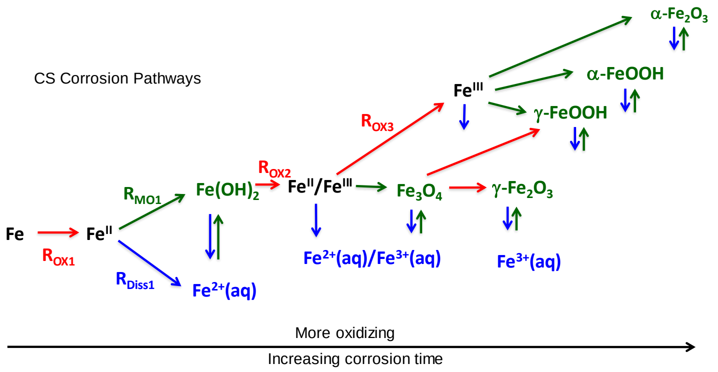
A recent US National Research Council report has identified ‘high-fidelity modeling for the prediction of corrosion degradation in actual service environments’ as one of the four grand challenges in corrosion research. Corrosion is a complex process involving oxidation of metal, reduction of solution species and interfacial transfer of electrons and ions. The transfer of metal cations to the solution phase can induce changes in the physical and (electro-) chemical nature of the interfacial region. Concentration gradients of dissolved metal cations may develop near the surface. The hydrolysis of metal cations can lead to the formation of metal hydroxide/oxides that may be present as a gelatinous solid, crystalline grains or thin films. Changes in the surface layer, in turn, can strongly affect the metal oxidation rate and alter the corrosion pathway. To develop a kinetic model that can predict the corrosion rate and its evolution as a function of environmental parameters, it is critical to understand and decouple the elementary processes involved in corrosion.

We have studied the corrosion kinetics of carbon steel in different environments to probe the elementary processes. The different environments are induced chemically, electrochemically and radiolytically. Ionizing radiation can change the redox activity of solution without affecting metal ion solvation properties and ion mobility in the solution. This technique provides a unique method to decouple the elementary processes involved in corrosion. This provides data for a mechanistic model for the evolution of corrosion as a function of exposure environments. The corrosion kinetics of metal coupons or electrodes are followed by performing various combinations of electrochemical, surface and solution analyses as a function of the corrosion conditions.

The experimental studies have led to the development of a carbon steel corrosion model, shown schematically in the figure below. The model includes all possible metal oxidation reactions. Each oxidized metal cation can follow one of two parallel reaction pathways, dissolution into the solution phase and/or incorporation into a solid oxide layer. The choice depends on the state of the oxide film, the interface and the environmental conditions. Different environmental parameters affect the competition kinetics differently and different combinations of these parameters can lead the corrosion of carbon steel to follow very different paths.

In this presentation, this model is used to explain the observed dependence of the evolution of carbon steel corrosion on the chemical and solvation properties of a solution. In particular we will discuss the dependence on the solution redox state (set by a flux of ionizing γ-radiation). The more oxidizing the solution environment is, the faster the initial rates of individual oxidation reactions. This can lead to enhance rates of metal dissolution, but this is strongly dependent on the solution pH. In small water volumes or in mildly basic solutions a higher initial in metal oxidation rate can lead to faster formation of an oxide layer that can suppress further corrosion.



Electrochemical Study of the Corrosion Resistance of the AlSi10Mg Alloy Obtained by means of LPBF

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Laser Powder Bed Fusion (LPBF) process is an additive manufacturing (AM) technology for the fabrication of near-net shape parts directly from CAD design data by melting a metallic powder with a laser source layer over layer on a building platform. Compared with traditional processes, AM saves time, costs, and has very few limits of complex geometries, with new design freedom and less scrap production. In the present work, the corrosion resistance in chloride solutions of a AlSi10Mg alloy obtained by LPBF process was evaluated. The alloy was studied by means of anodic potentiodynamic tests and electrochemical spectroscopy impedance, considering two superficial conditions: with the rough surface as produced by the LPBF technology or after mechanical polishing and passivation in air. The results show the effect of the surface conditions deriving from the production process and the microstructure.

A worsening of the resistance to the localized corrosion was observed for the alloy in the “as built” conditions, with decrease of the pitting potential and increment of passive current density compared to the polished and air passivated surface. A main role of chloride concentration in the initiation of localized corrosion was confirmed. The difference in the behavior becomes negligible with the increase of chlorides concentration.

EIS spectra showed the initiation of localized corrosion in the first time of immersion for the as produced surface; on the contrary, the passive film on the polished specimens showed a higher resistance than the hot formed film. The initiation of corrosion takes place by the selective dissolution of the α-Al phase at the edge of the melting pool, stimulated by nobler precipitates, especially silicon based.

Advancements in Corrosion Rate Prediction of Mild Steel in the Presence of Acetic Acid

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The recent developments on the mechanism of aqueous acidic corrosion of mild steel in the presence of acetic acid (HAc) suggest that this species is not significantly electro-active, in contrast to the common opinion [1]. It was shown that in the acetic acid concentration range commonly encountered in the oil and gas transmission pipelines, the charge transfer controlled currents are not affected by the presence of this weak acid [1]. However, the undissociated weak acid is known for its profound effect on the observed limiting currents. The term "weak acid" used to describe acetic acid, emphasizes that this species is only partially dissociated in an aqueous solution. Therefore, when the concentration of H^+ ion is depleted at the metal surface, as a result of its consumption in the corrosion process, acetic acid acts as an additional source of H^+ ion.

The existing corrosion rate predictive models does not included the more recent finding of the effect of acetic acid in the estimated values. To address this gap, a comprehensive mathematical model [2] is introduced based on these mechanistic developments. The kinetic parameters, describing the rate of underlying processes, were obtained based on a new set of experimental measurements. While these measurements confirmed the previous observations, they also suggest a rather significant inhibitive effect on both cathodic and anodic reactions. This latter observation was also included in the mathematical model by quantifying the surface coverage of the adsorbed undissociated acetic acid. It was found that acetic acid adsorption follows a Temkin type adsorption isotherm, while the characteristic parameters were different for the acetic acid adsorption during the anodic and cathodic polarization measurements. Furthermore, the effect of temperature on the rate of electrochemical reactions as well as the acetic acid adsorption were discussed.

A comparison of the experimental corrosion rate data and the predicted values is shown in Figure (1). The good agreement of the simulated results with the experimental data further supported the proposed mechanism. Therefore, the effect of acetic acid in the observed corrosion rates can be summarized as following:

- Acetic acid increases the corrosion current, if it is under mass transfer control.
- Acetic acid decreases the corrosion current, if it is under charge transfer control.

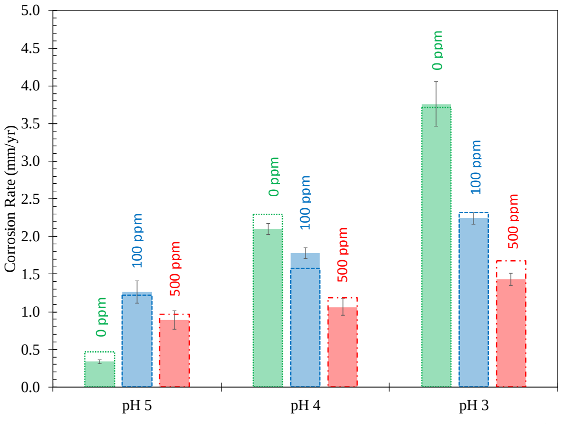

Figure 1. Comparison of the experimental and calculated corrosion rates of X65 mild steel in acidic solutions, at 30 °C, 0.1 M NaCl, 2000 rpm. Dashed boxed show the predicted values. Error bars represent the standard deviation of at least three measurements.

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Electronic Properties and Corrosion Resistance of Passive Films on Austenitic and Duplex Stainless Steels

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Due to their surface physico-chemical properties and their high corrosion resistance, stainless steels (SS) seem to be the most promising candidates for food and fine-chemical industry, for nuclear power industries and for maritime development [1-3]. Duplex stainless steels (DSS) are a combination of austenite and ferrite, replacing austenitic steels when a good compromise between the mechanical properties, the corrosion resistance and the economic advantages is required. DSS display the properties that are characteristic of both austenitic and ferritic stainless steels, showing high tensile strength and fatigue strength, good toughness even at lower temperatures, adequate formability and weldability, and excellent resistance to stress corrosion cracking [4-5].

The corrosion resistance of austenitic and duplex SS markedly depends on the composition, thickness, structure and electronic properties of the passive films covering their surface. It is commonly accepted that the native film on stainless steel surface is a chromium rich few nanometers thick oxide layer [1-3, 6-7]. However, SS are usually exposed for long time to aggressive media such as chloride containing solution, or highly concentrated organic and inorganic acidic solutions, hot alkaline solutions, therefore it is necessary to understand how passive films change as a consequence of the interaction with the environment. There is a large number of papers in the literature reporting on the characterization of passive films of Austenitic and Duplex stainless steels with a special focus on their electronic properties [1-5, 8-9]. Several authors base their conclusion on the interpretation of the dependence of the capacitance on electrode potential in the frame of Mott-Schottky theory with an approach sometimes questionable [2-3, 10].

In this work we report the results of a physico-chemial characterization on passive films on stainless steels in both acidic (H_2SO_4 at pH ~ 2), neutral (phosphate buffer pH ~ 7) and alkaline (NaOH pH ~ 13) solutions. The tested stainless steels are two austenitic (304L/EN 1.4307, 316L/EN 1.4404) and a duplex (2507/EN 1.4410) grades. For comparison we have also investigated the behaviour of a pure magnetron sputtered chromium electrode. Photoelectrochemical and impedance measurements were carried out in a very narrow electrode potential range around the open circuit potential in order to get information on the native films composition and on their electronic properties (band gap, conductivity type, polarization resistance). Passive films were then grown under constant polarizing voltage (below and above the transpassive potential) in all the investigated solutions. From the measured band gap values as a function of the formation conditions passive film composition was estimated, while the dependence of the photocurrent and of the measured capacitance on potential provided information on the conductivity type of the layers. The interpretation of the differential capacitance by a classic Mott-Schottky approach resulted to be not suitable to get information on the electronic properties (and indirectly on the corrosion resistance) of the passive films, due to the intrinsic difficulty in isolating the contribution to the measured capacitance arising from the layers. The experimental results were finally used to gain insight into the passivation mechanism of stainless steel at room temperature in aqueous solution.

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Corrosion of candidate materials for accident tolerant fuel cladding

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Since the Fukushima incident in 2011, the nuclear industry has sought to replace Zircaloy fuel cladding with a material which will better withstand a beyond-design-basis incident. A suitable material must possess superior oxidation resistance in high temperature steam (1200-1700°) to withstand a loss of coolant accident, while maintaining good hydrothermal corrosion properties for environmental compatibility during normal operating conditions (288-320°C water). In addition to corrosion issues, a suitable material must also demonstrate sufficient mechanical strength, creep resistance, radiation tolerance, and favorable neutronics.

Researchers at Oak Ridge National Laboratory are engaged in testing of two leading candidates for accident tolerant fuel cladding: iron-chomium-aluminum (FeCrAl) alloys, and silicon carbide ceramic matrix composites (SiC/SiC). FeCrAl alloys have shown excellent oxidation resistance due to the formation of a passive alumina film in high temperature steam, and a protective Fe-Cr spinel layer in water. SiC/Sic has shown excellent corrosive properties in high temperature steam, but a tendency to dissolve in LWR water. To improve performance during normal operating conditions, several protective coatings are under investigation

This talk will present results and analysis of experiments investigating corrosion of FeCrAl alloys and SiC/SiC with and without mitigation coatings during normal operating conditions, and during accident scenarios.

Effect of metal cations in model tap water on structure of passive film formed on aluminum alloys

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It is well known that the passive film structure is strongly depend on exposed environment, and it plays an important role in corrosion behavior of metals in various environments. The authors reported corrosion rate of aluminum alloys and steel is strongly depended on metal cations in model tap water[1-6)]. The effect of metal caions on corrosion rate can be classified by hardness of metal cation, X [7)]. It is expressed as $X = [X^0_M + (\sum I_n)^{1/2}]^2 / 10$, where X^0_M is the electronegativity of metal atoms, and $\sum I_\mathrm{n}$ is the total ionized potential from neutral metal atoms to a given oxidized state, n. However, the detailed effect of metal cations on passive film structure has not been clarified. The purpose of this study is to investigate the effect of metal cations on passive film structure formed on aluminum alloys in model tap water with different kind of metal cations by electrochemical and surface analysis techniques.

Aluminum alloys (A3003, A5052) sheets with 20 mm × 30 mm were used as specimens. Before the tests, specimens were chemically etched in 0.1 kmol m^3 NaOH solution, and then cleaned in highly purified water and ethanol in an ultrasonic bath. 0.5 kmol m^{-3} H_3BO_3 + 0.05 kmol m^{-3} $Na_2B_4O_7$ (Borate) was used as base solution because pH is closed to neutral in tap water. Borate solutions with five different salts such as Na_2SO_4, K_2SO_4, $MgSO_4$, $ZnSO_4$, $FeSO_4$, and $MnSO_4$ were used as test solutions. The hardness of metal cations, X, calculated by the equation increases in the order of K^+, Na^+, Mg^{2+}, Zn^{2+}, Fe^{2+} and Mn^{2+}. The concentration of added metal cations were controlled as 1 mol m^{-3}. A rest potential, E_{rest}, was measured for 600 s, and then potentiodynamic polarization measurements were carried out at E_{rest} – 10 mV to 1 V and scanning rate was 20 mV / min. Electrochemical impedance spectra were measured at E_{rest}, frequency range from 10 mHz to 10 kHz, and amplitude of the signal was 20 mV. The surface films were analyzed after immersed in the solutions by XPS using Mg Kα X-ray source. The analyzed area by XPS was 1 x 1 mm in the experiments, and depth profiles were obtained by Ar ion sputtering. The sputtering time was converted to depth by applying a sputtering-rate model assuming a sputtering rate of SiO_2.

The rest potential of A5052 tends to raise with increasing X, while its of A3003 was independent of X. Two active dissolution peaks and a kind of passive regions were observed at between -0.5 to -0.3 V (low potential region) and 0.3 to 0.8 V (high potential region) in potentiodynamic polarization curves of A5052. One active dissolution peaks and passive region was observed in potentiodynamic polarization curves of A3003. The average values of current density at high potential region of A5052 and passive region of A3003 were decreased with increasing X. From electrochemical impedance results, the film resistance was changed by added metal caion. From the XPS narrow spectra measured at binding energy region of each metal cation, no Na1s and K2s peaks were observed, while peaks related to hared metal cations, Zn2p, Fe2p, and Mn2p, were observed. These results suggest that hard metal cations were incorporated in all the passive films formed during immersion. In the case of A 5052, peak of Mg2p was observed independent of the depth. This may be related to the Mg in the substrate.

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In vitro corrosion of titanium implants and prosthetic metal alloys (Ni-Cr) in different electrolytic solutions.

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Despite the recent technological advances and remarkable progress in the design and development of dental materials for implants and prosthetic uses, corrosion is yet a critical phenomenon. Titanium alloys have excellent corrosion resistance due to the formation of a stable oxide film and some of these alloys have been chosen for surgical and dental implants because of their mechanical properties and biocompatibility. Alloys used in dental prosthesis as abutment, for example, Nickel-Chromium (Ni-Cr), have less resistance to corrosion, and when placed in solution together with nobler metals (for example titanium fixture) the galvanic corrosion can be evidenced. The toxicity of the alloying elements during the long-term use of implants still a concern, due to the continuous release of ions that are incorporated into the different sites of the organism. In the oral cavity these materials are exposed to different mechanical and chemical actions, resulting in a natural degradation process of the material due to the combined effect of corrosion and wear. The objective of this study is to evaluate the galvanic corrosion between titanium fixture and Ni-Cr abutment, observing surface alterations, composition and mass variations, after exposure in different electrolytic solutions in vitro, by scanning electron microscope. Fifteen external STRONG SW (4.1x3.75x13mm) hexagon implants were used, which were weighed and later washed with deionized water and sonicated for 15 minutes. The electrolytic solutions used were sodium fluoride (NaF) 1,500 ppm of Fluoride (pH 6,23), deionized water, coca soft drink (pH 2,72) and artificial saliva (pH 5,78). The corrosion was investigated for abutments and fixtures immersed coupled and also separated in the electrolytic solutions. A control group was performed the parts isolated, stored under atmospheric conditions, and not immersed. Samples were weighted then submitted to a 504 hour attack immersed in room temperature, and again weighed to calculate mass loss. Specimens were submitted to SEM and X-ray spectroscopy by energy dispersion (EDX). Significant changes were observed in the loss of mass Fig.1. Sodium fluoride and coca soft drink presented greater influence than deionized water in the loss of mass, suggesting interaction with the oxide layer present in the titanium fixture, which predisposes to galvanic corrosion. It was also seen that when the implant is attached to the prosthetic/abutment component there is greater loss of mass. The analysis of the microstructural changes by XPS Fig 2 has a higher specificity for the chemical composition of the constituents of the elements, especially in relation to the oxide layer and possible covalent carbon and oxygen bonds, which suggests corrosion of materials, as reported by Amin 2002. Fig. 3 shows SEM representative images, for fixture and abbutment components. It was evidenced through loss and mass transfer, EDX and MEV analyzes that occurred corrosion of the dental implants studied.

Fig.1: Mass loss study performed before and after exposure

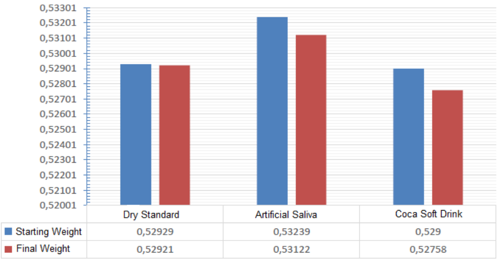
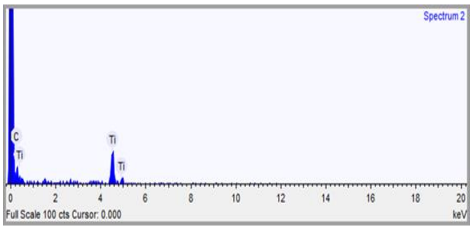
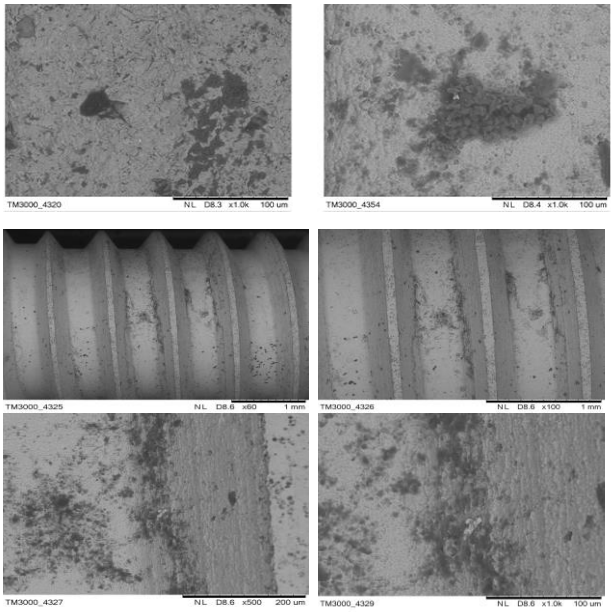


Fig.2: Analysis of the titanium implant microstructural changes by XPS



Element	Weight %	Weight %	Atomic %
Carbon	58.183	3.714	84.730
Titanium	41.817	3.714	15.270

Fig.3: SEM images of the implants submitted to sodium fluoride in different magnifications.



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Insight into the Origin of Crevice Corrosion of Magnesium

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Crevice corrosion is one of the most destructive forms of corrosion since it is a localized form of attack that occurs in occluded regions. It is generally accepted that crevice corrosion is the result of a differential aeration cell. The subsequent development of critical crevice solutions and/or critical ohmic potential drop leads to the depassivation of otherwise passivated material within the crevice and corrosion is therefore accelerated locally. Magnesium (Mg) alloys as engineering materials have many distinctive properties and are subject to extensive research recently. However, the possible susceptibility of Mg alloys to crevice corrosion is rarely studied because true crevice corrosion does not occur with Mg alloys for the following reasons [1]. Firstly, the dominant cathodic reaction is generally regarded as hydrogen evolution reaction (HER) and the necessary condition of differential aeration cell is not met. Second, local alkalization rather than acidification occurs for Mg alloys. Lastly, active-passive transition is rarely reported for Mg alloys due to the extremely low equilibrium potential and complication of HER. Contrary to the well-established theories for crevice corrosion, experimental evidence indicates that corrosion preferentially occurs at the Mg-epoxy interface and the corrosion rate for epoxy-mounted Mg sample can be three times larger than the "crevice-free" specimen. Furthermore, filiform corrosion, as a special type of crevice corrosion can also occur with the Mg alloys [2].

The present study aims to investigate the initiation and propagation of crevice corrosion of commercially pure Mg (99.95%) in 3.5 wt% NaCl solution. First, the multiple crevice assembly (MCA) described in ASTM G48 and G192 was used to study the susceptibility of Mg to crevice corrosion under both polarized and freely corroding conditions. Pitting corrosion was found on the surface outside the MCA and near the edge of footprints, but not underneath the footprints under potentiodynamic polarization. After long term immersion, minimal corrosion occurred underneath the footprints. However, severe localized corrosion was found between the footprints (i.e., gap) of the MCA. One observation during the immersion experiment was that large gas bubbles, presumably hydrogen, formed and trapped in the gap between footprints of the polymer-based MCA for long period of time. It was speculated that localized corrosion in the gap was associated with the attachment of hydrogen bubbles. To further understand the effect of hydrogen bubbles on the accelerated corrosion of Mg, a different crevice setup was adopted to monitor *in-situ* the initiation and propagation of Mg crevice corrosion under freely corroding condition. In this setup, a clear acrylic glass was fixed on an Mg plate with controlled crevice gaps. The acrylic glass partially covers the Mg plate for the possible separation of anode and cathode. The corrosion process was recorded in real time as well as the corrosion potential. An interesting phenomenon was observed that inside the crevice, small bubbles coalesced to form several large bubbles. Pits initiated at the edge of the large bubbles near the metal/gas/electrolyte tri-phase region. When large bubbles were forced out of the crevice, subsequent corrosion occurred rather quickly at the locations where the large bubbles previously resided. In contrast, the formation of large bubbles were absent outside the crevice and corrosion was uniform. The effect of hydrogen bubbles was further evaluated by altering the crevice orientation (horizontal vs. vertical). Reduced corrosion damage was found when bubble escape was facilitated. After immersion, samples were cleaned and corrosion damage was compared using 3-D optical microscopy. Selected samples were also examined by SEM/EDS/FIB to identify the corrosion products and also the sites for hydrogen bubble formation.

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Acknowledgement

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The Development of Corrosion Models for Nuclear Waste Disposal Systems

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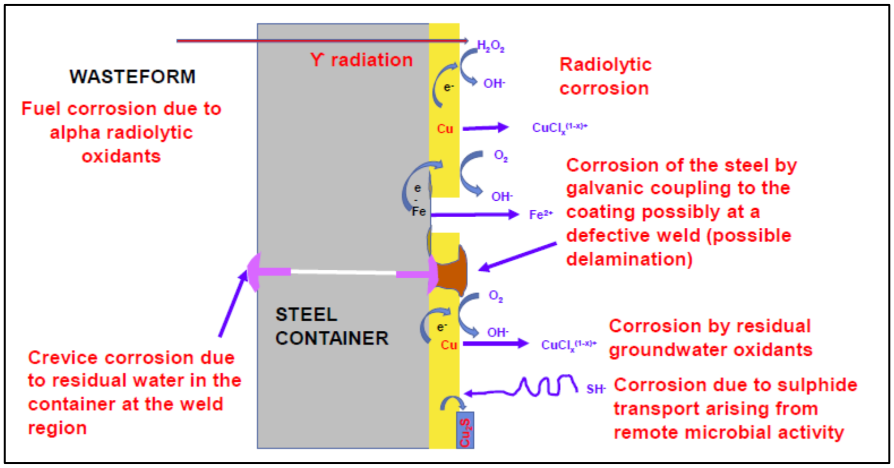
The internationally accepted solution for the management of high-level nuclear waste is deep disposal in a stable geologic formation. For many nations this means the direct disposal of the spent fuel. To ensure containment, the fuel will be sealed inside a corrosion resistant container capable of withstanding the anticipated hydrostatic lithostatic,and (in Canada) glaciation loads. In Canada, the present container design comprises a copper-coated fully welded steel vessel, with the coating applied using a a combination of electrodeposition and cold spray deposition.

Since the exposure conditions anticipated in a deep geologic repository will evolve with time from initially warm and oxidizing to eventually cool and anoxic, a number of container corrosion processes are possible, which change in importance as the environment evolves. In the unlikely event that the container fails within the required disposal period (many thousands of years), allowing groundwater to enter the container, corrosion of the wasteform due to the production of radiolytic oxidants could also occur. This last process would lead to the release of radionuclides from the fuel, the critical first step in their release to the environment. The key corrosion processes which could occur are summarized schematically in the Figure.



We have developed and are undertaking an extensive program to investigate the mechanistic details of the individual corrosion processes possible on both the container and the fuel wasteform. Our primary goal is to determine the extent, distribution and rate of accumulation of damage to the container, and, in the event of container failure, the rate of degradation of the fuel. Given the containment period required, this involves the specification of process models which aid the development of total system performance assessment models.

Two key corrosion processes will be discussed: (i) the radiolytic corrosion of copper during the early immersion period when the radiation fields emitted by the fuel waste form are significant and (ii) the radiolytic corrosion of the fuel inside the container once the container fails. The container process is being investigated by performing electrochemical and solution analytical experiments in a small cell containing aerated HNO_3, which is expected to form by the radiolysis of aerated water vapour. The reaction is being followed by electrochemically monitoring the polarization resistance and by measuring the evolution in pH which occurs due to the consumption of O_2 and HNO_3. The corrosion of the fuel (UO_2 doped with rare earth elements and intermetallic particles) is being modelled based on a wide range of electrochemical, surface analytical, and solution analytical measurements using COMSOL Multiphysics software. The redox conditions within the container are complicated by the simultaneous corrosion of the steel vessel. The interaction between the two corrosion fronts exerts a major influence on the overall corrosion process.

Inhibition of Flash Rusting by a Mussel Adhesive Protein: Characterizing the Interaction of MAP-5 on HY80, a High Strength Low Alloy Steel.

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A proteinaceous biopolymer, mussel adhesive protein #5 (MAP-5), isolated from the common blue mussel (*Mytilus edulis* L) has been investigated as a model for designing an aqueously soluble candidate corrosion inhibitor system that is non-toxic and environmentally friendly and that could inhibit the flash rusting of exposed high strength low alloy steel surfaces during the paint removal process. This protein is unique in containing 27% L-Dopa and 20% lysine, two unique amino acids containing catecholic and primary amine functional groups, respectively. It was found that when the MAP-5 protein was adsorbed onto HY80 steel and enzymatically cross-linked, a significant amount of corrosion inhibition was demonstrated upon subsequent exposure to a 100% relative humidity environment at 95°F (near 100% inhibition after 7 days). Indeed, these results were shown to surpass the performance of a commercially available flash rust inhibitor currently in use on maritime vessels. Currently, characterization of the interaction of the MAP-5 biopolymer on the steel substrate is underway to better understand its mechanism of corrosion inhibition. Energy dispersive spectroscopy (EDS) findings indicate that iron content is highest where the MAP-5 biopolymer is adsorbed onto the steel substrate at pH 5.5, exhibiting twice the content of the iron on the steel oxide surface alone; this intriguing result suggests that the iron atoms within the iron oxide/hydroxide film at the steel surface are undergoing complexation by the catecholic L-Dopa amino acids present in the MAP-5 polymer. This complexation can then allow for the adhesion to the metal substrate while simultaneously facilitating metal–mediated cross-linking of the polymer. When the enzyme catechol oxidase is added to a freshly adsorbed protein film, the biopolymer is enzymatically cross-linked on the steel surface at pH 5.5, and the iron content was found to decrease by 1/3 of that of the non-enzymatically cross-linked adsorbed biopolymer; this result suggests that when the enzyme is present, conditions for metal-mediated cross-linking by the protein may be less favorable. Analysis of the protein films on the steel surface by Raman infrared spectroscopy as well as FT-IR indicates that the L-Dopa and lysine amino acids may be involved in synergistic reactions at the oxide-covered metal surface. These results indicated that it is possible to utilize the biochemistry of a naturally occurring biopolymer isolated from a marine organism as a model to develop a non-toxic and environmentally friendly corrosion inhibitor.

Repassivation and Micro-phase Separation of Ti6Al4V Alloy Manufactured by Selected Laser Melting

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Additive manufacturing (AM) has revealed new trends in manufacturing industry by producing parts with complex geometry or personalized applications. Among the engineering alloys, Ti6Al4V (Ti64) is one of the most promising material due to its high strength, good corrosion resistance and good biocompatibility. However, the influence of high temperature sintering process when laser melting is used can impact the microstructure characteristics and the oxide formation can also result an obstacle when forming a dense and heterogeneous layer in Ti6Al4V. In this study, two synthesis path ways (vertical and horizontal) were employed to produce Ti6Al4V disks using high and low laser power resulting in two different thermo-history profiles. The corrosion potential of AM produced structure is more noble than cold-work products[1, 2].The performance of the AM produced Ti6Al4V disks have shown excellent corrosion resistance (10^{-4} mm/year) measured by anodic and cathodic polarization curve in order to eliminate the non-faradic effect [3]. Following a polarization plot we obtained a clear activation-diffusion transition for horizontal produced Ti64 during cyclic polarization test. Meanwhile, a series transient current was observed among vertical build Ti6Al4V group, which was confirmed to be selective dissolution of Al by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The repassivability of Ti6Al4V was measured under tribometer in Ringer's simulation body fluid against tungsten carbide. Zero resistance ammeter and electrochemical impedance spectroscopy were used to in-situ monitoring the passivation layer growth under sliding condition, among a loads range of (0.1-25 N) and speeds (1 - 10 mm/s).

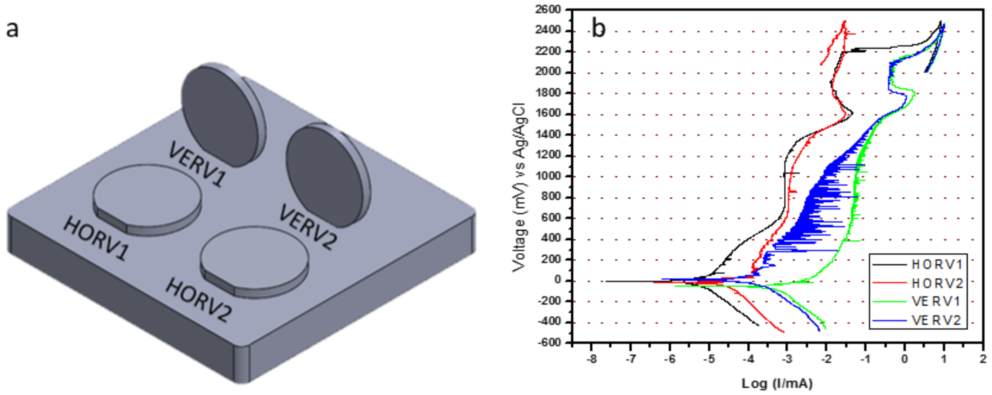

Figure 1. a) Illustration of horizontal and vertical AM build-up specimens and (b) its cyclic polarization curve.

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Influence of Humic Acid on the Corrosion of Zn And Galvanized Steel in Chloride Solutions

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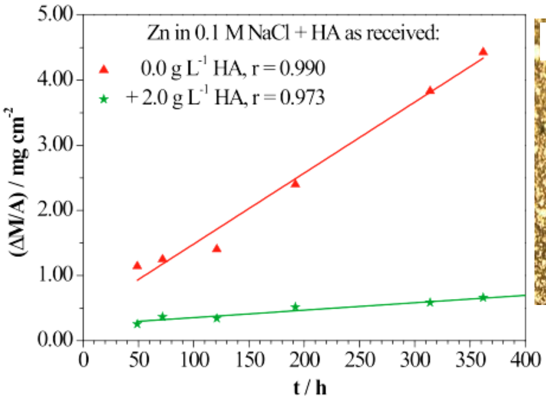
Buried steel structures are usually protected by Zn alloys applied as hot-dip coatings (HD-Zn) or as separated sacrificial anodes contacted to the structure. This arises mainly from the large galvanic potential difference between E(Zn^{2+}/Zn) and E(Fe^{2+}/Fe) and the deposition of Zn oxides and basic carbonates on cathodic steel areas where local pH increases, acting as a cathodic inhibitor. Particularly for the performance of Zn coatings, it is important that its consumption by reactions not associated to galvanic protection remains as low as possible, resulting in longer coating life. In this sense, the knowledge of the Zn corrosion rate not associated to the Zn-Fe galvanic pair is important for predictions of the durability.
Aiming to simulate the corrosion of galvanized steels in organic soils (peat soils) and in natural waters, the present study evaluates the corrosion behavior of pure Zn and HD-Zn coatings in 0.1 M NaCl with additions of humic acid (HA) in different concentrations. Studies of mass loss, electrochemical impedance spectroscopy, cyclic voltammetry and FTIR surface analysis were performed. The corrosion tests showed that small HA additions are able to inhibit the corrosion of zinc, with inhibition efficiency higher than 90%, as calculated from long-term mass-loss rate for HA additions of 2 g/L (**Fig. 1**). Moreover, humic acid also seems to be a cathodic inhibitor shifting the corrosion potential in the negative direction. Comparison between short-term (cyclic voltammetry, EIS) and long-term experiments (EIS, mass loss) showed that HA changes from corrosion promoter to inhibitor after exposures shorter than 48h. The extrapolation to t = 0 gives a positive intercept on the mass loss axis, indicating that the initial corrosion rates are higher. In chlorides, after pit nucleation the faster lateral growth of active fronts turns the localized corrosion into a uniform corrosion of the zinc surface, as shown on **Fig. 2a**. The effect of HA is not completely clear, however, it seems to avoid the lateral growth of nucleated pits (**Fig. 2b**).



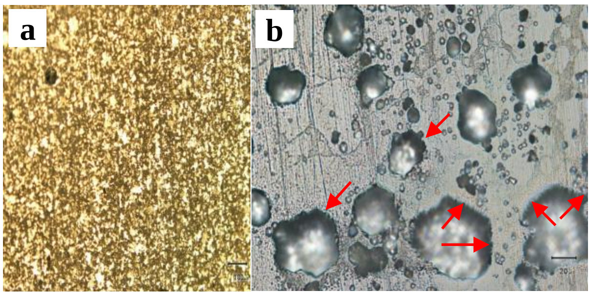


Fig. 1: Mass loss vs. time of Zn in 0.1M NaCl with and without additions of 2 g/L HA Fig.
Fig. 2: Corroded surface after 49 h exposure to (a) 0.1M NaCl and (b) 0.1M NaCl +2g/L HA (22°C) Arrows indicate the pyramidal (10$\underline{1}$0) pit sides.

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Quantitative imaging of intergranular corrosion of stainless steel using Hard X-Ray Nanoprobe

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The corrosion of steel components is a problem affecting a wide range of industries (from infrastructure and transportation to production and manufacturing), and results in estimated direct costs of 3.1% of the annual world gross domestic product (GDP). [1] During steel welding and fabrication, thermally activated segregation occurs, leading to the precipitation of Cr-rich carbides in the form of $M_{23}C_6$ at grain boundaries. This formation of Cr-rich carbides leads to Cr depletion within the matrix adjacent to grain boundaries, making them more susceptible to corrosion. Fundamental understanding of intergranular (IG) corrosion requires determination of local structure of grain boundaries and their role in Cr segregation at atomic and nanoscale. [2-3] To date, ability to monitor IG corrosion at grain boundaries at the atomic and nano-scale remains far below the level needed to elucidate the underlying physics and chemistry that governs IG corrosion, due to the lack of quantitative characterization tools with elemental, structural and chemical sensitivity at the nanoscale.

In our work, we utilize Hard X-ray Nanoprobe (HXN) (~ 20 nm resolution) to simultaneously probe the Cr segregation and phase contrast at grain boundaries in sensitized stainless steel.[3] Thin FIBed sections of stainless steel samples were corroded electrochemically in an aggressive electrolyte (KSCN in H_2SO_4) to observe corrosion. We provide quantitative characterization of Cr segregation at grain boundary inside the sensitized steel sample using X-ray Fluorescence (XRF). Tomographic image reconstruction of SS deteriorated by IG corrosion is combined with 3D imaging of phase contrast using Differential Phase Contrast (DPC) imaging. This combined structural and chemical analysis of the Cr segregation at grain boundaries allows us to understand IG corrosion in sensitized stainless steel at nanoscale. Such nanoscale understanding is critical for both – development of predictive multiscale corrosion models and engineering of corrosion resistant materials via bottoms up approach.

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New inhibition approach for active protective coatings on Mg alloys

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High susceptibility of Mg alloys towards corrosion attack is thermodynamically driven. However the fast kinetics of the process is often linked to presence of noble metallic impurities which serve as depolarization sites for the cathodic hydrogen evolution reaction. The enhanced hydrogen evolution and the high corrosion rate of Mg-based materials are correlated to the possible electrochemical re-deposition of a thin iron film on the corroding magnesium surface [1]. Re-deposition of the nobler metal increases the surface area with high electrochemical reactivity for cathodic hydrogen evolution reaction and in some cases becomes the determining process after an initial period. The revealed mechanistic details lead to new strategies for active control of Mg corrosion rate. It is suggested that iron complexing agents can serve as efficient corrosion inhibitors for structural Mg-based materials [2]. In the present work a large set of iron complexing agents was screened demonstrating dependence of corrosion inhibition efficiency on the stability constant of the inhibitors with iron cations among the main factors.

The selected inhibitors have been introduced into the protective coatings in order to achieve an additional active corrosion protection effect. The obtained thin coating system demonstrated a superior corrosion protection during immersion in chloride-containing environment. The electrochemical impedance spectroscopy revealed high values of impedance modulus even after a month of immersion. Even more importantly an active corrosion protection in artificial defects was clearly demonstrated using Scanning Vibrating Electrode Technique (SVET).

The presented results demonstrate a clear direction for new strategies on active corrosion protection of Mg based alloys.

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Anodic Films on Mg Alloys Formed in Glycerol/Fluoride Electrolyte

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Anodic treatments of magnesium alloys are commonly used to form oxide or more complex ceramic layers to enhance the corrosion and wear properties of magnesium alloys. Studies have been carried out on the formation of films under or in the absence of dielectric breakdown. Nevertheless, the formation mechanism and ionic transport within the films is only partially understood.

The present work systematically examines the findings of recent studies of the anodizing behaviour a wide range of magnetron sputtering-deposited model magnesium alloys, including Mg-Cu, Mg-W [1], Mg-Ag, Mg-Zr, and Mg-Fe alloys, as well as pure magnesium [2] and commercial magnesium alloys (AZ31 [3] and Mg-Zn-RE [4]). The specimens were anodized under galvanostatic conditions in a glycerol based electrolyte containing 0.35 mol dm^{-3} of ammonium fluoride and additions of water. The electrolyte enables the formation of the compact and uniform films suitable for the investigation of the formation mechanism and the behaviour of the various alloying elements. The effect of current density was studied by applying current densities in the range of 0.1 to 10 mA cm^{-2} in an electrolyte containing 5 vol.% of deionized water. Further, the influence of water content was studied by anodizing at a current density of 5 mA cm^{-2} in electrolytes containing 1, 5, 10, 20, 40 or 60 vol.% of water.

The mechanism of the film growth was studied using scanning and transmission electron microscopy (SEM and TEM) equipped with energy-dispersive X-ray (EDX) analysis facilities. Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA) were employed to quantify the elemental compositions of the anodic films and reveal the presence of alloying elements enrichments. Elemental depth profiling of the specimens was investigated by glow discharge optical emission spectroscopy (GDOES). X-ray diffraction was used to identify the phase composition.

The resultant films are shown to be nanocrystaline and to contain mainly fluoride and oxide species. The atomic ratio of O/F increases with increasing current density as well as with increasing water content [3]. A marker in the film is used to show that the films form by inward migration of F^- and O^{2-} ions and outward migration of Mg^{2+}. Fig. 1(a,b) presents an example of a film formed on a commercial alloy, revealing the local influence on the film composition of zirconium-rich second phase. Enrichments of the Zn, Cu, Al and Ag were observed in a thin layer immediately beneath the films. An example of an enrichment detected by RBS is shown in Fig. 1(c) indicating 5 x 10^{15} at cm^{-2} of zinc in the enriched layer. The migration behaviours and enrichments of the various alloying elements are discussed.

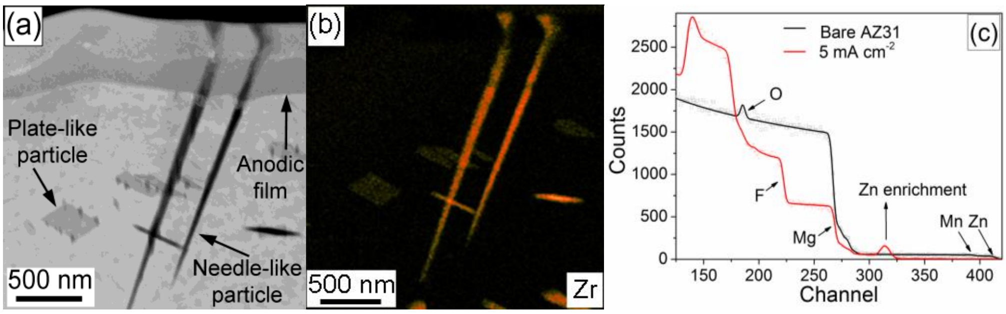

Fig 1. (a) Transmission electron micrograph and (b) EDX elemental map of zirconium for the Mg-Zn-RE alloy following anodizing at 5 mA cm^{-2} in a glycerol-based electrolyte containing 0.35 mol dm^{-3} of NH_4F and 5 vol.% of water [4]. (c) RBS spectra of AZ31 Mg alloy in the non-anodized condition and following anodizing at the same conditions as (a) and (b).

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Efficient pitting and breakdown of passivity for the AC electrograining of aluminium

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Pitting and breakdown of passivity generally have a negative influence on metal surfaces. However, the surface of certain materials can exhibit interesting properties when pitting corrosion is used as a surface treatment. Indeed, the AC electrograining process uses high current densities to induce controlled corrosion on aluminium surfaces. This is an energy-intensive process used for the production of printing plates for offset printing with a desired roughness and morphology. Because of the high current densities used, the electrochemical response of the system is complex. Three different stages are seen in this response, namely dissolution of second-phase particles, crystallographic attack of the aluminium, and development of the smut layer [1]. The graining conditions have a clear influence on the morphology, and on the electrochemical response. However, the influence of the graining conditions on the consumed electrical power has not yet been studied in detail.

In this work, different electrolyte additives are studied in a lab setup for electrograining. To simulate the different electrodes that are used in series in the production line, the measurement was split into different graining intervals and dead times. The graining interval time, dead time, and current density are varied. Hydrochloric acid is used as a base electrolyte in which the tested additives are added. The cell, working electrode and counter electrode potential are monitored, as well as the applied current. Based on these measurements, a detailed energy balance is calculated. In this energy balance the influence of the different graining conditions and electrolyte additives can be determined. These results are then compared with the surface morphology of the grained samples.

Initial results show that increasing the dead time between the graining intervals decreases the power requirements of the process, but it has a negative influence on the graining morphology. This could be due to the removal of the smut layer by the electrolyte, or by a change in the smut layer composition. Decreasing the current density decreases the power requirements and can still lead to a good graining morphology, but at the cost of longer production times. Different electrolyte additives show a vast difference in electrochemical response as well as a vast variation in the morphology with different settings. It is clear that the right combination of additives and graining settings has to be found to optimise the energy efficiency of the process and provide a good pitted surface topography.

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Corrosion reaction mechanism of the Ti/SBF in presence of fluorides determined under *operando* by means of Ambient Pressure XPS

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A novel *operando* Ambient Pressure Tender X-Ray Photoelectron Spectroscopy (T-APXPS) technique, newly developed by the beamline 9.3.1 at the Advanced Light Source (ALS)[1], allows for the first time to study on detail the corrosion phenomena at the metallic biomaterial/body fluid (SBF) electrified interface under *operando* electrochemical conditions. "Dip and Pull" method was used in order to form a stable nanometer-thick aqueous layer on the metallic biomaterial surface[1]. Keeping the bottom part of each electrode immersed in the electrolyte ensures ionically sustained electrical contact between the liquid layer on the sample surface and the bulk electrolyte. By using synchrotron radiation in the range of tender X-rays (at an energy of 4keV) it is possible to detect photoelectrons ejected from the solid/liquid interface, directly probing complex (electro-)chemical phenomena occurring at such important spatial region.

Polycrystalline titanium, employed widely in biomedical and dental applications[2], was characterized under potentiostatic conditions at applied potentials comprised in the different potential domains (cathodic, transition cathodic-anodic and passive domains) in *phosphate buffer solution* (PBS) with different fluoride concentration. T-APXPS measurements, acquired simultaneously with the electrochemical signal, allow us to determine variations of the oxide film composition under *operando* conditions with the applied potential. In addition, quantitatively variations of the oxide film structure were also determined using numerical simulations. Oxo-fluoride intermediate species (not observables under *in situ* measurements) were detected in presence of fluorides, which characterized the formation of the outmost oxide film formed on titanium, and consequently its corrosion phenomena and reaction rate. Mott-Schottky measurements shows a different conductivity of this oxo-fluoride layer in comparison with the $TiO/Ti_2O_3/TiO_2$ oxide film formed in presence of PBS. Potentiodynamic curves and electrochemical impedance spectroscopy confirmed that passive dissolution was enhanced with the anodic-passive applied potential and with the presence of fluorides. Thus, with all these results we were able to suggest the corrosion mechanism of the titanium in the studied SBFs, describing how fluorides can interact with the titanium enhancing the passive dissolution. The proposed reaction mechanism gives a depth insight about the possible reactions responsible of the failure in dental implants based on titanium.

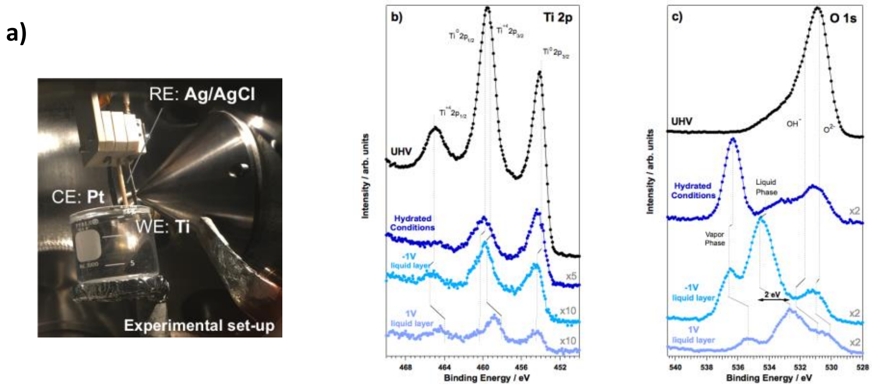

Figure 1(a) 3-electrode electrochemistry set-up into the APXPS chamber. **(b)** Ti2p and **(c)** O1s spectrum in UHV, under 16 Torr of water vapor pressure, and under cathodic ($-1V_{Ag/AgCl}$) and passive ($1V_{Ag/AgCl}$) conditions in 10PBS.

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Investigation by local electrochemical impedance spectroscopy and Raman spectroscopy of the corrosion inhibition of 2024 aluminum alloy

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Corrosion phenomena on aluminum alloy such as AA2024 are essentially linked to the local galvanic coupling between intermetallic particles and the surrounding matrix [1,2]. To have a better understanding of the action of different organic inhibitors on the aluminum alloy, a pure aluminum/pure copper model couple was used. This model couple was first designed to understand the corrosion phenomena associated with copper-rich intermetallics in aluminum alloys [2]. It was recently demonstrated, by using the Al/Cu model that in the presence of 8-hydroxyquinoline (8-HQ) or benzotriazole (BTA) alone, the galvanic coupling between copper and aluminum was poorly reduced and, conversely in the presence of the two compounds, the galvanic coupling was strongly limited [3]. Without inhibitor, a crevice was clearly observed at the Al/Cu interface whereas in the presence of the mixture, the Al/Cu interface remained undamaged [2, 3].

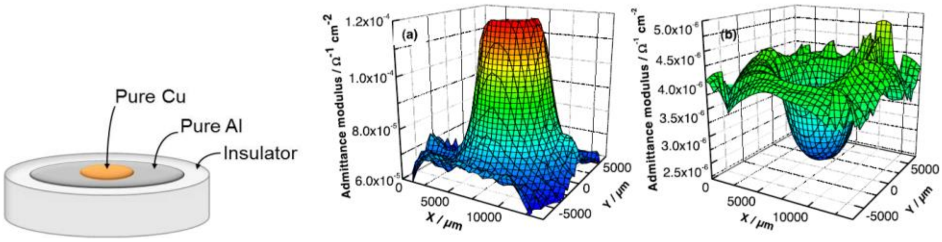

Fig. 1. Schematic representation of the model system
and example of mappings obtained (a) without and (b) with inhibitors (8-HQ+BTA) [3]

Following these encouraging results, we decided to investigate the action of various organic and inorganic compounds by using local electrochemical impedance spectroscopy (LEIS) on the Al/Cu model (Fig. 1). The influence of the concentration of the molecules was studied and the efficiency of each molecule was compared from the LEIS mapping. Moreover, some synergetic effects were identified and, in some cases, incompatibility between inhibitors were revealed.
Raman spectroscopy was used to characterize the molecules, first in solution and then on the Al/Cu model surface to provide a better understanding of the inhibition mechanism of the studied compounds.

By the combination of these techniques, a new methodology was proposed to evaluate different molecules, to compare their efficiency as potential inhibitors and to determine potential synergistic effects for a better protection of the 2024 aluminum alloy.

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Discussion on the relationship between passivity and reactivity of metals

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The relationship between passivity of metals and their reactivity is discussed through different examples in nitric acid solution. By passivity, it is meant the ability of the metal to protect itself from oxidation. Passivity was characterized by *in-situ* electrochemical methods (linear voltammetry – LV, electrochemical impedance spectroscopy – EIS) and by *ex-situ* X-ray photoelectron spectroscopy – XPS. By reactivity, it is meant the ability of the electroactive species present in solution to get reduced on the surface of the metal. Reactivity was also characterized by electrochemical methods (LV, EIS).

The first system concerns ferritic-martensitic steels in nitric acid solution with different chromium contents [1]. It was shown that passivity of those steels is governed by the chromium content in the oxide layer, which directly depends on the chromium content in the steel. A theoretical model was proposed to establish the relationship between the chromium content in the oxide layer and in the steel. Moreover it was shown that the kinetics of the nitric acid reduction slows down when the chromium content in the steel increases. In a second example, we studied the corrosion behavior of zirconium in nitric acid solution [2]. For that purpose, oxide layers with different thicknesses were electrogenerated on zirconium. It was shown that the thickness of the oxide layer governs both the oxidation rate of zirconium (through a high field mechanism) and the reduction rate of nitric acid (through the dielectric properties of the oxide). The last system described here concerns the comparison of the corrosion behavior in nitric acid solution of stainless steels doped with and without silicon. On the contrary to the two previous examples, it was concluded that the presence of silicon in the steel worsens passivity of the stainless steel, but also decreases the kinetics of the nitric acid reduction reaction.

From all these examples, it can be concluded that there is no systematic relationship between passivity and reactivity of metals. In most of the cases, the more passivated a metal is, the less it is reactive. But in some others, it is not true.

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Investigation on the stability of oxide films formed on magnesium rare-earth alloys

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Magnesium alloys are amongst the lightest industrial metallic materials. They have promising applications in many domains such as medical or transport industries. In a previous study, we have shown that corrosion rates of magnesium-based rare earths alloys in Na_2SO_4 solution were relatively similar to that of pure magnesium (results presented in the present annual ISE Meeting). This result was explained by the fact that for the alloys, the cathodic currents significantly increased due to the presence of intermetallic particle and the anodic currents were lower due to the alloying elements which improved the protection on the grain body. Hara *et al.* have shown that alloying elements have a strong influence on the passivity and thus on the breakdown potential of the films for pure magnesium or aluminum-magnesium alloys [1]. Some authors claimed that Y and Nd have a beneficial role on the oxide layer formed on the alloys surface and thus on their corrosion resistance [2,3]. Zucchi *et al.* also concluded that a more protective film was formed in the presence of rare earth elements and that chloride ions interfered with the maintenance of the protective layer in contrast to sulfate ions [4].

In the present work, two commercial magnesium alloys containing rare earth elements (WE43 and EV31) were compared to pure magnesium during immersion in 0.1 M Na_2SO_4 or 0.2 M NaCl solutions in order to investigate the role of the rare earths on the formation and on the breakdown of the surface films.

Polarization curves and electrochemical impedance spectroscopy (EIS) measurements were performed with a rotating disc electrode for different immersion times in the electrolytic solution. At the corrosion potential, the capacity of the oxide film was estimated by using the complex-capacitance plots [5] in order to determine the oxide film thickness. Tof-SIMS analysis were used to obtain information on the chemical composition of the oxide layers. Impedance measurements were also performed at different anodic overvoltages.

Polarization curves and impedance measurements performed at E_{corr} confirmed the presence of a protective oxide film that growth progressively and decreased the active surface area with increasing immersion time. The oxide film thickness (assumed to be mainly MgO) was relatively similar for the different alloys and for pure magnesium, about 3 nm. Impedance measurements carried out for different anodic overvoltages indicated a higher stability of the oxide film formed on the WE43 alloy, based on the breakdown potential values. The stability of the oxide layer for the WE43 alloy was also shown by the experiments performed in the NaCl solution. Complementary Tof-SIMS analyses are in progress to highlight the enrichment of oxide layer in Nd and Y oxides for the WE43 alloy.

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Corrosion behavior of Mg alloys in Na_2SO_4 solution: determination of the corrosion rate by EIS and ICP-AES

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With their low density (at least 33% lighter than aluminum), magnesium alloys represent an alternative for the transport industry willing to reduce the weight of their structures. Today, new generations of magnesium alloys containing rare earths resolve one of the main drawback associated to fire resistance [1]. However, their corrosion resistance remains the weak point. Several authors found that the addition of rare-earth elements improve the corrosion resistance of the Mg alloys [2-4]. For example, Ardelean *et al.* [2] claimed that the addition of Nd, Zr and Y improved the corrosion resistance of the WE43 Mg alloy by comparison with pure magnesium. However, in a recent review, Gusieva *et al.* [3] reported that the addition of yttrium could be beneficial or detrimental to the corrosion resistance of the alloys depending if it is added to pure magnesium or magnesium aluminum and of its relative concentration.

The aim of the present work was to evaluate and to compare the corrosion resistance of five commercial magnesium alloys. Three alloys containing rare-earths (WE43, EV31 and ZE41) and two magnesium-aluminum alloys (AZ31 and AZ91) were studied. Pure magnesium (99.95 wt.%) was also used for comparison. Polarization curves and electrochemical impedance spectroscopy (EIS) measurements were performed with a rotating disc electrode in 0.1 M Na_2SO_4. Inductive coupled plasma atomic emission spectroscopy (ICP-AES) analysis were conducted to quantify the dissolved Mg for different exposures times to the Na_2SO_4 solution. The corrosion rates measured from ICP-AES were compared to those calculated from the electrochemical techniques.

The polarization curves were corrected from the ohmic drop. After 24 h of immersion in the solution, all the Mg alloys exhibited higher cathodic current densities and lower anodic current densities than those measured on pure magnesium. The result was attributed to the presence of intermetallic particles which act as local cathodes and increase the cathodic currents; on the other hand, in the anodic range, the alloying elements modified the formation of surface films which were more protective for the Mg alloys than for pure Mg.

Independently of the immersion time, the impedance diagrams obtained at the corrosion potential for the Mg alloys presented the same phenomenology as that obtained for pure Mg: they were characterized by the presence of three time constants with the same characteristic frequency. Thus, in spite of the presence of intermetallic particles, the corrosion behavior of the alloys was close to that of pure Mg [5]. In agreement with the polarization curves, the impedance diagrams represent the corrosion of the grain body because the particles are cathodic and therefore protected against corrosion.

The corrosion current densities were calculated from the Stern and Geary relationship: the charge transfer resistance (R_{CT}) was extracted from the first capacitive loop of the impedance diagrams, and the anodic and cathodic Tafel slopes determined from the ohmic-drop corrected polarization curves. The corrosion rates were high and relatively similar to that of pure magnesium for the EV31, WE43, ZE41 Mg alloys and lower for the AZ series alloys. The mean corrosion rates obtained after 24 h of immersion from the electrochemical techniques and the ICP-AES were in good agreement. Furthermore, from the ICP-AES data it was observed that the corrosion rate decreased with increasing immersion time. This decrease was more significant for the WE43 Mg alloy between short and long immersion times than for the other alloys. This result would be linked to a slower formation of the oxide layer for the WE43 Mg alloy.

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Corrosion resistance of composition modulated multilayer Zn-Ni electrodeposited coatings, influence of the periodicity.

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Electrodeposited Zn-Ni coatings are widely used for the protection of steel structures and fasteners in automotive applications. Effectively Zn-Ni coatings present a very improved corrosion behavior compare with that of pure electrodeposited zinc coatings [2-4]. It is necessary to enhance both mechanical and corrosion properties in order to reduce the metallic release of heavy metals toward the environment and to improve the coating adhesion for fasteners. Composition modulated electrodeposited alloys could be an interesting configuration in order to improve the functional properties of the electrodeposited Zn-Ni coatings.

Reverse pulse electrodeposition was used in order to control the Zn-Ni composition and morphology. Zn-Ni alloys respectively with a composition of 14 and 7 wt. of nickel were deposited on a AISI 4135 steel. Multilayer configurations consisting on a layer alternation of 14 and 7wt% of Ni were characterized. Period was decreased in order to characterize its influence on the functional properties. Microstructure and morphology were characterized and the period decrease does not modify considerably the morphology of the films.

Functional properties were characterized. Reducing the periodicity leads to a slide increase of the micro-hardness of the multilayer coatings. Corrosion behavior of the Zn-Ni based coatings was characterized in a saline solution. Polarization curves and extended immersion test were realized. When the period is decrease, an improvement of the corrosion resistance is observed. Even if some defects are observed like cracks or pores, the increase of the number of interfaces could block the infiltration of the electrolyte inside the coating, reducing the impact of the galvanic corrosion on the global degradation of the Zn-Ni coating. The characterization of the samples after corrosion tests reveals that the corrosion mechanism is quite similar for all the configurations, even if a quite refinement of the microstructure occurs with the period reduction.

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Marine Microbial Corrosion: A Preliminary Interpretation Based on Electroactive Biofilm Corrosion Mechanisms

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Marine microbial corrosion is one of important corrosion phenomena in marine water environment. It is thought that most of metal materials are suffered the attack of microorganism. Ennoblement of open corrosion potential of passive noble metals and Sulfide derivitization of metals by sulfide-producing bacteria are two important corrosion phenomena. For the both sides, numerous researches have been conducted. Indirect and direct corrosion mechanisms have been suggested. The former is related to such as EPS, inorganic and organic acid corrosion, the latter is related to enzyme or direct bacterial cell corrosion. In this presentation, we are trying to suggest and interpret both corrosion phenomena from the viewpoint of electroactive biofilm mechanism. For passive stainless steel, natural seawater biofilm may induce ennoblement phenomenon with biofilm enzyme catalyzed oxygen reduction and electroactive biofilm cathode electron supplying/donor function. For alloyed steel, a kind of sulfate-reducing bacteria, which are suggested to siphon electron from the steel anode substrate or iron compound corrosion products, by catalyzing cathodic hydrogen production. The complex of microbial corrosion was also discussed to consider the different alloyed materials and microbial and other environment conditions.

Acknowledgements

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The Self-healing Effect of Polyaniline in an Epoxy Coatings for Carbon Steel Protection

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Epoxy coatings can protect metal substrate by blending active pigments and prevent the corrosive solution from contacting with metal substrate surface. Conducting polymers (CPs) catch people′s attention owing to their excellent inhibiting effect, e. g. polyaniline (PANI)[1], polypyrrole (PPY), polythiophene, etc. Because of high conducting, environment stability and ease of synthesis, PANI is the most widely used CPs for corrosion inhibition. Furthermore, PANI can be doped not only by inorganic acid (e.g. phosphoric acid[2], sulfuric acid [3], hydrochloric acid[4], molybdic acid[1], tungstic acid[5], perchloric acid[6]) but also organic acid (e.g. camphorsulphonic acid and phenylphosphonic acid [7], dodecylbenzene sulfonic acid (DBSA) [8], benzoic acid[9], oxalic acid[10]). But, there are some limitations for inorganic acid doped PANI: 1) the dedoped acid radical ions will catalyze the corrosion of carbon steel, e.g. Cl^- and $SO4^{2-}$; 2) some inorganic acid has poor solubility in water, e. g. molybdic acid and tungstic acid; 3) the chelation effect of inorganic acid is weak. Though organic acid doped PANI has good compatibility with resin, they have few functional group to chelate with irons and their chelation ability is also weak. Phytic acid has a good solubility in water and it is investigated as an eco-friendly corrosion inhibitor for many kinds of metals. The results show that phytic acid can dope with PANI directly and the synthesized PANI-PA has a good thermostability. Epoxy coating contained with 2 wt.% PANI-PA has the best inhibiting effect and the self-healing function of PANI–PA is attributed to the synergistic of the passivation effect of PANI and the chelation of the dedoped phytic acid ions with iron ions.

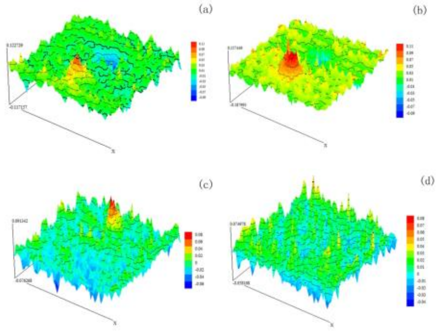

Fig.1 SVET 3D current density maps of mild steel coated with an epoxy coating containing (a) free inhibitors, 0h, (b) free inhibitors, 48h, (3) PANI-PA(2%), 0h, (4) PANI-PA(2%), 48h in 3.5% NaCl solution

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The Complex-Capacitance Representation: A Convenient Way to Follow *in situ* Modifications of the Thickness of an Oxide Layer during Electrochemical Polarization.

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Impedance data can be presented in different formats, depending on which specific behaviour has to be emphasized. The impedance format in Nyquist or Bode diagrams are widely used representations, providing interesting information in the low frequency domain, for reaction kinetics or mass transfer controlled reactions. However when the high frequency domain has to be investigated, the complex capacitance format is a more convenient representation and is especially useful for dielectric systems (called also Cole-Cole graphical representation). Accordingly it provides an easy determination of the capacitance value of the dielectric by extrapolation of the real part of the capacitance at infinite frequency. When the dielectric is an oxide layer, its thickness δ can be calculated using following equation:

$$\delta = \varepsilon\varepsilon_0/C_\infty$$

where ε_0 is the permittivity of vacuum ($\varepsilon_0 = 8.8542\ 10^{-14}$ F cm^{-1}), and ε is the dielectric constant of the layer.

The complex-capacitance representation was used in the present work to follow the modification of the thickness for an aluminium oxide layer during cathodic dissolution (Figure 1). The abrupt thickness decrease at E <-1.3V only obvious from the Cole-Cole plot could clearly be attributed to chemical dissolution of the oxide layer due to interfacial pH increase [1].

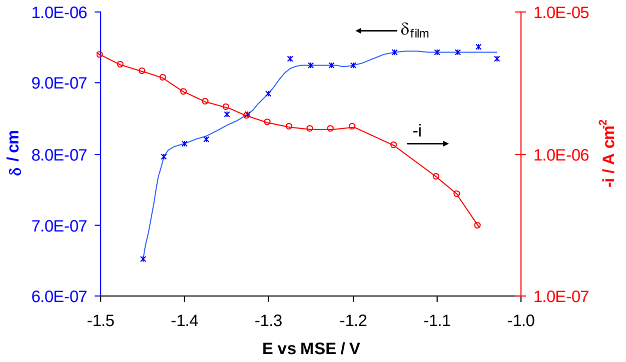

Fig 1: Comparison between the cathodic polarization curve and the variation of the layer thickness determined from Cole-Cole plots of an aluminium electrode in aerated 10^{-2} M Na_2SO_4 solution (immersion time: 2 h)

Some examples of capacitance determination are also given for iron oxide or titanium oxide.

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Influence of silicon on the transpassive behavior of austenitic stainless steel in acidic media investigated through innovative coupling of in-situ atomic emission spectroelectrochemistry and ex-situ analysis

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Because of their good resistance to corrosion in acidic media, austenitic stainless steels such as 18Cr-10Ni are largely used for equipment of the spent nuclear fuel reprocessing plants. Still, if the chemical environment becomes sufficiently oxidizing and thus lead them to their transpassive domain, they might corrode locally at preferential sites such as grain boundaries. However, with the addition of few wt.% of silicon to the 18Cr-10Ni stainless steel, the alloy loses its sensitivity to intergranular attack [1].

This work presents a novel method to measure the transpassive dissolution of stainless steels in nitric acid and to compare their corrosion behavior depending on their silicon concentration. Using the in-situ atomic emission spectroelectrochemistry (AESEC), chronoamperometries are performed at the same potential in the transpassive domain of each steel in nitric acid 4 mol L^{-1}, 40°C. During the potentiostatic transpassive dissolution of each sample, an inductive coupled plasma atomic emission spectrometer connected to a three electrode flow cell enables to quantify the dissolution rate of each major element. Comparing the total current measured and the elemental dissolution rates, the valence of each element dissolving is determined (Figure 1). In particular, the transition from third to sixth oxidation state of chromium is revealed.

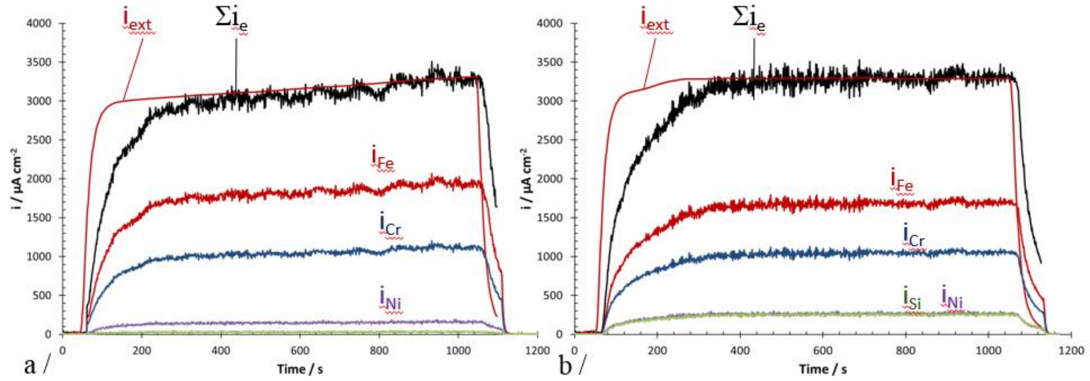

Figure 1. Dissolution signals of each major element of the stainless steels (a/ 18Cr-10Ni and b/ 18Cr-10Ni-4Si) during transpassive polarization (E vs NHE = 1.30V) expressed in µA cm^{-2}. Comparison between the total dissolution current Σi_e (black) and the external current measured with the potentiostat i_{ext} (light red)

Then, scanning electron micrographs enable the characterization of surfaces morphologies after corrosion. The 18Cr-10Ni displays a slightly selective dissolution and a severe intergranular attack meanwhile the silicon-rich stainless steel displays a non-selective dissolution behavior and a homogeneous surface morphology. Transmission electron microscopy is then used in addition to this work to compare the passive layers of each stainless steel in terms of morphology and chemistry, especially on top of grain boundaries. Energy dispersive X-ray spectroscopy reveals that silicon enriched stainless steel is protected by a homogeneous silicon rich passive layer, without segregation at grain boundaries, which would reduce any preferential attack during transpassive dissolution.

Both in-situ and ex-situ techniques converge to the conclusion that silicon modifies the transpassive dissolution of 18Cr-10Ni stainless steels by improving the homogeneity of the oxide layer and thus the electrochemical dissolution of the steel, following a mechanism that is described for each material.

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Composition Control for Multicomponent Electroactive Materials

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Lithium-ion (Li-ion) batteries are the most commonly used rechargeable batteries in the market due to many advantages including high capacity, high energy density, long cycle life, and safety. A new generation of Li-ion batteries of higher energy density, however, is still in great demand for electric vehicles and other energy storage applications. Among battery components, cathode materials play a major role in the cycle performance of the batteries, and many of the current and future cathode materials are multicomponent transition metal oxides, such as $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $LiNi_{0.5}Mn_{0.5}O_2$, and $LiMn_{1.5}Ni_{0.5}O_4$. Many of these multicomponent transition metal materials are reported to have electrochemical performance sensitive to the composition.

Co-precipitation is a popular, scalable route to synthesize precursors for the transition metal oxide cathode materials. First, a precursor is synthesized through co-precipitation using solution chemistry, followed by mixing the precursor particles with a lithium salt and calcining the mixture at elevated temperature to produce the final desired material. The particle morphology of the precursor can be well-retained even after high temperature firing, which makes this synthesis approach an attractive method to achieve control over particle size and shape; however, the deviation of the precursor composition from feed conditions is a challenge that has not been adequately addressed.

Using a target final material of the high voltage spinel $LiMn_{1.5}Ni_{0.5}O_4$ as an example, we show in this study that the compositional deviation caused by the co-precipitation reaction to form the precursor particles can play an important role in determining the electrochemical properties of the final active materials. A series of studies were conducted to understand the role of solution equilibrium and rate of precipitation of the transition metals during precursor formation. This knowledge was then used to provide rational control of the precursor composition and finally to synthesize, with high precision, the target stoichiometry necessary to produce $LiMn_{1.5}Ni_{0.5}O_4$. Electrochemical evaluation was then conducted to the cells using the stoichiometric and non-stoichiometric cathode materials, and the influence of transition metal stoichiometry on electrochemical properties was determined.

We show in this study that the deviation of composition can result in structural and elelctrochemical changes in final electroactive materials. Precise control of the material composition has great influence on electrochemical properties of the cathode materials. Similar analysis could be applied to many other multicomponent transition metal materials synthesized via co-precipitation of precursors. Such materials are broadly used by other research fields that require precise composition control, such as catalysis and ceramics.

Copper Hexacyanoferrate Hydrogel Electrodes for Cation Separations

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Chemical separations are of crucial importance and are used ubiquitously in the large-scale production of commodity chemicals and valuable species. However, as the purification steps in industrial manufacturing are often highly material and energy-intensive, there is a clear urgency for pursuing green engineering to develop and implement clean energy-efficient separation processes to reduce the economic and environmental impacts of high global energy consumption.[1,2] In particular, separations from aqueous media are of great interest. The removal of trace contaminants from water has been highlighted recently as a critical area for improvement, with applications to heavy metal recovery and seawater desalination.[2]

Electrochemical processes are an attractive platform for conducting separations, as they do not require solvents that change solution chemistry or impart environmental effects downstream, as well as heat and pressure inputs like conventional techniques.[1] Furthermore, they can be designed to target certain chemical species, whereas at the molecular scale, processes like distillation or chromatography can be inefficient.[1,2] Previously, redox-active materials such as metallopolymers have been shown to perform highly selective faradaic separations[3], as well as intercalating-type materials. One such crystalline candidate is the mixed-valence transition metal hexacyanoferrate class of compounds, whose analogues have been used in ion exchangers, ion-sensing, electrochromic applications, and lately, as an energy storage material for batteries[4,5,6].

We report a new surfmer-based method to produce functionalized redox-active copper hexacyanoferrate (CuHCF) composite hydrogels for electrochemically separating ions in aqueous media. The developed technique is a straightforward, inexpensive, one-pot preparation process that can consistently produce self-contained redox-active electrodes, without the need for manual filtration or grinding steps. The resulting electrodes are uniform, stable in water, and capable of withstanding up to ~100 separation cycles without gel leaching.

Furthermore, CuHCF exhibits strong redox response as well as affinity for cesium cations, whose radioactive isotope, ^{137}Cs, is present in nuclear waste and is both an environmental and health concern.[7] CuHCF nanoparticles can also be applied to remove other toxic heavy metal cations of concern with similar hydrated ionic radii.[4,6] We also discuss other methods to further improve the operation of the hydrogel in an electrochemical system by using specific dual-functionalized design schemes to tune the counter electrode[8], as well as analyzing energy consumption.

In conclusion, we present a novel technique to conveniently generate stable CuHCF composite hydrogels, which demonstrate robust redox activity.

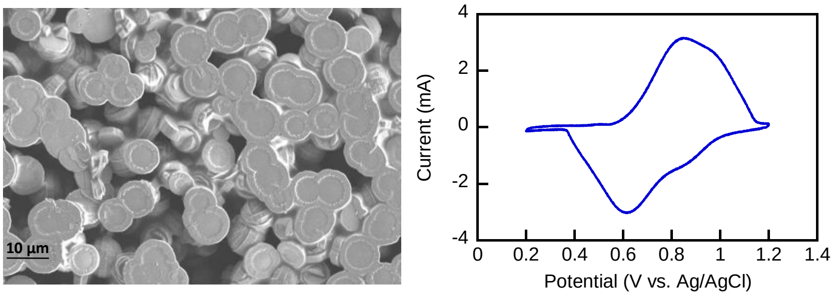

Figure 1. Scanning Electron Micrograph (SEM) of the porous hydrogel showing polymer-covered CuHCF nanoparticles (left). Cyclic Voltammogram (CV) in 1 M KNO_3, 2 wt% HNO_3 at 1 mV/s (right).

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Polymeric Sensing Electrochemical Motors. One Device with Two Tools Working Simultaneously: Mimicking Proprioception.

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Artificial muscles, actuators or soft motors generating reversible movements driven by reversible electrochemical reactions of conducting polymers are robust, reliable and reproducible motors. Oxidation/reduction reactions drive a cooperative actuation of the constitutive multi-step molecular motors (the polymeric chains) and the concomitant swelling/contraction of the material.

The flowing specific current (current per unit of polymer weight) controls the muscular displacement (linear or angular) rate. Muscle movement is controlled by the current flow and thus the sense of current flow controls the sense of the movement. The consumed specific charge controls the displacement amplitude[1]. This dynamic electrical control keeps whatever be the synthetic conditions of the electroactive material or the muscle's macroscopic dimensions.

The energy consumed by the driving electrochemical reaction senses the mechanical, thermal, chemical or electrical working energetic conditions[3]. One motor and several sensors work simultaneously in a physically uniform device driven by the electrochemical reaction of the constitutive material, as it happens in haptic muscles. Actuating (current and charge) and sensing (potential and electrical energy) magnitudes are present at any time within the only two connecting wires. No parallel device of such kind exists in present day technologies. Only haptic muscles are similar and, with brain and nerves, develop proprioception.

A basic proprioceptive equation, attained from basic electrochemical, polymeric and mechanical principles, describes the experimental results. A combination of sensing artificial muscles from conducting polymers, carbon nanotubes or graphene, a basic control chip designed using the basic actuating-sensing equation and the connecting wires, can generate the future basic artificial proprioceptive devices and robots.

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The electrochemical studies of new substituted olivine $LiMn_{1-x}VO_xPO_4$ as a cathode material in LIBs

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The olivine $LiMn_{1-x}VO_xPO_4$ has been successfully synthesized through a low-temperature (~130 ^oC) re-flux process. The VO^{2+} with 4+ Vanadium ion can easily substitute Mn^{2+} in a wide range of concentration ($0 \leq x \leq 0.30$). The significance of a re-flux process provides a homogeneous synthesized environment for possibly high production. The inert atmosphere in re-flux process also prevents the phosphate decomposition and makes organic additive (e.g. para-phenylenediamine, PPD) easily participated without oxidation. The concentration of Li^+ to Mn^{2+} can be maintained at 2:1 as using PPD during the synthesis, which prevent the waste of Li precursor. The size of $LiMn_{1-x}VO_xPO_4$ would be reduced by the amine group of PPD which traps on the surface of $LiMn_{1-x}VO_xPO_4$. Therefore, the pure $LiMnPO_4/C$ could exhibit the capacity of 125 mAh/g in an optima PPD/$LiMnPO_4$ ratio. Additionally, the $LiMn_{1-x}VO_xPO_4$ shows higher specific surface area than the pristine. The enhancement of VO^{2+} makes $LiMn_{1-x}VO_xPO_4$ particle grow through [011] direction, resulting a rice-like morphology. X-ray diffraction reveals no-impurity existing, yet a slightly lattice expansion after the $LiMn_{0.7}VO_{0.3}PO_4$ calcined at 600 ^oC for 2 hr. In electrochemical test, substitution of VO^{2+} prolongs the discharge plateau around 4.0 V, making the capacity increase to 150 mAh/g. This might indicate that a redox behavior of VO^{2+}/VO^{3+} is around the same voltage as Mn^{2+}/Mn^{3+}. The substitution of VO^{2+} improves the Li-ion transportation by lowering the charge-transfer resistance and enhancing the Li-diffusion diffusivity to an order of magnitude. In summary, the $LiMn_{1-x}VO_xPO_4$ is an potential cathode material that VO2+ can improve the Li-ion diffusion kinetic and provide additional redox behavior during cycling.

Modification of Carbon Nanocages Synthesis for Electrochemical Applications

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An increasing demand for reliable energy sources stimulates research towards devices that could equally efficient store and convert the energy in a convenient time. Few years ago the US Department of Energy ascribed the equal importance to two future energy storage technologies: batteries and supercapacitors. Since then the supercapacitor systems received increasing worldwide attention in research and industry. Supercapacitor, also known as electrical double-layer capacitor (EDLC), stores charge by adsorption of electrolyte ions onto the surface of electrode typically consisting of carbon-based materials. Recently**,** we synthesized carbon nanocages (CNCs) using organic precursor with metal salt.1) This is a nanoparticle templating method where one of the most important factors is that it involves only one annealing step over an entire synthesis. The method can produce nanocages with different sizes and shell thicknesses and for particular conditions gives the smallest uniform pores reported for this type of material.1) These nanocages, with their bilayer structure, unimodal pore size distribution and pore size of ~2.5 nm, approach the theoretical capacity of undoped bilayer graphene.

In a current work, we analyze how the synthesis procedure and precursor selection affect the properties of resulting carbon nanocages and influence the electrochemical performance of supercapacitor devices. In this study we use: HRTEM images of CNCs recorded in both, *in situ* (during a precursor annealing in TEM) and *ex situ* modes, BET, Raman, and XPS analyses. We correlate the graphitization degree, d-spacing, active surface area, pore size, and functionalization of CNCs with their capacitive behavior in varied electrochemical conditions. This helps to optimize the synthesis procedures for EDLC application. This synthesis method also allows for easy nitrogen doping through *in-situ* pyrolysis process (*i.e.*, during the carbonization reaction). We obtained N-doped carbon nanocages in which nitrogen atoms occupies mostly pyridinic sites. That expands the possible application range of this novel material.

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Cu Modified Tetrahexahedral Pd Nanocrystals for Electroreduction of Carbon Dioxide to Ethanol

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The electrocatalytic reduction of CO_2 to valuable products, especially alcohols, is a topic that has attracted the interest of many electrochemists. Among all metal electrodes, Cu is the unique metallic material for reducing CO_2 to hydrocarbons or oxygenates.[1,2] However, there are several fundamental challenges of Cu electrode in the electrocatalytic reduction of CO_2, such as high overpotential needed, poor Faradaic efficiency and lower selectivity for the C2 products of CO_2 reduction. Pd catalysts usually suffer from CO poisoning due to strong CO adsorption, and the main products of CO_2 reduction on Pd is mainly CO or formic acid.[3,4] CO_2 reduction is a surface-structure-sensitive reaction, changing the surface structure of the catalyst can certainly tune the activity and selectivity of this reaction. Hori et al. and Koper and co-workers have found that High-index facets have higher activity for CO_2 reduction.[5,6]

In this study, we combine Pd with Cu, the two metal with different CO binding energy by midify Pd NCs with Cu, and investigated their activity and selectivity of CO_2 reduction. Two kinds of Pd nanoparticles are prepared, i.e., {730}-faceted THH Pd NCs and {111}-faceted Pd NCs, by an electrochemical deposition method. Also, we tailor the selectivity of products on Cu/THH Pd NCs by varying the amount of Cu. Our results show the Cu_{1ML}/THH Pd NCs exhibit a higher activity and selectivity for CO_2 electroreduction, with ～20% FE towards ethanol at -0.46 V vs. RHE. Therefore, we conclude Cu overlayer modified Pd NCs with high-index facet show higher selectivity for CO_2 reduction to ethanol than that with {111} facets. The presence of undercoordinated sites are benefitial for C2 chemicals.

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Synthesis and characterization of modified electrodes based on Poly(o-ethoxyaniline) and Functionalized Carbon Nanotubes Composites

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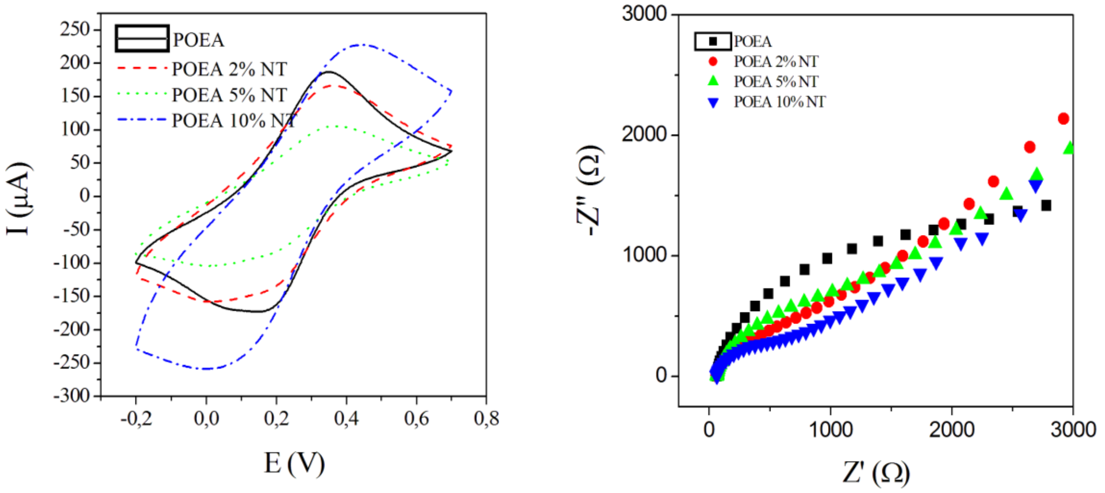
Modified Electrodes based on films of composites of conducting polymers and carbon nanotubes present advantages such as decrease of the capacitive current and charge transfer resistance[1,2]. In this work, poly(o-ethoxyaniline), POEA, and their respective composites with carbon nantoubes (MWCNTs), were produced by chemical polymerization of the monomer o-ethoxyaniline (o-phenitidine) with the dropwise addition of an ammonium persulphate solution (PSA) in HCl 1.0 mo L-1. POEA and their composites were produced in diferent mass reasons of MWCNT in relation to the mass of monomer (2%, 5% and 10% of MWCNT). The obtained POEA and its composites powders were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and the films of these materials, deposited onto glass substrates covered with Indium Tin Oxide (ITO), were characterized by electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Results showed a synergistic effect between the POEA and MWCNT capacitive current reduction and charge transfer resistance.



a) **b)**

Figure 1. Electrochemical characterization of POEA and its respective composites with MWCNT deposited onto ITO substrates, supporting electrolyte of HCl 0,1 mol.L^{-1}, reference electrode of Ag/AgCL. a) Cyclic voltammograms. v = 50 mV.s^{-1} b) Nyquist Diagrams (frequency of 0,1 Hz to 100 kHz)

Acknowledgments:
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Nano-structuring Nickel-based Catalysts for Oxygen Evolution

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Nickel based materials have been proposed as stable catalysts for oxygen evolution in alkaline water electrolysers. These include high area forms of metallic nickel, metal oxide/ hydroxide layers produced via cathodic deposition, spinels, and perovskites. Our previous research work indicated that nickel iron hydroxides are good catalysts for OER giving oxygen evolution overpotentials between 265 mV and 330 mV from varying catalyst compositions [1]. We believe that further decreasing the overpotential is highly beneficial to water electrolysis technology and this is only likely to be achieved by the identification of new families of OER catalysts.

This presentation will report studies of oxygen evolution at low cost, nickel based coatings on steel and nickel substrates. A number of binary and/or ternary mixed metal oxides (e.g. NiFe, NiCr, NiFeCr etc) will be prepared by cathodic electrodeposition and characterised. The composition of the selected catalysts will be optimised to give lower overpotential. In order to minimise IR drop and ensure a more reliable comparison of materials at the high current densities of interest for water electrolysers, the measurements will be carried out with microelectrodes (i.e. area $\approx 2 \times 10^{-5}$).

One method to further improve performance of the catalysts is utilisation of nano-structured materials to increase the surface area and loading of active material. Figure 1 illustrates the work carried out by the authors. A Ni/Co oxide nanowire array was prepared by a template-free growth method from hydrolysis of nickel/cobalt-ammonia complex ions [2]. The surface area of such a structured electrode can be increased significantly (e.g. by a factor of 10). We shall comprehensively investigate this method to prepare a nanowire array of active materials on substrates. **C**ombining the free-standing nanowire arrays with three dimensional substrates (e.g. nickel mesh, nickel foam), will result in nanostructured 3D electrodes that utilize more active material and possess superior mass transport properties, enabling higher catalytic activity for oxygen evolution reaction.

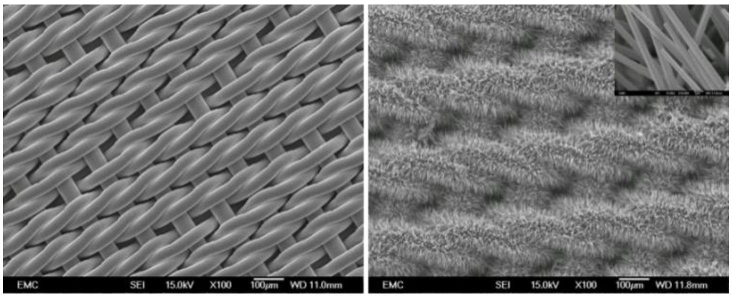

Figure 1 SEM images of Ni/Co oxide nanowire array that were prepared by a template-free growth method using nickel mesh as a substrate: (left) uncoated nickel mesh; (right) nickel mesh coated with Ni/Co oxide nanowire array (the inset is a high resolution image showing nanowires of diameter 500-600 nm).

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Cu Nanoparticle-Based Catalysts for Selective Electrochemical CO_2 Reduction

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The electrochemical reduction of CO_2 to useful products has been widely studied as a possible technique for the mitigation of atmospheric CO_2 and achieving "carbon neutrality" (net zero CO_2 emissions). The multi-electron/proton transfer processes and sluggish reaction kinetics determine that CO_2 electro-reduction involves very complicated reaction mechanisms and sometimes a wide product distribution. Therefore, viable electrocatalysts must be capable of lowering the CO_2 reduction overpotentials, inhibiting the competing hydrogen evolution reaction (HER) in aqueous media, and controlling the reaction pathways toward a specific product (to minimize the complexity of separation/purification processing).[1] Recent studies have indicated that when a right catalyst is used, certain degree of selectivity can be achieved, as demonstrated in the electrochemical reduction of CO_2 to CO on Au, Ag or to formate on In, Sn. To convert CO_2 to hydrocarbons, a specific form of Cu metal has to be used as the catalyst. Despite the extensive efforts devoted to both experimental and theoretical studies, the Cu-based catalysts studied for the CO_2 reduction tend to yield a diversity of hydrocarbon products and a practical approach to increase Cu catalytic selectivity towards a hydrocarbon molecule is still less explored.

Due to the recent synthetic advances in metallic nanoparticle (NP) synthesis, monodisperse NPs are routinely prepared with the desired dimension controls. Consequently, catalytic properties of these NPs can now be better studied to identify catalytically active sites for possible catalysis optimization.[2] For example, the preparation of monodisperse Au NPs enables identification of NP edges as the active sites for CO_2 conversion to CO,[3] which allows further tuning and optimization of the Au NP catalysis by developing monodisperse ultrathin Au nanowires as the most efficient catalyst for CO_2 conversion to CO.[4] In this presentation, our recent efforts in developing highly active and selective electrocatalysts for CO_2 reduction will be overviewed, with special focus on the efficient production of C2H4 and CO based on Cu NP-based systems.[5-6]

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Optimize the conductivity of PEDOT:PSS flexible transparent electrode with graphene

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As one of the most popular conductive polymers, poly (3,4-ethylenedioxythiophene):poly (4-styrenesulfonate) (PEDOT:PSS) has attracted wide attentions during these years. However, in the field of conductive transparent electrodes, supercapacitors and solar cells, the drawbacks of pristine PEDOT:PSS are inhomogeneous electrical properties, hygroscopic properties and poor long-term stability. Graphene is considered as an ideal additive for PEDOT:PSS to optimize its conductivity, due to its good performance in conductivity, transparency, flexibility and thermal stability. In this paper, high transparent, flexible and conductive PEDOT:PSS doped graphene modified with ethyl cellulose (EC) nanocomposite electrodes were fabricated on polyethylene terephthalate (PET) substrates, where the modified graphene powders were synthesized by electrochemical exfoliation and liquid ultrasonic exfoliation. The performance of nanocomposite electrodes can be greatly optimized by the modified graphene, showing a best sheet resistance ($R_{\square}$) of 54.8Ω/□ and a transmittance (T) of 76.3% at 550 nm, accompanying with excellent thermal stability and mechanical stability. The enhancement of conductivity is mainly attributed to the remove of the PSS chains of PEDOT:PSS and the rearrangement of the PEDOT chains. The PSS interacting strongly with the ethyoxyl groups from EC can promote the remove of PSS chains of PEDOT:PSS, while the highly uniform dispersion of electron conduction favored, EC modified graphene in the PEDOT:PSS matrix can achieve the rearrangement of the PEDOT chains with more expended conformation via the π-π interaction between graphene and PEDOT, so it can provide more conductive pathways for carriers. These results indicate that the PEDOT:PSS doped graphene modified with EC hybrid nanocomposite films fabricated by spin coating technique have great potential in next-generation optoelectronic devices, such as supercapacitors, solar cells, electronic paper, touch screens, low cost ITO-free flexible transparent electrodes and flexible displays.

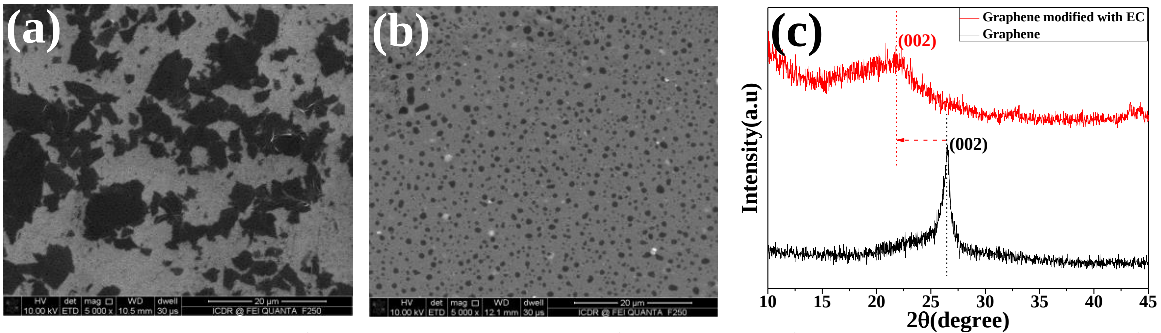

Fig 1. (a) SEM image of graphene; (b) SEM image of graphene modified with EC; (c) XRD pattern of graphene and graphene modified with EC

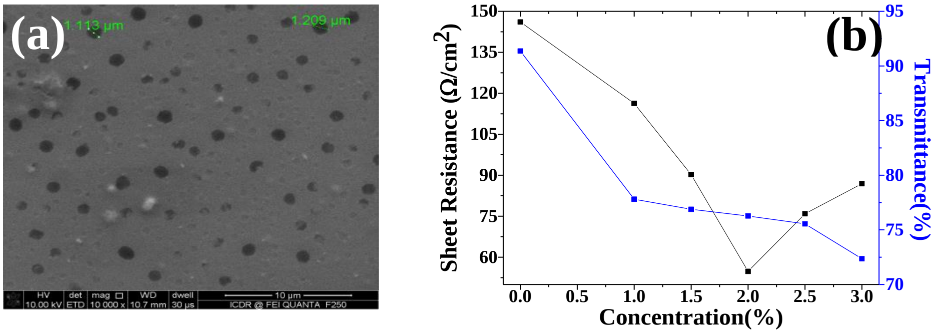

Fig 2. (a) SEM image of PEDOT:PSS doped graphene modified with EC nanocomposite film; (b) The sheet resistance and transmittance of PEDOT:PSS doped graphene modified with EC nanocomposite films at 550 nm via spin-coating process with different concentrations of EC modified graphene

Ceria Nanorods Supported on Vulcan XC72 Carbon as Electrocatalyst for Oxygen Reaction Reduction in Alkaline Medium

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Abstract: In recent years, electrocatalysts capable of generating hydrogen peroxide (H_2O_2) *in situ* in the reaction medium have been studied to subsequently promote the degradation of organic pollutants contained in water by advanced oxidative processes (AOP), thus reducing the cost and risks associated to transport and storage of H_2O_2 [1]. The ceria (CeO_2), like other rare earth compounds, is a powerful compound having superior physical and chemical characteristics, such as high corrosion and wear resistance [1] and the black carbon is a known cathode for the oxygen reduction via 2-electrons mechanism in alkaline solution, being an excellent choice as support for the electrocatalyst production due to its high surface area, strong corrosion resistance and low price [2]. This work aims synthesize electrocatalysts based on CeO_2 nanorods (NR) supported on Vulcan XC72 carbon and evaluate electrochemically its efficiency for the H_2O_2 generation. NR CeO_2 were synthesized by hydrothermal method[3] and were supported on Vulcan XC72 carbon by impregnation method [4] in different proportions (1, 2.5, 4, 5.5 and 10% w/w). In Figure 1 (a) is presented the X-ray diffraction (XRD) analyzes of the synthetized electrocatalysts confirming the presence of the NR CeO_2 (JCPDS 34-0394) [3], in Figure 1 (b) the transmission electron microscopy (TEM) images shows the NR CeO_2 on Vulcan XC72 carbon and in Figure 1 (c) are the polarization curves for oxygen reduction reaction (ORR) using a rotating ring-disc electrode (RRDE) measuring the efficiency of the electrocatalysts synthetized.

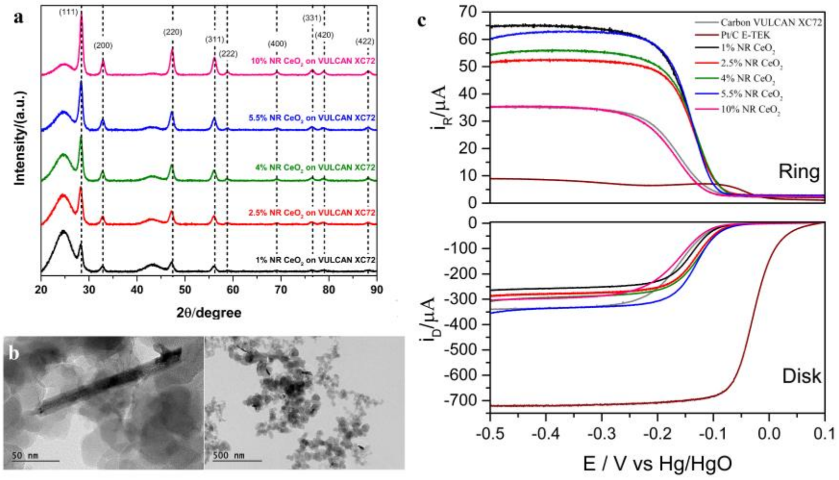

Figure 1. (a) XRD of the electrocatalysts synthetized. **(b)** TEM images of the electrocatalysts synthetized. **(c)** Polarization curves in NaOH 1.0 mol.L $^{-1}$ saturated with $O_{2(g)}$ using NR CeO_2 on Carbon Vulcan XC72 electrocatalyst in different proportions and the reference materials for 4-electrons (Pt/C E-TEK) and 2-electrons (Carbon Vulcan XC-72) in the ORR with RRDE, where the disk is of glass carbon (area = 0.2475 cm^2) and the ring is of gold (area = 0.1866 cm^2). In the disk was carried out an anodic scan (0.1 V to -0.5V) and the ring was polarized in 0.3 V.

By the calculation of the number of electrons transferred[1], we can conclude that the most promising electrocatalyst for the H_2O_2 electrogeneration is the one containing 1% NR CeO_2 (2.2 e^- transferred and 90% conversion of O_2 to H_2O_2). This electrocatalyst can be promising to degrade organics pollutants by Advanced Oxidative Processes.

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Synergic electrocatalysis based on Co_2SnO_4/graphene nanocomposite for hydrogen peroxide reduction

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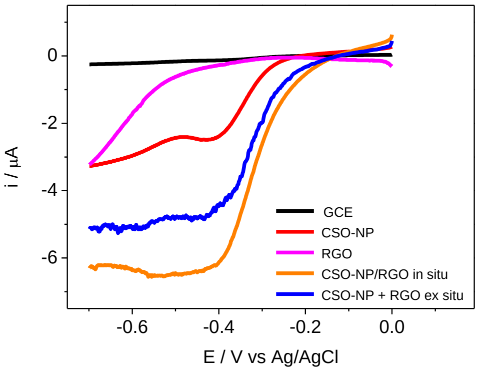
Nowadays, the fascinating advances in materials science research and biological diagnostics have led to the rapid development of different classes of sensors for a wide range of analytes detection with improved sensing characteristics. One of the most interesting analyte from the chemical and biological point of view correspond to hydrogen peroxide (H_2O_2), basically because it has important roles in the electron transfer process of hundreds of enzymes in biological systems and also it is present in several cleaning products or it is a by-product of several chemical reactions.

In the present study, nanoparticles of Co_2SnO_4 (CSO-NP) were synthetized alone and in the presence of reduced graphene oxide (CSO-NP/RGO *in situ*) via hydrothermal method and their electrocatalytic effect against the hydrogen peroxide reduction was tested.

Electrochemical studies were conducted in 0.01 M NaOH media (pH 12). Glassy carbon electrodes were modified by casting 10 µL of a 1 mg/mL (0.2 % Nafion in ethanol) dispersion of CSO-NP/RGO *in situ*. For comparative purposes *ex situ* mixture of CSO-NP and RGO were prepared (CSO-NP + RGO *ex situ*) in proportions of 4:0.25, 4:0.5 and 4:1).

SEM characterization showed that the morphology and size of CSO-NP are similar in both synthesis, alone and in the presence of graphene, with an average particle size of 100 nm. Using XPS, cobalt ions are shown to have an oxidation state of 2^+. TGA characterization confirmed the proportion of CSO-NP/RGO.

The electrochemical results were performed using linear sweep voltammetry (LS) at 5 mV/s. In the figure the LS voltammograms obtained using (4:0.5) nanocomposites modified electrodes are shown, also the voltammograms obtained using bare GCE, and electrodes modified using CSO-NP and RGO are included. Both nanocomposite modified electrodes (*in situ* and *ex situ*) exhibits excellent electrocatalytic activities against hydrogen peroxide reduction in alkaline solution. The onset potential is close to -170 mV (vs. Ag/AgCl), which is higher than obtained with CSO or RGO modified electrodes, -250 mV and -380 mV respectively. Meanwhile, the nanocomposites synthesized via *in situ* and *ex situ* showed similar onset potentials the *in situ* nanocomposite shows higher activity for hydrogen peroxide reduction compared to CSO-NP + RGO mixture.



On the other hand, when the quantity of graphene id higher in the nanocomposite, i.e. 4:1 proportion, more electrocatalytic effect was observed, mainly in the onset potential.

In Conclusion, graphene is an excellent support for CSO nanoparticles and demonstrate to be an effective ways to improve the catalytic activity probably by increasing the number of available electrocatalytic active sites at the surface and the electron transfer capability of the catalysts.

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Further Insight into the Electrochemo-Mechanical Behaviour of Electronically Conducting Polymers : Development of New Methodologies Involving Electrochemical Atomic Force Microscopy

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Electrodeposited films of electronically conducting polymer (ECP) films (polypyrrole, polythiophene and their derivatives) are insertion materials whose thickness is expected to vary in the course of electrochemically driven doping/undoping processes [1]. There are not so many techniques allowing in-situ measurements of thickness or thickness variations with a nanometric resolution. As a consequence, dimensional variations of thin films of insertion materials as a function of their redox state are only rarely investigated nowadays even though they give birth to more and more numerous risks arising from energy conversion or storage devices (see for example explosion of the battery of famous smartphones). In this talk, a brief overview of innovative methodologies associating in-situ atomic force microscopy (AFM) and various electrochemical techniques and dedicated to in-situ measurements of thickness variations of ECPs during their electrochemical conditioning will be introduced. Such methodologies can all be considered as different versions of the electrochemical atomic force microscopy (EC-AFM) technique. They actually associate usual working modes of AFM, such as contact mode or amplitude modulation-AFM (AM-AFM), with well adapted electrochemical techniques such as cyclic voltammetry (CV), chronoamperometry (CA) but also electrochemical impedance spectroscopy (EIS), sinusoidal voltammetry (SV), or advanced cyclic voltammetry (ACV). This latter technique is particularly interesting because it allows resting periods to be applied in between two consecutive potential cycles.

Throughout our investigations, our purpose was to establish, each time it was possible, correlations between the thickness variations measured using EC-AFM and ion and solvent exchanges occurring at the ECP film/solution interface as a result of the electrochemical doping/undoping of these ECP films. Other properties of ECPs can be measured in the course of EC-AFM experiments. Among them, one can cite absolute thickness or mechanical properties of ECPs such as hardness, expected to be directly related to their porosity, and/or to their permeability to the electrolytic solution, and our goal was to correlate them with data extracted from electrochemical techniques. Advantageously, such EC-AFM methodologies allow moreover many potential scans to be applied on the same sample, which allows other fascinating issues such as relaxation or ageing processes of ECPs to be further investigated. This contribution will be mainly focused on results obtained with polypyrrole or poly-(ethylene-dioxy-thiophene) thin films electrodeposited from aqueous electrolytic solutions in the presence of either bulky anions such as hexasulfonated calix[6]arenes [2,3] or dodecylsulfate anions or much smaller anions such as perchlorate anions.

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Synthesizing Catalyst Nanoparticles on Large Electrodes by Combining Inkjet Printing and Flash Light Irradiation

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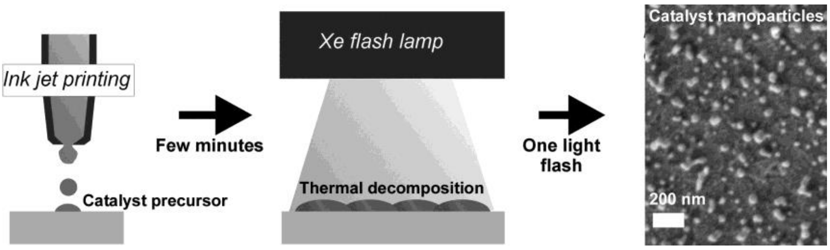
Catalytically active metal and alloy nanoparticles (NPs) play an important role applications and research fields including (photo)electrocatalysis and (bio)electroanalysis. The functionality of commercial devices and sensors containing NP-coated films and layers, such as polymer electrolyte membrane fuel cells, electrolyzers and biosensors rely on the superior properties of the NPs, such as catalytic activity, sensitivity and stability. These properties are a result of the NP composition, size, shape and synergistic effects with support materials. Nanoparticles made of noble metals, such as Pt or Au, are often used for the above listed applications. However, due to the price and scarcity of many noble metals and their corresponding precursors the relevant research to optimize the NP properties (e.g. sizing, shaping or alloying) can be costly. In addition, many efforts are made to lower the noble metal loadings in real devices while keeping or improving their functionality.

The preparation of NP-coated electrodes requires usually a prior NP synthesis, with or without support particles, before formulating an ink or paste that can be deposited onto the desired device structure. Afterwards, thermal post-processing guarantees the removal of ink/paste solvents and stabilizers in order to get catalytically active, well-adhered and conductive films.

Herein, we present a totally new approach, where inkjet-printed patterns of metal precursors, such as chloroplatinic acid, are irradiated with a high energy light pulse from a Xenon flash lamp [1]. The pulse is shorter than 1 ms and due to the absorption of the light emitted by the flash lamp by the precursor-coated electrodes temperatures of several hundred degrees Celsius are generated inside the printed films. This is enough to thermally decompose the precursor into pure metal. The flash light-induced process takes only a fraction of a second and generates gaseous and evaporated side products (e.g. HCl, Cl_2 and H_2O) [2-3].

We demonstrate how an integrated inkjet printing and flash light irradiation platform can be used to understand and optimize the relevant conditions (e.g. chloroplatinic acid precursor ink composition, printing parameters and Xe flash lamp settings) to decorate square centimeter sized indium tin oxide (ITO) coated glass slides within few minutes. The Pt NPs are free of chlorine, homogeneously distributed, well-adhered to ITO and show the catalytic properties expected for Pt. We further show how the demonstrated approach can be conveniently used to create combinatorial libraries of NP alloys to be analyzed by using electrochemical screening tools, such as scanning electrochemical microscopy (SECM).



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Molecularly Tunable Graphite-Conjugated Catalysts

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Immobilizing molecular catalysts onto electrode surfaces is an attractive strategy for creating catalytically active surfaces with molecularly well-defined active sites. However, methods currently employed for loading molecular units onto electrode surfaces use inert tethers that engender weak electronic coupling between the molecular orbitals of the active site and the delocalized states of the metallic electrode. In this talk, we demonstrate that we can synthesize electronically conductive tethers that are conjugated to graphitic carbon electrodes. These linkages are formed by reacting native surface defects of graphitic carbon with well-defined catalytic active sites under mild conditions. X-ray photoelectron and X-ray absorption spectroscopies establish the formation of surface-bound species with well-defined chemical environments. Electrochemical measurements and product characterization indicate that surface-bound organometallic catalysts retain their original catalytic activity and selectivity. This work establishes graphite-conjugation as a powerful strategy for generating well-defined, tunable, heterogeneous electrocatalysts on ubiquitous graphitic carbon surfaces.

Asymmetric Metallopolymer Redox-Electrodes for Pseudocapacitive Deionization and Selective Ion Separations

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Water purification is one of the greatest challenges of the 21st century. Capacitive-type deionization systems have come into play as an energy-efficient alternative for brackish water deionization.[1] Though porous carbon electrodes have been the conventional materials platform for deionization due to their robustness and costs, Faradaic materials have received increased attention in the rapidly developing field of hybrid and pseudocapacitive deionization.[2-6] These materials, often crystalline and battery-type compounds[2] but also polymeric,[3-5] possess high charge storage and can strongly enhance deionization capacity.

We present the novel capability of these redox-materials for achieving ion-selective separations,[3-6] as well as high-performance deionization at various electrolyte concentrations with an order of magnitude increase in capacity compared to solely capacitive systems. In our approach, we have relied on molecular design and materials synthesis to develop redox-electrodes based on electroactive metallopolymers, with ion-selective properties for both anions and cations. As shown schematically in **Figure 1**, these electrochemically-driven interactions allow for the targeting of a single ionic species over others in complex multi-ion systems.

First, we report our discoveries on metallocene-based chemistries for organic pollutant removal and remediation. Our iron and cobalt-based hybrid electrodes are shown to achieve separation factors >180 and uptake capacities >200 mg/g for target organic groups (carboxylates, sulfonates, phosphonates)[3] as well as heavy metal cations (cadmium and chromium) in complex multi-ion mixtures with over 300-fold competing electrolytes under <1.2 V windows. The molecular mechanisms for this specificity extend beyond size and charge properties, but rather rely on chemical binding effects, which include both redox-mediated hydrogen bonding and non-covalent cation interactions.

Second, we demonstrate that asymmetric electrochemical systems, in which both the cathode and the anode are functionalized in tandem with properly tuned polymeric electrodes, are more efficient for a variety of deionization applications. We can suppress water reduction, maintain solution pH and enhance ion separation, with current efficiencies of up to 96% towards selective ion-binding of micropollutants.[6] Finally, we show that through materials optimization (cross-linking and covalent routes), we have been able to significantly increase the cycling robustness in both flow and batch configurations.

In summary, we present redox-active organometallic electrodes as a robust asymmetric system for Faradaic-based deionization, and is of both scientific and practical interest for (a) sustainable water remediation and deionization, and (b) ion-selective purification of synthesis products in the chemical industry.

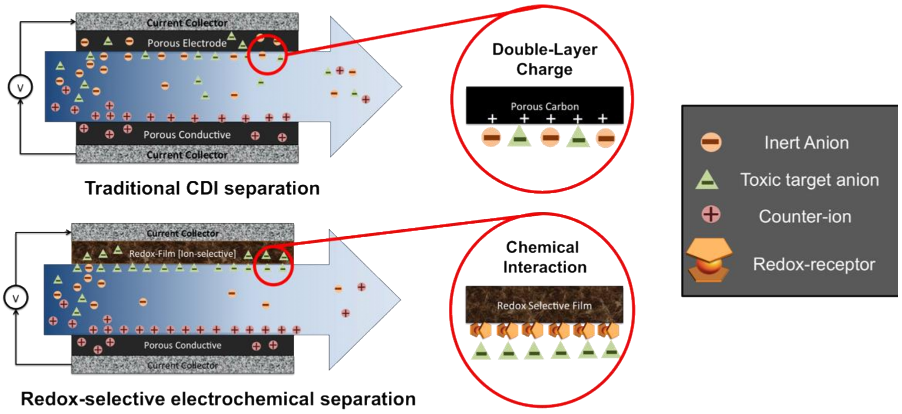

Figure 1. Top scheme shows the classical, non-selective capacitive deionization, and **bottom scheme** shows our ion-selective redox-mediated approach

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Modification of Gold Electrode with Monolayer of Environmentally Sensitive Microgels

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Polymer hydrogels are cross-linked hydrophilic polymer networks filled with an aqueous solution. The unique structure and environmental sensitivity make polymer hydrogels useful in various applications. Their environmental sensitivity is exhibited by the appearance of reversible volume phase transition. A change in the environmental conditions (e.g. in temperature, pH and light, and the presence of specific ions or molecules) may cause the reversible phase transition. When a swollen hydrogel undergoes the volume phase transition, water is ejected from the polymeric network.

From the point of view of exploiting the volume phase transition in potential applications, poor mechanical properties of the traditional gel materials, i.e. their big size and correspondingly slow response to changes in the environmental conditions are the major limitations. One possibility of dealing with these limitations is to work with very small particles of the gels. In recent years, the interest in micro- and nanogels increased significantly. The colloidal dimensions of the gels made them react very quickly to changes in the environmental conditions. Another possibility of elimination of the listed limitations assigned to the traditional gels is to work with a thin (a few hundred nanometer thick) layer of a gel anchored to the surface of a substrate, including the surface of an electrode. The attachment of smart gels to the surface of an electrode widens their usefulness in, for instance, the construction of switchable sensors/biosensors, switchable electrochemical systems and signal-responsive interfaces.

We have modified the surface of gold electrodes with a monolayer of environmentally sensitive microgels. To do it the disulfide bonds were inserted into the synthesized microgels. The synthesis was completed using the surfactant-free emulsion polymerization. Thanks to the strong interactions between gold and the sulfide atoms (present in the microgels) a strongly adhered monolayer of the microgels on the gold electrode was obtained. The build-up of a monolayer was inspected using a QCMB, see Figure 1. Additionally, the introduction of a conducting polymer, metal nanoparticles and electroactive groups to the microgels, led to formation of new electrochemical systems. The influence of changes in environmental conditions on the electrochemical properties of the modified electrodes will be presented.

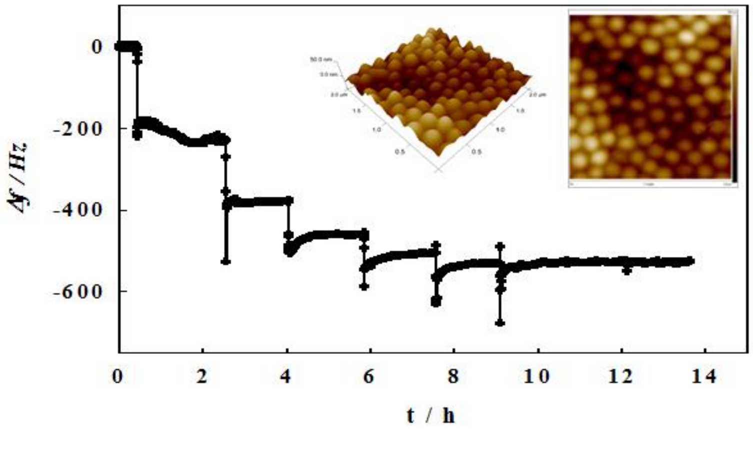

Fig. 1 Monitoring of the formation of the microgel monolayer on gold surface with QCM (drops in frequency are related with subsequent additions of microgel portions). Inset: AFM images of obtained monolayer of the microgels.

Achieving low turn-on voltage of hematite photoanode through sequential surface treatment for photoelectrochemical water splitting

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Hematite (α-Fe_2O_3) is a suitable candidate for solar oxygen production due to its well-suited band structure, stability and availability. However, it still exhibits low solar-to-oxygen conversion efficiency limited primarily by high charge recombination and poor surface catalytic activity. Here, we demonstrate a new sequential surface treatment approach on unintentionally Sn doped Fe_2O_3 photoanode. First, a heavily doped $Fe_{2-x}Sn_xO_3$ surface passivation layer was created by Sn^{4+} surface treatment which can robustly inhibit interfacial recombination. Then, NiOOH catalyst layer has been deposited that greatly enhance the charge transfer process across the passivated electrode/electrolyte interface. By exploiting this approach, the optimized sequentially treated photoanode (Fe_2O_3)/$Fe_{2-x}Sn_xO_3$/NiOOH) exhibits the lowest photocurrent onset potential of 0.49 V vs. RHE and a saturated photocurrent density of 2.4 mA cm^{-2} V at 1.5 V vs. RHE. Transient photocurrent and impedance spectroscopy measurements further reveal that the combined $Fe_{2-x}Sn_xO_3$/NiOOH layers reduce interfacial recombination and enhance charge transfer across the electrode/electrolyte interface. When the NiOOH was first deposited onto Fe_2O_3 surface and Sn^{4+} treatment later as over layer to form Fe_2O_3/NiOOH/Sn^{4+} (i.e., reversed surface treatment), 200 mV anodic shift in photocurrent onset potential and 41 % decrease in water oxidation photocurrent (at 1.23 V vs. RHE) were observed. The results are convincing evidences that it is possible to address the problems of surface trap recombination and sluggish catalysis independently by employing surface passivation layers first and catalysts later sequentially.

Viologen Based Redox Composite Films: Electrochemical Synthesis and Characterization

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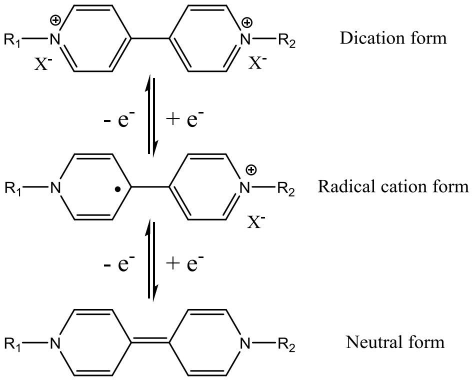
Viologens, usually named 1,1´-disubstituted-4,4´ -bipyridinium salts, have been in focus for increasing attention due to their unique properties.[1] The special colour change and the stable redox property are the two main features which made the viologens work as a frequently used functional material. The viologen can undergo two redox processes with three redox forms: dication form, radical cation form and neutral form, which are shown in Scheme 1. In previous work, varies viologen-based composite films have been synthesized electrochemically by cyanopyridine based precursors and other functional materials.[2, 3] The composite materials have been characterized by different electrochemical, physicochemical and imaging techniques. The resulted composite films have revealed that the good redox property from viologen has been maintained and the new functionalities have been introduced by new functional materials. The composite materials have huge potential to be applied in further applications.



Scheme 1. Three redox forms of viologen

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Metal precursor influence in the catalytic activity of pyrolyzed non precious metal catalyst.

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The discovery of Jasisnky in 1964 that the CoPc is active for the oxygen reduction reaction in acid media (1), implied the interest of scientific community in the study of catalytic activity and durability of different MN4 towards the ORR. However, the main problem of these MN4 catalysts is their poor stability in acid media. One of the most successful process to increase the activity and stability is the pyrolysis of MN4 catalysts under inert atmosphere above 500ºC. An important advance was then achieved by Yeager in 1989, when was revealed that often-expensive macrocycles could instead be substituted by carbon, nitrogen and salt metal precursors such as polyacrylonitrile (nitrogen and carbon precursor) with Co or Fe salts (2). Nowadays, one of the most promissory synthetic route to increase the activity and the stability is the heat treatment under inert atmosphere of carbon-nitrogen based polymers mixed iron or cobalt salts (3). In spite of the scientific efforts in this field, there are a lot of questions and uncertainties in the area of pyrolyzed catalysts, one of them is the specific role of the metal sources, which could be an integral part of the active site or only takes place during the pyrolysis process as catalyst of the formation of C-N active sites.

Present study is focused on the influence of the metal precursor in the catalytic and structure of the final pyrolyzed catalysts. In this work, two different iron sources, FeCl3 and Fe3O4 nanoparticles, are used as metal precursor; and polypyrrole, polyaniline and polydopamine are used as C/N precursor. To elucidate the metal role, four kind of pyrolyzed catalyst are evaluated towards the oxygen reduction reaction: (I monomer without metal, (ii) polymer with FeCl3, (iii) polymer adsorbed on Fe3O4 nanoparticles, and (iv) polymer with FeCl3 and Fe3O4 NP. The best system was the polymer heated in presence of NP and FeCl3, indicating that Fe3O4 induce the graphitization process and develop of nitrogen doped carbon and iron salts take place in the active site, increasing the activity of this kind of pyrolyzed non-precious metal catalysts.

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Electrochemically Prepared Oxides for Resistive Switching Devices

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Redox-based resistive switching memories (ReRAMs) are one of most promising candidates to be next generation nonvolatile memories. They meet all requirements for green IT e.g. low power consumption, high write, erase and read speed and can also be used for beyond von Neumann computing, alternative logic and neuromorphic operations. ReRAM devices have a simple structure, high scalability, data retention, endurance and can satisfy high-density integration criterion [1]. joined to a simple device structure. These systems are usually divided in two categories, ECM (Electrochemical Metallization cells) and VCM (Valence Change Memories), depending on the mechanism underlying the device operation [2]. The cell structure consists of a solid electrolyte, e.g. a metal oxide or a layered oxides structure, sandwiched between two electrodes with metallic behavior (metals, TiN or conducting transparent oxides). Despite the oxide films have macroscopic dielectric (high-*k*) properties, deposited as nanoscale thin films they behave as solid electrolytes [3]. Electrolyte for such devices are usually prepared by physical (e.g. sputtering, pulsed laser deposition) or chemical (atomic layer deposition, chemical vapor deposition) techniques. An alternative way to produce the metal electrode/oxide junction is the anodizing, an electrochemical technique that allows to grow oxides on the surface of valve metals or valve metals alloys such as Ta, Ti, Nb, Al, Hf and so on [4]. By easily adjusting process parameters, it is possible to tailor oxides features, such as thickness, morphology, structure and composition. Barrier-type anodic films seem to be suitable solid electrolytes for ReRAM devices since they are smooth, uniform in thickness and composition and show perfect adhesion to the metallic substrate.

In this work we present different valve metal/anodic oxide systems prepared by anodizing of metal thin films (namely Hf, Nb, Ta). Barrier-type anodic films were grown galvanostatically (5 mA cm^{-2}) or potentiodynamically (10 mV s^{-1}) to different formation voltages, in order to get oxides with different thickness. An investigation based on electrochemical impedance and photoelectrochemical measurements was carried out to get information on the solid-state properties of the anodic oxides (i.e. band gap, flat band potential and dielectric constant) as a function of the formation conditions.

Furthermore, we fabricated ReRAM-type devices by depositing Pt top electrodes on the anodic films surfaces. Electrical characterization was performed to check, first of all, whether these devices exhibit resistive switching and, in addition, they are suitable for the use in redox-based memories. In particular, cyclic voltammetry, dc I-V sweeps and pulse measurements were carried out to study the performances of the devices and to establish the kind of mechanism underlying the device operation [5].

The experimental findings (I-V sweeps stability, data retention and endurance) prove that anodic oxides can be considered promising electrolytes for ReRAM devices.

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Structural engineering of inorganic oxide semiconductor photoelectrodes

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The continuously growing concentration of atmospheric carbon dioxide (CO_2) is a major driving force of R&D activities, aiming towards efficient mitigation strategies. Among several different possibilities, solar fuel generation is an attractive remediation avenue, as it may reduce the quantity of CO_2, in conjunction with the production of useful fuels or other chemicals. For the direct photoelectrochemical (PEC) reduction of CO_2, p-type semiconductor photoelectrodes (cathodes) are required. Oxide semiconductors are promising candidates in this manner, because of their low preparation cost and relatively high stability compared to their elemental and chalcogenide counterparts. At the same time, novel synthesis methods are required allowing for the rational design of new materials, in terms of optoelectronic and morphological properties. Solution combustion synthesis (SCS) is considered a green and sustainable alternative to the widely employed energy- and/or time-consuming synthesis methods, and I will show two examples how it can be utilized to obtain nanostructured photoelectrodes.

Copper-based delafossites ($CuMO_2$, where M: Cr, Al, Fe, Rh, etc.) are attractive photocathode materials, because their conduction band position lies at a sufficiently negative potential, with respect to the thermodynamic potential of both carbon dioxide reduction. In the first part of my talk, I will present the synthesis of phase pure $CuCrO_2$ by SCS, via optimizing the reaction conditions. For the first time, PEC CO_2 reduction was studied on $CuCrO_2$ photocathodes and the formation of CO, CH_4, and H_2 was confirmed. Structure-property relationships were studied and an impressive PEC performance was found when $CuCrO_2$ had an interconnected nanostructure.

In the second part of my talk I will demonstrate that careful modification of the SCS protocol (by adding foreign ions of Fe(III) and Mn(II) into the precursor solution) can result in bandgap narrowing of $Bi_2Ti_2O_7$. Further, the phase composition of these materials and the amount of the foreign metal ions incorporated in the parent structure, could be effectively controlled. Finally, insights on the photoelectrochemical performance of these new materials are presented, taking into account all the governing parameters (e.g., surface area, light absorption, crystallinity, etc.).

Catalyst aging. Effects on the morphology and electrocatalytical activity of nitrogen-doped carbon nanotubes.

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The reduction reaction of oxygen (ORR) is the most essential reaction in life processes, *e.g.* biological respiration, and in energy-converting systems, *e.g.* zinc/air batteries and low-temperature fuel cells, in which ORR is the cathodic reaction. To cope with typical power requirements, ORR requires efficient and active catalysts; so far, platinum and platinum alloys nano-dispersed on active carbon proved to be the most active. Nevertheless, platinum cost, natural scarcity, and technological drawbacks (*e.g.* oxidation, dissolution and migration) hamper the commercialization of such energy converting systems. Thus, finding alternative, inexpensive materials is a necessary and very attractive challenge.

In the last years, many efforts have been devoted to demonstrate that nitrogen-doped carbon nanostructures, like graphene and nanotubes (N-CNTs), have great potential as Pt substitutes in ORR. Their electronic properties are extraordinarily improved by the presence of nitrogen species that perturb the uniform π-cloud of carbon nanotubes and increase the localized density of states at the Fermi level, thus acting as n-type dopants and enhancing the electrocatalytic activity. In addition, many recent works suggest the possibility of adjusting ORR activity of N-CNTs by varying preparation method, precursor nature, or composition of the catalyst used in the nanotube synthesis. In this work we present some data about the effect of the aging time of the catalyst used in the nanotubes synthesis on the morphology, surface composition and electrocatalytic properties of N-CNTs. Data from both surface-sensitive and bulk-sensitive techniques point to local changes in catalyst composition and morphology to explain the trend of electrocatalytic activity with time in N-CNTs.

Patterned graphene gold nanocomposites for electrochemical detection of microfluidic enriched biomarkers

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Graphene-based working electrodes are extensively used within biomolecular electrochemical sensors due to their wide potential window, rapid electron transfer kinetics and electrocatalytic abilities. However, immobilization of bio-receptors on graphene, for the purpose of selectively binding with target analytes, can degrade its electrical properties. Furthermore, for the purpose of detecting trace levels of analytes, there is a need to couple microfluidic enrichment of the biomarker with its *in situ* detection. We address these challenges by patterning graphene-gold nanocomposites (Gr-AuNs) with anchored bioreceptors within a nanoslit channel, so that dielectrophoretic enriched analytes can be locally enriched and selectively bound for enhancing detection sensitivity and selectivity. This patterned sensing platform on a plastic chip is fabricated by embossing on cyclic olefin copolymer via nanoimprint lithography.

Exfoliated graphene sheets were distributed at the water / n-heptane interface. Separately, thin sheets of cyclic olefin copolymer (COC) were spin coated with photoresist and exposed through a photomask to fabricate the pattern of choice, followed by baking and resist development. The patterned bilayer resist on COC was oxygen plasma treated and introduced at the heptane-water interface to enable the graphene film to climb over the substrate. The graphene covered substrate was heated (100°C for 1 hour) to stabilize the film. Following treatment in 5 % HF at 60°C for 15 minutes to enable hydrogen-termination, the graphene surface was immersed in 8 mM $HAuCl_4$ and HF for one hour to yield gold nanoparticle decorated graphene. Finally, patterning of these so-called graphene-gold nanocomposites was performed via lift-off process, by removing the pre-patterned photoresist using acetone. Receptors were immobilized on the gold nanocomposite surface using standard thiol chemistries. Microchannels connected to nanoslit were fabricated on a separate COC substrate by hot embossing. The COC substrate with channels was aligned via imprint lithography (as indicated schematically in Fig. 1a) and bonded to the COC cover slip with patterned Gr-AuNs, as per Fig. 1c. The bonding was done at room temperature with pressure applied only to the COC substrate with the fluidic channels, so that the bioreceptors immobilized on the COC coverslip were not damaged [1, 2]. Dielectrophoresis of neuropeptide Y (NPY) was performed at 3 MHz to enrich the biomarker within the nanoslit channel in vicinity of the immobilized aptamer receptors (Fig. 1c) and standard differential pulse voltammetry (DPV) techniques were used to quantify NPY (Fig. 1b). The presentation will also present the application of the immonoassays within this sensing platform [3].

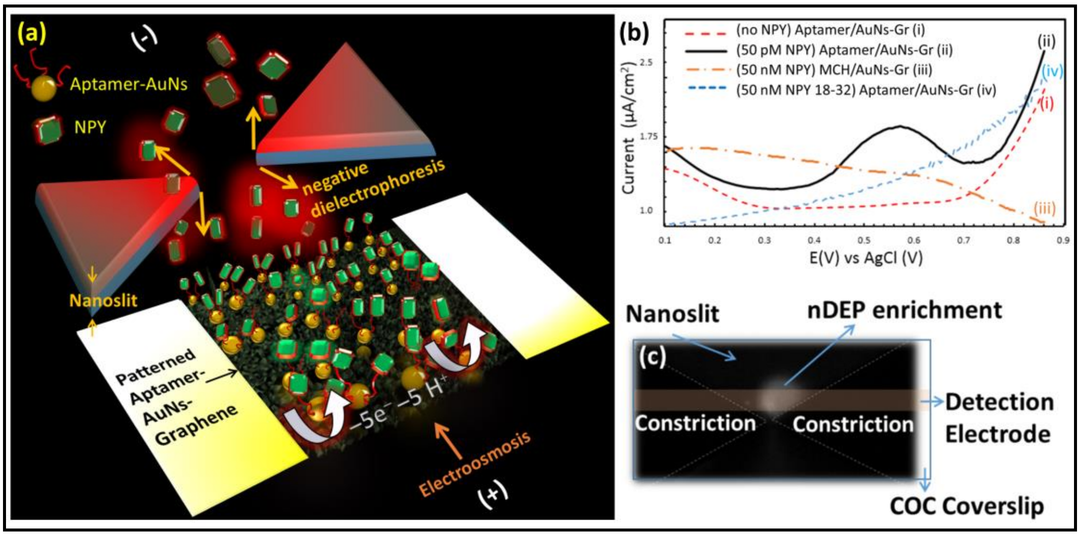

Figure 1: (a) Schematic of patterned Gr-AuNs inside nanoslit channel; (b) DPV for NPY quantification; (c) Dielectrophoretic enrichment of NPY in vicinity of the detection electrode to enhance sensitivity.

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Comparison of O_2 Reduction in Acid medium on Iron Phthalocyanines Axially Coordinated either to Pyridine or to Nitropyridine Anchored on Carbon Nanotubes

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Electrocatalysts with favourable characteristics to work as oxygen reduction reaction (ORR) cathode catalysts in fuel cells have been synthetized through the penta-coordination of iron phthalocyanine (FePc) with pyridine anchored on carbon nanotubes. Those catalysts mimic structures that exist in nature, such as the active site of the cytochrome c oxidase, and haemoglobin. In this work we have compared the electrocatalytic activity of FePc coordinated to either pyridine (to form FePc-Py) or 3-nitropyridine (to form FePc-3NPy) anchored on carbon nanotubes. We chose unsubstituted FePc because of its high activity as catalyst for the ORR via 4-electrons to yield water as by-product and because results show that the fifth coordination plays a major role in increasing its catalytic activity [1-3]. In order to probe the effect of the penta-coordination we compare it to a molecule with higher electron withdrawing capacity (i.e. 3-nitropyridine). Carbon nanotubes were used as base for the electrocatalyst synthesis because of their high conductivity and surface to volume ration and because of the easiness to be addressed by density functional calculations.

When FePc is coordinated to 3-nitropyridine, oxygen is reduced to water with smaller overpotential than when FePc-Py is used. Density functional calculations show that the ORR at the FePc-3NPy catalyst involves lower activation barrier, which is correlated with its higher turn over rate for the ORR. Finally, the activation barriers, the activities and the turn over rates of both catalysts (i.e. FePc-Py and FePc3NPy) are compared with the commercial standard 20% Pt/C.

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Self-Assembly of Fullerene-Graphene Supramolecular Hybrid and its Application as Pd Electrocatalyst Support for Direct Methanol Fuel Cells

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Direct methanol fuel cells (DMFC) have attracted enormous attention due to its promising prospect for clean energy power source. But the activity and durability of electrocatalyst for methanol oxidation reaction (MOR) must be improved before commercialization of DMFC. As a result, the development of stable support material has become an important issue to improve the performance of electrocatalyst. Nanocarbon materials such as fullerenes, carbon nanotubes, and graphene have been extensively investigated in supporting materials for electrocatalyst due to their excellent electronic and mechanical properties [1, 2]. As our continuous study on fabrications of nanocarbon material-based electrocatalysts for both MOR and biosensors [3-9], here we will present the facile preparation of fullerene-graphene nanohydbrid by self-assembly and its application as Pd electrocatalyst support for MOR. It has been found that the Pd catalyst on fullerene-graphene nanohydbrid showed an improved performance for MOR than on the graphene.

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Oxygen Reduction on Glassy Carbon Grafted with Anthraquinone-Modified Graphene and Multiwall Carbon Nanotubes

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In the present work, two carbon nanomaterials, graphene (GR) and multiwall carbon nanotubes (MWCNTs) were modified with anthraquinone (AQ) groups using the reduction of aryl diazonium salts [1,2]. Both nanomaterials (GR and MWCNTs) and corresponding diazonium salt (Fast Red AL salt) were of commercial origin [1]. The covalent modification of surfaces with different functionalities is efficient method for enriching the properties of materials surface [2,3]. This, in turn, broadens the field of applications of the modified materials [3,4].

For the surface functionalization, two different methods, electrografting and spontaneous grafting, were used for comparison purposes [2]. The AQ-modified nanomaterials were coated on glassy carbon (GC) electrode. In some cases, a layer of anion exchange ionomer (AS-04, Tokuyama Corp.) was additionally added on the carbon nanomaterial modified GC electrode. The composition of the prepared electrode materials was studied using X-ray photoelectron spectroscopy (XPS). The electrochemical characterization methods were used for the determination of the amount of AQ groups on the electrodes and in addition, for the investigation of electrocatalytic activity for oxygen reduction reaction (ORR) in 0.1 M KOH solution [1].

The XPS studies revealed the formation of azo linkages between the AQ groups in the modifier layers on nanomaterials which were electrochemically grafted. In case of spontaneously modified nanomaterials, no evidence for azo linkages was found. The study of electroactive AQ groups on the electrodes showed that the surface concentration (Γ_{AQ}) values were 10 to 25 times higher than in case of electrografted GC electrode. Corresponding phenomenon is related to the significantly higher surface area of GR and MWCNTs compared to the polished GC. The obtained Γ_{AQ} values suggest the suitability of this method for the application of carbon nanomaterials that need high loading of surface modifiers [1].

The increase in electrocatalytic activity toward the ORR was registered in case of spontaneously AQ-modified MWCNTs and OH^- ionomer coated GC electrode compared to the GC electrode coated with unmodified MWCNTs and OH^- ionomer. An analogous phenomenon was not evidenced in case of GR-based electrodes. Additionally, the long-term ORR tests showed that the OH^- ionomer coating on GR nanomaterial is preferred for sustaining the electroactive functional groups on GR, but in time the inhibiting effect on the ORR intensity was observed most likely due to OH^- ionomer [1].

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Photoelectrochemical Activity of Mesoporous TiO_2 Films Formed by Anodizing in Hot Phosphate/Glycerol Electrolyte

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Anodizing of metals is a simple and effective electrochemical process to form self-ordered porous oxide structures. The most well-known nanostructured anodic oxides are highly ordered porous anodic alumina films with honeycomb morphology, which are formed in acid electrolytes, such as sulfuric acid, oxalic acid and phosphoric acid. When titanium is anodized in fluoride-containing electrolytes, nanotube array films are usually formed. The anodic films thus formed are amorphous, but converted to crystalline anatase after heat treatment at ≥673 K. We have also found that anatase crystalline mesoporous films are formed by anodizing of titanium in hot phosphate/glycerol organic electrolytes at 433 K [1]. The characteristic features of this anodic film are 1) small pore sizes of ~10 nm, leading to high surface area, and 2) direct formation of anatase phase without heat treatment. The as–formed crystalline anatase films are photoelectrochemically active [2, 3], but it would be further improved since the anodic oxides contain an amorphous phase as well. In this study, we have formed the mesoporous anodic TiO_2 films by anodizing at several voltages up to 90 V. Cathodic treatment of the anodized titanium was also carried out to introduce the electron trap sites in the band gap of TiO_2 and to enhance the photoelectrochemical activity.

Mesoporous anodic films of ~4 μm thickness were formed by anodizing of 99.5% pure titanium sheet at 20, 60 and 90 V in glycerol electrolyte containing 0.4 mol dm^{-3} K_2HPO_4 and 0.4 mol dm^{-3} KH_2PO_4 at 433 K. Anatase phase was found in the anodic films formed at all formation voltages, but rutile phase was also found at 90 V. Photocurrent was measured during cyclic voltammetry under UV light irradiation in 0.1 mol dm^{-3} $HClO_4$ solution. It was found that photocurrent decreases largely with an increase in the formation voltage despite increased crystallinity at higher formation voltages. The electrochemical impedance spectroscopy (EIS) measurements of the anodized specimens indicated that the resistance of the anodic films increased as the formation voltage rose.

Thus, in order to reduce the resistance of the anodic films, cathodic treatment of the anodized titanium was conducted at -1.4 V vs Ag/AgCl in 0.1 mol dm^{-3} Na_2SO_4. The EIS measurements disclosed that the resistance of the anodic films was remarkably reduced for the specimens anodized at all voltages. Associated with the reduction of the resistance of the anodic films, the capacitance of the anodic films were also highly enhanced, suggesting the large increase in the effective surface area. Consequently, we found large increase in the photocurrent of the anodized titanium after the cathodic treatment. Hydrogen gas treatment of TiO_2 at elevated temperatures has been often used [4], but the present study demonstrated that the cathodic treatment is also useful to enhance the photoelectrochemical activity of TiO_2.

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(Photo)Electrochemically Active Functional Hybrids of Multilayer CVD Graphene Decorated with Colloidal TiO_2 Nanocrystals

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A direct and facile solution-based procedure has been implemented for manufacturing optically transparent and UV-light photoactive hybrids based on graphene (from one to 5 layers), grown by Chemical Vapor Deposition (CVD) and decorated with TiO_2 nanocrystals (NC) surface functionalized with 1-pyrene butyric acid (PBA). PBA functionalization was obtained by a capping exchange procedure onto pre-synthesized organic-capped NCs [1].

An in-depth characterization by SEM, EDS, AFM, Raman spectroscopy, Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements demonstrated the successful immobilization of the colloidal NCs on the graphene multilayers, which preserves or even enhances the graphene intrinsic structural properties. In particular, we observed an electrical conductivity higher than that measured for bare graphene, which has been accounted for by a p-doping effect of graphene, due to a hole transfer from the nano-objects to graphene, mediated by the short aromatic ligand acting as a charge channel.

The hybrid~~s~~ properties are strongly dependent on the number of layers of CVD graphene. The use of two redox mediator probes [inner-sphere, surface sensitive ($K_4Fe(CN)_6$) and outer-sphere, surface insensitive ($Ru(NH_3)_6Cl_3$)], in a synergistic CV and EIS study, allowed to understand these features from a morphological point of view. The results showed a strong difference between the mono-, the bi- and the other multi-layers, in terms of different diffusional mechanism and redox active sites [2-4].

Moreover, the stacked layers of the pyrene-coated TiO_2 NCs are found to increase the electroactivity, the capacitive behavior, as well as the photo-electrical response of graphene, concomitantly maintaining its high charge mobility. The photoelectrical conversion of the hybrid is enhanced of 50% with respect to the bare graphene, with a long recombination lifetime of the photogenerated electron-hole pairs.

For all the above reasons, the photoactive composite has a great potential as an optically transparent component for manufacturing photoanodes to be integrated in solar cells or photodetectors and in FETs or (photo)electrochemical sensors, also exploiting the possibility of photorenovate the sensor surface [5].

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Electrochemical Conversion of CO_2 into Formic Acid on Boron-Doped Diamond Electrodes

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Introduction

In the past few decades, CO_2 conversion into useful chemicals has been attempted by various methods.[1] Electrochemical CO_2 reduction has attracted much attention as one of the most promising methods because it can be performed under ambient temperatures and pressures without using the special reagents and catalysts. On the other hand, it is known that the absorbing ability of the intermediate, $CO_2^{\bullet-}$, on electrodes affect the selectivity of the final products.[2] Formic acid can be produced from CO_2 on Sn, Pb, Hg, and In electrodes. Although these electrodes enable us to produce formic acid at very high faradaic efficiency due to high hydrogen overpotential, there are problems of their toxicity and stability.[3] Therefore, we focus on boron-doped diamond (BDD) electrodes which exhibit wide potential window and high durability. In this work, we investigated the electrochemical reduction of CO_2 using BDD electrodes to produce formic acid.

Experimental

BDD electrodes were prepared onto silicon wafer substrates by a microwave plasma-assisted chemical vapor deposition method, and evaluated with Raman spectroscopy and a scanning electron microscope (SEM). The electrochemical experiments were performed in a two-compartment cell separated by Nafion® membrane with three electrode system (working electrode: BDD, counter electrode: Pt, reference electrode: Ag/AgCl). N_2 gas was bubbled into the electrolytes to remove oxygen. Then, CO_2 gas was bubbled into the electrolytes to obtain CO_2 saturated solution. The electrolysis of CO_2 saturated solution was performed at -2 mA/cm^2 for 1 hour. The products were analyzed by a gas chromatography and a high-performance liquid chromatography.

Results and Discussion

Raman spectrum showed two wide bands at around 500 cm^{-1} and 1200 cm^{-1}, which are attributed to B-B and B-C vibrations, respectively. In addition, a peak was observed at around 1300 cm^{-1}, which is attributed to the center zone optical phonon of diamond. SEM images showed the polycrystalline nature with grain size of about 5 μm. Consequently, polycrystalline BDD films were synthesized successfully.

Formic acid was obtained as the main product by the electrochemical reduction of CO_2 on BDD electrode at -2 mA/cm^2 in NaOH, KOH, RbOH, and CsOH aqueous solution saturated CO_2. In RbOH aqueous solution saturated CO_2, the faradaic efficiency for the production of formic acid reached to the maximum, and the hydrogen evolution was suppressed. This is because Rb cations strongly adsorb and completely cover BDD surface. As the result, the atomic hydrogen arising from the decomposition of water molecules cannot occupy any surface sites. In addition, more than 75% faradaic efficiency was kept for 48 hours using BDD (Fig. 1). After 48-hour electrolysis, the morphology of BDD electrode was examined by SEM, which showed no significant change in comparison with that before electrolysis.

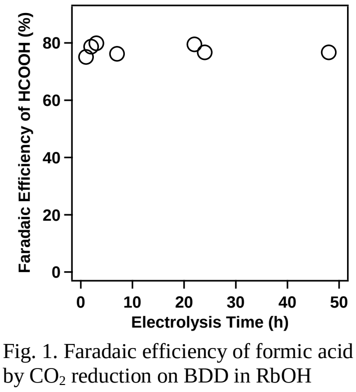

Fig. 1. Faradaic efficiency of formic acid by CO_2 reduction on BDD in RbOH aqueous solution for 48 hours

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Advanced Electrochemically Active Materials Based on Lignosulfonates

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Renewable and easily accessible materials are nowadays requested for production of environmentally friendly and cost efficient electrochemical devices. Biopolymers with redox functions such as lignin derivatives are promising electroactive materials, which can be used in the development of chemically modified electrodes for electrocatalytic, electrochemical sensing and charge storage purposes [1-3]. The biopolymer lignin is found in green plants, and makes up 20-30 % of the weight of wood while lignosulfonates arises from pulp and paper industry as a byproduct of paper manufacturing. From chemical point of view lignosulfonates have no regular structure, however, they are mainly composed of phenylopropane segments (C_9 units) having hydrophilic sulfonic grups and electroactive methoxyphenol grups [4]. Being polyphenolic compounds lignin derivatives show substantial electroactivity especially in the range of anodic potencials. This is due to the fact of developing of quinone/hydroquinone redox couple during oxidation process. Thus, they can be generally classified into quinone based redox polymers undergoing fast proton-coupled reversible redox transitions over wide pH range [2].

There are several types of hybrid and composite materials consisting of lignosulfonates or other technical lignins. Multifunctional lignin structure makes it hardly possible to clearly divide the materials described in literature. These materials differ from each other with the physical interactions occurring between them, such as, electrostatic interaction, intermolecular π–π interaction or Van der Waals interaction. Composites in which lignin was covalently bound to other components have also been tested; hydrogen bonds have also occurred [1-7].

Generally, following types of material groups can be distinguished:

a) Lignin/conducting polymer materials;
b) Lignin/carbon materials;
d) Lignin/nanoparticles materials;

Recently, a great interest of application of lignin derivatives in the development of charge storage devices can be observed. So far, the most promising results have proved that lignin derivatives can be considered as a electroactive materials for the application in light and inexpensive organic batteries or supercapacitors [1,5]. In the course of our research, we also found that lignosulfonates are excellent marterials for the development of conducting polymer based electrocatalytic materials [3]. Moreover, one of the most promising application of lignosulfonates is the synthesis of noble metal nanoparticles, were this biopolymers can play the role of both reducting and stabilizing agent [6]. Taking into account relatively dense aromatic structure of lignosulfonates, they possess a tendency to adsorb on both insulating and conducting surfaces. Therefore, this biopolymers may be used to tune carbon surfaces due to strong π–π interactions and hydrophobic attraction of alkyl chains in lignosulfonate [7].

With this talk the results regarding the synthesis and electrochemical performance of different lignin-based electroactive materials will be presented in order to allow a broad view on the such materials nowadays.

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Electrochemical Activation of a Boron-Doped Diamond Electrodes by Cathodic Reduction Treatments

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Introduction

It is widely known that boron-doped diamond (BDD) electrodes have excellent properties such as wide potential window, low background current, and high durability. Therefore, BDD electrodes are attractive for wide variety of applications. On the other hand, the electrochemical properties of BDD are affected by surface condition.[1] It is well known that hydrogen-terminated BDD exhibits greater electrochemical activity and sensitivity in comparison with oxygen-terminated BDD. Therefore, many researchers use cathodic reduction (CR) treatment before measurements to obtain hydrogen-terminated surface.[2,3] However, the conditions of CR treatments conducted in several reports differ from each other, and there are little knowledge about what factors of CR treatments influence the surface hydrogenation. Herein, we investigated how the various conditions of CR treatments had effect on the electrochemical properties and surface condition of BDD electrodes.

Experimental

BDD electrodes were prepared onto Si(111) wafer substrates by a microwave plasma-assisted chemical vapor deposition method. The boron-to-carbon ratio in feed gases was 1000 ppm, and deposition time was 6 hours. Anodic oxidation (AO) treatments were performed in 0.1 M H_2SO_4 aqueous solution at +3 V *vs*. Ag/AgCl for 5 minutes. Then, CR treatments were conducted with variation of applied potential and the pH of electrolytes. The electrochemical properties and the surface condition of BDD before and after CR treatments were examined by cyclic voltammetry (CV) in 1 mM $K_3[Fe(CN)_6]$ aqueous solution containing 1 M KCl and X-ray photoelectron spectroscopy (XPS), respectively.

Results and Discussion

CV measurements were conducted after each treatment with variation of the pH of electrolytes (pH 0.9 ~ 13.0). The peak-to-peak potential separation (ΔE_p) decreased after CR treatments with the lower pH solution (Fig.). Additionally, after CR treatments with variation of applied potential (−1.5 V ~ −5 V *vs*. Ag/AgCl), ΔE_p decreased with applying more negative potential. It is well known that heterogeneous electron transfer is accelerated by CR treatment on BDD. Based on the results, the electrochemical activation of BDD could be accelerated by applying more negative potential in lower pH solution.

In the C 1s peaks deconvoluted from XPS spectra before and after CR treatments, peak area of the component attributed to C-H bond increased, and that attributed to C-O bond decreased with decrease in the pH of electrolytes and applied potential for CR treatments. These results indicated that applying more negative potential in lower pH solution could accelerate the surface hydrogenation of BDD, which led to the electrochemical activation.

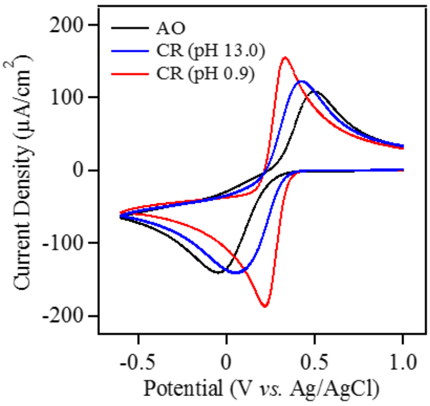

Fig. CVs of 1 mM $K_3[Fe(CN)_6]$ + 1 M KCl aqueous solution after CR treatments in different pH solution.

In previous work, the active sites on the surface of BDD can be deactivated by surface oxygen functional groups, and re-activated by all-around surface hydrogenation with hydrogen-plasma treatment.[4] In contrast, our results suggested that partial hydrogenation by CR treatment also can activate BDD. Therefore, it is implied that the hydrogenation by CR treatments could occur at the electrochemical active sites preferentially.

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Tuning the size and shape of novel nanoscale metal oxide photocatalysts using the cathodic corrosion method

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Growing energetic demands, in conjunction with the ever-growing consensus surrounding the increasing adverse effects of climate change and global warming, have led to much research dedication to the development of renewable energy technologies. A hydrogen economy has long been sought after, but with most the earth's hydrogen stored in water and the main source of hydrogen production involving the burning of fossil fuels, a widely applicable alternative is required.

Transition metal oxide semiconductors were first shown to be active towards hydrogen evolution from water under UV-irradiation by Fujishima and Honda.[1] Nanoscale photocatalysts are desired to overcome the limitations surrounding the low natural abundance of solar UV light by modifying the semiconductor band gaps to harness more of the visible spectrum and minimize ion carrier migration distances. Current state-of-the-art photocatalysts include TiO_2, $FeTiO_3$, H_2WO_4, $BiVO_4$ and their metal-doped analogues.

Cathodic corrosion[2–4] is a powerful tool for the electrochemical synthesis of nanomaterials with enhanced electrochemical properties. Here we demonstrate that the particle size and shape of mixed transition metal oxide semiconductor nanoparticles can be tuned by changing the synthesis conditions. This has resulted in an effective way to change the photocatalytic properties of the nanomaterials. The structure-reactivity relationship for the photocatalytic water oxidation will be presented.

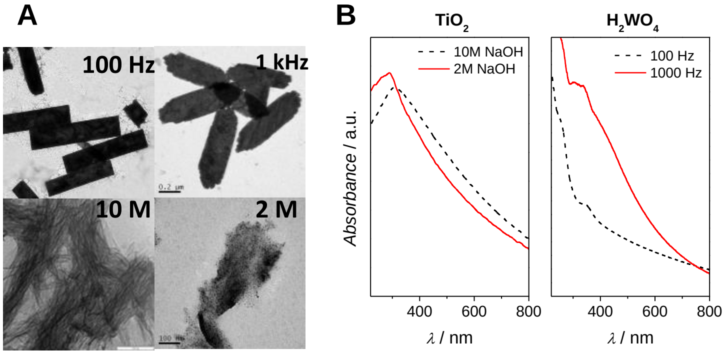

Figure 1. (A) TEM images of H_2WO_4 (top) and TiO_2 (bottom) nanoparticles synthesized by cathodic corrosion using varying conditions as indicated in the figure; frequency of the square wave form and concentrations of NaOH (B) UV-vis absorption spectrum of the H_2WO_4 and TiO_2 nanoparticles.

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Constructive Impact Experiments of Single $HAuCl_4$ Micelles

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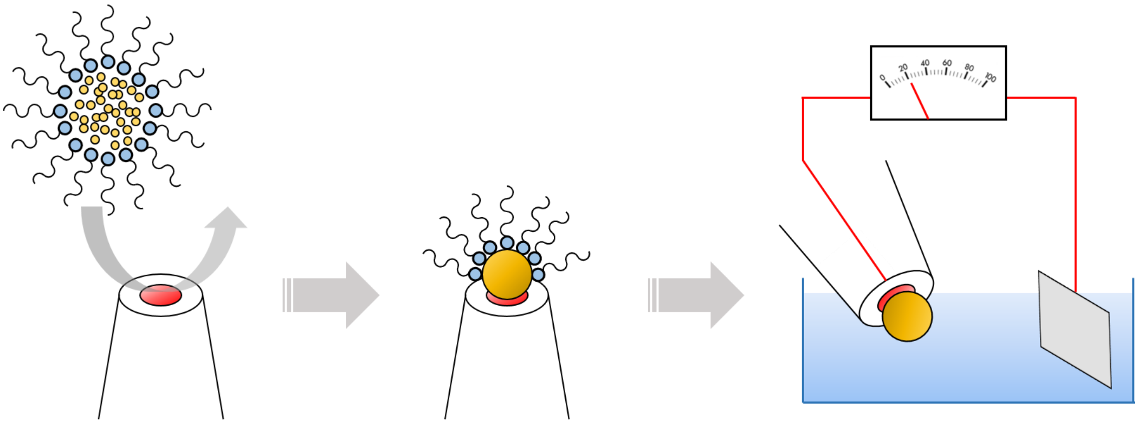
Nanoparticles are used in a variety of fundamental to applied research owing to their optical properties and reactivity. However, most electrochemical studies that employ nanoparticles are focused on ensembles instead of single entities. These studies commonly yield an average or sum of the properties of the size-distributed particles. Inactive nanocatalysts are, thus, hardly distinguishable from highly active particles. Single nanoparticle modified electrodes allow to resolve the shortcomings of ensemble studies by enabling low-current investigation of single objects. Using easily accessible techniques, a far deeper understanding of processes at and of nanoparticles is gained. One by one, the size, catalytic activity or formation process and many more features can be probed.[1]

Especially the lower size regime of nanoparticles, roughly from 40 nm and below, is of tremendous interest for biomedical application such as cancer treatment, industrial applications like catalysis, and environmental applications in solar cells and contamination sensing in water. This size regime is governed by extraordinary catalytic activity, optical behavior but also by remarkable changes thereof depending on the size. Removing or changing only a small part of a nanoparticle can cause a large change in properties. The nucleation and growth of a nanoparticle is a core piece in understanding how to afford a particular size and monodisperse product, and how this correlates with their physicochemical properties, for which nano-impacts are one of the most suitable analysis techniques.[2,3]

Herein, we present the constructive impacts of single $HAuCl_4$ micelles that are protected with a diblock copolymer, so as to form monodisperse nanoparticles of precisely known individual size by means of electrochemistry. Instead of a chemical reduction and therefor post-treatment analysis, using the electrical potential at an electrode and measuring the individual reduction charge transferred per particle formed, provides information of the underlying processes. By these means, also the addition of chemical reducing agents such as $NaBH_4$ is avoided and therefore purification of the product material is simplified. The clean functionalized electrodes may conveniently be tested for their electrochemical features.



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Electrochemical and Physical Properties of Prussian Blue (PB) composites: stable electrocatalytic materials.

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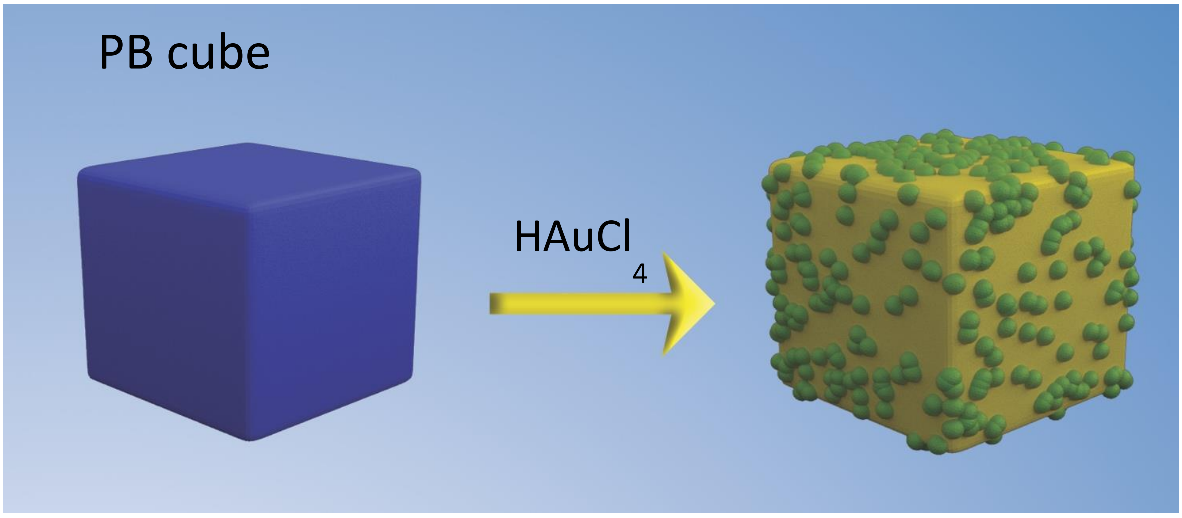
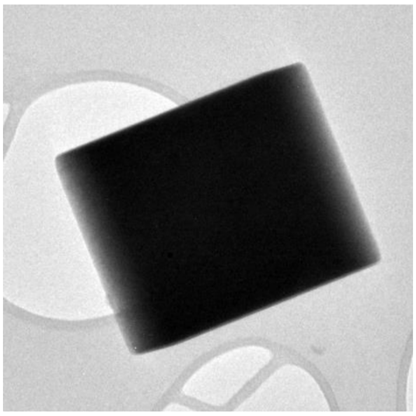
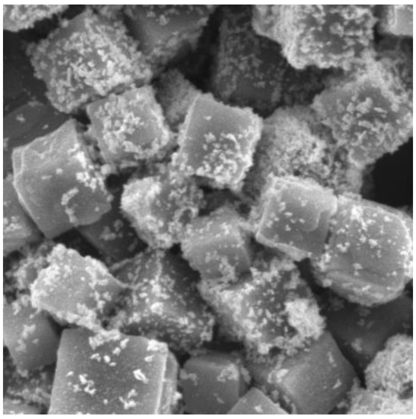
Galvanic replacement of Prussian Blue cubes with $HAuCl_4$ leads to a stable AuCN/Prussian Blue (PB) Nanocube composite. The composite has an increased surface area and pore volume, but smaller surface pore sizes than pure PB cubes. For electrocatalysis and sensing, the AuCN/PB composite has much improved stability, leading to improved limit of detection and sensitivity for H_2O_2 sensing. This stability was attributed to the stabilization of the surface of PB with AuCN, which prevents decomposition of the reduced $Fe^{II}Fe^{II}$ derivative of PB during electrocatalysis. The new material shows that redox active Molecular Organic Frameworks (MOFs) used for electrochemical sensing or catalysis can be tuned for surface porosity, and stabilised via galvanic replacement with a noble metal salt, leading to improved electroanalytical performance. A range of similar materials under development will also be discussed.





Schematic of composite synthesis (above), and images of PB (left) and PB composite (right)



Modification of Gold Nanoparticles on Nickel Electrodes by a Galvanic Replacement Reaction

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Metal nanoparticles (NPs) have been attracting active attention as functional units for electrode modifications because they can change the electronic communications on the conductive materials. If we would like to attach gold NPs (AuNPs) on the ITO surfaces, the functional bridging reagents such as (3-mercaptopropyl)-trimethoxysilane have been adopted. While many successful results have been obtained using the bridging reagents, our group proposed a simple methodology to attach AuNPs on the ITO surfaces. Namely, by applying a seed-mediated growth method, which was originally developed for synthesizing metal nanorods in aqueous solution, to the surface modification, the crystal growth of AuNPs on the ITO surfaces could be performed from the Au nanoseed particles physically adsorbed on the ITO with keeping adhesion contacts [1]. As the results, successful electroanalysis could be performed using thus prepared AuNP-attached ITO electrodes [2].

While we have been utilizing Au nanoseed particles followed by the nanostructural growth in growth solutions for several years, only the attachment of Au nanoseeds might change the electrochemical characteristics of the base conducting materials. Although the effects of Au nanoseeds on ITO electrodes were relatively scarce, it was found that the electrochemical characteristics of a Ni electrode could be changed by modifying Au nanoseed particles, whose amount was very small, to those of Au-based electrodes [3].

Although we utilized the absorption of Au nanoseed particles on Ni surface in the previous work [3], Au can be attached or deposited on Ni surface using a very simple method. That is, because the oxidation potential of nickel to nickel ions is relatively negative, it is expected that Au deposits on Ni electrodes by the simple galvanic replacement reactions. When we use a wire of Ni as a base electrode, the modification of AuNPs was possible by just immersing a Ni wire into an aqueous solution of $HAuCl_4$. The modified states of Au were evaluated by observing SEM images and cyclic voltammograms of H_2SO_4 and glucose. As the result, it was found that the immersion time and the concentration of $HAuCl_4$ significantly affected the modification of Au. The progresses of this approach will be presented in the meeting.

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1D core-shell nanostructures formed by electrodeposition of metals and metalloids in anodic TiO_2 nanotubes

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The anodizing is a high-voltage electrochemical conversion process that forms barrier-type oxides or nanoporous/nanotubular layers on valve metals and alloys mainly depending on the composition of electrolyte used.[1] The key to achieve the ordered nanoporous/nanotubular structures is a displacement of the film material above the original surface position due to synergistic effect of pits generation (field assisted oxide dissolution), stress generated at the metal-oxide interface including electrostriction and plastic oxide flow switching the growth of the barrier-film to nanotube/nanopore. Typically, the TiO_2 nanotube array formed in organic electrolytes such as glycerol, dimethyl sulfoxide, ethylene-glycol is obtained in the form of close packed structure in which the nanotubes nearly stick together with the tube walls. A fundamentally different nanostructure from that is obtained in diethylene-glycol electrolyte. The nanostructure is characterized by free standing nanotubes separated by an interconnecting space much bigger than the thickness of nanotube wall (Fig. 1). [2,3] Such geometry gives possibility for deposition of secondary materials using electrochemical processes in view of improved wetting behavior of the nanostructure. [4] Herein we report on how to control the synthesis of nanotubes to achieve unique oxide geometries, we discuss functional properties of nanostructures and report an examples of composites formed between oxide layer and Si, CdSe, Au, Pt. An examples of the nanostructured energy storage devices will be demonstrated. [4]

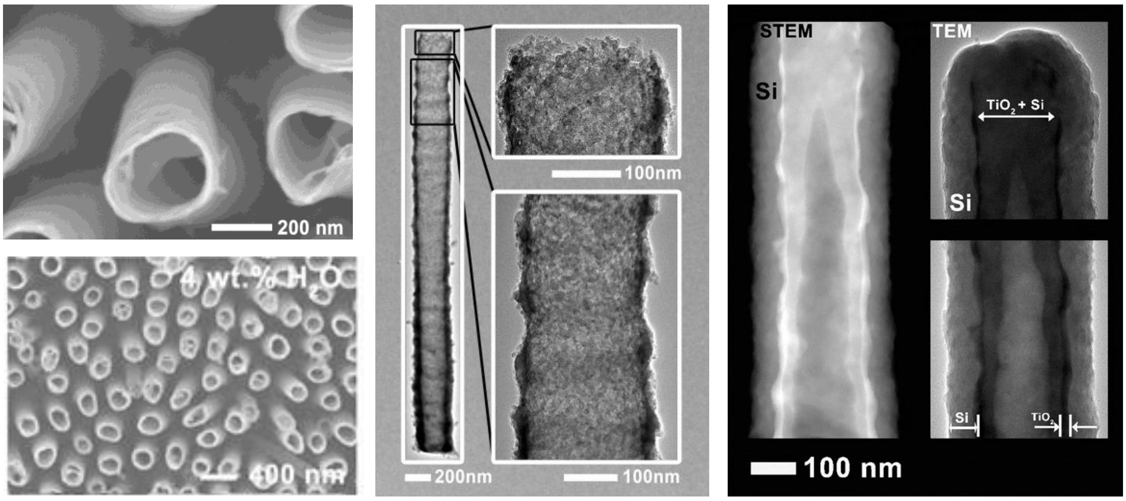

Fig. 1 SEM and TEM images for TiO_2 nanotubes formed at 60V and 70V for 16h in diethylene glycol electrolyte containing 0.1M HF and H_2O 2-4 wt.%. The right figure shows STEM and TEM images for Si electrodeposited on TiO_2 nanotubes and applied as negative electrode in lithium ion battery.

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Optimization of Composite Sensing Material Properties for Simultaneous Temperature and Humidity Monitoring

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Temperature and humidity micro-sensors are of great interest in mobile applications, such as micro-mlectro-mechanical systems (MEMS) and industrial environments. Conventional temperature and humidity sensors are separated sensing devices and usually horizontally integrated in different circuit loops. In this work, all the circuit components are inkjet-printed on flexible plastic films with sensor dimension less than 1 X 1 mm. The electrochemical properties can also be accurately controlled by adjusting ink composition. Temperature sensing is achieved by measuring the electrical resistance change of a printed nickel oxide (NiO) thin film, while humidity sensing is obtained by the capacitance change of a printed Nafion film. Instead of horizontal integration, the temperature and humidity sensors are vertically integrated into a single RC parallel circuit to realize size reduction. However, the high resistance of nickel oxide thin film at room temperature leads to measurement obstacles for the printed RC circuits. In order to solve this problem, Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate ionomers mixtures (PEDOT:PSS) is added to the NiO nanoparticle ink to reduce the resistance. To optimize the circuit effectiveness, detail RC circuit simulations is also performed to provide design guidelines for the printed circuits. To conclude, a micro tempaerature and humidity sensor combinaiton circuit is successfully fabricated. The device performance follows Arrhenius relation as well as isotherm adsorption with wide range of relative humidity (RH 35–85%) and temperature (20-80 °C). The printed circuits can be miniaturized and integrated with electronic devices to achive wireless sensing network for smart buildings.

Elucidating Next Generation Battery Materials with *in situ* Raman Spectroscopy Coupled to Scanning Electrochemical Microscopy

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Understanding the fundamental connection between structure and reactivity in next generation battery materials is paramount for predicting long-term cyclability, stability, and efficacy. Here we describe the implementation of simultaneous, *in situ*, and spatially-resolved measurements using scanning electrochemical microscopy (SECM) and Raman spectroscopy. This integrated instrument enables correlation of redox reactivity with electronic structure of operating battery materials by using a versatile toolbox of chemical imaging including local electronic and ionic conductivity and surface reactivity.

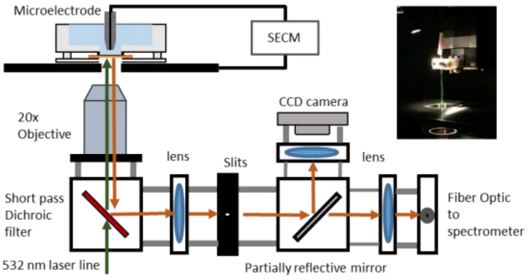

Fig 1. Schematic for Raman-SECM setup.

The setup, Figure 1, consists of a laser line of a Raman microscope aligned to the electrode probe of a SECM. Co-alignment of the laser line to the probe of the SECM enables access to a range of electrodes from 50 nm to 25 µm, allowing the resolution of the redox probe to match or surpass the spectroscopic resolution. The time scale of acquisition for Raman data can reach the second regime, without surface-enhancement, facilitating the tracking of electronic and ionic events in solution and at surfaces in relevant time periods. This arrangement has allowed for the study of various battery materials such as redox active colloids (RACs) for flow batteries, and graphene for conventional ion intercalation batteries.

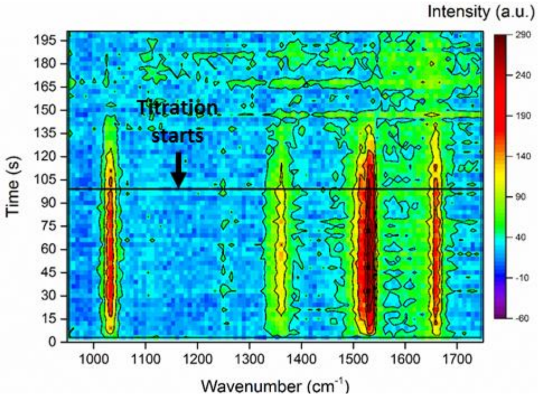

Fig 2. Raman intensities of viologen RAC vibrational modes when charged then subsequently discharged via titration a redox species generated at the SECM probe.

RACs are an attractive material for redox flow batteries because of their modular redox properties, and size tunability.[1] However, in these materials a careful balance between ionic and electronic transport is required to afford optimal performance. The combination of Raman spectroscopy and SECM has enabled us to explore these two coupled charge transport parameters. Viologen RACs become more Raman active once reduced because of the resonance Raman effect allowing for studies of monolayer films without requiring surface-enhancement.[2] With our current spectroscopic setup aligned to an SECM probe, we can monitor the vibrational changes associated with a RAC film when electrochemical interrogated by an SECM probe (Fig 2.). Additionally, recent experiments in our lab have also enabled us to follow electronic and ionic processes on thin graphite electrodes undergoing lithiation.[3] In both cases, the merging of these two powerful analytical techniques helps elucidate the correlation of electronic and ionic reactivity with surface structure. Which promises significant progress in next generation battery materials and can be applied to our understanding single particle electrochemical reactivity, catalysis, and other approaches such as tip-enhanced Raman spectroscopy and scanning electrochemical cell microscopy.

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Poison-Tolerant Catalyst for Electrocatalytic Production of Formate from CO_2

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The growing world energy demand and adverse environmental effects of fossil fuel usage have prompted the need for clean, carbon-neutral, and sustainable forms of energy. This global challenge can be addressed by gaining fundamental and predictive understanding of how to transform and store carbon dioxide into fuel and chemicals in a selective and efficient manner. Here, we describe the electrochemical production of formate, a high-value chemical commodity used in industry and fuel cells, using a robust, poison-tolerant Pd catalyst. Pd-based nanoparticles are very efficient and selective for reducing CO_2 to formate, however, their performance is marred by poisoning by CO, which is produced as a minor product under catalytic turnover. We will demonstrate a simple new Pd-based catalyst to overcome this challenge. The synthesis, function, CO resistance and mechanism of the catalyst will be discussed in detail.

Electrochemical detection of trace heavy metals using bismuth particles/polypyrrole film/ionic liquid modified carbon paste electrode

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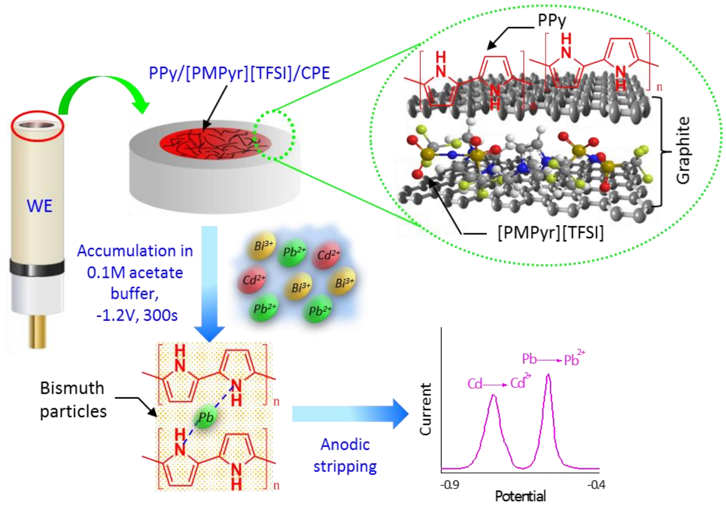
Heavy metal contamination is one of the major problems for environment and human health due to high toxicity, are also a major environmental contaminant found in air, soil and drinking water. Lead ion, Pb^{2+}, is one of the most toxic environmental pollutants even at very low concentrations. Thus, developing sensitive and selective strategies for Pb^{2+} detection has been of great concern in the past decades as well as recent years. The electroanalytical techniques are one of the most techniques used for detection and analysis of trace heavy metals ions, because of their attractive features, including easiness, robustness and their low cost.

Different approaches have been used to develop high-performance electrochemical sensors based on modified electrodes by conducting polymers[1]. Polypyrrole (PPy) is one of the most investigated conducting polymers, because of its facile synthesis, good conductivity, redox properties, long-term environmental stability and biocompatibility. PPy has shown also promising applications including sensors, photovoltaic/solar cells or corrosion protection.[2]

Room Temperature Ionic Liquids (RTILs) are a new class of purely ionic, salt-like materials that are liquid at unusual low temperatures. Because of their high stability, fair electrical conductivity, and very low vapor pressure, ILs hold a great promise for green chemistry applications in general and for electrochemical applications in particular.[3]

In the present work a new composite carbon paste electrode based on bismuth particles, PPy film and ionic liquid, 1-methyl-1-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide [PMPyr][TFSI], has been fabricated. This modified electrode shows very attractive electrochemical performances compared to other modified electrodes previously reported in the literature, notably in terms of sensitivity and stability. The interface properties of the obtained composite were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and the morphology was examined by scanning electron microscopy (SEM-FEG). This new composite demonstrated interesting performances for heavy metals detection, and also a better sensibility, and stability.



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Dry Transfer Method of Graphite onto Paper for High Performance Flexible Electrochemical Sensors

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There is an increasing interest on flexible carbon-based electrodes with high performance [1-3]. We will demonstrate a direct, simple, and dry transfer method of graphite onto paper with unprecedented electrochemical features on flexible substrates. We have selected soft pencils to transfer graphite onto paper and achieved comparatively low sheet resistances (45±2 Ω sq^{-1}). The sluggish electron transfer observed on bare pencil drawn surfaces was enhanced by two steps. The surface was first electrochemically oxidized and reduced. The standard heterogeneous rate constant was found 5.1×10^{-3} cm s^{-1}, which is the highest reported so far for pencil drawn surfaces. The origin of such unprecedented performance was characterizaed by atomic force microscopy, laser scanning confocal microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, and contact angle measurements. We observed that the oxidation process causes the formation of a few microcracks on the electrode surface. Also, different chemical groups are formed and reduced due to the electrochemical treatment. Some of the weakly attached graphite particles and carbon nanodebris are detached from the electrode surface after the electrochemical treatment. Our results suggest that oxidation process leads to chemical and structural transformations on the electrode surface, and these transformations are responsible for the electrode response improvements. As a proof-of-concept, we have modified the pencil drawn surface with Meldola's blue to electrocatalytic detect nicotinamide adenine diclucleotide (NADH). The electrochemical device exhibited the highest catalytic constant (1.7×10^{5} L mol^{-1} s^{-1}) and the lowest detection potential for NADH reported so far in paper-based electrodes. The electrochemical detection of NADH was also evaluated in artificial blood serum samples and the results are very promising toward the development of NADH-based biosensors.

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Metal nanoparticles - polysaccharides hybrids for electrode modification

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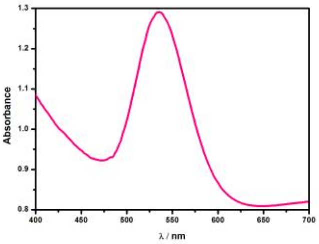
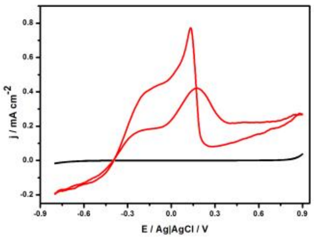
Synthesis of new, environmental friendly materials with catalytic properties consume a lot of time of scientists in 21st century. Here we would like to demonstrate a new type of polymer/polysaccharide matrix, based on pectin as a host for noble metal nanoparticles (gold, platinum). Pectin are cheap, readily available and edible. They could be found in apple, citrus, or citrus peels it means, and may be possessed from waste or buy in any grocery shop.
First we will present optimised conditions for synthesis metal (Au, Pt) nanoparticles - pectin gel hybrids and results of their physicochemical studies. They are formed by reduction of a given noble metal precursors as $HAuCl_4$ or H_2PtCl_6 and the absence of any additional reducing agent, under stirring. The obtained samples exhibits UV-vis spectra characteristic for the presence of metal nanoparticles. They have somehow fibrous structure with most metal nanoparticles placed next to the fibers as seen on TEM images.





Next we will to present an electrochemical properties of gelled and ungelled matrix deposited on the electrode surface. The electrodes modified with this material exhibit cyclic voltammograms characteristic for a given metal indicating formation of percolation paths by nanoparticles. In alkaline solution they exhibits electrocatalytic properties towards glucose oxidation.

Electrocatalytic Properties of Modified Carbon Paste Electrodes with Nanostructured Carbon Materials and Ionic Liquids.

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Carbon paste electrodes (CPE) offer several advantages in comparison with other types of modified electrodes, mainly due to the easiness of its preparation by a direct addition of the modifier agent into the electrode material [1]. Regarding this subject, the simultaneous use of ionic liquids (ILs) and nanostructured carbon materials has been successfully applied for the sensing and quantification of several compounds [2].

In this work a comprehensive study of the electrochemical response of several redox probes such as dopamine (DA), norepinephrine (NE), 4-nitrocatechol (4-nitCHT), potassium ferricyanide (FICN) and ferrocenemethanol (FCM) over carbon paste electrodes modified with ionic liquids and nanostructured carbon materials is presented. The ionic liquids used in this work as co-binders in the presence of paraffin oil (PO) for the electrode modification were selected by means of its structural features in order to study the influence of this factor on the electrochemical response of the redox probes. Other factors, such as ionic liquid/paraffin oil ratio, the heating of the carbon paste before its use, and the addition of multiwalled carbon nanotubes and carbon nanofibers into the paste were also studied by square wave and cyclic voltammetries. ILs used in this work were the bis(trifluoromethyl)sulfonylimides of 1-ethyl-3-methylimidazolium (IL1), 1-methyl-3-propylimidazolium (IL2) and 1-butyl-3-methyl imidazolium (IL3) and the hexafluorophosphates of 1-butyl-3-methyl imidazolium (IL4) and 1-butyl-3-methylpyridinium (IL5). 50 mM, pH 7.0 aqueous Britton-Robinson buffer was used as the supporting electrolyte for DA, NE, 4-nitCHT, while for FCM and FICN a solution of 0.2 M aqueous KCl was employed. All potentials were measured against Ag/AgCl reference electrode.

In general, the addition of ionic liquid as co-binder increases the signal for every redox probe, finding an optimum IL/PO ratio (between 20-40% w/w) for which the response reaches its highest value, followed by a gradually decrease for higher IL contents.

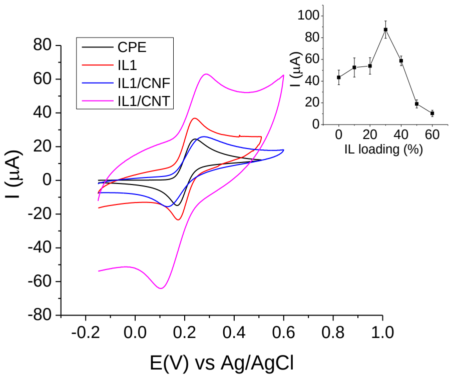

Fig. 1. CVs for 1 mM DA in Britton-Robinson buffer pH 7.0. on different electrodes. Inset: SWV currents for DA oxidation varying the amount of IL1 used as a co-binder.

The addition of carbon nanotubes (10% w/w against graphite) in the presence of ionic liquid further increased the signal for all the redox probes, and for some of them an increment of electrochemical reversibility was also detected. On the contrary, the addition of carbon nanofibers had no impact on the signal, obtaining almost the same results than in the case of the electrode prepared using only graphite as the carbonaceous phase. Despite the signal enhancement observed for the modified electrodes using ionic liquids in the absence or presence of carbon nanotubes, an increase in capacitive current is also observed. Heating the carbon paste (80°C, 5 min) did not improved the signal and a slight increase in capacitive current was observed for the electrodes contrary to some reported results [3].

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Light activated electrochemistry on silicon electrodes: opportunities and challenges

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Light-addressable potentiometric sensors (LAPS) based on silicon use AC photocurrents to detect changes in the capacitance of the semiconductor depletion layer, making possible LAPS to sense changes of pH, redox potential and ions concentration in aqueous solutions. However, LAPS remain as chemical sensors with no DC currents crossing the interface. A crucial step for achieving faradaic silicon-based devices capable of operating in aqueous environments consists on avoiding the growth of the insulator SiO_x layer. An elegant solution relies on protecting silicon with a self-assembled monolayer based on 1,8-nonadiyne that is still sufficiently thin for allowing electron transfer through it, so electrochemical information can be either read from or written onto these surfaces by using light.[1]

This is possible because the electronic properties of silicon can be tuned by controlling the type and the level of doping species. Generally, non-degenerated n-type silicon ($N_D < 10^{18}$ cm^{-3}) is suitable for studying photooxidative processes of redox molecules attached over the SAM and non-degenerated p-type silicon ($N_A < 10^{18}$ cm^{-3}) can be employed for photoreduction reactions. Since the surface remained in the dark is not active for electrochemistry, distinct spots can be individually read/modified by positioning the spotlight in the desired location. That is, dynamic electrochemistry can be performed whenever you want by turning light on/off and wherever you want by controlling the position of the light beam on the surface. If the spotlight presents micrometer dimensions, an array of microeletrodes can be thought by only using a connection wire and with no need of microfabrication pre-steps. This possibility is promising as it may overcome a central tenet of electrochemistry in which any electrode in an array must be connected to an external circuit via a wire, which demands considerable space and requires pre-organization of the surface.

DNA-based diagnostic tests are considered here to illustrate relevant opportunities in the field. The experiments consisted on monitoring the hybridization of probe nucleic acids immobilized on a silicon-based substrate with target nucleic acids present in solution. Interestingly, electrochemical signaling approaches based on labelling DNA molecules with intercalators capable of being allocated between adjacent pairs of double-stranded DNA after hybridization occurs has shown capability to discriminate between a complementary sequence and a non-complementary sequence.[2] Whether DNA duplexes were formed at individual spots of a silicon-based surface was determined electrochemically by scanning the light source across the array, such that an enhanced current was observed when the light scanned past a spot containing duplexes. We believe this opens space for the electrochemical sensors start to compete with optical methods in terms of being able to form high-density arrays.

With this aim, improving the spatial resolution of the technique is another topic of our interesting and it is illustrated here as a current challenge. By using illumination from the non-solution side, or backside, the spatial resolution is limited by the finite thickness of silicon wafer. This happens because the photoexcited carriers in silicon can diffuse laterally, as well as to the silicon surface, thus making the electrochemically active area larger than the illumination spot. Interestingly, when the spatial resolution of light activated electrochemistry was monitored using topside illumination (illumination from the solution side), a spatial resolution of ~30 μm was achieved, which is a 20 times improvement compared with the backside illumination design.[3].

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Photoelectrochemical properties of original hybrid organic – inorganic porphyrin – polyoxometalate thin film: from flat to mesoporous ITO electrodes

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Polyoxometalates (POMs) are anionic metal oxide molecular analogues presenting a great diversity of structures and applications. In particular, the development of hybrid polymers incorporating POMs is a promising approach to elaborate new functional materials. To expand the practical applications, their association to a visible-light photosensitizer is so far a prerequisite since POMs themselves are mainly photoactive in the UV domain of the solar spectrum, which strongly limits the use of POMs in solar visible light conversion materials. In this context, we have developed a method of electropolymerization of POMs based on nucleophilic attack onto the electrogenerated porphyrin dications.[1-2] The formation of hybrid POM-porphyrin copolymeric films (Fig. 1, film I) can be obtained by the electro-oxidation of porphyrin in the presence of the POM bearing two pyridyl groups (Py-POM-Py) [3]. This process is feasible for various type of POMs such as Dawson, Lindqvist or Keggin type POMs [4-6].

A second methodology is also proposed to form hybrid POM-porphyrin films (Fig. 1, films II or III): first the formation of cationic polyporphyrin electropolymer. Then, by metathesis reaction, the (partial) exchange onto the surface of the initial counter ions by the POM^{n-} or by the nanoparticles stabilized with POM^{n-} (POM^{n-}@M, M = Ag, Au, Pt, etc.). A second approaches is also used: preparation of modified ITO electrode with POM^{n-}/graphen or POM^{n-}@M/graphen, then electropolymerization of porphyrin. All the electropolymers have been studied by spectroelectrochemistry (UV-vis-NIR-IR), EQCM, AFM, XPS and impedance measurements.[7]

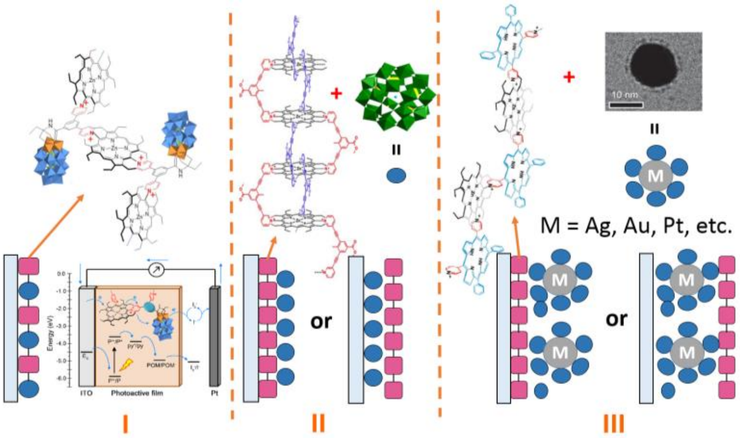

Fig. 1: Various type of porphyrin-POM films.

The photovoltaic performances of these hybrid materials have been investigated by photocurrent transient measurements under visible-light illumination [8-10] given by now good efficiency. In order to increase the efficiency, mesoporous ITO electrodes (nanofiber formed by electrospun or porous ITO electrode obtained using a colloidal co-assembly approach) have been used and will be discussed.

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Curved Polyaromatic Hydrocarbons.
An Electrochemical Route to Generate Graphen-like Structures

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Planar and curved Carbon nanostructures, and in particular graphenes, in principle could be obtained following a bottom-up approach by synthesizing large polycyclic aromatic hydrocarbons (nanographenes)[1] starting from suitable precursors. Their subsequent intermolecular condensation into progressively more extended structures can produce macroscopic graphene films.

Amongst the polycyclic aromatic hydrocarbons, Corannulene is a bowl-shaped species recalling the fullerene surface. It is particularly intriguing, for its unique redox and luminescent properties, to develop new materials. Its electrochemical behaviour for the reduction processes has been recently reinvestigated over a large range of experimental conditions, by using "traditional" and "unconventional" solvents.[2]

As for the oxidation, which has been so far scarsely investigated, it is a completely irreversible process that brings about a passivation of the electrode surface.[3] The adoption of suitable ultra-dry solvents and electrolytes, with very high oxidation resistance and low nucleophilicity, allowed to explore the reactivity of the electrogenerated corannulene carbocations.

In this communication the interesting redox, spectroelectrochemical, luminescence and electrochemiluminesce properties[4] of corannulene and derivative species, together with the structure of their electrochemically generated films, will be discussed.

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Solar fuel generation using organic semiconducting polymer photoelectrodes

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Photoelectrochemistry is an attractive way to convert CO_2 into fuels and chemical substances, thereby lowering the atmospheric concentration of this greenhouse gas and reducing the consumption of fossil fuels. Research in this area mainly focuses on inorganic semiconductor photoelectrodes, however, organic semiconductors can be even more promising in terms of their facile electrosynthesis, tunable chemical structure, and low cost [1]. Conducting polymers (CPs) in their reduced state are mostly p-type semiconductors and their band structure makes the photoelectrochemical CO_2 reduction thermodynamically possible. Recently we reported that polyaniline, as a first example of a CP, can photoelectrochemically reduce CO_2 [2]. Based on these results, we started the systematic investigation of the photoelectrochemical properties of different CPs, with particular focus on their photoelectrocatalytic behavior towards CO_2 reduction and H_2 evolution.

We started with polymers, obtained by polymerizing commercially available monomers (e.g., polypyrrole, polythiophene, poly(3,4-ethylenedioxythiophene), polyindole, polycarbazole, poly(o-aminophenol)). We aim to shed light on the factors dictating the photoelectrochemical performance of these polymers. By uniting that knowledge, we design new CPs with functional moieties advantageous for the photoelectrocatalytic purposes. For example, (i) CPs with reduced bandgap (i.e., in the range of the visible light) can be synthesized from monomers containing both electron donor and acceptor groups, (ii) CO_2 adsorption can be enhanced by introducing primary or secondary amino groups, (iii) attaching electrocatalytic functional groups to the polymer backbone can improve the electron transfer kinetics. Some proposed monomer structures are presented in **Fig.1**.

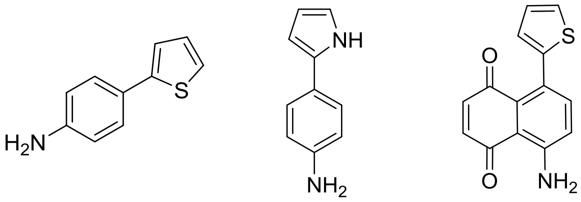

Figure 1: Structure of monomers of some custom-designed CPs for photoelectrocatalytic applications.

In my presentation I will report on the detailed electrochemical, photoelectrochemical and (photo)electrocatalytic characterization of the above mentioned polymers. Starting from the synthesis (to find the optimal conditions for obtaining the best photoelectrochemical performance) to the analysis of the reduction products, we will establish structure-performance relationships for the photoelectrocatalytic properties of these organic semiconductors.

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Hydrogen/Nitrogen Doped Anatase TiO_2 for Photoelectrochemical Splitting of Water

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Anodized TiO_2 nanotube arrays (NTs) are widely investigated for photoelectrochemical water splitting, despite the fact that pristine TiO_2 suffers both from a low electrical conductivity and a rather large band gap (3.2eV, $\lambda < 387$ nm), limiting light absorption only to the UV region of the solar spectrum.[1] Both limitations however can be overcome by generating suitable defects; for example, electrochemical or thermal treatments of TiO_2 under reducing conditions have been shown to generate substoichiometric, high-conductivity TiO_{2-x} materials such as Magneli phases, potentially providing higher conductivity and increased light collection.[2] In similar efforts, increasing the disorder of the crystal structure at TiO_2 NT surfaces may lead to color changes, also resulting in improved light absorption properties.[3]

Herein we report two distinct methods to induce formation of substoichiometric phases, enhance surface disorder and thus reduce band gap by modification via hydrogen or ammonia gas. Annealing in partial hydrogen pressure (5 at%) results in a gradual loss of the nanotube morphology, accompanied by the transformation of the anatase structure to various Magneli phases, yielding improved photoelectrochemical response (up to ~2.2-fold improvement) and more negative onset of the photocurrent (~20mV). Annealing in ammonia yields limited N incorporation but a significant negative shift (~100mV) and a 4 to 5-fold photocurrent improvement. In order to characterize the catalytic and electronic properties of these modified materials, electrochemical impedance spectroscopy (EIS) was employed to evaluate the efficiency of water splitting at the interface,[4] while we demonstrate that selective hydrogen or nitrogen doping can improve the number density of charge carriers by up to 3 orders of magnitude.

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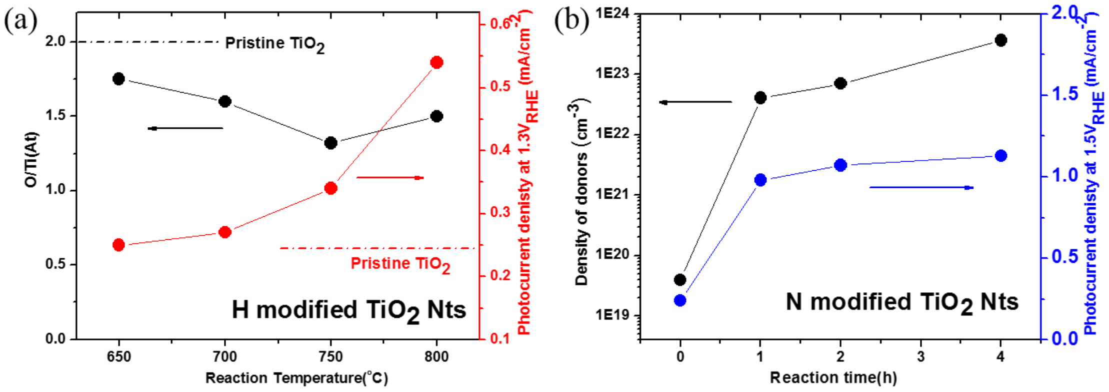
Figure 1. (a) Atomic composition of H-treated TiO_2 NTs measured by EDS and the corresponding photoresponse at $1.3V_{RHE}$ under AM 1.5 simulated sunlight in alkaline solution. (b) Density of donors of N-treated TiO_2 NTs measured by Mott-Schottky method and the corresponding photoresponse in the same conditions as (a).



Electrodeposition of Metals on Porous Polymeric Templates for Raman Spectroscopy and Sensing

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Electroplating can be employed for a controlled growth of metals and conducting polymers with several distinct morphologies, which are expected to present different properties and thus expanding the amount of possible useful applications, such as SERS spectroscopy, electrochemical (bio)sensors, photonics and catalysis[1].

In this sense, the association of this technique with templates may increase even more the diversity of platforms produced, with special importance concerning the exposed area and the respective boundary geometry. Spin-coating porous PMMA templates is presented as a low-cost, simple and fast method to obtain thin films with pores presenting a few hundreds of nanometers of diameter[2], providing an interesting path to restrict the maximum size of plated structures.

In the present work, one can report the synthesis of a platform with agglomerated gold nanoparticles, exhibiting enhanced Raman signal, Fig. 1, and are expected to be improved towards a reusable SERS-active platform, with simple cleaning procedures.

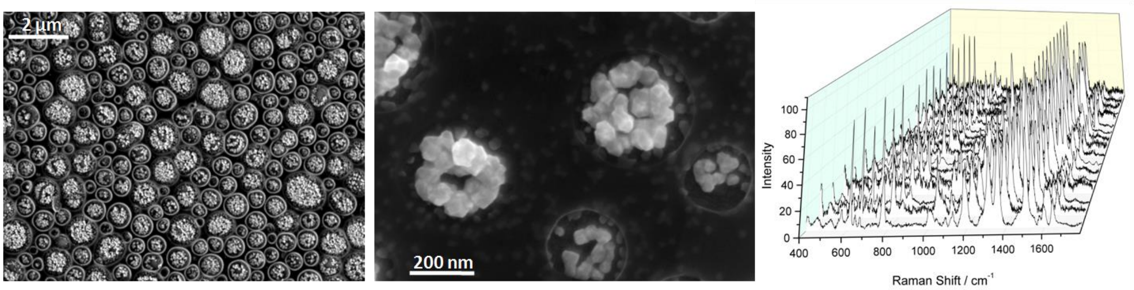

Fig 1. Rough gold nanoparticles delimited by PMMA template (left), morphology highlighted (centre), Raman spectra of Rhodamine 6G on several distinct spots (right), with 785nm laser wavelength.

Nickel is also an interesting metal to work with, due to its diverse forms, and the electrodeposition of convertible nickel metal, oxide and hydroxide was successful, with the special feature of the nanocubic structures obtained during the hydroxide electrochemical formation, thus presenting a promising structure for selective catalysis and sensing, Fig 2.

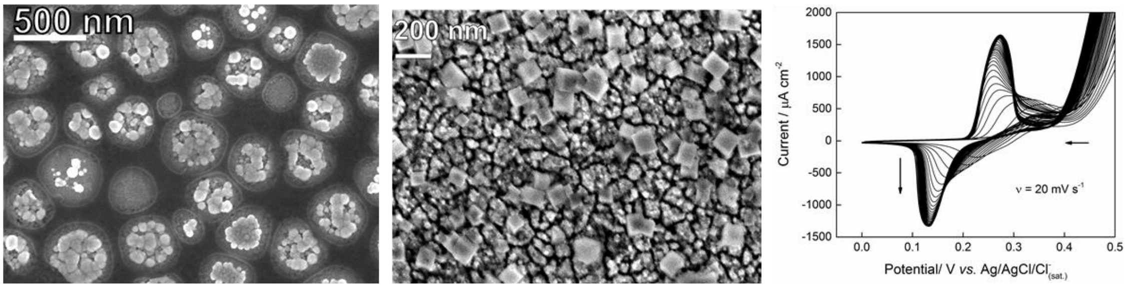

Fig 2. Electroplated nickel particles on PMMA porous template (left), nickel hydroxide nanocubes formed by electrochemical cycling on concentrated KOH (centre), cyclic voltammogram of cubic particles registered on 7M KOH (right)

Tailoring bismuth electrodeposits morphology is another important and non-trivial task with great importance concerning heavy metal detection and quantification, in this topic advances were achieved by controlling deposits concavity from an array of flat microdisks to nanorings.

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Ultrathin Co-based metal-organic framework nanolamella on graphitic carbon as OER electrocatalyst precursors

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The development of noble metal-free, carbon-based electrodes for electrocatalytic reactions such as the oxygen evolution (OER) holds the key for renewable energy technologies [1]. Electrically conductive composites comprising 2D nanomaterials currently attract a great deal of attention as precursors for such electrode materials, which could be integrated in ultrathin functional devices [2]. Herein, novel electrode materials have been developed by the integration of nanosized 2D fluorine-functionalized cobalt-based metal-organic framework (MOF) crystals and graphitic carbon nanosheets.

After synthesis and decomposition of the macromolecular MOF precursor at different pyrolysis temperatures, the electrocatalytic properties have been examined for the OER in alkaline media using a rotating electrode following a standardized experimental protocol. Figure 1a displays the electrocatalytic properties of these Co-MOF/exfoliated graphite composites for the OER in alkaline media as a function of the pyrolysis temperature, which is in turn directly related to the metal dispersion and speciation. Pyrolysis at 250 °C resulted in a notably increase in the electrocatalytic activity with respect to the pristine composite, pointing to the high intrinsic activity of the supported CoF_x nanoclusters existing in the sample after this mild pyrolysis treatment. High-resolution transmission electron microscopy (HRTEM) showed small (2-5 nm) metal nanoparticles with lattice spacings consistent with CoF_2 nanoclusters, which are stabilized within a matrix of amorphous carbon, derived from the decomposition of the organic linkers in the MOF precursor, supported on the exfoliated graphitic carbon (Figure 1b). However, the activity dropped significantly after a pyrolysis treatment at 550 °C, due to the segregation of fluorine and cobalt species and the significant aggregation of the metal. The results highlight the synergetic role of Co and F for the creation of the most active sites. More broadly, our studies show how 2D MOF nanostructures can be used as a macromolecular "shuttle" to introduce dispersed metal species on highly conductive graphitic substrates, and control their direct chemical vicinity via selection of the organic linker in the macromolecular precursor.

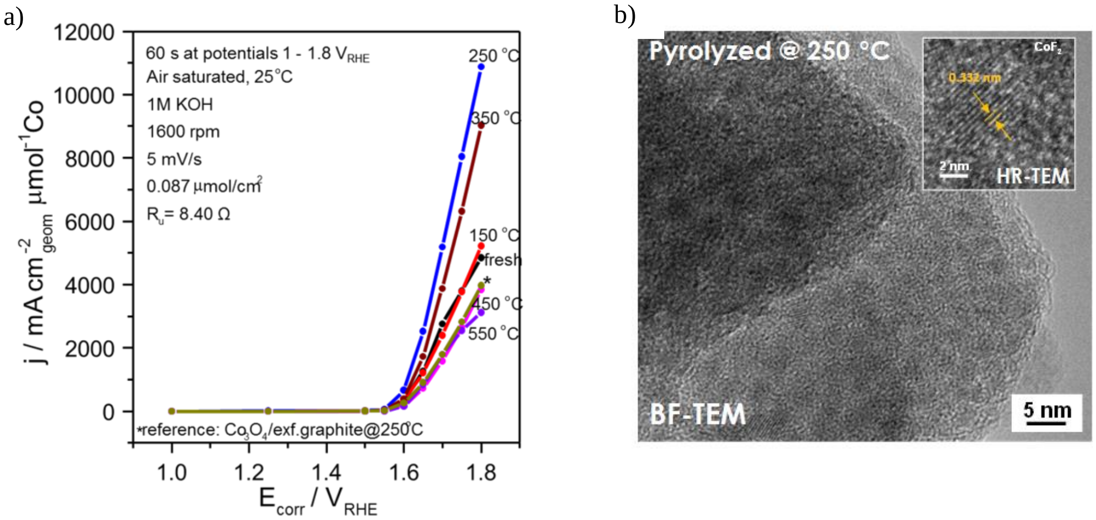

Fig. 1. a) Metal-normalized OER geometric activity determined under stationary polarization conditions for the F-Co-MOF crystals supported on exfoliated graphite annealed at different temperatures. b) (HR)TEM micrographs showing CoF_x nanocrystals within a carbon matrix after pyrolysis of the MOF/C composite at 250 °C.

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Preferentially Oriented TiO_2 Nanotubes as Anode Material for Li-Ion Batteries: Insight into Li-Ion Storage and Lithiation Kinetics

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Self-organized and highly ordered TiO_2 nanotubes (NTs) are a promising, cost effective and safe anode material which, due to its parallel oriented pore structure, allows one-dimensional electronic and ionic conductivity. In addition, the thin walls provide short pathways for Li-ion diffusion and high tolerance to structural changes, i.e. in volume, occurring during charge/discharge cycling.[1] The synthesis of TiO_2 NTs with a specific and controllable crystallographic orientation is highly desirable for gaining fundamental understanding of the performance of this anode material in Li-ion batteries. In the present study, self-organized TiO_2 NTs are anodically grown in a 2 wt% H_2O and fluoride containing electrolyte and annealed at 450 °C in air.[2] The resulting NTs are mostly vacancy-free and possess exceptional crystallographic preferential orientation along the [001] direction (PO TiO_2 NTs). To ensure an accurate comparison, reference TiO_2 NTs with similar morphology are produced, using 10 wt% H_2O in the electrolyte, and annealed under identical conditions, leading to randomly oriented NTs (RO TiO_2 NTs). In this work, the intrinsic kinetic and thermodynamic properties, as well as the effect of crystallographic orientation on the lithiation/delithiation process have been investigated by a multiple-technique approach, including cyclic voltammetry, galvanostatic cycling and electrochemical impedance spectroscopy. In addition to gaining a new understanding of the origin of preferential orientation, it is found that PO TiO_2 NTs demonstrate a superior performance in Li-ion batteries compared to the reference NT array. The main reason for this is faster Li insertion/extraction kinetics. The determined thermodynamic properties, which describe the ability of the host material to intercalate Li-ions, are found to have a negligible influence on the superior performance of PO TiO_2 NTs. These insights confirm the importance of the crystallographic properties on the Li intercalation process.[3] The presented analysis method has high potential for a straight forward evaluation of battery materials in terms of their lithiation/delithiation thermodynamics and kinetics, in general.

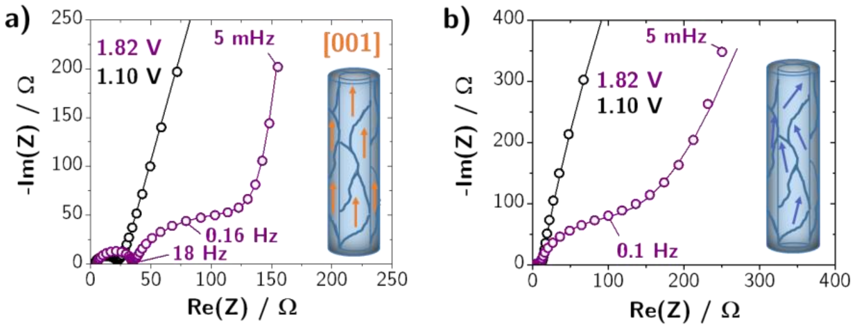

Figure 1: Electrochemical impedance spectroscopy measurements: Nyquist plots for a) PO TiO_2 NTs and b) RO TiO_2 NTs at selected lithiation potentials.

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Binary Nickel and Iron based Porous Nanocubes as High-efficient Electrocatalysts for OER

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Exploring low-cost and high-efficient electrocatalysts toward oxygen evolution reaction (OER) is of great significance for the development of sustainable energy systems (e.g. water electrocatalysis and metal-air batteries)[1-2]. Presently, Ir- and Ru-based materials have been demonstrated as the most efficient catalysts for OER[1]. However, the large-scale application are largely restricted due to the limited reserves and high-cost of precious metals [1]. Therefore, it is extremely essential to explore high-efficient non-precious electrocatalysts for OER. Numerous researches have shown that the morphology and the introduction of foreign element play a significant role in enhancing the electrocatalytic activities[3]. Metal-organic frameworks (MOFs) are an ideal and appealing precursors for the preparation of three-dimensional nanomaterials due to their desirable properties including large specific surface area, high porosity and well-defined structure[4].

In this work, heteroatoms (P, B, S) were introduced into NiFe-based nanocubes (Ni-Fe-P, Ni-Fe-B, Ni-Fe-S) by direct calcination of MOFs and small molecules containing heteroatoms. All the three materials maintain the cube structure of MOFs with remarkably porous feature (Figure 1a-c). Besides, the introduction of heteroatoms could tune the electronic structure of the catalysts. Electrochemical tests demonstrate that all the three NiFe-based nanocubes exhibit excellent OER electrocatalytic activities in alkaline media (Figure 1d), even much better than Ir/C. The superior activities could be attributed to the unique morphology and composition. The distinctive porous nanocubes offer lots of channels for the fast mass transfer, enable the adequate contact between the catalysts and electrolyte. The amorphous structure could provide much more unsaturated atoms as active sites, which are favorable for the enhancement of the catalytic activities. In addition, the introduction of heteroatoms could modify the electronic structure, and promote the water absorption, and thus expedite the reaction rate.

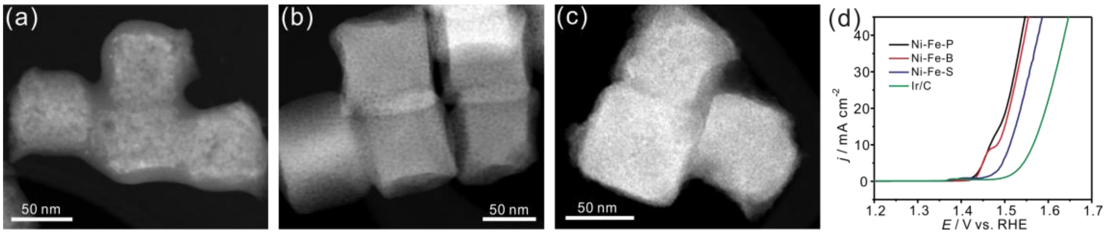

Figure 1. S-TEM images of Ni-Fe-P (a), Ni-Fe-B (b), and Ni-Fe-S (c). LSVs of NiFe-based catalysts in 1 M KOH(d).

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Enhancing Charge Transport in Redox Active Polymers Through Molecular Design

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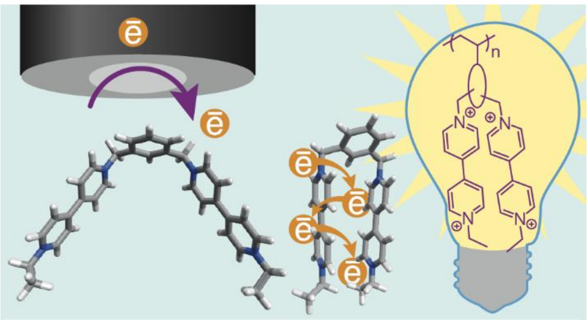
Non-aqueous Redox Flow Batteries (NRFBs) are emerging devices for electric grid storage applications. A major challenge in redox flow batteries is enhancing the ionic conductivity across the membrane while preventing the crossover of the anolyte and catholyte .[1] Recently, we reported that using redox active polymers (RAPs) in combination with size exclusion membranes, in contrast to ion selective membranes, provides a viable alternative that addresses these challenges and enables NRFBs.[1]

The electron transfer kinetics of large RAPs mediators with hundreds to thousands of redox active centers in solution are not well understood.[2-3] In addition, the existence of a preceding chemical step that mediates the redox chemistry of RAPs in solution highlights the importance of charge hopping on these polymers.[2] In order to gain a better understanding of the electrochemical properties of RAPs, we use a systematic molecular design approach to investigate the impact of backbone and redox-pendant electronic interactions on the performance of viologen RAPs. We used different electrochemical techniques to study the redox properties, charge transfer kinetics and self-exchange of electrons through redox active dimers and their equivalent polymers. Our studies provide insides on how the modulation of RAP inter-pendant interactions decisively impacts charge transfer. Stark contrast was observed between the electrochemical properties of viologen dimers and their corresponding polymers. However, there is a limit to how close pendants should be brought together. Limitations in counter-ion transport towards buried redox groups upon electron transfer and the well-known formation of irreversible dimers from radical species, which are favored at short inter-pendant distance, could adversely impact polymer charge storage performance (scheme 1).[3] While polymers with optimized macroscopic reversibility were obtained, the microscopic trends describing small molecule electrochemistry did not hold for polymers, showing anti-Marcus effects that require further investigation. The present/on-going studies give us the necessary fundamental tools to understand and act on charge transfer effects that we need to improve the performance for RAPs and give us the knowledge to design new and better performing polymers.



Scheme 1. Exploring structure chemical interactions generated after a redox process at its effects on the electrochemical performance of soluble polymers.

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An Enhanced Electrochemical Biosensor Based on 3D Pt Nanowire Array/Au Nanoparticle Hybrid Structure

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In recent years, vertically aligned nanowires have been investigated in a range of sensor development for high sensitivity and selectivity detection. In this research, a novel hybrid structure based on vertically aligned Pt nanowire array (PtNWA) coated with Au nanoparticles has been developed as a highly sensitive electrochemical biosensor. The vertical Pt nanowire array has been prepared onto an Ag substrate by an electrodeposition method within anodic aluminum oxide (AAO) membranes; then a controllable electroless plating procedure was applied to deposit Au nanoparticles onto the surface of the vertical Pt nanowires (Figure 1(A)). This new sensor structure would avoid several shortcomings of the conventional nanowire modified electrodes. For example, no coating layer (such as Nafion) is needed for nanowire fixation so there is no serious bubble-trapping problem, which makes this structure more stable and durable. Also, without the nanowire overlapping issue, the well-aligned array structure makes it possible that every nanowire has full contact with the analyte for better electrochemical performance. The electroless plated high density of Au nanoparticles (Figure 1(B)) enhanced enzyme immobilization, and the electron transfer could also be intensified by the 3D vertically aligned Pt nanowire array, leading to higher signal to noise ratio, which makes this structure a promising design for various electrochemical biosensing applications (Figure 1(C)). Herein, we immobilized glucose oxidase (GOD) enzyme on to the surface of the Au nanoparticles with two widely used enzyme immobilization methods, 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide/N-hydroxysuccinimide (EDC/NHS) and glutaraldehyde crosslinking, respectively. The prepared electrode (EDC/NHS) showed high sensitivity of 184 µA mM^{-2} cm^{-2}, a limit of detection of 15 µM, and high selectivity toward the detection of glucose (Figure 1(D)). This PtNWA/Au nanoparticle hybrid structure, with different enzyme immobilization, can be used as a new electrochemical sensor platform for the quantitative detection towards various biomolecules.

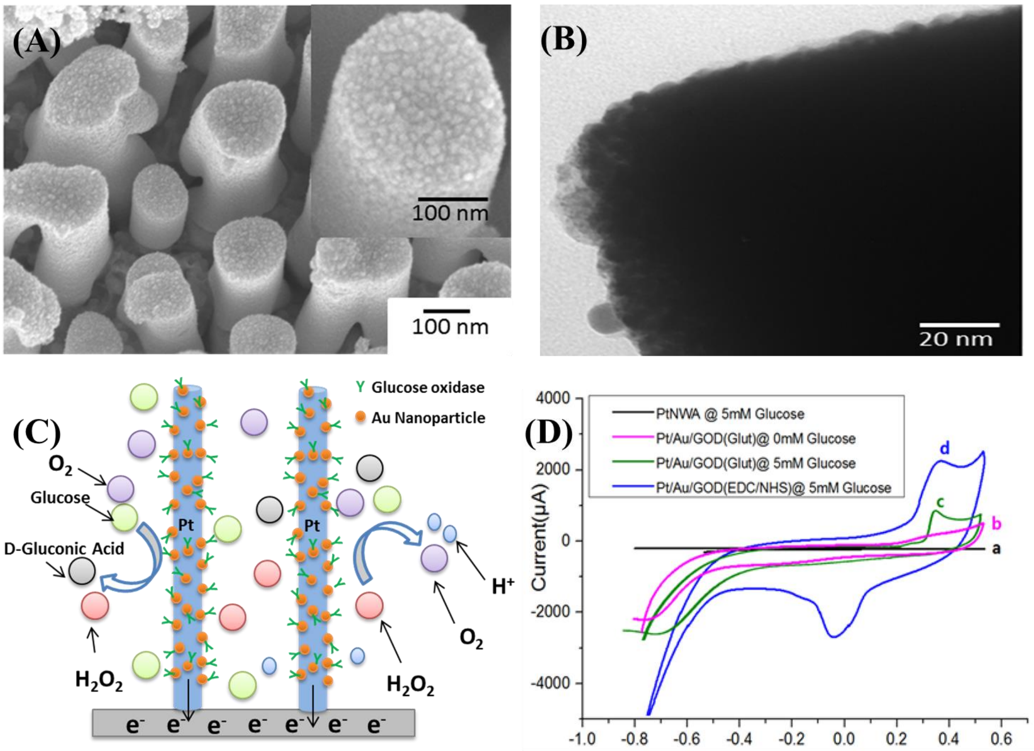

Figure 1: (A) SEM image of PtNWA/AuNPs hybrid array structure; (B) TEM image of tip area of a Pt nanowire coated with AuNPs; (C) Schematic illustration of the reaction occurring on the PtNWA/AuNPs electrode; (D) Cyclic voltammetry test results toward glucose detection.

Performance of capacity enhanced conducting polymer based cathodes for lithium ion battery

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Since their discovery, conducting polymer has generated great interest as an electrode material for electrochemical storage systems. This is due to their stable reversible redox activity combined with their insolubility in organic electrolyte as well as the ability to conduct both ions and electrons. However, their low practical capacity has greatly limited their use in the field of electrochemical storage. One of the strategy to increase their energy density, is to form an hybrid material with the addition of an organic redox molecule.[1] This presentation will focus on our development of capacity enhanced poly 3,4-ethylenedioxythiophene (PEDOT) using electron rich aromatic moieties.[2,3,4] The capacity enhanced PEDOT shows an additional reversible redox activity around 4.2 V vs. Li/Li$^+$ (fig. 1). Furthermore, the interaction between different pendant redox moieties with the conducting polymer backbone is explored via in-situ Raman and UV-vis spectroscopy.

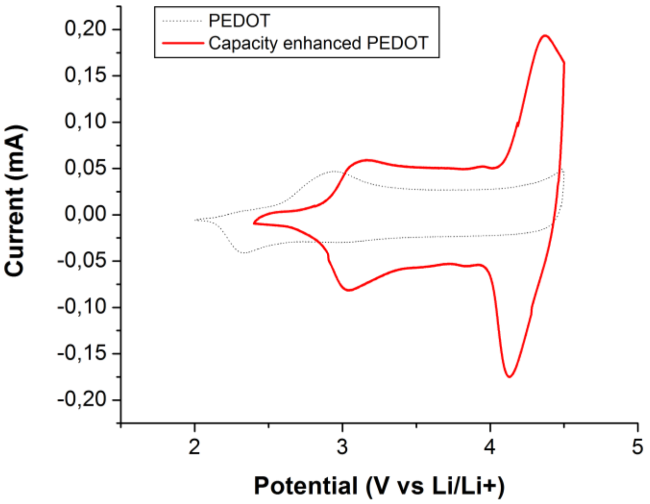

Figure 1. Cyclic voltammetry of PEDOT/Capacity enhanced PEDOT electrodes in solution of 0,1M TBAClO$_4$ in acetonitrile

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Pencil-Urchin-Like $CoSe_2$ Catalytic Film as the Electrodes for Dye-Sensitized Solar Cell and Hydrogen Evolution Reaction

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A good electrocatalyst normally has two parts. Firstly, the intrinsic property of the material, namely its standard heterogeneous rate constant, should possess an attractive value. Secondly, the material should offer a sufficient surface area with some structures. Nanoparticle is considered to have high surface areas, while nanorod structure is advantageous to promote electron transfer. In this study, a novel pencil-urchin-like (PUL) structure based on cobalt diselenide ($CoSe_2$) is synthesized for the use as the counter electrode (CE) in dye-sensitizes solar cells (DSSCs) and for the use in hydrogen evolution reaction (HER). We aim to prepare the $CoSe_2$ crystals with a structure of pencil urchin via a surfactant-assisted hydrothermal technique using a cation surfactant, namely, cetylmethyl ammonium bromide (CTAB). The prepared $CoSe_2$ is dropped on an FTO substrate and annealed at 450 °C for 30 min for both applications. As shown in Fig. 1(a), the $CoSe_2$ crystal possesses a hierarchical pencil-urchin-like structure, *i.e.*, a nanoparticle-assembled sphere (diameter about 50 nm) with the extended hexagonal long rods, whose length is about 1-3 μm. This synthesized $CoSe_2$ PUL is expected to possess both large active surface areas and directional electron transfer capability. The $CoSe_2$-PUL-1.4 CE has the best performance among all CEs with different $CoSe_2$ loadings. At 100 mW cm^{-2} (AM 1.5G), a DSSC with the $CoSe_2$-PUL-1.4 on its CE reached a power conversion efficiency (η) of 9.29% with an open-circuit voltage (V_{OC}) of 0.82 V, a fill factor (FF) of 0.70, and a short-circuit current density (J_{SC}) of 16.09 mA cm^{-2}. This $CoSe_2$-PUL-1.4-based DSSC performs better than the cell with a Pt-based DSSC (η: 8.33%, V_{OC}: 0.81 V, FF: 0.70, J_{SC}: 14.81 mA cm^{-2}). Fig. 3 gives the cathodic HER polarization behavior of various $CoSe_2$-PUL in 0.5 M H_2SO_4, including $CoSe_2$-PUL-0.05, $CoSe_2$-PUL-0.15, and $CoSe_2$-PUL-0.25, which correspond to the overpotentials of 407, 397, and 405 mV, respectively. The results suggest the possibility of $CoSe_2$ to replace Pt in both applications.

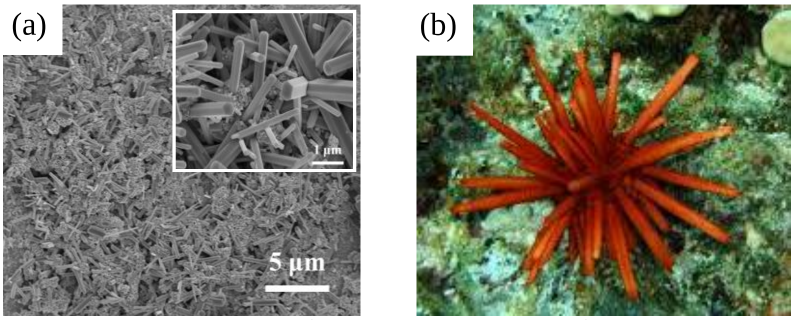

Fig. 1 (a) FE-SEM image of urchin-like $CoSe_2$. (b) Image of pencil urchin.

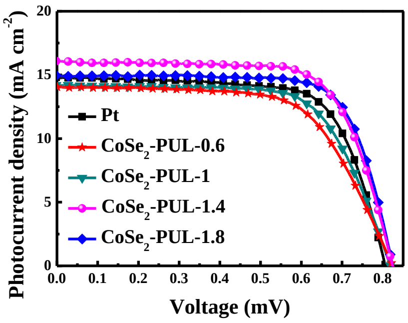

Fig. 2 Photocurrent density-voltage curves of the DSSCs with the Pt and various $CoSe_2$-PUL on their CEs, measured under 100 mW cm^{-2} (AM 1.5G).

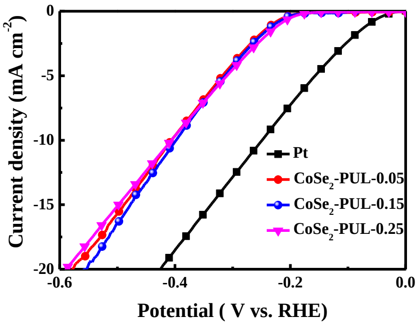

Fig. 3 Comparison of HER polarization curves for various $CoSe_2$-PUL CEs in 0.5 M H_2SO_4 and the Pt CE.

Tube-Array of S-P3MEET/PEDOT-MeOH as Electro-catalytic Counter Electrode for Dye-Sensitized Solar Cells

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Optimization of the counter-electrode (CE) material of a dye-sensitized solar cell (DSSC) is an important task not only to enhance the performance of the cell, but also to reduce its cost of fabrication. Polymer-based CE materials are a cost-effective alternative for the expensive platinum in a DSSC; they can be processed by rather simple methods. In this study, we synthesized a film of tube arrays (TA) on an FTO glass, where each tube consisted of an inner layer of poly (hydroxymethyl 3,4-ethylenedioxythiophene (PEDOT-MeOH) and an outer layer of sulfonated poly(thiophene-3-[2-(2-methoxyethoxy) ethoxy]-2,5-diyl) (S-P3MEET). The PEDOT-MeOH is a kind of conducting polymer with hydroxymethyl functional group that enhances the conjugation, and thereby resulting fast electron transfer. We designate this film as S-P3MEET/PEDOT-MeOH TA. The inner layer (PEDOT-MeOH) was obtained under controlled electro-polymerization at 0 ˚C, while the outer layer was obtained by drop coating of S-P3MEET on the inner layer. The inner layer was intended for unidirectional electron transfer and the outer layer for enlarging the surface area of the whole film, both being for enhancing the electrocatalytic ability of the whole film. A DSSC fabricated by optimizing the CE film (S-P3MEET/PEDOT-MeOH TA) has exhibited a power conversion efficiency (η) of 9.09% at AM 1.5 G light illumination, while the DSSC with a platinum CE has shown an η of only 8.80% (Fig. 1); the η's are 8.31% and 5.31% for the DSSCs with bare TA of PEDOT-MeOH and bare film of S-P3MEET, respectively. The morphologies of the electrodes were observed by Field-emission scanning electron microscopy (FE-SEM). It can be seen that these tubes (Fig. 2(a)) with diameter of 1-2 μm were covered by S-P3MEET and increase tube thickness (Fig. 2(b)). Suitable amount of dropping could properly cover the tube surface for enhancing the electro-catalytic ability and still maintain the tube shape. The catalytic abilities of the electrodes were analyzed by cyclic voltammetry (CV), Tafel polarization plots, electrochemical impedance spectroscopy (EIS), and data from rotating disc electrode (RDE). Moreover, incident photon-to-current conversion efficiency (IPCE) spectra were used to substantiate the photovoltaic performances. It may be concluded that S-P3MEET/PEDOT-MeOH TA is a promising electro- catalytic material to replace the expensive platinum in DSSCs.

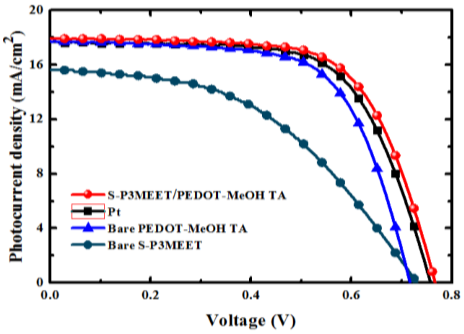

Fig. 1 Photocurrent density-voltage curves of the DSSCs with the CEs of S-P3MEET/PEDOT-MeOH TA, Pt, Bare PEDOT-MeOH TA, and Bare film of S-P3MEET.

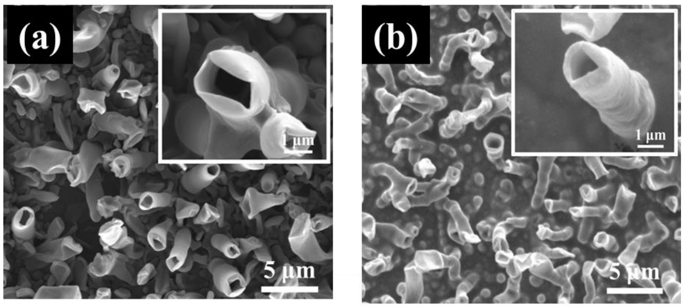

Fig. 2 FE-SEM image of different dropping amounts of S-P3MEET on the top of the PEDOT-MeOH TA. (a)Bare PEDOT-MeOH TA.(b) S-P3MEET/PEDOT-MeOH TA

Electrodeposition of High Porosity Cu Alloy Layers and their Use as Efficient Electrodes for Nitrate Reduction in Alkali

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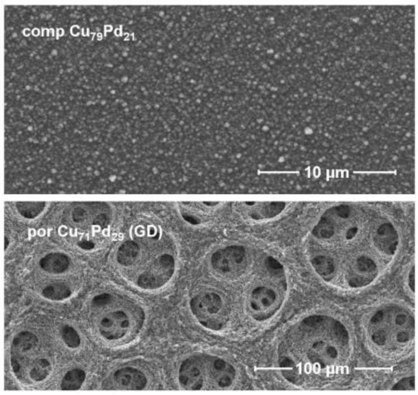
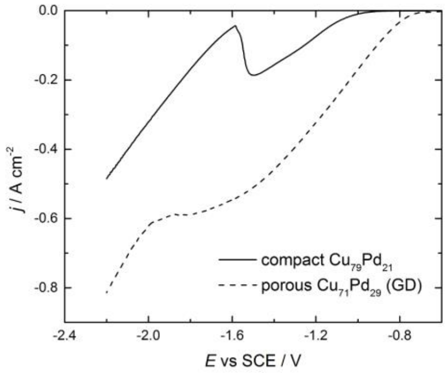
Porous electrodes are attracting much interest due to their promising characteristics in numerous applications like reactors, fuel cells, batteries, sensors. An established preparation method is templated electrosynthesis, based on slow metal electrodeposition in the pores of solid templates and final removal of the latter, typically by etching or dissolution [1]. This method offers excellent control of the deposit properties and appears suitable for the synthesis of one-dimensional nanomaterials, or ordered porous materials [1], but is costly and difficult to scale up.

When order requirements on the deposit are not particularly strict, an alternative simple approach may be considered, the dynamic hydrogen bubble template (DHBT) electrodeposition method [2]. This approach exploits the action of confinement and stirring provided by gas evolution during cathodic deposition with a large current flow. The method has been used for the deposition of porous layers of various common metals including Cu, Sn, Ni, Co, Pb [2]. The obtained deposits are robust and show large area, hierarchical porosity and increased transport, all properties favorable to the use as electrodes.

We present here the deposition of various compact and porous Cu alloys like Cu-Ni [3], Cu-Zn [4], Cu-Pd [5]. The porous materials are obtained with the DHBT method. Comparative X-ray diffractograms show interesting differences. For Cu-Ni and Cu-Zn the dependence of lattice parameter on composition is similar for both compact and porous alloys: for Cu-Ni, the Vegard's law is valid over the entire composition range; for Cu-Zn it applies only to the Cu-rich region (metallurgic α phase). For Cu-Pd, conversely, two types of materials are obtained: i) solid Cu-Pd solutions respecting Vegard's law for slow alloy formation processes (e.g., electrodeposition of compact materials at low current densities); ii) biphasic structures, including pure Cu and a $Cu_{17}Pd_{83}$ phase in different ratios, for fast alloy deposition (DHBT) from a chloride bath.



Porous Cu alloy electrodes show markedly improved performances in comparison with their compact counterparts for nitrate reduction in alkali (right figure, reduction of 0.1 M $NaNO_3$ in 1 M NaOH at a Cu-Pd RDE): better efficiency; comparable selectivity (main product is NH_3); superior current stability, due to better resistance to poisoning. This method of electrode surface modification with a thin porous layer may be easily applied to substrates of large dimensions and complex shape, with a potential practical interest.



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An Electrochemical Study of the PbO_2/Mn^{2+} Galvanic Displacement Reaction

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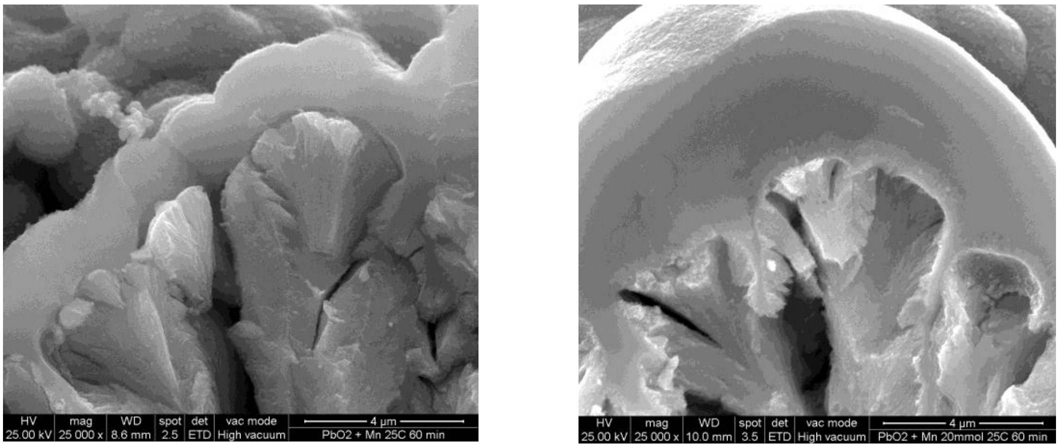
Porous PbO_2 layers can be prepared by oxygen bubble–templated anodic deposition [1]. Galvanic displacement reactions may provide a route to other porous oxides that are interesting as electrode materials but cannot be obtained with the same method. In a recent paper [2], we have shown that the reaction between porous PbO_2 layers and mildly acid acetate solutions of Mn^{2+} proceeds with the reduction of PbO_2 to Pb^{2+} ions, which become dissolved, and the deposition of an MnO_x layer on top of the remaining PbO_2. We have further studied this galvanic displacement reaction, using electrochemical, microscopic and spectroscopic methods. The main experimental variables of the study were reaction duration, Mn^{2+} concentration and solution temperature.

Adopting an approach typical of corrosion studies, quasi steady-state current potential curves for the partial reactions involved in the galvanic displacement, i.e. PbO_2 reduction and Mn^{2+} oxidation, have been recorded and compared using Evans' diagrams. Analysis of these diagrams provided information on dissolution/deposition rates, and allowed the interpretation of the evolution of the open circuit potential during the galvanic displacement reaction.

By recording cross-sectional SEM images of deposits obtained under different experimental conditions, the growth kinetics of the MnO_x layer was investigated. We found that, at 25°C, the layer thickness grew faster when the Mn^{2+} concentration was lower (e.g. 0.020 M vs. 0.200 M). This result was similar to those reported for some metal/metal galvanic displacement reactions in which the deposited layer completely blanketed the sacrificial metal [3,4], and suggested that the rate of the PbO_2/Mn^{2+} reaction was controlled by the availability of bare PbO_2 areas where the cathodic partial reaction could occur, and that more concentrated Mn^{2+} solution yielded MnO_x layers which coated PbO_2 more efficiently.

Some preliminary tests were carried out by reacting PbO_2 with Co^{2+} solutions. A displacement reaction did occur, with formation of a CoO_x layer on top of PbO_2. The reaction rate was much lower than that for the PbO_2/Mn^{2+} system, in agreement with the lower thermodynamic driving force.



Cross-sectional SEM images of porous PbO_2 layers after reaction with 0.200 M Mn^{2+} (left) or 0.020 M Mn^{2+} (right) at 25°C during 60 min. The MnOx layer grew thicker in the less concentrated solution.

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Electroactive Supramolecular Ionic Material for Biosensing and Electronic Device

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Over the past two decades, functional supramolecular materials prepared with noncovalent interactions have attracted enormous attention because of their unique applications in electronics, photonics, light-energy conversion, biosensing, and catalysis. Recently, supramolecular materials with water-stability and adaptive encapsulation properties have become particularly attractive especially in biosensor development since most biological processes take place in aqueous environments and biological molecules such as proteins and enzymes are generally active in water. Moreover, the ability to encapsulate functional molecules in supramolecular networks enables the materials to hold great promise in tailoring and improving their functions for target-oriented applications. So far, several kinds of water-stable and adaptive materials have been developed, mainly based on metalcoordination interactions. As a result, it is imperative to explore other kinds of noncovalent interactions for the development of water-stable and adaptive materials with excellent properties.

Ionic interaction between oppositely charged species represents one of the strongest noncovalent interactions and has been widely used in self-assembly, typically as electrostatic self-assembly in solid state and ionic self-assembly in solution. All this work suggests that Coulombic interaction could be used as the noncovalent interaction to form supramolecular materials by self-assembly. While wide availability of charged species and the simplicity of their synthesis allow the ionic interactions to be used in synthesis of various functional materials, it remains a great challenge to utilize this kind of interaction to develop functional supramolecular materials with water stability and adaptive encapsulation property. This is because, on one hand, most of the charged species could easily dissolve in water because of the high dielectric constant of water ($\varepsilon = 78.5$, at 25 °C) and thus the electrostatic interactions become significantly weakened in water. On the other hand, the large lattice energy in ionic compounds essentially limits their encapsulation property. Very recently, this interaction was utilized to create supramolecular ionic networks and supramolecular polymers by using multiple electrostatic bonds. This implies that ionic interaction could potentially provide the possibility to form water-stable and adaptive supramolecular materials by rationally designing the structure of the building blocks. However, such potential has not been explored so far.

Herein, we demonstrate a series of water-stable, adaptive, and electroactive supramolecular ionic materials (SIM) that is formed from the aqueous solutions of imidazolium-based dication and dianionic through ionic self-assembly. The formed SIM not only shows good thermostability and unique optical and electrochemical properties that are raised from precursors of the SIM, but also exhibits good water-stability, salt-stability, and adaptive encapsulation properties toward some heterocyclic cationic dye molecules. Firstly, we systematically studied the self-assembly behavior based on different carbon chains in imidazolium dications and its structure. Secondly, we found these SIM bears good adaptive inclusion property towards organic dyes and inorganic salt. Based on this, some kinds of biosensors including fluorescence and electrochemistry have been developed. Finally, the electronic property of this kind of SIM was investigated. And we found its electric conductivity was strongly dependent on the humidity. Based on this property, the solid electronic device with high sensitivity and stability was developed. The present study not only opens a new avenue to the preparation of the supramolecular materials, but also provides a versatile platform for (bio)sensing and electronic devices.

Enzymatic catalysis for H_2/O_2 biofuel cells: from Self-Assembled-Monolayers to mesoporous carbon materials

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One of the challenges in the large scale development of H_2/O_2 fuel cells is the replacement of platinum catalysts required to accelerate both hydrogen oxidation and oxygen reduction. One alternative is the use of enzymes as biocatalysts. Enzymes are involved in energy metabolic chains of microorganisms to convert efficiently hydrogen and oxygen. We previously explored the biodiversity and ability of some organisms to survive in extreme environmental conditions, and demonstrated the feasibility of the use of O_2- and CO-tolerant hydrogenase for H_2 oxidation, and multicopper bilirubin oxidases for O_2 reduction into water in H_2/O_2 enzymatic biofuel cells [1]. Although very efficient compared to platinum, the nanometric size of the enzyme with an active site isolated in the protein moiety imposes to develop interfaces with: i) suitable chemical functionalization for proper orientation of the enzyme required for fast interfacial electron transfer rate, ii) large surface/volume ratio to enhance the amount of enzymes participating to the catalysis.

Distribution of orientation of enzymes can be determined by studying enzyme immobilization on Self-Assembled-Monolayers on gold electrodes, while carbon nanotube (CNT) networks may serve as platforms to enhance the catalytic currents. In this work we discuss how the molecular basis for proper orientation obtained on SAMs can be extended to mesoporous conductive networks. We illustrate this issue by examining the intriguing behavior of two different hydrogenases for H_2 oxidation, and two different bilirubin oxidases (BODs) for O_2 reduction. We focus on their functional immobilization on CNTs presenting surface chemistry with different functionalities and charges.

Aquifex aeolicus is a hyperthermophile ancestral bacterium that harbors an O_2- and CO-tolerant membrane-bound hydrogenase. Molecular dynamic and electrochemistry coupled to PMIRRAS and Surface Plasmon Resonance provided the tools to determine the required functionalities for efficient direct electron transfer, and to propose a model for the orientation of the enzyme as a function of hydrophobicity and charges [2]. Accordingly, the enzyme immobilized on CNTs exhibited the expected catalytic efficiency according to CNT functionality. *Ralstonia eutropha* is another bacterium which also harbors an O_2-and CO-tolerant hydrogenase which shares more than 60% homology with *A. aeolicus* hydrogenase. However, a very different behavior was observed on charged CNTs, that we will discuss on the basis of detergent content in the membrane-bound enzyme sample [3].

We also determined the molecular determinant for functional orientation of BOD from the fungus *Myrothecium verrucaria*. As for *A. aeolicus* hydrogenase, the key parameters obtained on SAMs were suitable to get a proper orientation on functionalized CNTs [4]. However, BOD from the bacterium *Bacillus pumilus*, that is preferable than *M. verrucaria* BOD because it is thermostable, failed in direct electrical connection to the CNT-based electrode in the same conditions as the *M. verrucaria* BOD. To establish the molecular basis for such different behaviors, we undertook an in-depth multidisciplinary study of the interactions between the two BODs and the various CNTs. Comparative modeling of the enzymes allowed to point out the differences in surface charges near T1 copper center, the entry point of electrons, as well as in dipole moment of the two BODs as a function of pH. Catalytic current for O_2 reduction by BODs immobilized on the surface of different CNTs was then followed by electrochemistry. A discussion on the proportion of well oriented BOD for direct electron transfer and forces governing this orientation can be drawn from these studies [5].

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One-Step Electrodeposition of Nanocrystalline $Zn_xCo_{3-x}O_4$ Films with High Activity and Stability for Electrocatalytic Oxygen Evolution

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The development of highly active, low-cost, and robust electrocatalysts for the oxygen evolution reaction (OER) is critical for generating hydrogen fuel through electrochemical (EC) and photoelectrochemical (PEC) water splitting.[1,2] Here, we report a new and facile one-step electrodeposition of nanocrystalline spinel-type $Zn_xCo_{3-x}O_4$ films from an alkaline Zn^{2+}-Co^{2+}-tartrate solution. To the best of our knowledge, $Zn_xCo_{3-x}O_4$ has never been directly electrodeposited. Previously reported synthetic methods for $Zn_xCo_{3-x}O_4$ usually involved high-temperature annealing of the hydrothermally or electrochemically synthesized Zn-Co precursors,[3-5] which were time-consuming and not suitable for the direct synthesis of catalysts on semiconducting substrates like Si. In contrast, in this work The electrodeposited $Zn_xCo_{3-x}O_4$ electrode could be directly used as the anode for the water electrolysis without any post treatment. The $Zn_xCo_{3-x}O_4$ film shows a low and stable overpotential of ~0.33 V at 10 mA cm^{-2} (and ~0.35 V at 20 mA cm^{-2}) for over 10 hours and a Tafel slope of ~39 mV dec^{-1} toward the oxygen evolution reaction (OER) in 1 M NaOH (as shown in Fig. 1), comparable to the best performance of the non-precious OER catalysts reported for alkaline media. The enhanced OER activity of $Zn_xCo_{3-x}O_4$ compared to Co_3O_4 could be attributed to the surface structural modification and higher density of the accessible active Co^{3+} sites induced by the incorporation of Zn^{2+}. The electrodeposition method in this paper could also be used to synthesize other binary and ternary metal oxide-based catalytic electrodes for reactions like OER and oxygen reduction reaction (ORR).

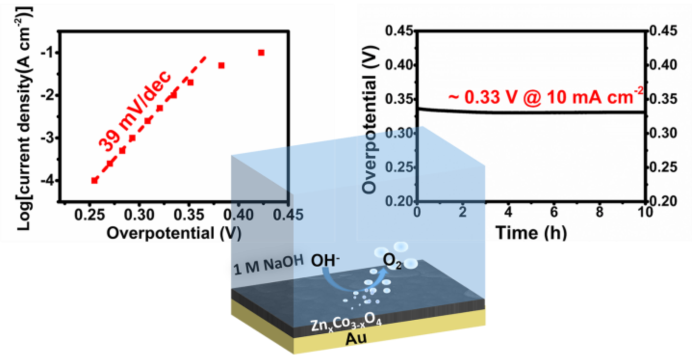

Fig. 1. Tafel slope and long-term stability test of the electrodeposited $Zn_xCo_{3-x}O_4$ film in 1 M NaOH at room-temperature.

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Hydroxide Ion Oxidation in Aqueous Solutions Using Boron-doped Diamond Electrodes

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Hydroxide is used worldwide in many industrial processes and research, including in the electrochemical field application, making the study of this compound is important to this field.[1,2] The electrochemical oxidation of hydroxide ion occurs at high overpotential, usually in the region of 1.30 to 1.60 V (vs. SCE).[2,3] In aqueous solution, this high overpotential makes the phenomena quite difficult to be observed due to overlapping of the oxidation wave with the oxygen evolution reaction (OER). On the other hand, the used of boron-doped diamond (BDD) as electrode materials gained much attention due to its high durability, small background current, and high overpotential of water oxidation compared to conventional electrode.[4] Since BDD have high overpotential of water oxidation, it should be possible to distinct the oxidation wave of hydroxide ions with the OER. This makes study of hydroxide ion oxidation easier to be observed, without the needs of particular geometry or electrode system. Herein we report the study of hydroxide ion oxidation at BDD electrode in basic aqueous solutions.

A well-defined voltammetric wave attributed to hydroxide ion oxidation was observed at ~1.25 V versus Ag/AgCl in 100 mM $NaClO_4$ with the presence of 1 mM NaOH at anodic-oxidized BDD (10 voltammetric cycle between 0 V and 3.0 V in 100 mM $NaClO_4$ before measurement, referred as AO-BDD). Moreover, the hydroxide ion oxidation behavior was found to be affected by the surface condition of the BDD electrode. When cathodic-reduced BDD (10 voltammetric cycle between −3.0 and 0 V in 100 mM $NaClO_4$ before measurement, referred as CR-BDD) was used as the electrode, the hydroxide ion oxidation peak was observed at slightly less positive potential. Additionally, a shoulder wave (referred as pre-peak) was observed at potential ~0.90 V. Considering that the peak was not observed at AO-BDD, the pre-peak was interpreted as the oxidation of hydroxide ion at "reduced surface" of the BDD, while the peak observed after that was interpreted as the oxidation of hydroxide ion at the "oxidized surface" of the BDD. Furthermore, various cycle number of cathodic pretreatment was conducted. It was found that the pre-peak was increase along with the increase of the number of cycle at the cathodic pretreatment. This might be due to the increase of the "reduced surface" of the BDD with the increase number of reduction cycle, leads to the increase of the current signal at the pre-peak. Although the hydroxide ion oxidation profile was slightly different between AO- and CR-BDD, the peak current was found to depend linearly on NaOH concentration at both electrodes. Lastly, the LSV measurements using different kind of bases shows similar peak profile, further confirmed the hypothesis that the peak was due to the hydroxide oxidation.

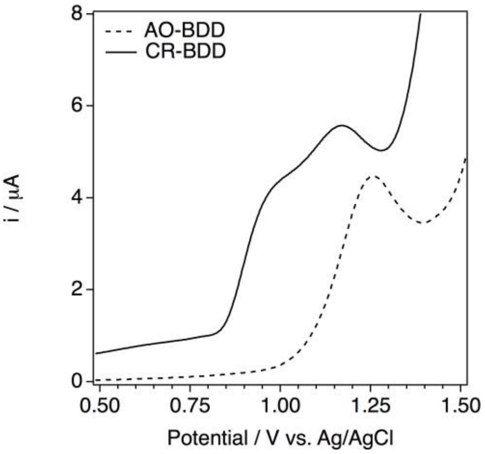

Figure. LSVs measurements in 100 mM $NaClO_4$ aqueous solution with the presence of 1.0 mM NaOH at AO-BDD (dotted line) and CR-BDD (solid line).

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New Organometallic Tracers for the Development of Electrochemical Affinity Biosensors

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The detection of endocrine disruptors in the environment is a current analytical challenge, especially with regard to the estrogenic hormones estradiol (E2) and ethinylestradiol (EE2). In the European Union, these substances have been recently included in a watch list of harmful chemicals (2015/495) in the frame of water regulation policy (Water Framework Directive). Affinity sensors based on antibodies and aptamers appear as promising alternative analytical tools for the detection of these estrogenic hormones that do not display any electrochemical and enzymatic activity. Classically, target-antibodies or target-aptamers interactions are revealed using enzymatic labelling, which is sensitive to interfering compounds and involves additional incubation and washing steps. In order to circumvent these problems, hormones derivatives were chemically-modified using metal complexes, detectable by electrochemical methods, and the resulting tracers were subsequently used in immunosensors operating in competitive mode. Detection limits in the order of 4 ng L^{-1} were obtained using salan oxovanadium complex as marker, these performances were comparable with those achieved using enzyme-labelled immunosensors[1] [2].
More recently, our works were focused on the synthesis of bis-1,2,3-triazole ligands and their corresponding metal complexes. A great coordination sphere allowing the complexation of copper and oxovanadium was proved. The complexation reaction was studied by spectrophotometric titration, which showed an intense absorption around 400 nm, corresponding to ligand metal charge transfer. Additionally, the X-Ray Structures of bis-triazole ligand and their corresponding metal complexes showed the co-existence of a dinuclear coordination complex, which can explain the important amplification of electrochemical signal. A good stability and solubility, up to 1 mM of metal complexes in phosphate buffer at pH 7 was demonstrated. These new complexes based on bis-triazole ligands show promising ability for antibodies and aptamers labelling.

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Designing low cost Na-ion batteries

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Li-ion batteries are starting to reach their limits in terms of energy density, cost and abundance, and progress is slower than expected. Thus, researchers are currently re-investigating other alkali metals as Li substitutes, mainly focusing on Na. This system has been considered to be purely academic, and no real applications or prototypes have been developed to investigate its viability or possible commercialization, the only exception being the high temperature Na-S system, which was commercialized in the 1960s. Recently however, the amount of research and number of papers devoted to the development of active materials for Na-ion batteries has increased exponentially, leading the community to consider the commercialization of Na-ion batteries in the near future. To achieve commercialization, suitable anodes and cathodes must be developed and studied in depth as the Na-system is often not analogous to the Li-system.

After establishing a careful guideline to optimize the electrode engineering and the electrolyte formulation both of which strongly influence electrochemical cycling performance, we developed new materials (negative and positive electrodes) for cheap Na-ion batteries. For the former, the most common binder used in Li-ion batteries, polyvinylidene difluoride, was found to be unsuitable for Na-ion batteries due to it decomposing to form NaF [1]. Additionally, a systematic investigation of particle size, binder and conductive additive ultimately led to an optimized electrode composition consisting of 70wt% micron-sized active material, 18wt% carbon black and 12wt% sodium carboxymethyl cellulose (Na-CMC) binder [2].

For the latter, we have developed a new research direction to drastically reduce the cost of the Na-ion batteries by making carbonaceous materials (negative electrodes) based on bio-wastes (Figure 1) and by developing new cathode materials based on the 20th more abundant elements in Earth crust [3-4].

Along this talk, we will review the synthesis procedure, the characterization of those novel materials and finally reveal their electrochemical performances in half-cell Na-ion batteries but also in full-cell configuration.

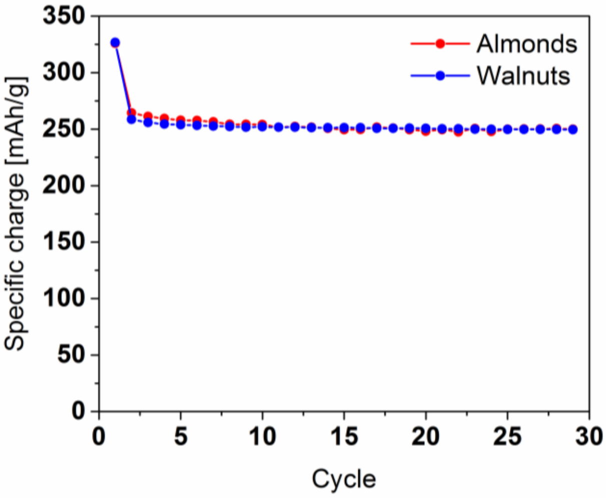

Figure 1. Cycling stability of biowaste carbonaceous materials obtained from walnuts and almonds calcination

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Solid State Electropolmerization of Manganese Phthalocyanine coated with Langmuir-Blodgett and Click Electrochemistry

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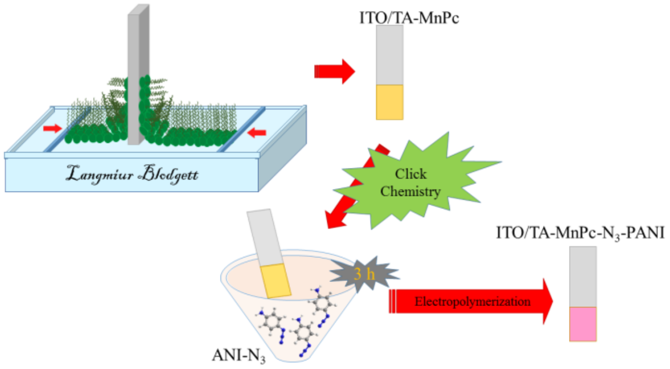
Recently, electrochemical biosensors are highly used in environmental monitoring, process control systems in the food manufacturing industry, and in biomedical analysis. Electrochemical techniques by comparison with conventional techniques for pesticide determination have excellent properties such as rapid response time, high sensitivity, fast, low cost [1-4]. Among the various functional materials, metallophthalocyanines (MPc) as sensing materials have been intensively studied due to highly conjugated, high thermal stabilities, photovoltaic effect, redox activity, and strong absorbance in the UV-visible regions. Applications of MPcs usually acquired a thin film deposited on a solid substrate such as ITO, FTO electrode etc. MPc films may be obtained by different deposition techniques: spin coating, physical vapor deposition, molecular beam deposition, Langmuir–Blodgett deposition (LB), electropolymerization, electrodeposition or covalent anchoring [1]. Here, we selected the LB technique for the preparation of terminal alkynyl substituted manganese phthalocyanine (TA-MnPc) thin film due to its excellent properties like molecular orientation, molecular arrangement, constructing supramolecular assemblies or ultrathin molecular film arrangement of functional materials. One of the main problem of LB films is the leakage of the films from the substrate, which decrease stability of the modified electrodes constructed with LB technique. This problem was tried to solve by electropolymerization of the LB film of MPc.

A mimic enzymeless electrochemical sensor based on terminal alkynyl substituted manganese phthalocyanine (TA-MnPc) was constructed and tested as selective and sensitive sensor for various pesticides. The sensor was constructed with sold stated electropolymerization of the functional materials coated on ITO electrodes. TA-MnPc was deposited with Langmuir Blodgett (LB) technique. Then 4-azidoaniline (PANI-N_3) was bonded to the terminal alkynyl substituents of TA-MnPc (ITO/TA-MnPc-N_3-ANI) with click chemistry (CC) and finally solid TA-MnPc-N_3-ANI film on ITO electrode was oxidatively electropolymerized to ITO/TA-MnPc-N_3-ANI electrode. The structure of ITO/TA-MnPc-N_3-PANI electrode was characterized using square wave voltammetry (SWV), X-ray diffraction (XRD), scanning electron microscope (SEM), and Fourier transform infrared (FT-IR). This electrode was tested for detection of various pesticides via SWV technique. Different voltammetric responses were observed for each pesticide, which showed selectivity of the electrode. The limits of detections (LOD) (0.49 μM for fenitrothion, 0.88 μM for eserine and 0.62 μM for diazinon) were considerably lower than reported ones with AChE based electrochemical sensors. As a real sample application, the mimic enzymeless electrochemical ITO/TA-MnPc-N_3-PANI sensor was successfully employed for determining the fenitrothion residue in rosehip sample.



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Color changeable gold luster polymer apply for energy storage smart window

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There are two important energy solution strategies, harvesting renewable energy and using energy efficiently. Renewable energy can be harvested by natural energy, for example sun light. For instance, energy from sunlight has been used increasingly in recent years. On the other hand, multifunctional device called energy storage smart window (ESS window) was designed to use energy efficiency.[1] ESS window is not only electrochemical capacitors but also able to change color and transmittance by stored energy in itself. Although this device is very interesting, the variation of colors is little. Creating more variation of colors is essential for the development of this device.

In this study, we made color changeable gold luster polymer from 3,4-ethylenedioxythiophene (EDOT) and aniline. PEDOT has high conductivity and that is derivative of thiophene polymer which can indicate gold luster.[2] Aniline polymer (PANI) change color and transmittance with small voltage application. Polymer film was made by electropolymerization (Fig. 1) and the color was valued by total reflectance (Fig. 2). The total reflectance of this gold color film was changeable with voltage application. Although the color of this polymer was gold at 1.0 V, it was gray at -0.5 V (Fig. 3). This gold color is made by only polymer and has supercapacitor function. This research is attractive to make gold color ESS window.

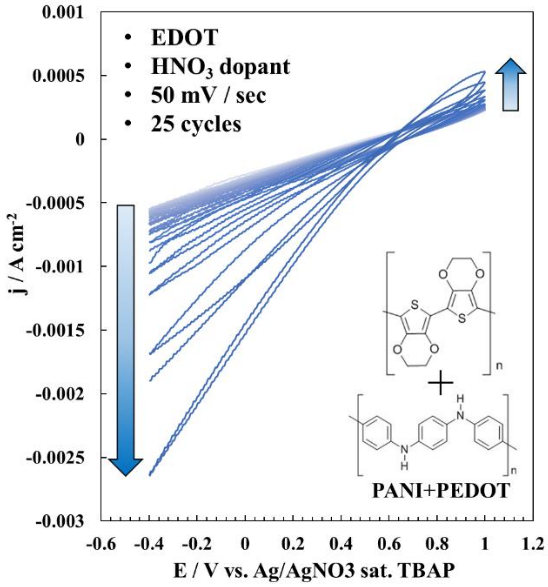

Figure. 1 CV carb of PEDOT + PANI

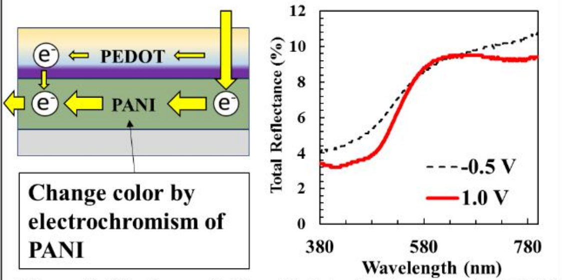

Figure. 2 Film image (left) and total reflectance spectra (right)

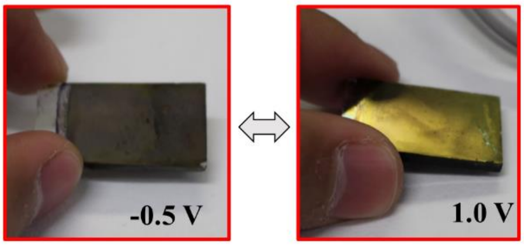

Figure. 3 EC of PANI + PEDOT

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Nanochannel Arrays for Molecular Sieving and Electrochemical Analysis by Nanosphere Lithography Templated Graphoepitaxy of Block Copolymers

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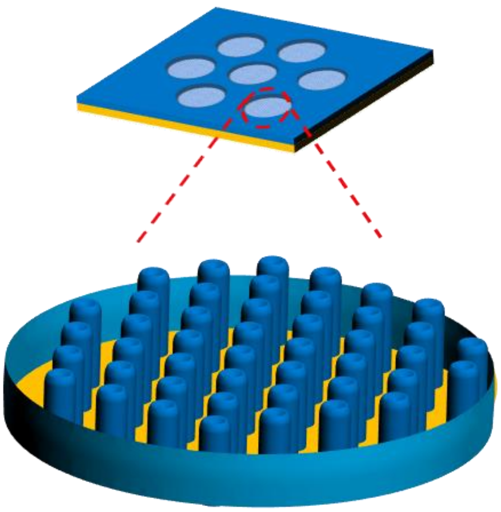
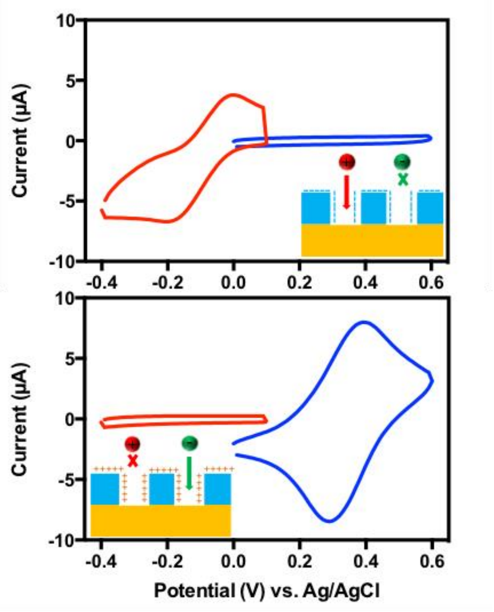
The ability to design, fabricate, and manipulate materials at the nanoscale is fundamental to the quest to develop technologies to assemble nanometer-scale pieces into larger-scale components and materials, thereby transferring unique nanometer-scale properties to macroscopic objects. In this work, we develop a new approach to the fabrication of high-density ordered nanoelectrode arrays that employs nanosphere lithography to template the graphoepitaxy of polystyrene-polydimethylsiloxane, PS-b-PDMS, di-block copolymers. By optimizing the chemical composition and molecular weight of the PS-b-PDMS copolymers under well-controlled solvent vapor annealing and overcoating conditions and the subsequent reactive ion etching processes, silica nanochannel (SNC) arrays with areal densities, ρ_A, approaching 1000 elements μm^{-2}, were obtained over macroscopic scales. The integrity of the SNC arrays was tested by using them as permselective ion gates, in wafer-scale nanoelectrode arrays (NEAs). These permselective NEAs allowed cations to pass into the nanochannel, but rejected anions, as demonstrated by cyclic voltammetry. The ion gating behavior could be reversed by chemically inverting the surface charge from negative to positive. Furthermore, conformal SNC array structures were obtained which could easily lifted off, detached, and transferred to another substrate, preserving the hierarchical organization while transferring the nanostructure-derived properties to a different substrate. This proof-of-concept sets the stage for potential applications in pre-concentration of target molecules and improved electrochemical selectivity for electrode materials not capable of supporting the SNC fabrication process directly.





Oxygen Reduction Catalyst Ni_3S_2 Oxidative Surface Restructuring and Application in Membrane-free Fuel Cells

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The interconversion of water and oxygen is a central chemistry underlying the storage of renewable electricity in energy dense chemical bonds. First-row transition metal oxides and chalcogenides have been found to rival or exceed the performance of the precious metal-based catalysts for both the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR). We have found that Ni_3S_2 efficiently catalyzes ORR under neutral conditions and outperforms Pt in the long-term electrolysis. The tolerance to small organic molecules and the selectivity towards the ORR made it possible to construct a membrane-free formate fuel cell with Ni_3S_2 as the cathode. In fact, we have found out that the Ni_3S_2-based fuel cell generates ~1.8 times power density than the Pt-based one, which further demonstrates that first-row transition metal compounds are promising electrocatalysts in the renewable electricity conversion and utilization.

The high lability of the first-row transition metals leads to surface dynamics under the conditions of catalysis that result in active site structures different from the bulk phase. While these surface transformations have been well-characterized on many metal oxides, the surface dynamics of chalcogenides under electrocatalytic conditions are largely unknown, particularly for the ORR. Herein, we combine electrochemistry, surface spectroscopy and high resolution microscopy techniques to characterize the surface dynamics of Ni_3S_2 under ORR catalytic conditions. We show that Ni_3S_2 surfaces undergo self-limiting oxidative surface restructuring to form ~2 nm amorphous surface films with an approximate composition of Ni:S 1.0:1.0. The formed amorphous surface structure exhibits similar ORR catalytic activity to the independently prepared amorphous and crystalline NiS. Both experimental and computational results indicate that the local coordination environment of the active sites instead of the bulk crystalline structure determines the ORR catalysis.

Tuning surface composition of Pt_3Co electrocatalysts and performance for enhancing CO tolerance

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Carbon supported Pt-based catalysts are recognized as the best catalysts that widely used in proton exchange membrane fuel cells (PEMFCs) and direct alcohol fuel cells (DAFCs). Currently in industry, most of H_2 was produced from hydrocarbons (CH_4, C_3H_8, or kerosene) reforming, while small amounts (ca.100 ppm) of CO was present in as-produced H_2. On the other hand, adsorbed CO are generated as an intermediate species during alcohol electro-oxidation. It has long been recognized that Pt is very susceptible to CO poisoning, even when the concentration of CO is as low as 10 ppm. Due to the strong adsorption, CO can block the active Pt sites and thus cause a great decline in fuel cell performance.

In this work, we tuned the surface composition of Pt_3Co nanocatalysts by heat treatment under different atmosphere (Air, Ar, H_2). The results of atomic-resolution HAADF-STEM, XRD, XPS and electrochemical characterization demonstrated that the surface composition of Pt_3Co catalysts with Co-increased, Intermetallic and Pt-increased were obtained by metal segregation approach. The unique surface composition on three catalysts causes the huge difference in both electronic effect and oxophilic effect. Correspondingly, their CO poisoning tolerance is also significantly different. Due to the differences in the surface atomic distribution and alloying extent, the nanocatalysts show different CO poisoning tolerance in the order of Co-increased > Intermetallic > Pt-increased. CO stripping voltammetry and in-situ Fourier transform infrared spectroscopy (FTIRS) were used together to investigate the origin of varied CO poisoning tolerance on three Pt_3Co catalysts. In−situ FTIRS shows that electronic effect plays a major role in weakening CO adsorption on Pt_3Co nanocatalysts and thus promoting CO oxidation to form $COOH_{ad}$ intermediate consistent with Langmuir−Hinselwood mechanism. Oxophilic effect promotes the oxidation of $COOH_{ad}$ intermediate into the final products CO_2/CO_3^{2-}. Therefore, careful tuning surface composition of Pt_3Co catalysts with the optimal electronic effect and oxophilic effect, the CO tolerance would be improved greatly. The conclusions drawn from this work can be extended to design efficient catalysts for other important reactions such as HOR, MOR, and hydrogenation.

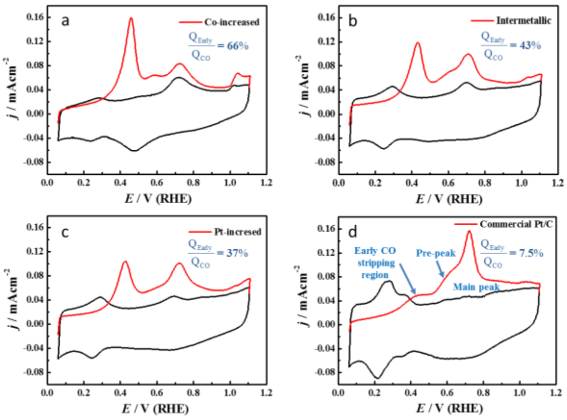

Figure 1 CO stripping voltammograms of catalysts in CO-free 0.1 M NaOH. Q_{Early} are obtained from integrating charges for early CO stripping from 0.35 to 0.5 V, and Q_{CO} for total CO stripping region.

This work was supported by National Science Foundation of China (Grant No. 21273180).

Core-shell carbide-derived carbons as platform for high performance electrochemical energy storage and electrocatalysis

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Porous carbons are a key component for supercapacitors and electrocatalysis. The electrode performance is strongly dependent on the structure of the pore network and carbon, which affect processes like surface interactions, sorption, reactions, or mass and electron transfer. Hierarchical structures are needed for an optimized balance of these processes and a core-shell architecture is particularly attractive. We recently presented two synthesis methods leading to new core-shell carbons. The basis for both routes is the reactive extraction of carbides to obtain carbide-derived carbons (CDC). Crucial for the core-shell design is a high control of the partial degree of conversion leading to carbon/carbide intermediates. We achieved precise control over the degree of conversion either by adjusting the conversion time [1] or limiting the amount of reactive extraction agent [2]. From the resulting well-defined carbon/carbide intermediates, we have derived three advanced core-shell materials for different electrochemical applications (Figure 1):
1) *Vanadium pentoxide / CDC core-shell hybrid particles* resulted after oxidation of the carbide cores. The redox activity of the vanadium oxide leads to an attractive lithium intercalation capacity while the surrounding porous carbon provides supercapacitance [3]. With this material, high specific energies up to 80 Wh kg^{-1} was achieved in organic electrolyte.
2) *All carbon core-shell structure* showing a mesoporous graphitic shell and a microporous amorphous carbon core were obtained after an additional reactive extraction of the carbide cores. Electric double-layer capacitor electrodes operating in with organic electrolyte were made from this material. The microporous core leads to high specific capacitance (93 F g^{-1}), while with the presence of the graphitic shell the electrodes show a high electrical conductivity [1]. The beneficial mass transfer provided by the mesopores of the shell allowed us to combine a high specific power with a high specific energy (14 Wh kg^{-1} @ 20 kW kg^{-1}).
3) *Hollow mesoporous and graphitic carbon spheres* were obtained after oxidation of the microporous carbon core of the all carbon core-shell structures. Electrocatalysts for the *methanol oxidation* were prepared by immobilizing platinum nanoparticles (NPs) on these hollow spheres. Conventional carbon black with 4 nm Pt NPs showed a mass activity of 220 A g_{Pt}^{-1} @ 0.6 V; for comparison, the pore structure of our hollow spheres allowed to obtain 2 nm Pt clusters, which showed a remarkable activity of 390 A g_{Pt}^{-1}@ 0.6 V. The hollow sphere based catalyst also featured excellent stability over 500 cycles of cyclic voltammetry with no activity loss, while the carbon black based catalyst drops in activity by 25%.

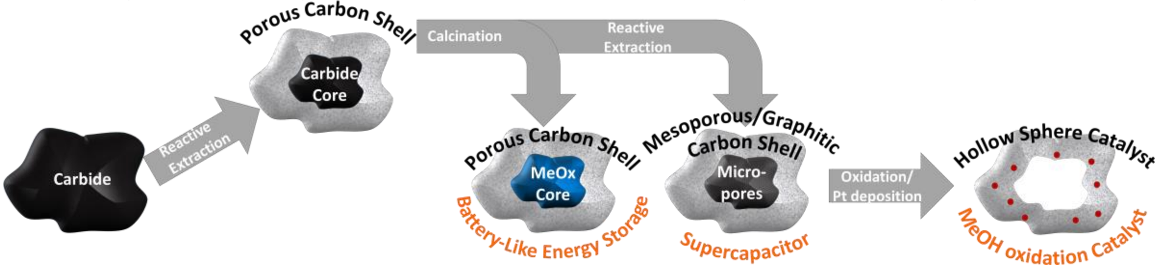

Figure 1: Scheme on synthesis platform allowing to obtain three different core-shell materials for different electrochemical applications.

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Panoramic Overview on the Enantioselection Performance of Inherently Chiral Surfaces: a Comparison between Systems with Different Atropisomeric Cores and Stereogenic Elements

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Enantiorecognition is a key issue in advanced analytical chemistry, particularly concerning the biological and pharmaceutical field. Enantiomeric molecules, being mirror-image structures, have identical physico-chemical scalar properties, but opposite pseudo-scalar ones. When interacting with a racemic probe, chiral molecules are able to recognize the enantiomers through diasteromeric interactions.

Similarly, chiral electrodes are required for enantioselective electroanalysis, and the development of "intelligent" electrodes capable of discriminating enantiomers, in particular molecules of biological and pharmaceutical importance, remains as one of the major challenges in electroanalysis.

We have recently proposed the first synthetic inherently chiral electrode surfaces able to neatly discriminate as separate peaks (in terms of potential values) the antipodes of model chiral probes, also drugs, both as enantiopure and racemate. [1-2] We have also verified the general validity of the inherently chiral concept, which does not depend from the chemical nature of the atropisomeric scaffold, testing chiral surfaces electrooligomerized from starting monomers with different molecular design (*i.e.* bithiophene, bibenzothiophene, biindole and paracyclophane cores) and different stereogenic elements (stereogenic axis *vs* helix *vs* plane). In order to fully elucidate the enantioselection capability of all of these heteroaromatic systems we propose a detailed comparison (an example in Figure) of our inherently chiral surfaces with different atropisomeric core *vs* thiahelicene-based films *vs* "two floor" paracyclophanic oligomers.

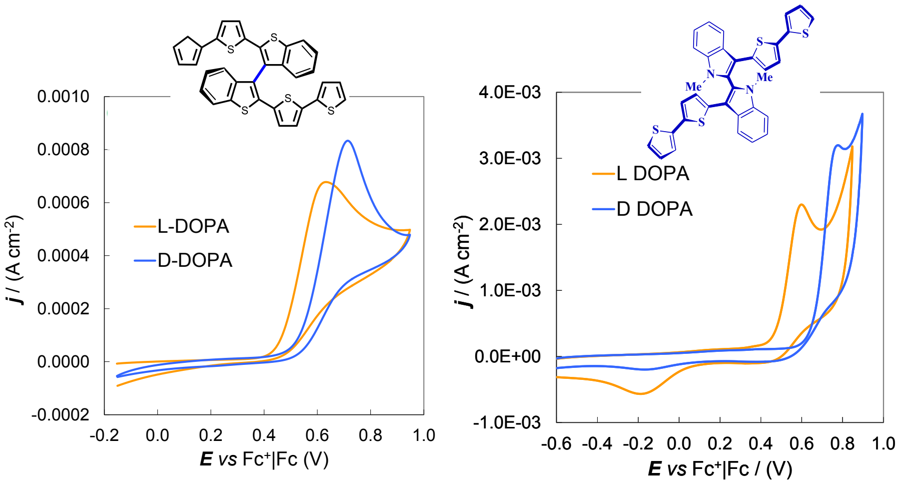

Figure. Enantioselection properties of inherently chiral oligomers with bibenzothiophene and biindole units towards L- and D-DOPA probes.

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Electrochemical sensing of glucose by reduced graphene oxide-zinc ferrospinels

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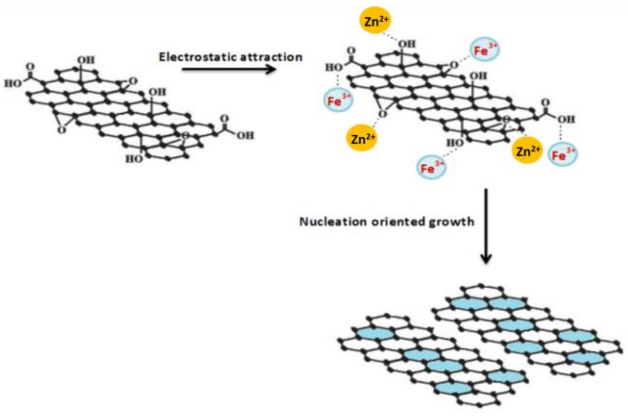
We have developed $ZnFe_2O_4$ magnetic nanoparticles/reduced graphene oxide nanosheets modified glassy carbon ($ZnFe_2O_4$/rGO/GCE) electrode as a novel system for the electrochemical glucose sensing. Via a facile in situ hydrothermal route, the reduction of GO and the formation of $ZnFe_2O_4$ nanoparticles occurred simultaneously. This enables the $ZnFe_2O_4$ nanoparticles dispersed on the reduced graphene sheet. Characterization of nanocomposite by X-ray diffraction (XRD) and transmission electron microscopy (TEM) clearly demonstrate the successful attachment of $ZnFe_2O_4$ nanoparticles to graphene sheets. Electrochemical studies revealed that the ZnFe2O4/rGO/GCE possess excellent electrocatalytic activities toward the oxidation of glucose and the performance of sensor is enhanced by integration of graphene nanosheets with $ZnFe_2O_4$ nanoparticles.



Scheme 1. The synthesis process of the ZnFe2O4/rGO nanocomposite

Molten salt synthesis of nitrogen doped porous graphitic carbon: A new preparation methodology for high-volumetric capacitance electrodes materials

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To meet the ever-increasing needs for high-efficiency energy storage in the modern society, porous carbon materials with large surface areas are typically employed for electrical double-layer capacitors to possess high gravimetric performances (up to 250 F g^{-1}). However, due to their low packing density (typically less than 0.5 g cm^{-3}) [1, 2], the specific volumetric capacitance[3, 4], another more important parameter in evaluating a material using in supercapacitor, is usually lower than 200 F cm^{-3}. Beside, both physical and chemical activation methods involve multiple steps to obtain the final products, which drive the expense for scale-up. Thus, the search is still on novel methods to synthesize porous carbon materials with high volumetric capacitance for EDLCs.

Here, a novel and one-step molten salt synthesis of three-dimensional, densely nitrogen-doped porous carbon (NPC) material by using low-cost and eco-friendly tofu as the nitrogen-containing carbon source is proposed(Figure 1). During the process, the low melting point molten salts act as in-built template that prevents the adjacent tofu from fusion/agglomeration during the carbonization. At the same time, $LiNO_3$ is introduced into the modern salts can act as activating agent by using the principle of black powder for the construction of porous carbon framework. Consequently, the as-obtained functionalized NPC has high surface area (1202 m2 g^{-1}), high bulk density (about 0.84 g cm^{-3}), high nitrogen doping (4.72%) and hierarchically interconnected porous framework. As such, the as-obtained NPC shows an ultrahigh volumetric capacitance of 360 F cm^{-3} and gravimetric capacitances of 429 F g^{-1} in KOH and excellent cycling stability (100% capacitance retention after 10000 cycles at a current density of 10 A g^{-1}). The high specific gravimetric/volumetric capacitance, outstanding rate capability and stable cycling performance of these NPC are very promising for the development of compact, high-performance supercapacitors.

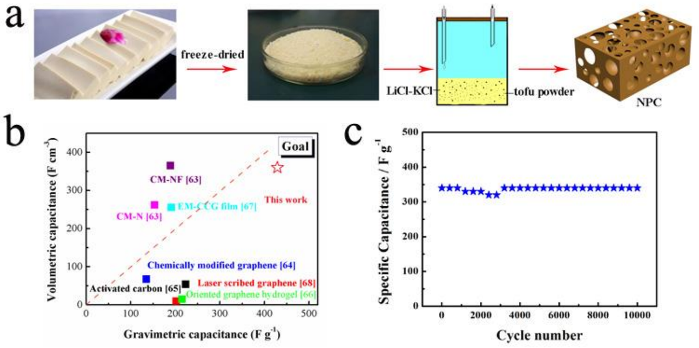

Figure 1 (a) Schematic illustration of the formation of NPC. (b) Comparison of the volumetric and gravimetric capacitances of the NPC-750-0.25 electrode with those of other carbon electrodes in aqueous electrolytes. (c) Cycling stability of the NPC electrode after 10000 cycles.

Acknowledgments

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Initial Stages of Sn Electrodeposition on Glassy Carbon. Effects of Temperature and Thiourea Addition

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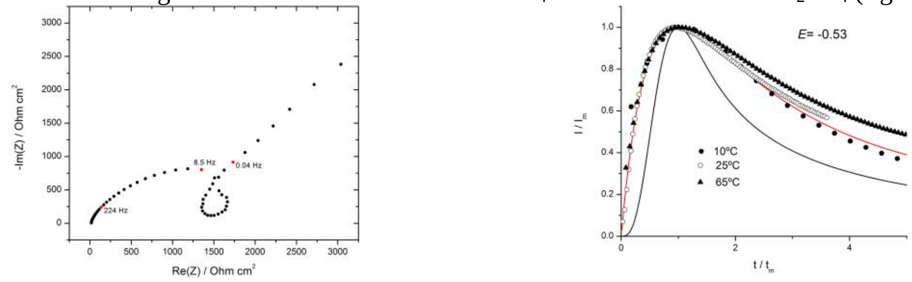
Among other uses, Sn has been proposed as part of a composite anode material for lithium batteries, particularly because of its excellent intercalation properties for lithium ions. An interesting possibility is the development of carbon based electrodes, such as graphite or graphene, coated with Sn. In order to advance in the knowledge of the electrodeposition of Sn on carbon substrates, we have studied the electrodeposition of Sn on glassy carbon (GC) electrodes for temperatures between 283 and 338 K ~~C~~ in sulphuric acid solutions in the absence and the presence of thiourea, (TU). Experiments involved voltammetric runs, potential steps and electrochemical impedance spectroscopy together with SEM analysis. The voltammetric runs show a single cathodic current peak that shifts to less positive potentials (measured vs Ag/AgCl reference electrode) as the TU concentration is increased, and, at the same time, the threshold potential for the hydrogen evolution reaction decreases. Analysis of the current transients related to the electrodeposition of Sn at constant potential shows that the corresponding current peaks appear at longer times in the presence of TU along with a change in the nucleation mechanism. Thus, in the absence of TU, the adimensional analysis of the current transients fits a model associated with an instantaneous nucleation and 2D growth under diffusion control. The presence of TU in the platting solution apparently (?) changes the mechanism to a progressive nucleation process, seemingly due to the adsorption of the molecule blocking active surface sites. SEM images show that Sn particles deposited from TU-free solutions exhibit a rather cubic shape with a mean size of about 2x10^{-9} cm^2, and are well distributed on the electrode surface. Conversely, deposits formed from TU-containing solutions exhibit comparatively very large and dispersed particles, particularly at the lowest temperature. It can also be observed the presence of dispersed aggregates formed by rather large sticks grown at right-angles. The Nyquist plots obtained in TU-free solutions between 60 kHz and 10 mHz, show two time constants at high frequencies followed by an inductive loop, assigned to the relaxation of an adsorbed intermediate, and finally a Warburg impedance at low frequencies, which is related to the transport of ions to the reaction interface. On the other hand, Nyquist plots obtained in TU-containing solutions exhibit a single time constant, at least in the 60 kHz – 10 mHz frequency range.

SEM image of Sn deposited on GC at -0.53 V during 0.5 s at 298 K from 0.01 M $SnSO_4$ in 1 M H_2SO_4 (left) and -0.58 V during 25 s at 283 K from 0.01 M $SnSO_4$ + 0.01 M TU in 1 M H_2SO_4 (right).



Nyquist plot for the electrodeposition of Sn on GC at -0.52 V and 283 K (left); Reduced variables tests (I/I_m vs. t/t_m) obtained for E= -0.53 V at different temperatures (right). 0.01 M SnSO4 + 1 M H_2SO_4.

Potential Controlled Electrolysis as a New Industrial Scale Electrochemical Process of Metals Recovery and Manufacturing

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Due to expansive economic development and growing industrialization, the demand for base and precious metals is constantly growing. At the same time resources and quality of ores and metals concentrates are significantly declining, what results in increasing costs of metal production. Therefore, alternative sources of metals like industrial waste and spent electrolytes should be explored. There is a variety of methods in use for recovery of heavy metals, including hydrometallurgical, pyrometallurgical, and bio-hydrometallurgical [1-8]. However, among electrochemical methods especially, a new and patented method of potential controlled electrolysis (PCEl) of mass metals electrowinning/electrorefining [1-8] has a potential to meet the challenges of 21 st century challenges. It has been shown that electrowining of copper can be carried out at the very low copper concentrations even below 1 g/l which might simplify existing metals recovery from by-products and spent electrolytes of mining and metallurgy industries. On the other hand potential-controlled industrial electrorefining of e.g. copper can be potentially realised at the very high current densities (as high as limiting current densities) even above 500 A/m2 and cathodic current efficiencies above 98% with a purity of copper even higher than 99.995% and relatively low power consumption [6-7].

The most important advantage of potential-controlled electrolysis is that current density might change according to the changes of actual conditions of the industrial electrolysis. Consequently, a high purity metals can be obtained by potential-controlled electrolysis even when such fundamental conditions of e.g. copper electrodeposition process as copper concentration, temperature, concentration of additives (e.g. animal glue and thiourea) change with time and site of the electrolytic cell. Presently, the current-controlled (galvanostatic) copper electrolysis processes are very sensitive to changes of the copper electrolysis conditions. As it is shown in pilot and laboratory scale experiments the power consumption of metals electrowinning is lower than for existing electrometallurgical processes [6-7].

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Electrokinetic Technologies for Dewatering Phosphatic Clay Suspensions

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The current methods in the phosphate-mining industry for processing phosphatic clay waste streams are costly and slow due to the poor-settling behavior of the phosphatic-clay effluent, which hinders the separation of the component clay and water. Gravity settling takes 25 to 50 years to achieve the required minimum solid-weight fractions when starting with suspension that are initially 2 to 3 wt. % solids. This process occurs in large man-made lakes called clay-setting areas (CSAs) which occupy significant amounts of land and water. The objective of the present work is to develop an economically viable method for separating the clay and water by use of electrokinetic phenomena.

The effluent is a colloidal suspension consisting of charged clay particles in water that was added for the flotation process. The charged nature of the clay particles has prompted interest in the utilization of electrokinetic phenomena to accelerate the clay-water separation. When the suspension is under the influence of an applied electric field, the particles and water move under the mechanisms of electrophoresis and electro-osmosis, respectively. Electrokinetic dewatering (EKD) is a method that has been investigated over the past 50 years as a possible method for accelerating the dewatering process as opposed to current mechanical methods, but these studies often resulted in the assessment that EKD is cost prohibitive.

Previous work by our group has shown, through the development of EKD prototypes, that the efficacy of EKD can be improved, increasing the viability of EKD as a possible industrial method. Initial batch-scale EKD cells provided proof-of-concept, achieving a 40 wt. % solid cake and the development of a constitutive relationship between the rate of dewatering and final achievable weight percent as a function of applied electric field and residence time. Further development improved on the efficiency of the process by converting the previously studied EKD process from batch to a semi-continuous which improved the separation as experimentally observed in the production of low-turbidity supernatant water with measured transparencies below 1 NTU. The most recent prototype moved to a fully-continuous-separation process which significantly reduced the power consumption of EKD.

Current work is to improve the efficiency of the separation through the design of the next generation of the EKD process. Optimization involves the development of a mathematical model that can adequately represent the EKD process. From a better model, the underlying electrochemical processes can be quantified to develop more comprehensive constitutive relationship between applied electric fields, dissolved ionic species, clay composition, and geometry. From iteratively designed prototypes, the physical process can be improved by optimizing the mechanical efficiency, by studying the rheological behavior of the viscoelastic phosphatic clay suspension, and by refining the fully continuous design.

The development of EKD as an industrially viable process will have significant effect on reducing the environmental footprint of the phosphate mining industry in the reduction of the land required for CSAs and the minimization of the required water resources for the beneficiation of the phosphate ore. EKD ultimately can be applied to other mining operations that utilize flotation and produce charged-particle effluent streams. Examples may include mining of many ores and extraction from oil sands.

Synergetic effects of electrochemical precipitation and cathodic oxidation on removal of ammonia in wastewater

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Abstract: An electrochemical reactor used Mg plate and modified graphite felt as electrodes was developed to remove ammonia nitrogen in waste water. Experimental results showed that the reactor achieved 74.58% removal rate of ammonia which was higher than a Pt/steel electrode reactor at reaction time of 1.0h and electric current density of 4mA • cm^{-2}. Reaction time prolongation resulted in decreasing of ammonia removal rate because of part of the precipitation dissolved. Electrochemical precipitation plays the main role in removal of ammonia nitrogen which contributed to 76.7% of removed ammonia nitrogen. Air floating was responsible to less than 3.0% amount of ammonia nitrogen removed. The modified graphite felts cathode produced H_2O_2 that could oxidize ammonia to nitrogen and improve the removal rate of ammonia nitrogen. Therefore, the synergetic effects of cathodic oxidation and electrochemical precipitation can effectively improve the removal of ammonia nitrogen in water. The results enlightened significance for the development of enhanced electrochemical ammonia removal process.

Keywords: ammonia nitrogen; electrochemical; cathodic oxidation; struvite; wastewater treatment

Comparison of the effect of Ti/RuO_2 and Ti/IrO_2 anodes on the purification of phenolic wastewaters

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Phenolic compounds, typically found in olive mill wastewaters (OMW), are difficult to be removed through biological processes due to their recalcitrant character and seasonality. This situation led to the search for new depuration technologies operating at room conditions of pressure and temperature. Among them, the electrochemical oxidation (EO) emerged as a promising solution with generally simple operations and inexpensive equipment. This technique is versatile, robust and amenable to automation.

In this context, an EO process was applied to the treatment of a synthetic OMW in a batch-stirred reactor by testing the Ti/RuO_2 and the Ti/IrO_2 materials as anodes. After 180 min of reaction, each electrode allowed a total phenolic content (TPh) abatement and 100 % or 84.8 % of COD removal for the ruthenium or iridium materials, respectively, with the following conditions, 10 g $L^{-1}$of NaCl, 119 mA cm^{-2} and initial pH 3.4. Although no morphological differences were observed between the fresh and used Ti/RuO_2 anode, the surface of Ti/IrO_2 evidenced some changes, maybe because of a corrosion phenomenon. In recent years, diseases of the central nervous system that are affecting a growing number of people limiting their everyday life are one of the main focus of biomedical research. In particular, synaptic activity and its major property, plasticity, which is involved in cellular learning, may be highly affected by pollutants of industrial origin. Therefore, the impact in neuronal activity of the untreated and treated phenolic effluents was evaluated through the formation of synaptic reactive oxygen species (ROS). The treated effluent caused a smaller depression and a larger potentiation upon its removal than the untreated one, probably due to the formation of end products obtained. In addition, the depuration of real undiluted OMWs (COD_0=6.5 and 23 gO_2 L^{-1}) with both active anodes revealed a high ability to remove phenolic content, achieving only COD removal around 17 %. Conversely, when a diluted OMW (COD_0=1.1 gO_2 L^{-1}) was tested with Ti/IrO_2 material, there was an increase of the COD abatement to 62.8 %.

The results ensure the applicability of these approaches as pre-treatment processes.

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Stability of Organic and Organometallic Flow Battery Reactants

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To address the intermittency of renewable energy sources such as wind and solar, much effort has been focused on reducing the cost of electrochemical energy storage. Flow batteries with lower cost reactants have the potential to become less expensive than conventional closed-cell batteries for long duration utility scale applications. Aqueous-soluble organic reactant molecules which can be easily synthesized from earth abundant elements are currently being developed for this purpose. A necessary criterion for the success of this technology is the long-term stability of these reactants molecules. In this work, we report on the chemical and electrochemical stability of several organic and organometallic redox reactants in aqueous electrolytes. Several analytical methods such as NMR, UV-Vis spectroscopy and three electrode cyclic voltammetry are used to assess reactant concentration over time. In addition, electrochemical stability is further characterized by long-term cycling and capacity monitoring of symmetric two electrode cells. Specific fade rate mechanisms are proposed for each reactant.

Effect of water hardness during the BDD-anodic oxidation of wastewater containing with an azo dye

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The cations Ca^{2+} and Mg^{2+} are commonly present in drinking water and industrial effluents. These cations represent the water hardness and depending on their quantity, they can restrain the efficacy of the treatment method used to eliminate the high toxicity level of organic pollutants[1]. Electrochemical Advanced Oxidation Processes (EAOPs) are characterized by the *in situ* generation of reactive oxygen species such as the hydroxyl radicals ($^\bullet OH$). These radicals have a high standard power of reduction $E^\circ(^\bullet OH/H_2O)=2.80$ V/SHE that promotes the mineralization of the organic pollutant to CO_2, H_2O and inorganic ions[2]. The AO has been the most employed EAOP for treating organic pollutants, due to simplicity combined with high performance. In this process, when boron doped diamond (BDD) is applied as anode, is formed the physical adsorbed $^\bullet OH$ on its surface from water oxidation, as shown in reaction: $BDD + H_2O \rightarrow BDD(^\bullet OH) + H^+ + e^-$. However, the efficacy of the elimination of organic pollutants depends on several operaing parameters and the physical-chemical conditions of water. Therefore, the effect of the hardness can be a significant circumstance that should be studied in order to understand the effect during the electrochemical treatment of organic pollutants, such as dyes, pesticides, hydrocarbons, etc. In the case of anodic oxidation (AO) by using BDD anode, no attempts have been reported in the literature yet about the positive or negative effect of water hardness.

The experiments of AO were performed with 0.21 mM of the Eriochrome Black T (EBT) dye, different current density (j) and pH 10. The results demonstrated a significant decrease on the efficiency for color and chemical oxygen demand removals (Fig. 1) due to the formation of the complexes of Mg^{2+} and Ca^{2+} with EBT. These complexes are stable, limiting the fragmentation of the chromophore group (-N=N-) by the $^\bullet OH$ radicals and diminishing the removal of the organic matter. The reaction is of pseudo first order, with the values of the kinetic constants (k) of $k_1 = 0.0075$ min^{-1}, $k_2=0.0088$ min^{-1} and $k_3 = 0.016$ min^{-1}, for values of j of 25, 50 and 75 mA cm^{-2}, respectively. For higher j as the case of the 75 mA cm^{-2}, it was observed a decrease in the discoloration kinetics; this can be justified by the occurrence of the parasitic reactions of the $^\bullet OH$ radicals. The main conclusion of this work is that the hardness of the wastewater is an important parameter to be taken into account when applying an AO process because at high water hardness, longer treatment times are necessary, and consequently, increasing the costs.

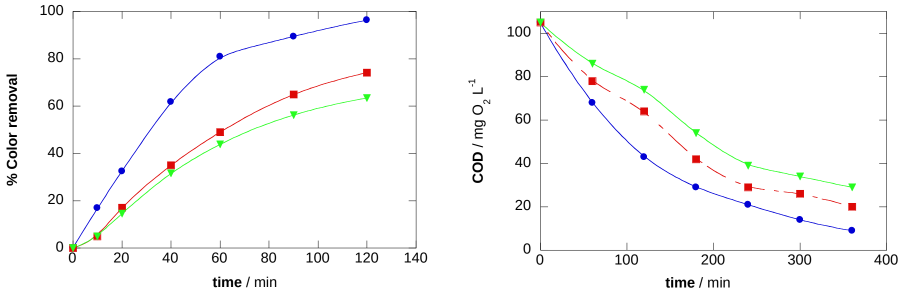

Fig 1. (a) Percentage of color removal (b) COD abatement achieved by AO treatment of 100 mL of 0.21 mM EBT solutions at j = 50 mA cm^{-2} under different water hardness matrix: (●) 0 mg L^{-1} of $CaCO_3$ or (■,▼) 500 mg L^{-1} of $CaCO_3$ water hardness due to (■) Ca^{2+} or (▼) Mg^{2+}.

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Shock Electrodialysis and Shock Electrodeposition for Sustainable Water Treatment

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Securing clean water is a global challenge made even more difficult in areas of high population density and sparse surface water. In India, though some of the groundwater available has relatively low salinity, the water often requires significant purification before it would satisfy the World Health Organization's drinking water standards[1]. Wells across the nation are poisoned with intolerably high levels of arsenic, nitrates, fluoride, metal ions, etc[2]. If not for these trace toxic ion impurities, these low-salinity aquifers could help address India's growing water demands. While many established water treatment technologies are available, few are well equipped to efficiently treat low salinity sources. Shock electrodialysis (SED) is a water purification technology, recently developed in our lab[3–6], that promises to completely eliminate ionic impurities in water with significantly lower energy overhead when compared to incumbent technologies like reverse osmosis. SED, much like electrodialysis (ED), passes an electric current perpendicular to flow in order to guide ions out of a purified stream of water and into a concentrated brine to be disposed. To contrast ED, the separation of fresh and brine is not achieved by a physical barrier like a membrane. Instead, the streams are separated by a stable concentration "shock" that arises from passing overlimiting current (defined as current requiring ion transport faster than is possible by diffusion alone) between the electrodes. This shock is stable in flow and possible only because of the SED device's carefully chosen porous media, which must have pores small enough to prevent the formation of vortices and have enough surface charge to promote the surface conduction of oppositely charged ions. Using a combination of this technology with shock electrodeposition, another recent advance from our research lab[7], it is possible to achieve the deionization of water without the costly water splitting reaction at the electrodes while collecting a significant portion of the impurities in a solid waste stream when removing certain metallic contaminants.

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Are N-volatile Species Released During Mineralization of Organic Pollutants by Hydroxyl Radical on Boron-Doped Diamond Anodes?

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The treatment of N-containing aromatic pollutants in waters such as amines and nitro-derivatives is of great relevance due to their carcinogenicity. The mineralization of nitrogen-containing pollutants yields N-species apart from the expected CO_2 and water. Generally, the main considered N-species are NH_4+, NO_2^- and NO_3^-. Nonetheless, taking into account these species, the nitrogen mass balance is in general terms incomplete. The evolution of hazardous NOx during the water treatments by •OH has been suggested to explain the loss of nitrogen during the mass balances, but unfortunately this hypothesis has not been demonstrated experimentally.

The research undertaken in this work aimed at identifying the formation of N-volatile species from their oxidation mediated by •OH to gain a better understanding of the oxidation reactions of reactive oxygen species (ROS) with organic pollutants. Four N-containing organic compounds with different functional groups were selected as model pollutants and treated by electrochemical oxidation (EO) using boron-doped diamond (BDD) anode. In EO, •OH is electrogenerated on the surface of oxygen terminated BDD anode from water oxidation reaction (1), which could be obtained at high applied potentials.

$$\text{H2O} \rightarrow \bullet\text{OH} + \text{H+} + \text{e}- \qquad (1)$$

In this work, the release of NOx has been ascertained and the overall current efficiency of conversion of N-containing pollutants to CO_2 and NOx was estimated semi-quantitatively using differential electrochemistry mass spectroscopy (DEMS) during electrochemical advanced oxidation process with boron-doped diamond (BDD) anodes. To identify the N-volatile species, the EO was carried out using Differential Electrochemical Mass Spectroscopy (DEMS). This analytic technique allows the on-line and simultaneous detection of volatile reaction products after their formation during cyclic voltammetry assays. Thereby, during the potential sweep, the faradaic current and the ionic currents of $m/z = 44$ (CO_2), $m/z = 46$ (NO_2) and $m/z = 30$ (NO) were simultaneously recorded during pollutants oxidation allowing the identification of these N-volatile species that have not been reported before in literature.

The systematic study of model organic compounds containing organic nitrogen has provided valuable information on the relationship between NOx species released with the nitrogenized functional groups, as it will be discussed for nitro group and primary, secondary and tertiary amino groups. Furthermore, the quantification of released species from the current efficiencies highlighted the low extent of NOx species evolved from the •OH oxidation of amino and nitro functional groups, which are ca. three orders of magnitude lower than the initial dissolved organic nitrogen in solution far from hazardous NOx concentrations stated by law of 40 $\mu g\ m^{-3}$. Thus, despite of being released NOx species, the EO with BDD anodes can still be considered an environmental friendly alternative to depollute wastewaters containing organic pollutants. On the other hand, the results suggest that similar trend could be observed in other advanced oxidation processes where the organics oxidation is produced by hydroxyl radical.

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Electrochemical Reduction of CO_2 to Formate on Nanostructured Bismuth Electrodes

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The electrochemical reduction of CO_2 to useful products including formate/formic acid, methanol, ethanol, methane and some others, represents an interesting alternative not only to mitigate global warming effects but also to produce valuable chemicals. In this sense, very relevant efforts have been recently made about this important topic [1-4]. In this contribution we present our recent results dealing with the electrochemical reduction of CO_2 to formate/formic acid on nanostructured bismuth (Bi) electrodes. Unsupported and carbon-supported Bi nanoparticles (about 10-12 nm) were prepared using an easy and fast methodology at room temperature. Once characterized by different physicochemical techniques (TEM, XPS and XRD), the samples were air-brushed on a carbon paper (Toray Paper TGPH-90). The nanostructured Bi electrodes showed not only high selectivity towards the product of interest (formate/formic acid) but also an important stability. The results will be discussed and compared with recently reported results obtained with nanostructured tin (Sn) electrodes [5].

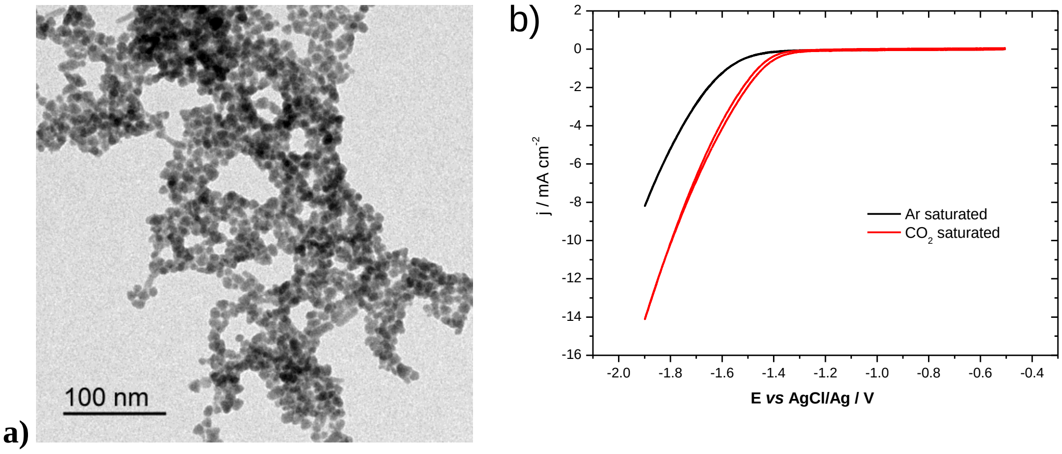

Figure 1. a) Representative TEM image of the prepared Bi nanoparticles and b) voltammetric response of a nanostructured Bi electrode in Ar and CO_2 saturated 0.5 M $KHCO_3$ solutions, scan rate 50 mV s^{-1}.

Acknowledgements
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Hydroxyl Radical Effect on Helminth Ova

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Introduction

Helminthiasis is a common disease around the world, 25–33% of population is affected in developing countries. There are several kinds of helminthiasis, most of the people affected are children under 15 years [1]. Helminths are pluricellular worms, their eggs are microscopic with a complex life cycle, and different from bacteria and protozoan, which are well known microbes in the wastewater treatment field. A common characteristic of helminths is that they reproduce through eggs that differ in shape and size, but in general, possess a shell that consists of three basic layers secreted by the egg itself; this is a lipoidal inner layer, a chitinous middle layer and outer proteinic layer. All these layers give high resistance to eggs under several environmental conditions [2], even resistant to common disinfection treatments with sodium hypochlorite [3]. There are some methods reported to remove Helminth ova: waste stabilization ponds, reservoirs constructed wetlands, coagulation-flocculation, rapid filtration, UASB (Upflow Anaerobic Sludge Blanket) [4]. The problem related to this processes is that Helminth ova are inactivated but not destructed. However, there are some alternatives that promote disinfection of water through hydroxyl radical, a powerful oxidant with a potential of 2.8 V, vs NHE via Advanced Oxidation processes (AOP) [5, 6]. The objective of this research was to study the effect of hydroxyl radical on Helminth ova in water, obtained via electro-Fenton.

Methods

A three-compartment electrochemical reactor was used, activated carbon was placed in the central compartment and an ionic exchange resin was placed in side compartments. Reagent H_2O_2 was electro-generated via oxygen reduction reaction on the cathode, the ionic resin in one side supplied ferrous ion, and ferric ion was recovered by other resin compartment, product of Fenton reaction.

Results and conclusions

In order to compare the effect of radical hydroxyl, traditional Fenton was analyzed, Figure 1 shows Helminth ova behavior before and after hydroxyl radical contact. It clearly shows Helminth ova disintegration due to the presence of radicals. After this result, electro-Fenton system was studied in order to simplify reagents use. Figure 2a shows the presence of Helminth ova on activated carbon in the reactor. Once hydroxyl radicals react to helminth ova, these eggs were disintegrated by its effect, Figure 2b.

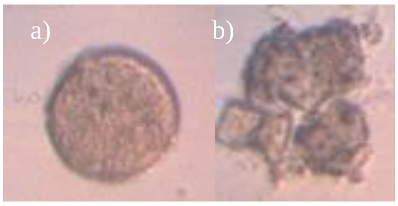

Figure. 1. Helminth ova disintegration by hydroxyl radical effect, a) before hydroxyl contact, b) after contact.

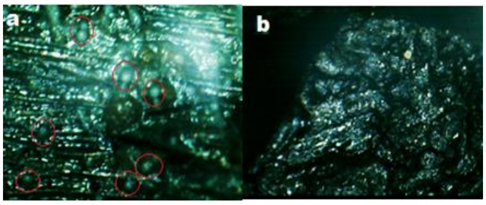

Figure. 2. Helminth ova disintegration in an electro-Fenton reactor, a) before treatment, b) after contact with hydroxyl radical.

According to results, our electro-Fenton reactor promotes an efficient disintegration of Helminth ova. This is a promising alternative to wastewater disinfection.

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Electrochemical Engineering Of The Molten State: A Path Toward Sustainability?

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Metals remain at the basis of modern society and their affordable and environmentally respectable extraction and recycling is required. In the context of 9 billion people by 2050 and issues such as greenhouse gas emissions, developing alternative approaches for metals extraction and processing is necessary. The electrochemistry of the molten state is an integral part of such endeavor, compatible with the deployment of sustainable electric power generation [1]. This presentation offers to report electrochemical studies of a subset of molten oxide [2,3] and sulfide [4] systems. Our results show that molten state electrolytes offer unique functionalities (enhanced mass transport, high conductivity, electronic conductivity, thermoelectric power) and that their engineering in electrochemical reactors remains to be tackled. Recent experimental results suggest that the specificities of the molten state require special attention to issues such as natural convection or anode design for enhanced gas recovery.

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Increasing Salt Adsorption Capacity Using Prussian Blue Analogues Electrodes for Cation Intercalation Desalination

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Many advances have been made in the development of capacitive deionization (CDI) devices for desalination applications through the use of novel cell architectures (e.g., flow-through electrodes, suspensions, and fluidized beds). When electric double-layer charging is used as the primary electrosorption mechanism, salt adsorption capacity of these devices is fundamentally limited by the surface area of the capacitive material. As such, alternative charge storage mechanisms are desired to increase salt adsorption capacity. Intercalation host compounds (IHCs), commonly used in rechargeable batteries, provide an alternative mechanism for charge adsorption where ions are stored within the interstitial sites of a solid-state material. The "Desalination Battery"[1] and hydrid CDI cells,[2] in particular, function with a scheme where one electrode adsorbs cations and one electrode adsorbs anions, similar to CDI, but with cations adsorbed via an Na-ion IHC instead of a capacitive electrode. Smith and Dmello (SD)[3,4] proposed desalination with Na-ion IHC electrodes having identical chemical composition. Referred to here as Cation Intercalation Desalination (CID), this innovative cell design was proposed where porous IHC electrode films are placed on either side of a separator layer with feed water in a "flow-through" mode directed through the electrode, along the separator layer. SD showed that for an IHC that is cation-adsorbing, the separator layer must be cation-blocking to achieve high salt removal, i.e., an anion-exchange membrane (AEM) must be used. In so doing, these simulations predicted salt removal capable of seawater level concentrations, in contrast to the typical brackish desalination capability of CDI.

In this talk we demonstrate the cation intercalation desalination concept for the first time experimentally.[5] We use electrodes incorporating nickel hexacyanoferrate (NiHCF) Prussian Blue Analogue nanoparticles to exchange Na^+ ions with solution, while Cl^- ions transport simultaneously between electrodes through an AEM. We choose NiHCF amongst many other IHCs for its long cycle life, facile intercalation kinetics, and suitable reduction potential. Experiments performed with brackish water feed solution (20 mM) show that, compared to capacitive deionization using porous carbon electrodes, a higher salt adsorption capacity per cycle is achieved, much lower cell voltages are needed, and the energy costs of desalination can be significantly reduced. Furthermore, computational modeling of CID predicts that NiHCF is capable of desalinating seawater level salt concentrations.[6]

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In Situ Characterization of Electrolytic Plasma Polishing Correlated with Effective Surface State Changes in Ti Anodes

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Electrolytic plasma processes are a group of electrochemical methods that allow the controlled transformation of metal electrode surfaces to achieve surface polishing, cleaning, case-hardening, oxidation and/or create micro- and nanostructures. Unlike many other electrolytic or chemical surface treatments, they use mild, REACH-compliant electrolytes. Their hallmark lies in the formation of a continuous gaseous envelope around the working electrode under high applied potentials (typically in the order of hundreds of volts). Micro-discharges, or a more stable plasma region giving the processes their generic name, form spontaneously and allow the flow of current through the gas layer.

While these processes are being used in industrial settings, their larger deployment is significantly hindered by the time required to optimize the appropriate set of parameters for each material and target surface states. Developing relevant process control protocols can therefore be expected to benefit greatly to a larger integration of the method in the industry. Real time data on the ongoing process are however difficult to collect, because the local conditions at the interface are relatively extreme and constitute a challenge to most conventional measurement equipment.

The focus in this work is placed on the exploration of this approach for the case of electrolytic plasma polishing (EPPo) of Ti. This method removes material to yield a smoother surface, partially through anodic dissolution. Accessible in situ information is gathered, and put into the perspective given by changes in surface state as characterized before and after the treatment. Depending on the material, process parameters and study goals, techniques such as voltammetry, electrochemical impedance spectroscopy, as well as optical emission and absorption spectroscopies can be exploited to probe the physics, chemistry and electrochemistry at play in EPPo. The evolution in the state of the interface as well as that of the gaseous envelope is of interest, with a focus on the phenomena ultimately controlling the charge transfer mechanisms through the interfacial region.
The topographical state of the surface before and after treatment is characterized, and described mainly through laser confocal profilometry, as illustrated in figure1. Alterations in chemical and mechanical surface state are also monitored with for example changes in hardness due to dealloying, or in corrosion resistance following surface restructuration of oxide layers, being the subject of particular attention.

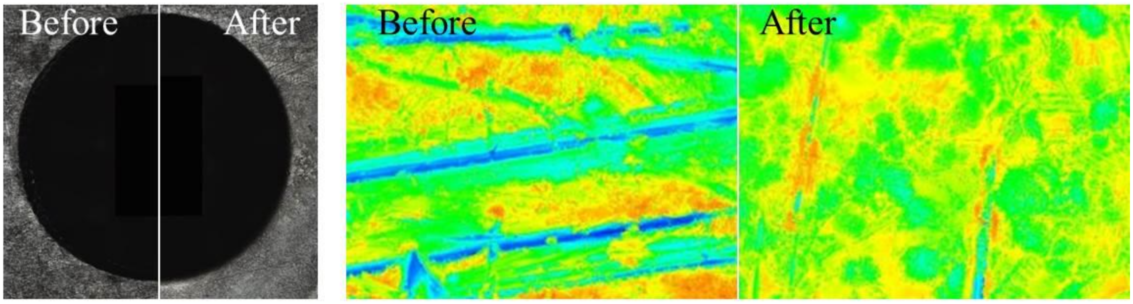

Figure 1 Titanium alloy pieces before and after EPPo treatment. Left: optical microscopy, image height 3mm. Changes in surface textures and edge rounding can be observed. Right: Height maps obtained by confocal microscopy, dimensions ca. 100µm x 70µm, color map scale blue to red 2µm.

In developing methodologies that allow an effective and quantitative description of key process phenomena, the prospect of delivering a practical feedback for EPPo opens up. The method holds the decisive advantage over mechanical finishing of being largely shape-independent. This makes the inherently environmentally friendly technique an excellent contender for the treatment of all small-throughput metallic production, key to the future of innovative design, such as additive manufacturing or 3D printing. Moreover an extrapolation to other electrolytic plasma processes can be offered, since they are all susceptible to share profound similarities in the gaseous envelope and charge transfer behaviors.

Stimulation by Electric Fields of the Germination and Growth of Different Species of Plants Using IrO_2-Ta_2O_5 | Ti Electrodes

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Plants are sensitive to many different forms of stimuli, and they respond to many well-known environmental conditions such as temperature, light quality, moisture, and gravity, among others. Electro-culture or electro-farming consists of stimulation by electric fields applied in the soil in order to improve germination rate, growth rate, yields and crop quality [1]. This technology has been used for different purposes including seed treatment, seedling growth, plant growth, insect control, among others [2].

The goal of this research was develop the electro-culture process for different species of plants as *Arabidopsis thaliana* [3] and *Mammillaria mathildae* [4] using IrO_2-Ta_2O_5|Ti with a titanium cathode applying a constant electric field with direct current. The germination and growth rate were observed by the increase of plant's cotyledons, leaves, and roots in the early stages of *A. thaliana* growth, and the size of the cactaceae *M. mathildae*.

This process was beneficial due to the fact that the ions undergo electro-migration and permeate the nutrients across the seeds. Furthermore, a decrease in pH was observed nearby the IrO_2-Ta_2O_5|Ti via electrolysis of the water during the electro-culture process (pH = 1), and generation of hydroxyl radicals ($^\bullet$OH) was shown during the electrolysis when the seed was exposed to low electric fields in a short time with direct current.

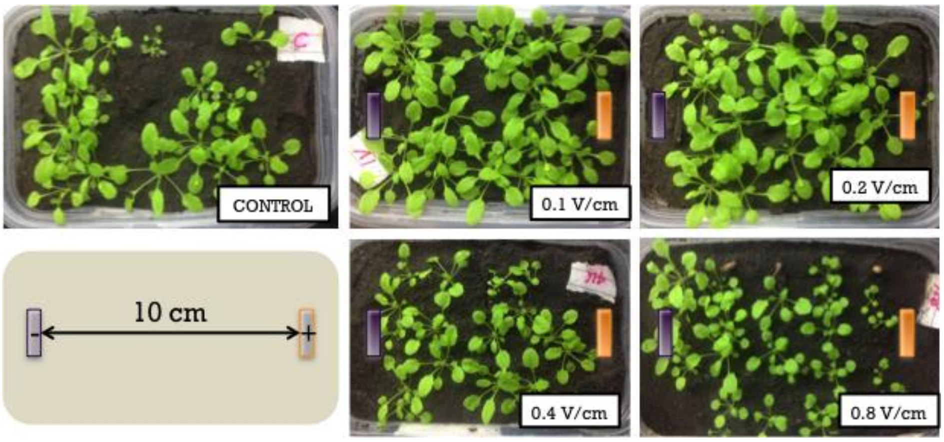

Figure 1. Stimulation by different electric fields (0.1, 0.2, 0.4 and 0.8 V/cm) of the germination and growth of *Arabidopsis thaliana* plants using IrO_2-Ta_2O_5|Ti and Ti electrodes.

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Exploring a novel tetrapolyphosphate/electro-Fenton system at near-neutral pH with a Ni-Fe-Foam cathode for the treatment of electronics wastewater

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Over the last years, electrochemical advanced oxidation processes (EAOPs) have emerged as a powerful green solution for wastewater treatment, pointing out the advantages of electrochemistry for the preservation of our water resources that will guarantee the catering of clean water for future generations. Among EAOPs, the electro-Fenton (EF) process has stood out as one of the most promising technologies due to its versatility, high efficiency, environmental compatibility, cost-effectiveness and facile operability. EF is based on the in-situ cathodic production of the Fenton's reagent, Eq. (1) and (2), which promotes the generation of $^{\bullet}OH$ via Eq. (3) [1]. Despite the manifest potential of EF, one of the constraints still limiting its application at industrial scale is the restricted pH interval of operation (between 2.5 and 3.5).

Within the industry, the electronic sector has been identified as one of the focus targets for water reuse and recycling because the manufacturing process of increasingly miniaturized devices requires very high purity water. It is thus imperative that electronics companies explore novel alternatives for wastewater management. In this scenario, the present study investigates the application of an efficient EF process for the treatment of electronics wastewater at near-neutral pH using a safe chelating agent, sodium tetrapolyphosphate (TPP) as supporting electrolyte. Two cathode materials were tested for comparison: a porous Ni-Fe-foam composite and a conventional carbon brush (CB) cathode for exhaustive production of H_2O_2. Over 70% of total organic carbon (TOC) removal following 4 h of electrolysis was achieved under optimal conditions with both Ni-Fe-foam and CB electrodes (Fig. 1). Besides its function as a complexing agent, TPP (in the form of TPP-Fe(II) complex) also activates the reduction of O_2, promoting the chemical formation of H_2O_2, which in turn enhances the production of $^{\bullet}OH$ [2]. For the TPP/Ni-Fe-foam system, the mineralization efficiency increased with the current from 19% to 75% at 100 mA and 300 mA, respectively, but then dropped to 55% at higher current of 500 mA (Fig 1). This behavior could be explained by the increasing cathodic reduction of Fe^{3+}/Fe^{2+} ions as current rose, which reduced the amount of Fe^{2+} ions in detriment of the active TPP-Fe(II) complex. Interestingly, despite the greater capacity of carbon materials to produce H_2O_2, a CB cathode with the same geometric area and an optimal concentration of Fe^{2+} ions (3.1 mM, data not shown) did not result in a mineralization rate increase (only 70% of TOC removal under similar experimental conditions), which can be accounted for by the effective regulation of Fe^{2+} ions released from the Ni-Fe-Foam cathode. These results highlight the potential of high-surface area, robust and resistant Ni-Fe-Foam electrodes as an alternative to carbon materials for the EF process without external addition of Fe^{2+} unlike conventional EF systems. In conclusion, the use of TPP allowed conducting EF at near-neutral pH for the efficient treatment of electronics wastewater, a remarkable feature for practical applications. Furthermore, the use of a Ni-Fe-foam electrode opens the door for new research directions on EF as a sustainable solution for industrial wastewater treatment.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$
$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (2)$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

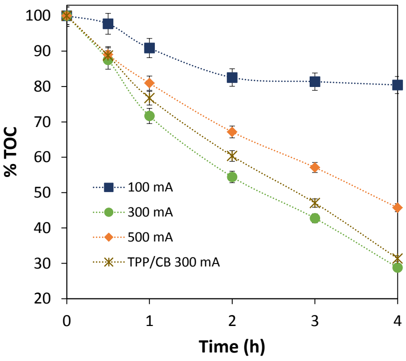

Fig. 1. TOC removal during EF treatment. V= 200 mL of electronics wastewater with 60 mg L^{-1} of initial TOC, TPP 0.05 M as supporting electrolyte, pH=6.0, Ni-Fe-Foam cathode (50 cm^2) and Pt anode. In the case of TPP/CB, carbon-brush (CB) cathode was used with $[Fe^{2+}]$= 3.1 mM.

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Enhancement of hydrogen peroxide generation through a graphene-based gas diffusion cathode and its application for the mineralization of real electronic wastewater by electro-Fenton.

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Over the years, despite improvements in water technologies, water pollution remains a pervasive threat, emphasized by the proliferation of recalcitrant contaminants. A clear example is the electronics industry, which in order to survive the constant technological evolution and meet the product demand, requires large amounts of ultrapure water. The implementation of water reuse is necessary to maintain the water supply in the manufacturing process, however, the recalcitrant nature of this type of water, limits it reuse. In the recent years, electro-Fenton (EF) has emerged as a promising solution for the mineralization of these non-biodegradable compounds[1]. Among the different electrodes used in EF, gas diffusion electrodes (GDEs) have shown to be one of the most efficient in achieving high mineralization of pollutants[2]. GDEs usually incorporate PTFE that imparts some hydrophobic character to the electrode, providing an additional gaseous interface which, in conjunction with the solid and liquid interfaces, enhance the availability of O_2 and therefore the generation of H_2O_2. However, this PTFE layer increases the resistance of the electrode, diminishing its efficacy.

In this study, we coated for the first time a waterproof carbon cloth GDE (CC-PTFE-GDE) with graphene in order to improve the generation of H_2O_2 and thus the mineralization of pollutants in wastewater. The coating of graphene allowed doubling the concentration of H_2O_2 accumulated by the CC-PTFE-GDE from 135 to 280 ppm (Figure 1a). In comparison, carbon cloth in a non-GDE configuration (CC-PTFE) – used as a negative control – led to very little H_2O_2 accumulation (13 ppm). Electrochemical Impedance Spectroscopy (Figure 1b) showed a modification of the surface of the electrode caused by graphene. The equivalent circuit that best fitted the CC-PTFE without graphene was represented by a resistance in series with a constant phase element (CPE), meaning that the electrode behaved as a capacitor with a rough surface. Meanwhile, the CC-PTFE with graphene displayed a charge transfer resistance and the admittance of the CPE attributed to CC-PTFE was 0.001 mho, almost 70 fold higher than the electrode without graphene, which is reflected in a lower resistance and higher oxygen reduction in the system. As a result, the EF process using CC-PTFE-GDE coated with graphene was more efficient than in the absence of graphene, achieving almost total mineralization of real electronic wastewater (95% of total organic carbon removal) after 180 min under optimum operating conditions (14 mAcm^{-2} and 0.2 air Lmin^{-1}) . In conclusion, this study demonstrated the benefits of coating CC-PTFE-GDE with graphene, improving the attractiveness of GDEs for real applications for the electro-Fenton process.

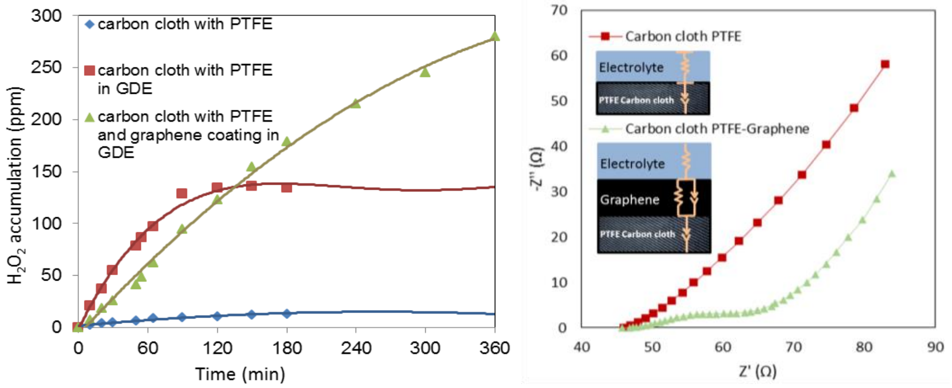

Figure 1. a) Hydrogen Peroxide accumulation trough the time and b) Nyquist plot for CC-PTFE and CC-PTFE coated with graphene

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Zinc concentration as critical parameter for dendritic growth of deposited zinc in rechargeable zinc-oxygen batteries

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Zinc–air batteries are characterized by their high theoretical energy density, low costs, good availability of zinc, and high safety level. Rechargeable zinc-air batteries have a great potential to be the next generation of secondary batteries [1, 2]. With special electrode design even high current density can be reached [3]. Unfortunately, morphological changes of the zinc electrode usually occur after a few charge and discharge cycles. Formation of needle shaped zinc (dendrites) during the charging process is one of the main challenges concerning a possible commercial application. In this contribution the influence of zinc ion concentrations in the electrolyte at the zinc electrode surface is discussed. The overall question is how to avoid dendrites. Dendritic crystals occur when the growth rate is limited by the rate of diffusion of zinc ions to the electrode surface.

In our investigation we used two different experimental set ups. The first one is an unstirred cell (20mm*20mm with an electrolyte gap of 10mm), the second one is a comparable cell where the electrolyte was fed by pumping through the cell (stirred cell). As zinc deposition material a brass foil was used, the counter electrode was a commercial titanium plate electrode coated with an iridium mixed oxide (from Magneto). A standard power supply from BaSyTec GmbH was used to perform the electrodeposition experiments. The electrodeposition was stopped after a specific time, e.g. after 500 s, and dendrite formation was investigated with a Keyence VHX-2000D microscope. A high resolution scanning electron microscopy (Carl Zeiss DSM 982 Gemini) took the SEM images to characterize and validate the morphology of one deposition experiment compared to optical microscope results.

We show that dendritic structures will occur at every current density investigated in this work in an unstirred system. Five different current densities 15, 20, 25, 30 and 40 mA cm^{-2} in a 40 wt.% potassium hydroxide solution were investigated. The deposition times where dendrite structures are starting to grow are used to describe the zinc ion concentration behavior within the cell with a numerical model. We demonstrate that dendritic structures are independent of the current density and are depending on the zinc ion concentration at the zinc electrode surface. Pulsed current technique during charging can positively influence the obtained structures in an unstirred system but dendritic growth even using this deposition method occurred. The zinc ion concentrations where dendritic growth was detected were almost the same in every deposition experiment. With the knowledge of the critical surface zinc ion concentration the current density in a stirred system could be chosen to avoid these concentration region. The combination of an appropriate flow rate with pulse current deposition technique leads to the favored boulder structures with every current density and deposition time (Fig.1).

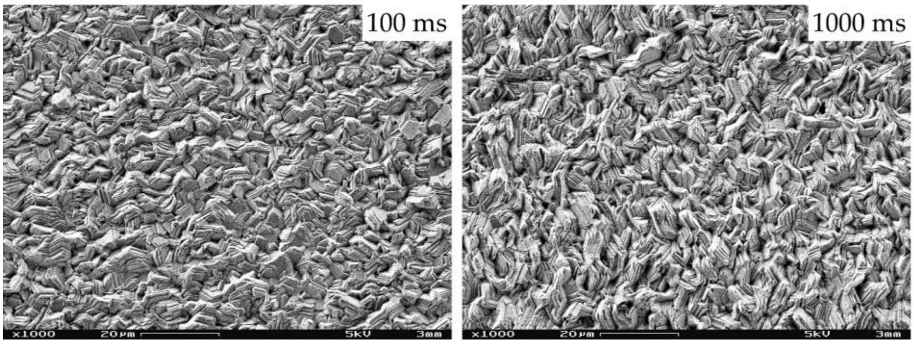

Figure 1: SEM images after 1800s of Zn deposition with pulse technique at an on/off ratio of 1 and two different on times (left 100ms, right 1000ms), 80mA/cm² mean current density, 40 wt.% potassium hydroxide solution with 4 wt.% zinc oxide dissolved

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Nafion® as a Solid Polymer Electrolyte under Elevated Temperature and Pressure

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Perfluorinated sulfonated acids are typical representatives of highly conducting and at the same time highly chemically and mechanically stable polymer electrolytes. They are therefore considered for a broad range of applications having extraordinary requirements on this component of an electrochemical cell. One typical example of such application is proton exchange membrane (PEM) water electrolysis. As this process is extremely demanding also in the case of the remaining cell components, it is characterized by a high costs related to the cell production. An endeavor is therefore visible in a numerous laboratories around the globe to increase PEM water electrolysis efficiency and intensity in order to minimize its specific capital costs. An attractive solution represents increase of the operational temperature. However, it is known from the PEM fuel cell technology, that when approaching/exceeding boiling point of water allowing PFSAs rapidly lose their ionic conductivity. This is due to the loss of solvation water. It on one hand impedes PFSAs dissociation and consequently decreases a content of the free charge carriers. On the other hand, it leads to a collapse of the ion conducting pathways. In the case of water electrolysis, however, situation is different from the fuel cell technology. Here, water represents the main reactant. Thus, increase of the operational pressure allows to keep the water inside the system liquid and thus to avoid drying out of the membrane at the operational temperature higher than 100 °C. At the same time, reactant starvation is not an issue. Moreover, elevated pressure reduces volume of the gaseous phase evolved and thus reduces its negative impact on the cell performance. The main question, however, represents a long term stability of the PFSA membrane under these conditions. This is mainly because the glass transition temperature (T_g) of this material (in a H^+ form) has a typical value of 110 to 130 °C.

This question was addressed in our previous study [1]. As it was found, during prolonged exposure to the temperature above 100 °C and to the elevated pressure, Nafion® 117 membrane has shown loss of the ionic conductivity. The rate of the conductivity decline was increasing with the raising temperature and pressure. Performed spectroscopic and NMR analysis did not confirm chemical degradation of the material. Instead, a change of the internal polymer structure was proposed as a true reason for the observed behavior of the polymeric membrane.

In the present study the problem of the Nafion® 117 changes introduced by the above mentioned exposure is being addressed. Besides the ionic conductivity changes also impact on ion exchange capacity of the membrane was followed. The results observed were discussed in terms of results of the AFM with current sensing probe and SAXS analysis of the samples exposed to the environment under various temperature, pressure and duration. The results obtained confirm the changes in the PFSA internal structure. The main changes are related to the decrease in the average diameter of the ionically conducting micelles in the structure of the polymer. The indicated expansion of the membrane internal structure was beside the observed increase in the membrane sample dimensions during the exposure documented also by AFM experiments indicating significant protuberations on the membrane surface once exposed to the conditions under study. Moreover, these protuberations exhibit higher ionic conductivity when compared to the average membrane surface. The theory on the membrane internal structure changes can thus be considered as proven. The main challenge now is to minimize its occurrence/impact of these effects by selection of suitable membrane and/or by the appropriate membrane preparation.

Acknowledgement

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Electrochemical and Photoelectrochemical Study of Tungsten Oxide Based Nanomaterials for Environmental and Energy Applications

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Heterogeneous photocatalysis has been playing important roles in addressing the pressing environmental and energy issues. As tungsten oxide (WO_3) possesses a lower band gap in comparison to titanium oxide, it may be employed as a solar light-driven photocatalyst. Due to its ability to absorb in the visible light region, along with other properties, WO_3-based nanomaterials have been gaining in popularity for their use in photoelectrochromic “smart” windows, solar energy conversion, storage cells, solar water-splitting cells, and as a potential catalyst enhancer for fuel cells, photocatalysis, batteries, and gas/chemical sensors [1-4]. In this presentation, we report on the synthesis, electrochemical and photoelectrochemical studies of WO_3-based nanostructured materials for environmental and energy applications.

Platelet-like structures comprised of WO_3 with variable dimensions were directly grown on the W substrate via a hydrothermal method. The electrodes were subsequently electrochemically treated, which resulted in the removal of the surface layer, whereupon WO_3 nanospheres were obtained. During electrochemical treatment, the color of the electrode was altered from yellowish green to black; the obtained nanospheres had a lustrous purple color. Interestingly, the nanospheres exhibited a 7-fold enhancement in the photoelectrochemical activity when compared to the parent WO_3-platelet electrode.

Unique WO_3-based bifunctional electrodes were also prepared with the aim of achieving optimal photocatalytic and electrocatalytic activities of WO_3 nanoplatelets and Pt nanoparticles, respectively. WO_3 nanoplatelets with a high visible light response were directly grown on both sides of a tungsten substrate. Pt nanoparticles were deposited on one side of the WO_3 electrode, where they served as the electrocatalyst. The prepared electrodes were characterized by X-ray diffraction, scanning electron microscopy, electron dispersive X-ray spectroscopy and electrochemical methods. The bifunctional electrode exhibited far greater activity as compared to the WO_3 electrode as the sole photocatalyst and WO_3-Pt as the sole electrocatalyst, promising for environmental applications.

Further, a novel supercapacitor electrode based on WO_3/IrO_2-Ta_2O_5 nanocomposites with a high specific capacitance and high charging/discharging stability was demonstrated, where WO_3 nanoplatelets served as the substrate; and IrO_2-Ta_2O_5 provided a reservoir for the storage of charge. A rectangular shape of the cyclic voltammogram was attained for the fabricated WO_3/IrO_2-Ta_2O_5 electrode even tested at high potential scan rates. The synergetic effect of the trimetallic oxide nanocomposite on the significant enhancement of the capacitance is discussed.

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Prediction of Photo-anode Current Densities for Modelling Scaled-up Water-Splitting Reactors

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We studied the photocurrent behaviour of spray-pyrolysed Sn^{IV}-doped α-Fe_2O_3, annealed in air at 400-500 °C for different times, and developed a model to predict that behaviour from experimentally-determined parameters. Photo-anodes were characterized using photo-electrochemical impedance spectroscopy (PEIS) [1], cyclic voltammetry in the presence and absence of hole scavengers [2], open circuit potential under high intensity illumination and incident photon to current Efficiency (IPCE). Mott-Schottky analysis was used cautiously to estimate donor densities (n_D). Morphological and optical parameters, such as absorptivity, were also used as inputs to a modified version of the Gärtner-Butler (GB) equation [3,4]. The shift in the onset potential for water splitting and the maximum photo-current density will be discussed in terms of the re-distribution of Sn^{IV} after annealing. The semi-empirical model was used to predict successfully experimental photocurrent densities, j_{photo} (Figure 1) in terms of measureable parameters, following a procedure similar to that proposed previously [2]:

$$j_{\mathrm{photo}} = j_{\mathrm{photo(GB)}} \times \Phi_{\mathrm{surface}} \times \Phi_{\mathrm{bulk}} \tag{1}$$

where $\Phi_{surface}$ is the surface electron-hole recombination, which can be estimated from PEIS measurements as a function of the applied potential [1]. Bulk recombination (Φ_{bulk}) was estimated from the ratio between the photocurrent obtained experimentally in the absence of surface recombination, e.g. using a hole scavenger, and the ideal photocurrent density, $j_{photo(GB)}$, obtained from a modified Gärtner-Butler equation [5] accounting for incident photon flux (I_0), transmitted (unabsorbed) flux (I_x), absorption coefficient (α_λ) and band bending ($\Delta\phi_{sc}$). The model can be used to predict the behaviour of scaled up reactors, the effect of current density distribution and (H_2-O_2) cross-over losses.

$$j_{\mathrm{photo(GB)}} = \left[2e \left\{ \sum_{\lambda} (I_0 - I_x)\alpha_\lambda \right\}^2 \varepsilon_0 \varepsilon_r \Big/ n_D \right]^{1/2} (\Delta\phi_{sc})^{1/2} \tag{2}$$

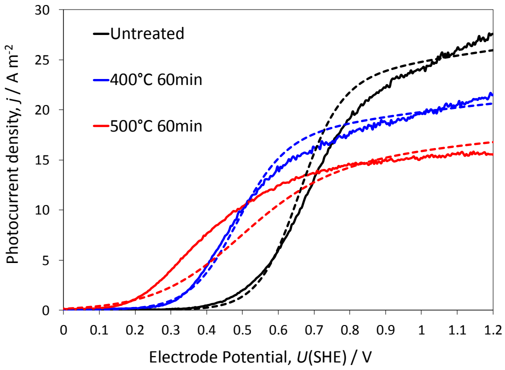

Figure 1. Predicted (dashed) and experimental (continuous) effects of potential and annealing temperature on photo-current density of Ti | Sn^{IV}-doped α-Fe_2O_3 samples in 1 M NaOH electrolyte; potential scan rate: 10 mV s^{-1}. Xenon arc lamp: 3000 W m^{-2}.

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Fabrication of an Expanded Graphite Supported p-n MoS_2-SnO_2 Heterojunction Composite Photo-Electrode for Enhanced Photo-Electrocatalytic Degradation of Pharmaceutical Pollutants

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Pharmaceutical pollutants from industrial wastewaters have been found in the environment due to poor or improper treatment of these wastewaters by the conventional methods [1], and this has necessitated the search for effective and efficient wastewater treatment method. In this regard, a novel photo-electrode consisting of a p-n MoS_2-SnO_2 heterojunction anchored on an expanded graphite (EG) was fabricated and applied in the photo-electrocatalytic degradation of pharmaceutical pollutants in water. The MoS_2-SnO_2 p-n heterojunction nanostructures were synthesised by a modified facile hydrothermal method [2]. Then the nanostructures were anchored on the EG using a wet chemical method after the intercalation and expansion of the graphite [3]. SnO_2, an n-type semiconductor having a wide band gap, has been employed as sensors, transistors and as photocatalysts [2]. On the other hand, MoS_2, a p-type semiconductor with a narrow band gap, has a high surface area, good optical property and electrical conductivity (2D material). Hence the doping of SnO_2 with MoS_2 to fabricate a p-n heterojuction of MoS_2-SnO_2 would result in effective charge separation and enhanced visible light absorption of the SnO_2 [2, 4]. The EG supported MoS_2-SnO_2 composite was characterised using cyclic voltammetry, linear sweep voltammetry, chronoamperometry, X-ray diffractometry, UV-Visible-diffuse reflectance spectroscopy, Raman and Fourier transformed infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, and energy dispersive X-ray spectrometry. The photo-electrocatalytic capability of the MoS_2-SnO_2 anchored on EG as a photo-electrode was tested by the removal of ciprofloxacin as a target pharmaceutical pollutant in 0.1 M Na_2SO_4 solution using a current density of 0.01 Acm^{-2}. The removal efficiency was monitored using a UV-Visible spectrophotometer and the extent of mineralisation was measured using a total organic carbon (TOC) analyser. Efforts were made to investigate the intermediate products during the degradation process. The photo-electrode displayed a better removal efficiency (78.5%) and mineralisation (over 35%) in comparison to EG, SnO_2-EG and MoS_2-EG electrodes. Thus, the presence of p-n heterojunction in the nanocomposite rendered the electrode a good photo-electrode due of its higher degradation efficiency which resulted from the effective charge separation and transport from the SnO_2 to the MoS_2 and EG.

Key words: Photo-electrocatalytic degradation, tin (IV) oxide, molybdenum disulfide, expanded graphite, pharmaceutical, ciprofloxacin

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Degradation of carbofuran in aqueous solutions by electrochemical advanced oxidation processes: Study of parameters and by-products

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Remediation of wastewater contaminated with hazardous organic compounds like agricultural pesticides has been recognized as a major environmental concern due to their toxic properties. Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is a well-known methylcarbamate pesticide used to inhibit insect activity. The use of carbofuran has caused concerns not only due to its extensive use but also due to its high oral toxicity [1,2]. It exhibits refractory character to conventional methods of wastewater treatment. The electrochemical advanced oxidation processes (EAOPs) are characterized by the electro-production of extremely reactive and unselective hydroxyl radical ($^{\bullet}OH$), which is able to oxidize and mineralize almost all organic compounds to CO_2, water and inorganic ions [3].

In this work, the treatment of 2.5 L of carbofuran solutions in 0.050 M Na_2SO_4 at pH 3.0 has been investigated by electrochemical oxidation with electrogenerated H_2O_2 (EO-H_2O_2), electro-Fenton (EF) and photoelectro-Fenton (PEF) processes using a lab-scale pilot plant containing an undivided filter-press reactor equipped with a DSA®-Cl_2 anode and an air-diffusion electrode (ADE) as cathode. The two latter processes were made by adding 0.50 mM Fe^{2+} as catalyst. A 160 W UVA lamp was used to illuminate the solution in PEF. The performance of each treatment was assessed by TOC, HPLC and GC-MS analyses. The slowest degradation of carbofuran was observed in the EO-H_2O_2 treatment, achieving 55% removal after 360 min. The EF and PEF processes led to a remarkable enhancement of degradation, with an almost total carbofuran removal after 120 and 90 min, respectively. Moreover, the PEF process was the most effective technology for mineralization. TOC was quickly abated for 120 min, achieving 75% mineralization. At longer time, the presence of highly recalcitrant products caused a strong deceleration of TOC decay. The effect of some relevant operation parameters such as the applied current, the nature and concentration of supporting electrolyte and the initial concentration of carbofuran on the process efficiency and the formation of intermediates was thoroughly evaluated. Finally, considering all the products detected in the present study, the evolution from carbofuran to the final products is proposed in a general reaction scheme.

Acknowledgments

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Remediation of soils polluted with organochlorinated compounds using surfactant-aided soil washing and electrochemical oxidation

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In last years the removal from soils of hazardous species is an environmental priority in order to avoid the further magnification of the problem with the later pollution of water reservoirs [1, 2]. Electrochemical technologies have been developed to remove pollutant from soils and recently the implementation of a combined process with surfactant-aided soil-washing (SASW) and advanced electrochemical oxidation processes (EAOP) have been the aim of many research works [3]. In this study, the treatment of soil spiked with lindane was studied using a SASW process. This compound has been banned as agricultural pesticide in the numerous group of countries that signed the Stockholm Convention on Persistent Organic Pollutants, but it is still produced and used as a pharmaceutical product in such countries and as an effective pesticide in non-signing countries. Regarding to this, the removal of lindane has been faced with different AOPs technologies but in this work, it is evaluated the complete treatment of polluted soils.

Results demonstrate that this technological approach is efficient and allow to remove this hazardous pollutant from soil. They also pointed out the significance of the ratio surfactant/soil in the efficiency of the SASW process and in the performance of the later electrolysis. To clarify the degradation mechanism involved in the electrochemical treatment of the lindane emulsion, TOC and pesticide concentrations and particle size distribution were monitored. Results show that oxidation of lindane is very rapid and only one intermediate (2,3,4,5,-Tetrachlorocyclohexene (IV)) was detected by HPLC and it was removed fastly. On the contrary, surfactant is removed more slowly with the release of sulfate ions which can be further oxidized to peroxosulfate. They are very reactive and high concentration are not detected in the solution. Larger values of the ratio surfactant/soil lead to effluents that undergo a very efficient treatment which allows the depletion of lindane for applied charges lower than 15 Ah dm^{-3} and the recovery of more than 70% of the surfactant for the regeneration of the soil washing fluid.

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Rechargeable Zinc-Oxygen Flow Battery with High Power Density

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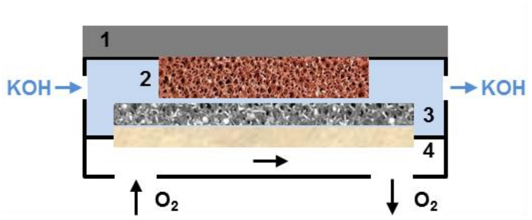
Zinc–air batteries are characterized by their high theoretical energy density, low costs, good availability of zinc, and high safety level. While primary zinc-air batteries have been used as hearing aids or flashing lights for long time, electrically rechargeable zinc–air cells still suffer from low efficiency and unsatisfactory cyclability [1]. The main problems of secondary zinc–air batteries are dendritic or mossy growth of zinc resulting in morphology and shape change during charge as well as self-dissolution and passivation of the zinc electrode during discharge. An interesting option for overcoming these problems is the use of flowing alkaline electrolyte to enhance the liquid-solid mass transfer [2].

We have recently demonstrated an electrically rechargeable alkaline zinc-oxygen flow cell on the basis of copper foam as substrate for zinc deposition and nickel foam as oxygen evolution electrode (OEE) combined with a silver-based oxygen depolarized cathode (ODC) [3]. Copper foam (Alantum) with 2 cm^2 geometric surface area, 2.4 mm thickness, 800 µm nominal pore size, and a porosity of 91% was used as substrate for zinc deposition. For oxygen reduction, a silver-based ODC (Covestro) with a geometric surface area of 5 cm^2 was employed, while nickel foam (Inco) with 97% porosity, 110 PPI pore density, a geometric surface area of 5 cm^2 and a thickness of 1.5 mm was used for oxygen evolution (Fig.1, left). All tests were performed in 30 wt.% KOH electrolyte with 2 wt.% ZnO. A small gap between the copper foam and the oxygen electrodes was used to avoid the need for a separator. The electrolyte was pumped through the cell at a volume flow rate of 0.4 L/min, while pure oxygen was supplied at a flow rate of 0.2 L/min. The overpotentials at the zinc electrode were measured with a reversible hydrogen reference electrode (RHE) HydroFlex® (Gaskatel). Figure 1 (right) shows exemplary results for the overvoltages of the full cell in comparison with overvoltages of a zinc electrode during charge and discharge at room temperature. One can see that very high current densities (with a peak power density of 270 mW cm^{-2}) can be applied and that the main contribution to the losses comes from the oxygen electrodes.



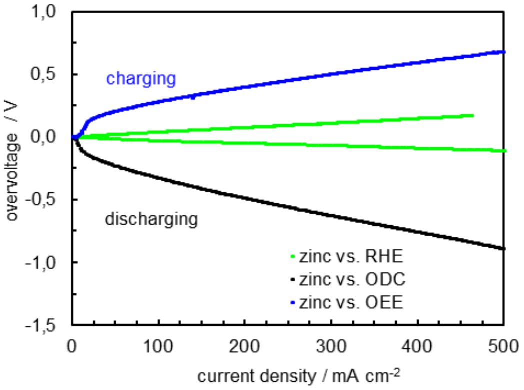


Fig. 1: Schematic of the testing cell, (1) zinc plate, (2) copper foam, (3) nickel foam, (4) silver electrode (left), overvoltages of full cell and at zinc electrode as a function of current density (right) [3]

The corresponding voltage efficiencies decreased from 50% at 100 mA cm^{-2} to 25% at 500 mA cm^{-2}. The cyclability of the battery was investigated at a current density of 50 mA cm^{-2}. In order to suppress formation of dendrites during zinc deposition, the charging process was performed at pulsating current. Stable cyclic behavior was observed for more than 300 cycles, before inhomogeneous zinc deposition led to short circuits in the cell. Further improvements might be achieved by using a separator between copper and nickel foam or by simplifying the arrangement through use of a bifunctional oxygen electrode.

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The Role of Nickel-based Surfaces in Electrochemical Valorization of Glycerol: PM-IRRAS Insight

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The biodiesel production from vegetable oils or animal and/or waste fats has attracted considerable attention as an alternative to petroleum diesel, however it led to a tremendous increase of glycerol by-product overproduction. This has sparked the need for glycerol valorization to justify biodiesel technology [1] by means of heterogeneous catalysis. One of the efficient ways of transforming glycerol to value-added products is electrochemical partial oxidation of glycerol in alkaline media. Due to complex electro-oxidation pathways, a large number of high value-added chemicals may be produced [2]. The control of selectivity and activity can be achieved through formulation of novel, nanostructured electro-catalysts. In this work, glycerol electro-oxidation reaction (GOR) was investigated on bulk Ni electrode and Ni-based mono and bi-metallic (Ni_xPd_{1-x}, x = 95 and 90) nanoparticles in 1M KOH. Limited studies have reported the electrocatalytic property of glycerol on nickel catalysts in contrast to noble metals such as Pt, Ag, and Pd [3].

First, the detailed electrochemical study has been carried out on bulk Ni electrode followed by an electrochemical sinusoidal-wave treatment in a solution of 0.1 M Na_2SO_4 + 30mM ascorbic acid to modify the Ni surface and increase its catalytic activity [4]. Results indicated that the Ni electrode was able to catalyze the GOR at the NiOOH surface, well known as the active species [5]. This treatment proved to enhance the catalytic activity of Ni towards the GOR. The current of GOR increased almost four times and was accompanied by the onset potential shift to lower values by 35 mV, while the electrochemical active surface area showed a six-fold increase. The Ni surface before and after the electrochemical treatment was characterized using XRD, SEM and XPS to clarify the role of the treatment and analyze Ni surface chemistry. XPS confirmed that before the treatment there is a presence of Ni metal in addition to $Ni(OH)_2$, whereas after the treatment Ni is mostly present as nickel hydroxides.

Moreover, the Ni-based mono- and bi-metallic Ni_xPd_{1-x} nanoparticles were synthesized by hydrazine reduction in ethylene glycol. Their physicochemical characterization (TEM, SEM, XRD and XPS) and detailed electrochemical study have been performed in combination with *in-situ* polarization modulation infrared-reflection absorption spectroscopy (PM-IRRAS) measurements. PM-IRRAS allowed us to follow the adsorbed intermediates and reaction products on the electrode surface and in the solution during glycerol electro-oxidation on both Ni bulk and Ni-based nanoparticles [6]. The correlation between electrocatalytic performance and nanoparticle size, surface and bulk composition, as well as structure of Ni-based nanoparticles will be discussed in terms of mass activities and product distribution during GOR.

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Active Functionalization of Plasma Electrolytic Oxidation Coatings

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The aim of this work is to develop ceramic coatings with self-healing ability based on active functionalization through encapsulation of corrosion inhibitors using plasma-assisted electrolytic treatments of magnesium alloys.

The growing interest to magnesium in weight-sensitive applications has attracted attention to surface modifications techniques that can enhance metal properties, in particular corrosion resistance. Amongst them stand out Plasma Electrolytic Oxidation (PEO), which is a high voltage electrolytic-plasma surface treatment capable of obtaining highly stable ceramic coatings with excellent hardness, adhesion, corrosion and wear resistance. One of the major advantages of this technique over other electrolytic methods is the possibility of modifying the coating composition by incorporating elements from the electrolyte, which allows the improvement of specific properties. For instance, it has been demonstrated that the incorporation of ZrO_2 and CeO_2 nanoparticles increases the corrosion resistance, Al_2O_3 and SiC enhance the tribological behaviour and the incorporation of Ca- and P-rich compounds enhance the biocompatibility of PEO coatings. This opens up new opportunities in the active functionalization of ceramic coatings, since the incorporation of active agents from the electrolyte enables specific interactions between the coating and the environment.

The active function relies upon material ability to release on-demand active species as a selective response to certain triggers (e.g. time, pH and mechanical damage). Therefore we discuss possible approaches to develop self-healing PEO coatings capable of mitigating corrosion attack by releasing encapsulated inhibitors when detecting electrochemical activity. In the present work, halloysite nanotubes loaded with different corrosion inhibitors by vacuum-induced capillarity are used as nano-containers that are incorporated into the PEO coatings. The main challenge here is to achieve the non-reactive incorporation of the loaded nanotubes since the high temperatures and pressure reached during the coating synthesis might compromise the 3D integrity of the nano-containers. The obtained coatings are evaluated in terms of microstructural characteristics and corrosion resistance. The proposed approach is expected to enable the use of PEO coated Mg components in demanding environments, including high-performance components of machinery, consumer products and biomedical devices, e.g. drug-loaded coatings for orthopaedic implants.

Improving Negative Electrodes in Secondary Alkaline Zn/Ni Batteries

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Zinc-based alkaline secondary batteries [1] (e.g. Zn/Ni or Zn/Air) could be wide-scale energy storage devices, owing to their energy-density, power-density and environmental friendliness (they use abundant elements, and non-toxic materials and processes). Despite these advantages, their development is hindered by the drawbacks of the negative zinc electrode: dendrite growth, shape change and/or solubility of zinc discharged products in concentrated KOH electrolytes yield severe and gradual capacity loss [2]. So, anode additives mitigating these issues are under emphasized focus [3–7]. One of the most common additive is calcium hydroxide: its reaction with zinc oxide during discharge [8] leads to the *in situ* formation of solid calcium zincate (equation 1):

$$2\ ZnO + Ca(OH)_2 + 4\ H_2O \leftrightarrow Ca(OH)_2{,}2\ Zn(OH)_2{,}2\ H_2O \qquad (1)$$

The lower solubility of calcium zincate compared to commonly used zinc oxides in strong KOH electrolyte drastically reduces the zinc redistribution within the electrode and improves the cyclability [8].

In the present study, homemade 10 mAh Zn/Ni Swagelok batteries using calcium zincate negative electrodes (synthesized through the hydro-micromechanical synthesis method) were characterized. The distribution of zinc, calcium and conductive additive within the electrode was characterized using a complete set of experimental tools (X-ray radiography, cross-section photography, and Scanning Electron Microscopy), during a prolonged charge/discharge sequence. Mechanisms of redistribution of these elements in the course of charge/discharge cycles were unveiled, a first step towards mitigation strategies of the shape change of the zinc electrode.

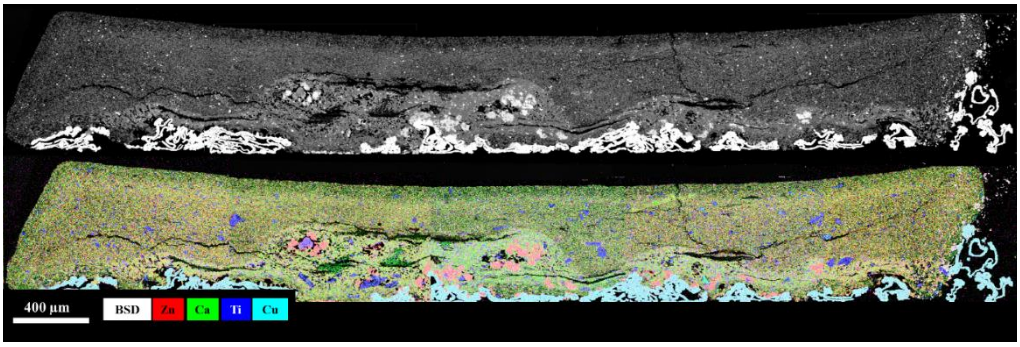

Fig. Highlighting zinc segregation within the thickness of the negative electrode after only one cycle

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Electrochemical CO_2 conversion system based on dental amalgam electrode

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CO_2-to-Formate or Formic Acid Process is one of the actively pursuing CCU technologies. The dental amalgam is formed on the porous copper foam for fast conversion of CO_2 at high current density in flowing condition. We succeeded in producing formate of 1.2 M concentration for 30 hrs electrolysis using 9 cm x 9 cm electrode. The current efficiency of 80~90% was obtained at 50 mA/cm^2 and at 100 mA/cm^2. The electrolyzed could be operated more than a week.

Influence of Dissolved Ions on The Water Purification Performance of TiO_2-Impregnated Porous Silica Tubes

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TiO_2-coated porous silica glass tubes containing macropores were fabricated [1] and evaluated for their water-purification capacity using aqueous solutions of methylene blue. Evaluation of these tubes confirmed that they are suitable for the purification of water [1]. However, there are several important points regarding environmental conditions that must be contemplated when considering their application. For example, groundwater contains variable concentrations of inorganic ions. Therefore, to determine the influence of ions on the degradation efficiency of methylene blue, we examined both Milli-Q water (soft water) and Contrex water (hard water) as solvents, and we found that the adsorption and photodegradation rate of methylene blue was significantly lower for Contrex, which contained a number of inorganic ions. It was therefore considered that the presence of inorganic salts decreased the photocatalytic efficiency. Following treatment of Contrex water with ion-exchange resins, the decomposition ability of the cation-free solvent (pH 2) was higher than that of the anion-free solvent (pH 11), although the decomposition ability of the non-treated Contrex water (pH 7) was superior to the cation-free and anion-free solvents. Finally, we concluded that the efficiency of photocatalytic decomposition of TiO_2 was influenced by multiple parameters, including the presence of anions and cations, and the solution pH. These results are expected to contribute to a better understanding of how environmental conditions can affect the photodegradation ability of catalysts for the purification of groundwater.

Fig.1 Schematic representation of the water purification test using the TiO_2-impregnated a-silica tube.

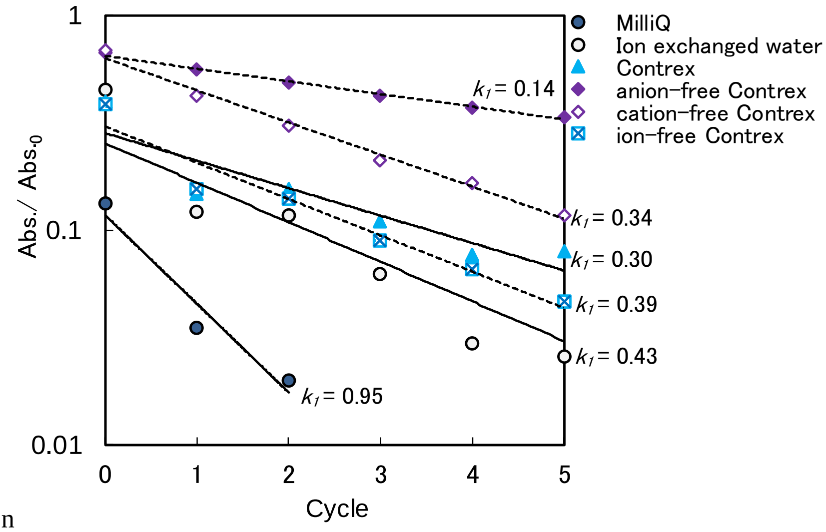

Fig.2 Photocatalytic degradation of methylene blue in the various aqueous solvents.

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Electrochemical Activation of Natural Gas Liquids in Petrochemical Manufacturing

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The shale gas revolution in the United States in recent years has resulted in an oversupply of methane and ethane (the major components of natural gas and natural gas liquids, respectively), and this trend will continue for the foreseeable future. Due largely to these cheap resources (e.g., the current price of ethane is less than 20 cents/gal), the chemical industry has moved manufacturing plants back to the United States, creating thousands of jobs, while enjoying healthy margins compared to international rivals that typically use more expensive oil-based naphtha as feedstock. However, today ethane is solely used to produce ethylene, a chemical feedstock for plastics manufacturing, by steam cracking followed with ethylene purification. These purely thermal-based processes have a very high-energy intensity and carbon footprint.

To overcome these problems and create value-added products, transformational oxidative and non-oxidative electrochemical processes have been investigated in ethane activation at intermediate temperatures (400–600°C, compared to steam cracking of ~850°C) by means of deprotonation and coupling reactions to produce butylene (or higher hydrocarbons), and power or hydrogen, respectively. The rate of reaction is controlled by the flux of oxygen ions or protons passing through the membrane (electrolyte) as well as the kinetics of oxygen reduction, ethane oxidation, and ethyl coupling reactions in the oxidative process; and ethane deprotonation, ethyl coupling, and hydrogen evolution reactions for the non-oxidative process.

The unique advantages of the proposed oxidative and non-oxidative electrochemical ethane activation over the ethane steam cracking are: (1) these are low-thermal budget processes with the reactions carried out at 400-600°C or even lower, so long as there is sufficient oxygen ion / proton conductivity at the temperature; (2) the ethane oxidation and hydrogen evolution reactions are fairly low overpotential processes at elevated temperatures with relatively small electrical energy input; and (3) the ethyl coupling reaction is a chain reaction that can be tuned to control the product, and it is likely the rate-limiting step dominated by the thermochemical properties.

In this presentation, we will discuss our recent progress in electrochemical ethane activation, including the configuration and structural modification of electrochemical membrane reactors, the bi-functional electrocatalysis for electrode reactions, and product characterizations.

Simulations of two-phase flow during the cathodic H_2 evolution in a pre-pilot multi-electrode stack having 12 cells in continuous mode

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1. INTRODUCTION

Gas evolution is presented in many electrochemical systems, either as the main product or unwanted by-product [1]. The current efficiency and the electrolysis energy consumption of many electrochemical processes are affected by the existence of bubbles or bubble curtains [2,3]. There are many works on modeling and simulation of electrochemical reactors using computational fluid dynamics (CFD), but in the literature there are few works that include biphasic simulation for the development of new geometric designs of electrochemical reactors.

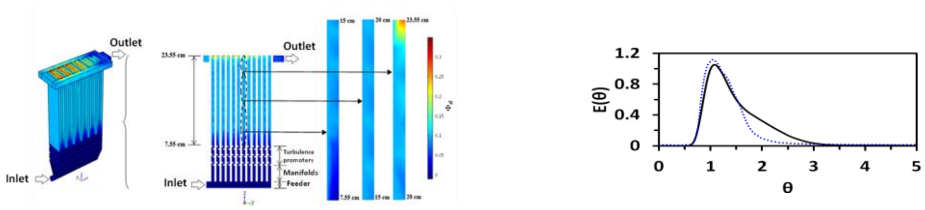
In this work we present the simulation of the biphasic flow in an electrocoagulation reactor of novel design. Two-phase flow simulations were performed by solving, on one hand, the Navier-Stokes (NS) equations, and on the other hand, the Navier-Stokes Reynolds Averaged (RANS) equations with the standard $k\text{–}\varepsilon$ turbulence model, in both cases under the Euler-Euler approach. Theoretical residence time distributions (RTD) were calculated by solving the diffusion-convection and the averaged diffusion-convection equations for NS and RANS equations, respectively. The commercial package COMSOL Multiphysics® was employed for the numerical calculations. Experimental RTD tests were performed to validate the simulations.

2. METHODOLOGY

The hydrodynamic behavior of the two-phase flow (H_2-water) was simulated for different reactor geometries; afterwards, a novel electrocoagulation reactor was built based on the optimum simulation results. For the novel reactor, different inlet flows between 0.5–3 L min^{-1} were simulated in laminar and turbulent regime. These simulations were validated with experimental RTD tests.

3. RESULTS

Figure 1 shows the isometric and segmented interelectrodic gap views of the volumetric H_2 fraction simulated in laminar regime, while Fig. 1 (b) depicts the theoretical RTD and experimental RTDs.



(a) (b)

Figure. 1. (a) Isometric and segmented interelectrodic gap views of the H_2 fraction simulated in laminar regime. (b) Theoretical (—) and experimental (…) RTDs. Tests performed at 2 L min^{-1}, 298 K.

4. CONCLUSIONS

The best agreement between theoretical and experimental RTD was obtained by the laminar two-phase flow model, showing that non-ideal flow is mainly produced by the presence of low velocity zones, which are created by the extensive area of the multi-electrode stack having 12 cells. Analyses of particle image velocimetry to validate our approaches are in progress.

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Development of Concentration Strategies for the Improvement of the Efficiency of Electrochemical Degradation Technologies

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The potential applications of electrochemical technologies to a wide spectrum of environmental applications have remarkably increased within the last decades. For the particular case of the removal of organic pollutants, many studies have researched the optimization of operation conditions or the combination of different processes, with the final aim of attaining high degradation efficiencies in the depletion of these hazardous species.

Despite these important efforts, several drawbacks are still to be overcome. One of them can be found when using electrochemical degradation technologies to treat organic pollutants in low concentration, a common case for many persistent and emerging contaminants. It is well-known that the higher the concentration of the pollutant, the higher is the current efficiency of the electrochemical treatment process [1]. Thus, mass transfer control is expected when low concentrated wastes are treated, limiting the maximum removal rate and lowering the current efficiency of the process.

This work reviews the different approaches that have been researched to increase the efficiency of electrochemical degradation technologies to treat low concentrated wastes. Moreover, we present new data about the integration of degradation and concentration technologies with the aim of increasing the rate and the global efficiency of the treatment process.

When combining degradation and concentration technologies, the approach depends on the nature of the pollutant: ionic or non-ionic. For the former, it is possible to use electrodialysis to perform the simultaneous removal and degradation of the pollutant by a proper placement of the ion exchange membranes. As an example of ionic pollutant, the degradation rate of 2,4-D was studied and compared with two different systems: single electro-oxidation and combined electrodialysis and electro-oxidation. It was observed that it is possible to concentrate and to deplete simultaneously 2,4-D, increasing significantly the rate and the efficiency of the process, thus lowering the environmental impact and the cost of the treatment.

A different approach should be done for non-ionic pollutants as these are not transported in an electrodialysis cell. In this case, electrocoagulation can be employed to concentrate the contaminant prior to its degradation by a suitable electrochemical technique. First, it is necessary to trap the pollutant into the growing flocs and, subsequently, to dissolve the solid in a reduced volume of acid, thus producing a much concentrated solution. This approach has been evaluated using oxyfluorfen as model of non-ionic pollutant and iron as anode. As it was the case of 2,4-D, it was observed that it is possible to concentrate oxyfluorfen by electrocoagulation and to increase the rate and the efficiency of the treatment of organic non-ionic pollutants.

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Acknowledgments

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Arsenic and fluoride removal from groundwater by electrocoagulation process in a continuous filter-press multistack reactor

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The problems related to water scarcity in several regions in the world have forced to communities to use groundwater (used for potable purposes) which contains inorganic constituents that may become in a major public health problem. The most significant inorganic pollutants in groundwater affecting human health at the global scale, according to the World Health Organization (WHO), are arsenic (*As*) and fluoride (F^-) [1], their drinking water standards are set at 10 µg L^{-1} and 1.5 mg L^{-1}, respectively. Arsenic is classified as a Group I carcinogenic substances to humans based on epidemiological evidence. Fluoride with an excess of fluoride in drinking water (> 1.5 mg L^{-1}) can lead to dental and skeletical fluorosis [2]. In Mexico, approximately 75% of total population relies on groundwater for drinking that contains fluoride and arsenic levels above the International standards.

The electrocoagulation technique (EC) has been considered as an alternative to remove arsenic and fluoride from drinking water because it provides some significant advantages [3]. Aluminum is the most used material as sacrificial anode in EC studies reaching high removal efficiencies through a substitution reaction for fluoride $\left[Al_nF_m(OH)_{3n-m}\right]$ and an adsorption reaction for arsenic $\left[Al(OH)_3\cdot HAsO_4^{2-}\right]$.

In this communication, groundwater was used for EC treatment (fluoride 5.4 mg L^{-1}, arsenic 50.4 µg L^{-1}, hydrated silica 132.0 mg L^{-1}, sulfate 40.0 mg L^{-1}, nitrate 6.7 mg L^{-1}, phosphate 0.55 mg L^{-1}, hardness 23 mg L^{-1}, alkalinity 59 mg L^{-1}, pH 8.0 and conductivity 805.4 µS cm^{-1}). The EC system consists of a continuous filter press multistack reactor coupled to a flocculation-clarification unit (jar test). Aluminum electrodes (99.7% purity, in monopole configuration) were used as anodes and cathodes. EC tests were performed with current densities of 5–7 mA cm^{-2} under different hydrodynamic conditions (0.23 – 0-93 cm s^{-1}). Arsenic and fluoride were analyzed in the resulting clarified solution. SEM-EDAX, XRD and FTIR analyzes were performed to the flocs.

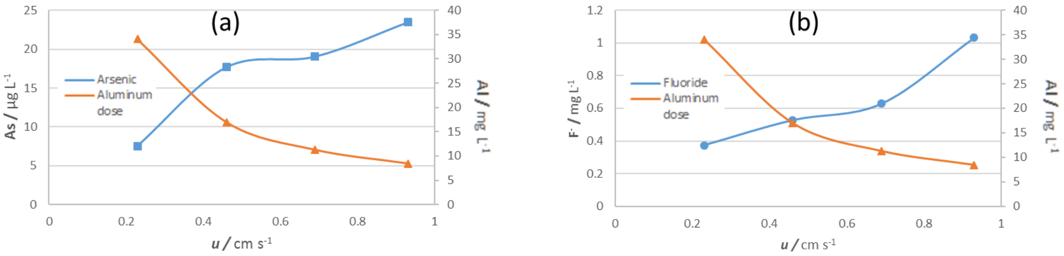

Fig. 1. Influence of the mean linear flow rate and aluminum dose on the residual arsenic (a) and fluoride (b) concentration.

Fig. 1 shows the residual arsenic and fluoride concentration as a function of mean linear flow rates in the EC reactor at a current density of 7 mA cm^{-2}. The theoretical aluminum dose is also shown. At 0.23 cm s^{-1}, we obtained values below the maximum permissible limit for both pollutants. XRD, FTIR and SEM-EDAX analyses performed to aluminum flocs revealed a nanometric amorphous floc which are composed by aluminum silicates. Arsenate, sulfate and phosphate are adsorbed on aluminum flocs. Fluoride might replace hydroxyl groups from flocs.

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Ultramicroelectrode Studies of the Additive Derived Critical Breakdown in S-NDR Copper Electrodeposition

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Copper electrodeposition is widely used in integrated circuit manufacturing, ranging from damascene plating of sub-100 nanometer features to deposition of micron-scale through-silicon-via (TSV) interconnects used for 3D-chip stacking.[1] Electrodeposition of void-free copper structures in high aspect ratio cavities is achieved with various suppressing, accelerating, and leveling organic additives which enable superconformal, bottom-up filling of the recessed features. Recently, the use of a single suppressing organic additive has been demonstrated and modeled in a variety of different metal systems (Cu, Ni, Co) for TSV-scale feature filling.[2-4] In these systems, bottom-up filling is derived from an S-shaped negative-differential-resistance (S-NDR), generating active plating regions at the bottom of the TSVs and passive regions along the walls and surface. This active/passive bifurcation is driven by adsorption/desorption kinetics, mass-transport, and the TSV geometry. Additional studies of S-NDR systems demonstrate that in the absence of any geometric constraints the bifurcation occurs in random Turing-like patterns[2]. In other reaction systems, such bifurcating active-passive reactions are found to be dependent on the electrode size such that for reduced electrode dimensions the ability to bifurcate is frustrated and a homogeneous surface reactions occurs across the electrode.[5]

In this work, ultramicroelectrodes (UMEs) are employed to further examine acid copper sulfate electrolytes containing a single organic suppressor to better understand feature filling for TSVs. The negligible IR-drop and high mass-transport rates inherent with UMEs provides new insight into the critical breakdown behavior of S-NDR systems relevant to industrial applications. Additionally, more precise kinetic relationships are derived at UMEs with dimensions less than the critical dimension of the spatial instability in an S-NDR system; a result enabled by the homogeneity of the reaction across the electrode surface. The effect of chloride content, cuprous ion concentration, copper crystal structure, and electrolyte conductivity (regulated by sulfuric acid concentration) on the critical breakdown of the chloride-polymer suppressor layer is explored by cyclic voltammetry and linear galvanodynamic measurements on both UMEs and macroscopic electrodes. In addition, scanning electron microscopy of copper electrodeposition in microwell arrays of varying dimensions demonstrate the effect of electrode size on active/passive spatial bifurcation and subsequent pattern formation.

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Carbon nanotubes electrosynthesized from CO_2 for efficient, cost incentivized greenhouse gas removal

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As the levels of carbon dioxide (CO_2) increase in the Earth's atmosphere, the effects on climate change become increasingly apparent. An incentive to remove the greenhouse gas carbon dioxide is provided here by its low energy, low cost, high yield conversion to valuable carbon nanotubes products. We've previously shown that carbon dioxide can be captured directly from the air at solar efficiencies as high as 50%, and that CO_2 associated with cement formation and the production of other commodities, such as ammonia and iron, can be electrochemically avoided in the STEP process.[1-3]

Here we show the effective capture of the greenhouse gas CO_2 and its conversion at high yield to carbon nanotubes at low energy and high yield by dissolution in molten carbonates and splitting by electrolysis in molten carbonate to carbon nanotubes and oxygen.[4-12]

Displaying superior strength, conductivity, flexibility and durability, carbon nanotube (CNT) applications had been limited due to the cost intensive complexities of their synthesis. We present an inexpensive, high-yield and scale-able synthesis of CNTs. We show that common metals act as CNT nucleation sites in molten media to efficiently drive the unexpected, high yield electrolytic conversion of CO_2 dissolved in molten carbonates to CNTs. We accomplish this by electrochemically reducing CO_2 on steel electrodes in a molten carbonate electrolyte. The CNT structure is tuned by controlling the electrolysis conditions, such as the addition of trace common metals to act as CNF nucleation sites, the concentration of added oxide, the addition of initiators and the control of current density. The process can be driven by efficient solar, as well as conventional, energy. Scalability of the process is demonstrated from 1 A to 100A. An inexpensive source of CNTs made from carbon dioxide will facilitate the rate of its adoption as an important societal resource for the building, aerospace, transportation, renewable energy, sporting and consumer electronics industries, while concurrently consuming carbon dioxide.

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Lithium-6 Enrichment using Innovative Electrodialysis Method with Lithium Ionic Superconductor

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Tritium needed as a fuel for fusion reactors is produced via neutron capture by lithium-6 (^{6}Li). However, natural Li contains only about 7.8% ^{6}Li, and enrichment of ^{6}Li up to 90% is required for adequate tritium breeding in fusion reactors. The mercury amalgam method is superior to some of the lithium isotope enrichment methods. In Japan, lithium isotope enrichment methods have been developed to avoid the environmental hazards of using mercury. However, the isotope separation coefficient and efficiency is too low to meet the practical need of large mass production of ^{6}Li.

Therefore, new Li isotope separation technique using a Li ionic superconductor functioning as a Li isotope separation membrane (LISM) have been developed. First of all, I investigated the ionic mobility of lithium isotopes in ionic superconductor. Combing the first principle and the kinetics Monte Calro simulation, we calculate the diffusion constant of ^{6}Li and ^{7}Li. We show the two important effects for the difference in the mobility between isotope of lithium. The first is the quantum effect, which decrease the diffusion barrier for lithium ion and increase the ratio of the diffusion constant of Li isotopes. The second is the correlation effect between ^{6}Li, ^{7}Li and vacancy. I also discuss the preferable chemical composition enhancing the Li isotope effect.

Furthermore, examinations of Li isotope separation using lithium ion superconductor with electrodialysis ware performed. Li ions move by electrodialysis through LISM between the cathode and the anode in lithium solutions [1]. Because the mobility of ^{6}Li ions is higher than that of ^{7}Li ions, ^{6}Li can be enriched on the cathode side of a cell (Fig.1). Using $Li_{0.29}La_{0.57}TiO_3$ (LLTO) as the Li ionic superconductor was prepared, and the relationship between the ^{6}Li separation coefficient and the electrodialysis time was investigated. After electrodialysis, we obtained a maximum of 1.04 for the ^{6}Li isotope separation coefficient. This result showed that the ^{6}Li isotope separation coefficient of this method is the same as that of the amalgamation process using mercury (1.06).

These results show this method has the potential to be a superior ^{6}Li enrichment method to produce 90% enriched tritium breeder for fusion reactors.

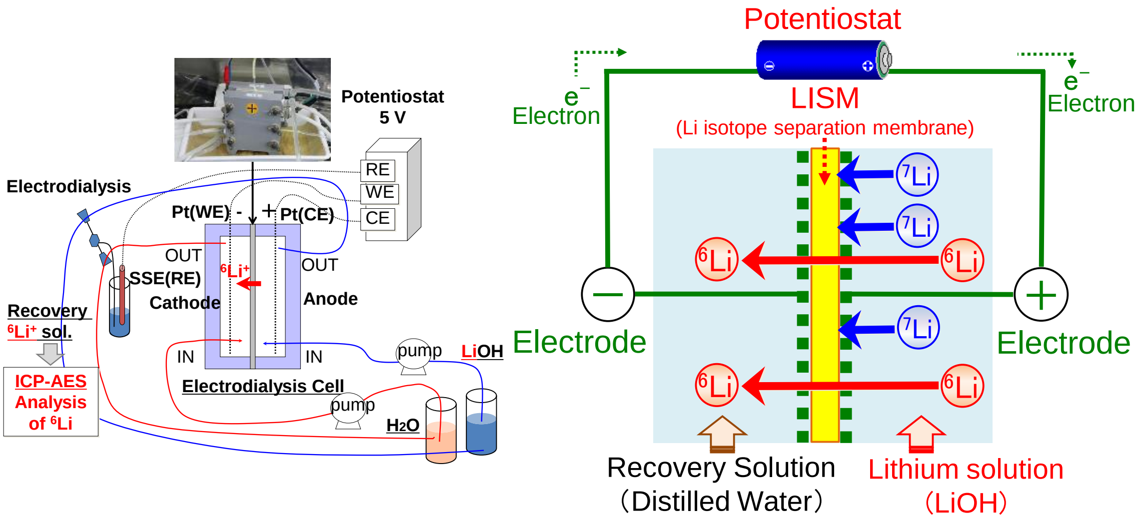

Fig.1 Schematic of ^{6}Li enrichment from Li solution using the proposed electrodialysis method with Li isotope separation membrane (LISM).

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Electrochemical Micro/Nano-Machining

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Micro/nano-machining (MNM) is becoming the cutting-edge of high-tech manufacturing because of the increasing industrial demand for supersmooth surfaces and functional three-dimensional micro/nano-structures (3D-MNS) in ultra-large scale integrated circuits, microelectromechanical systems, miniaturized total analysis systems, precision optics and so on. Taking advantage of no tool wear, no surface stress, environmental friendliness, simple operation, and low cost, electrochemical micro/nano-machining (EC-MNM) has an irreplaceable role in MNM. However, because the thickness of the electrolyte solution between the tool electrode and the workpiece are usually at micro/nano-meter scale, it is a challenge to solve the problems of potential distribution and mass transfer in the ultra-thin layer electrolyte cell. In this presentation, we will introduce our recent work on the external physical field induced electrochemical reactions in which there is no need of 2-electrode or 3-electrode system in the conventional electrochemical system. Figure 1 gives an example on the contact electrification induced electrochemical reactions and its application in nanoimprint lithography.

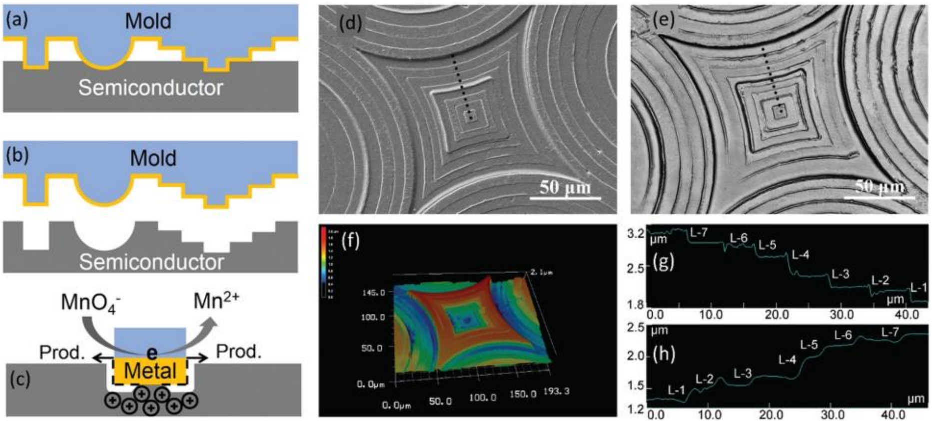

Fig. 1 (a–c) The schematic of ECNL; (d) the SEM image of a diffractive microlens on a catalyst mold. (e) The confocal laser microscopy image of a diffractive microlens fabricated on GaAs. (f) The AFM image of (e). (g and h) The cross-sectional profiles of eight-phase levels on a catalyst mold and GaAs outlined by the black dotted lines, respectively.

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Traceable High Precision Biofuel Conductivity Measurement

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Here we present the factors involved in the design, testing and data analysis techniques employed to obtain an instrument for the highly precise measurement of electrolytic conductivity on volatile liquids.

With the increased focus on renewable energy generation, much work has looked into either the total or partial replacement of petroleum fuels in motor vehicles. At the current time, bioethanol is generally considered the most technologically feasible. Bioethanol has multiple advantages, including: that it can be produced from various crops and trees, in many different climates, or even from biomass, of being liquid and being capable of utilizing the existing distribution network for petroleum fuels with few modifications [1].

It is important to ensure the purity of the ethanol used in motor vehicle engines against the various impurities which may arise from either manufacture or storage. Impurities such as acetic acid, which is produced by the oxidation of ethanol, water or chloride salts. The presence of these will reduce the lifespan of an engine due to the corrosive effect they exhibit towards engine materials, for example steel. Testing for the presence of these impurities in bioethanol can be performed, in combination with other techniques, using conductivity measurements; this method of analysis is chosen due to the low conductivity of ethanol and the relatively large effect on conductivity of small quantities of impurities. In many countries this is enforced by a maximum conductivity value for bioethanol for motor vehicles, e.g., the Brazilian government limits the maximum to 500 µS/m [2].

Reliable measurements of the electrolytic conductivity of ethanol for biofuels are difficult due to the volatility of ethanol and the instability, during measurement, of ethanol based solutions. The developed conductivity measurement system is traceable to the SI system of units, via a primary cell for electrolytic conductivity, which has been developed at DFM, and which has demonstrated electrolytic conductivity measurements down to 5 µS/m with an expanded uncertainty < 0.5%.~~As a National Metrology Institute with experience in highly precise electrolytic conductivity measurements, including aqueous solutions down to the ultra-pure water level, DFM has the capability to create a system that is traceable to the SI, via DFM's primary cell for electrolytic conductivity.~~

DFM has, therefore, undertaken to expand its activities in the field of electrolytic conductivity. With the *VolaCond* system, on which we report here, DFM will be able to measure low conductivity levels in volatile solutions such as ethanol. The system is designed to run automatically once the sample has been loaded onto the system, minimizing exposure to the air, with flexibility to adjust experimental conditions to ensure high performance for various sample types over several decades of electrolytic conductivity.

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Recycling the Rare Earth Elements from Permanent Magnets by Electrochemistry in Ionic Liquid

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Thanks to their high magnetization and low mass, permanent magnets (NdFeB and SmCo) have quickly become essential for new energies (wind turbines, electrical vehicles…). They contain large quantities of neodymium, samarium and dysprosium, that have been recently classified as critical elements and that therefore need to be recycled. Electrochemical processes including electrodissolution followed by electrodeposition are an elegant and environmentally friendly solution for the recycling of such rare earth elements (REEs) contained in permanent magnets. However, electrochemistry of those REEs is a real challenge as their standard potentials are highly negative (around -2.5V vs ENH). Consequently, non-aqueous solvents are required. Ionic liquids (ILs) are novel electrolytes exhibiting physico-chemical properties that fulfill many requirements of the sustainable chemistry principles, such as extremely low volatility and non-flammability. Furthermore, their chemical and electrochemical properties (solvation of metallic ions, large electrochemical windows, etc.) render them very attractive media to implement alternative and sustainable processes in view of integrated processes.

All experiments that will be presented were carried out using 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([BMPyrr][Tf_2N]). Linear sweep voltammetry, cyclic voltammetry, galvanostatic and impedance electrochemical techniques were used. The reliability of electrochemical experiments, performed without glove box, for the classic three electrodes cell used in this study has been assessed. Deposits (Nd, Sm, Dy, Pr) were obtained by chronopotentiometry and were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (DRX).

The electrochemical behavior of pure IL has been examined for various constraints (N_2, Ar, O_2, or H_2O content) and several electrode materials (Pt, Au, GC). The maximum cathodic potential value is -3V *vs* Fc^+/Fc (Ar, GC) thus allowing a reduction of REEs. However, the reduction potentials of Nd, Sm, Dy and Pr vary with time and are more negative than -3V *vs* Fc^+/Fc. The impedance analysis evidences a varying capacitance as a function of applied potential and, more importantly, IL electrochemical properties are strongly affected by the metal addition.

The individual deposits obtained are porous and oxidized. Selective deposition of neodymium in presence of dysprosium was also studied and will be discussed.

Electrodissolution of a real permanent magnet sample was monitored kinetically. Then, the sequential electrodeposition of REEs contained in the IL was investigated. Yields, quality of the deposits and consumption of chemicals will be discussed in depth, in view of the industrial feasibility of this process for real permanent magnets recycling.

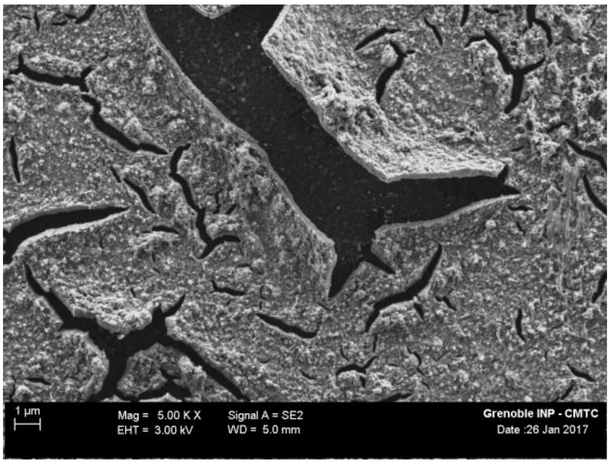

Figure 1 – Deposit of Neodymium in [BMPyrr][Tf_2N] on glassy carbon electrode

Understanding the mechanism and kinetics of electrochemical wastewater treatment at oxygen evolving anodes

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Electrochemical oxidation is a promising technology to treat a wide range of compounds in both industrial and domestic wastewater streams [1, 2]. However, despite the success of electrochemical oxidation in treating a range organic species, the high energy requirements of the process limits the commercial viability of electrochemical wastewater treatment [2]. In many cases, the high energy requirements are linked to the low current efficiency due to the oxygen evolution reaction (OER) which occurs in parallel to the organic oxidation reaction at the anode. To avoid this, anodes with very high overpotentials for the OER are often used [1, 3-5]. These anodes oxidise the wastewater compounds via the hydroxyl radical formed at high potentials [6, 7], although this approach inevitably leads to high energy requirements due to the high cell voltages applied. One option to solve this problem is to develop electrocatalytic anodes with high activity for organic oxidation and low selectivity for the OER at low potentials. However, this approach is complex as the mechanism for organic oxidation involves an intermediate species of oxygen evolution [6], and thus completely avoiding the OER is unlikely.

To better understand how the reaction kinetics and the mass transport influence the treatment process, a model incorporating both the kinetic and mass transfer controlled regimes has been developed. Importantly the model uses an established OER reaction mechanisms and can predict both steady-state polarization curves and bulk electrolysis behavior, and has been validated against a range of experimental data. This model shows that while multiple sets of kinetic parameters can predict almost identical OER behavior, these sets of kinetic parameters can result in very different organic oxidation kinetics. The information obtained from this model provides useful insights into the ideal characteristics of an electrochemical wastewater treatment anode.

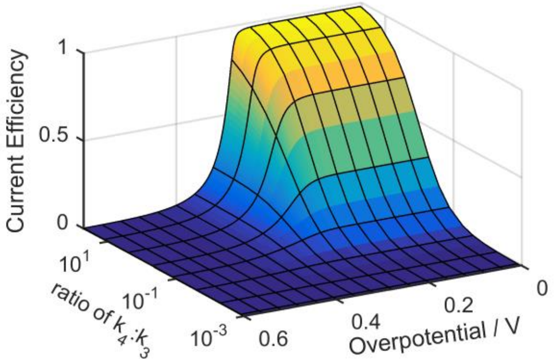

Figure 1: An example simulation showing how the current efficiency varies as a function of overpotential and the ratio of the rate constants of key steps in the reaction mechanism.

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Experimental study and modelling of electrochemical oxidation of pharmaceuticals using a boron-doped diamond anode

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Electrochemical oxidation is a potentially promising alternative technology for elimination of pharmaceuticals from water, in particular using a boron doped diamond anode (BDD). The strong ability for organic oxidation of BDD is well known and attributed to the electrogeneration of hydroxyl radical ($^{\bullet}OH$) from the water discharge. Hydroxyl radical is the most powerful oxidant in water (standard potential E_0 = 2.74 V / SHE). It reacts unselectively and rapidly with a large variety of organics (i.e., kinetic constant $k_{\bullet OH} > 10^9$ M^{-1} s^{-1}). Thanks to the wide electrode potential window of the BDD anode, direct electron transfer reactions are also available for the electroactive species.

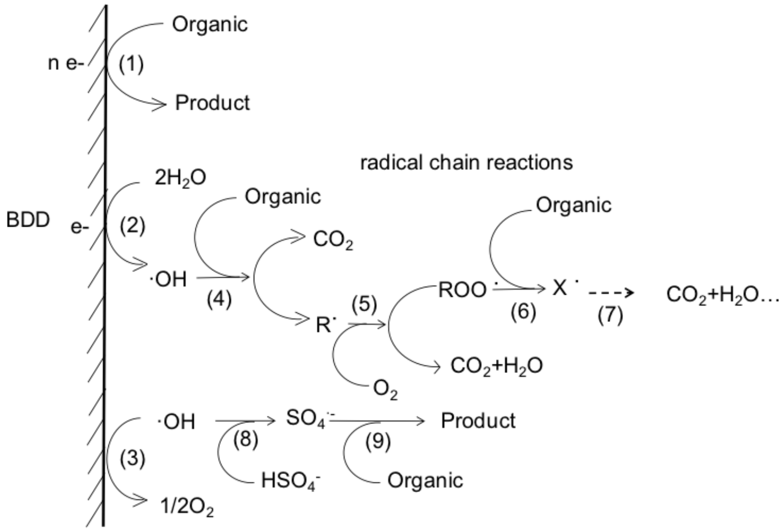

Fig. Oxidation pathways of organic with BDD anode: (1) direct electron exchange, (2) electrogeneration of $^{\bullet}OH$, (3) generation of oxygen (4) formation of organic radicals via reaction between organics and hydroxyl radicals, (5) reaction between O_2 and organic radical, (6) reaction between peroxy radicals and organic in the solution, (7) complete mineralization, (8) formation of sulfate radicals, (9) reaction between sulfate radicals and organics.

With a view to treat hospital wastewater at source, an experimental and theoretical study was performed to demonstrate the great ability of the BDD anode to efficiently destroy a wide range of refractory pharmaceuticals.

This study is devoted to establish an easy-to-use model taking into account all types of transfer:

(i) the contribution of the direct oxidation (electrons),
(ii) the reaction with hydroxyl radicals (transfer of oxygen atoms)
(iii) the reaction with electrogenerated strong oxidants (such as sulfate radicals)

Because the composition of wastewater is complex, different compositions were tested experimentally and simulated: concentration of sulfate, current densities, presence of electroactive and electroinactive pharmaceuticals in the solution. For every case, the model has been validated experimentally.

Anodic Oxidation of Organic Compounds Using TiO_x Membrane as Porous Anode Material

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Introduction

This study focuses on anodic oxidation for remediation of water pollution caused by biorefractory organic pollutants. The cost-efficiency of the anodic oxidation process tightly depends on improving mass transfer of organic pollutants from the bulk to the anode surface [1].
In this study, sub-stoichiometric titanium oxide (TiOx) membrane was used as anode material in a flow-through reactor during filtration/electro-oxidation experiments [2]. The originality of this approach lies in the production of hydroxyl radicals within the pores of the conductive membrane.

Methods

Experiments were performed using a cross-flow filtration setup in inside-out mode. TiOx membranes were used as anode, while stainless steel rod was used as cathode. Paracetamol (PCT) was selected as model organic compound. Voltage, flow, PCT concentration, total organic carbon (TOC), degradation/mineralization by-products and biodegradability evolution were monitored.

Main results and discussion

This study focused on the assessment of organic compound oxidation during filtration through the TiOx membrane. Initial pollutant concentration, current intensity and flow rate are critical parameters for process efficiency. After a single passage through the membrane, total degradation of 0.18 mM of PCT was observed and the mineralization rate reached more than 95% during the whole experiment (Figure 1) with an energy consumption of 1.0 kWh/g(TOC). By comparison, PCT degradation rate in the retentate was only 10% after 80 min; PCT oxidation occurs mainly within the pores of the TiOx membrane. The high efficiency observed during these filtration experiments is explained by the increase in the convective mass transport of pollutants, compared to the use of conventional plate electrodes.

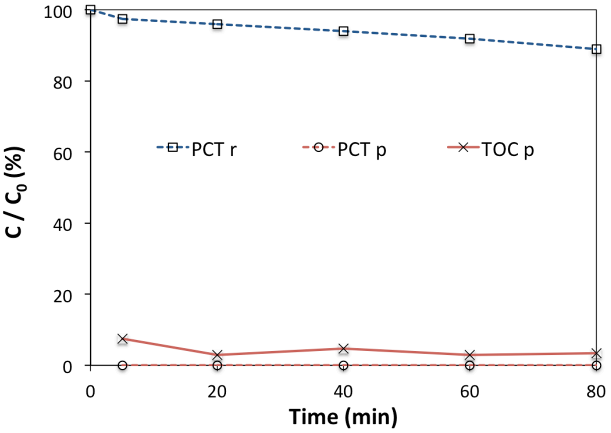

*Figure 1. Evolution of [PCT] ($[PCT]_0$ = 0.18 mM) and TOC (TOC_0 = 17.7 mg L^{-1}) in the retentate (r) and in the permeate (p) after a single passage through TiOx membrane (*I = 30 mA/cm^2 ; Flow = 116 $L/m^2/h$*).*

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Electrochemical Production of Ammonia in Alkaline Media

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Ammonia is produced commercially via the Haber-Bosch (HB) process. However the HB process requires high temperatures and pressures and as a result it can only be done in large plants which consume large amounts of power and generate large quantities of CO_2 from the fuels used to power the process, such as natural gas [1,2]. It is estimated that the HB process accounts for nearly 1% of the entire global power consumption [3]. Due to the sheer scale of the HB process, distribution from the point of production to the point of use becomes an additional carbon and energy burden. Alternative methods of manufacturing ammonia that enable small scale, distributed generation at the point of use using renewable energy and sustainable feedstocks could have a great impact on global CO_2 emissions. Electrochemical synthesis of ammonia at low temperatures and pressures is one promising solution that has recently begun to gain more attention as a viable method of sustainable, on-site generation of NH_3. Furthermore, ammonia generation at the point of use can also facilitate applications for energy storage via ammonia fuel cells and ammonia electrolysis technology [4].

Several electrochemical approaches to NH_3 synthesis have been reported in the literature with varying success, including high temperature proton-conducting ceramic electrolytes, molten hydroxides, PEM membrane and AEM membrane systems [5-7]. Most low temperature and low pressure production rates range between 10^{-12} and 10^{-8} mol NH_3 cm^{-2} s^{-1} with Faradaic efficiencies that are typically very low due to the competing hydrogen evolution reaction (HER) [5-7]. Cathode catalysts that enable increased NH_3 production rates while suppressing the HER are critical to realizing the benefits of sustainable electrochemical synthesis of ammonia. By utilizing alkaline media, non-platinum group metals (PGMs) may become feasible catalysts, thus lowering costs and use of very limited global supply of PGM.

Recently, Botte has demonstrated the electrochemical synthesis of ammonia in alkaline media according to reactions (1), and (2) [8].

$$N_2 + 6H_2O + 6e^- \rightleftarrows 2NH_3 + 6OH^- \qquad (1)$$

$$3H_2 + 6OH^- \rightleftarrows 6H_2O + 6e^- \qquad (2)$$

The overall reaction leads to the synthesis of ammonia with a theoretical cell voltage of 0.059 V. In this talk, recent advances on the process will be presented including the effect of the electrocatalyst composition, loading, and process parameters.

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Homogeneous Catalysis and redox shuttle for non-aqueous Li-O_2 cathode

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Non-aqueous Li-O_2 batteries have been under extensive focus in the last decades, owing to their high theoretical energy density[1]. However, such theoretical promises are yet to be validated in practice, owing to the multiple limitations of the oxygen positive electrode. Among others, the recharge of the Li_2O_2 formed during discharge is awkward because of its insulating behavior. To mitigate this, redox shuttles have been proposed[2].

In the present contribution, a redox shuttle compound is tested. Electrochemical characterizations in a three-electrode setup demonstrate that it is efficient to promote oxygen evolution reaction (OER, the charge reaction of the oxygen positive electrode in a non-aqueous Li-O_2 battery), and notably to regenerate the surface of Li_2O_2-covered carbon electrodes (Figure 1). Moreover, it promotes an efficient homogeneous catalysis of the oxygen reduction reaction (ORR, the discharge reaction of the oxygen positive electrode in a non-aqueous Li-O_2 battery), the onset potential of the ORR being shifted positive compared to redox-shuttle-free electrolyte (Figure 2). DEMS and UV-Vis characterization further confirms the catalysis and a simple mechanism is proposed. Li-O_2 full cell experiments will also be presented, and the value of this redox shuttle compound for practical systems will be discussed.

Figure 1: Evidence of the interest of a Redox shuttle for the regeneration (recharge) of Li_2O_2; CV scan rate 100 mV/s in 0.1M LiTF DMSO in presence of the redox shuttle, O_2 saturated.

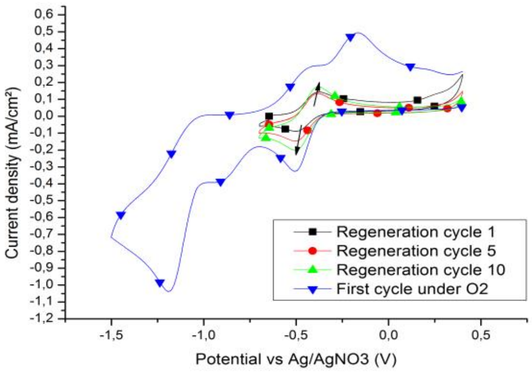
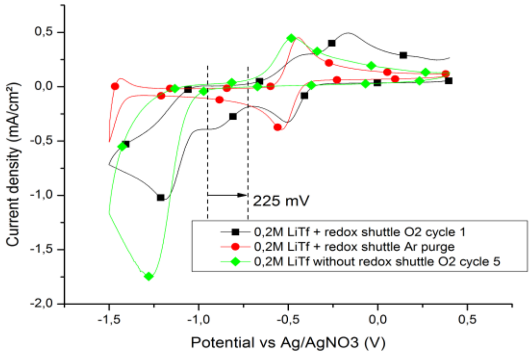


Figure 2: Evidence of Homogeneous Catalysis; CV scan rate at 100 mV/s in 0.1M LiTF DMSO, Ar or O_2 saturated.



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Alternating Current Output from a Photosynthesis-Inspired Photoelectrochemical Cell

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Photosynthesis involves two opposite directions of proton flux across the photosynthetic membrane through embedded proton pumps and proton channels,[1] which provides a biological prototype for designing new photovoltaic systems with alternating current (AC) generation. We recently found that, platinum nanoparticles (Pt NPs) unilaterally covered TiO_2 nanoporous membrane has several characteristics quite similar to the natural photosynthetic membrane: (i) harvesting light and achieving charge separation across the membrane like a photosystem complex;[2] (ii) forming a transmembrane proton gradient through asymmetric photochemical reactions on both sides, acting as a proton pump protein embedded in natural photosynthetic membrane;[3] (iii) providing nanochannels for protons pass through as proton channel proteins.[4] Therefore, Pt NPs unilaterally covered TiO_2 nanoporous membrane is employed to construct a photoelectrochemical cell with AC output through the combination with electron donor and acceptor. In this cell, ultraviolet light (UV) irradiation induces protons consumption and generation respectively in the two parts of solution across the membrane via asymmetric photochemical reactions.[5] The resulting concentration gradient of HCl powers the generation of a forward photocurrent. Turning UV illumination off causes a reversed transmembrane HCl concentration gradient mainly because hydrogen atoms adsorbed on Pt NPs are oxidized to be protons, which leads to a reversal in the direction of the current. Upon illumination periodically switching on and off, a continuous and steady AC is generated from the photoelectrochemical cell. Moreover, the waveform of AC is adjustable, and a stable square-wave signal can be obtained by optimizing light on/off frequency and proton source concentration in this system. This photoelectrochemical cell shows potential useful in photoelectric conversion, and the proposed mechanism for AC output in this work may provide new ideas for solar energy utilization.

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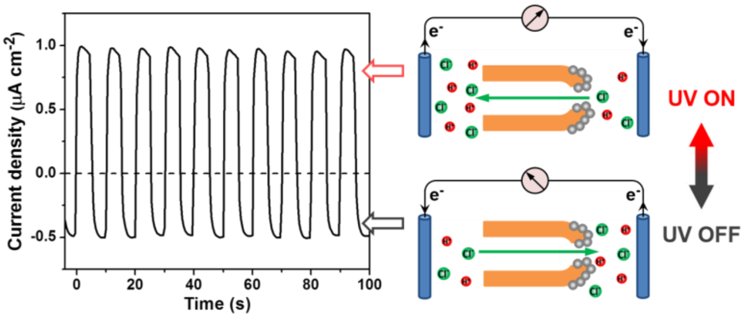

Figure 1. Alternating current output in response to periodic UV illumination and proposed mechanism based on transmembrane HCl concentration gradient inversion.

Unraveling the Potassium Storage Mechanism in Graphite Foam

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Potassium ion batteries (KIBs) are promising alternatives to LIBs in grid-scale electrochemical energy storage, owing to their comparable energy density, good rate performance, and economically viability. However, very little is known about the K^+ storage mechanism in graphite, and the understanding of the complex kinetics and thermodynamics that control the reactions and structural rearrangements is highly desirable. Here in operando studies including *in-situ* Raman and *in-situ* XRD characterizations, *ex-situ* XPS analysis and density-functional theory (DFT) calculations are carried out for correlating the real-time electrochemical K^+ intercalation/de-intercalation process with structure/component evolution. The experiment and theoretical calculation results reveal that potassium graphites of stages III (KC24), II KC16, and I (KC8) form in succession upon potassiation without the signature of dilute staging. The graphite recover back through phase transformations in an opposite sequence when depotassiation. The K^+ diffusion coefficients are found to be GIC stage dependent based on GITT and EIS results, highlighting the diversity in K^+ intercalation pathways. The establishment of clear property-structure relations in this work promotes better understanding of the K^+ storage mechanism in graphite and opens up a new exciting direction for designing new materials for K-ion Batteries.

AC voltammetric Sensing of Wastewater Polyaromatic Hydrocarbons

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There is much concern globally regarding the potentially harmful effects of organic pollutants, particularly because of an escalation in the rate at which they are being released into the environment. Among these pollutants are polyaromatic hydrocarbons (PAHs) which are known to present significant latent risk to humans and the ecosystem through the food chain. There is, therefore, a great need for their continuous monitoring and it requires simple, low cost, robust and sensitive signalling devices. In this study, novel generation-3 poly(propylene thiophenoimine)-co-poly(3-hexylthiophene) dendritic star co-polymer-on-gold sensor system (i.e. Au/G3PPT-co-P3HT) was developed for the determination of anthracene (AN), phenanthrene (PHE) and pyrene (PY) in oil-polluted wastewater. Electrochemical characterization and sensor application of the Au│G3PPT-co-P3HT electrode were performed by alternating current voltammetry (ACV), in a supporting electrolyte of 0.1 M Bu_4NClO_4 in acetonitrile. A good linearity calibration curves were obtained and the limit of detection were ranging between 1.34 - 2.33 nM. The results obtained from the proposed AC voltammetric sensing were comparable with other electrochemical analysis. The sensor developed presented an attractive alternative sensing methodology to the existing methods for the detection of PAHs wastewater.

Electrochemical Peroxidation – Electro-Fenton Integrated Process for Sludge Treatment: a Real Case Study

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As a consequence of the growth of human population, the number of wastewater treatment plants (WWTP) has significantly increased worldwide over the recent years. These facilities produce large quantities of hazardous sludge, which has become an important environmental concern in many developed and developing countries. In fact, the complex characteristics of sludge render its treatment and disposal difficult and expensive and as a result, sludge management already represents over 60% of the total costs of conventional WWTPs [1]. Conventional biological and physico-chemical methods for sludge treatment require high energy consumption and long retention time and their efficiencies are limited. Thus, there is an urgent need for sustainable and cost-effective treatment technologies and there is hope that electrochemical methods – with the advantages of being clean and energy-efficient – could be applied to sludge dewatering and stabilization [2]. However, results so far have not been conclusive and the removal of organic matter has remained low.

In this study, we present a sequential electrochemical process for anaerobic sludge treatment combining electrochemical peroxidation (ECP) and electro-Fenton (EF). Sludge samples (with 20,000 mg L^{-1} of initial chemical oxygen demand (COD) content) were obtained from a large egg-producer farm in Singapore, which faces issues because of the important amount of sludge it generates from its anaerobic digestion system. In the first step, ECP – consisting of H_2O_2-assisted electrocoagulation with iron electrodes – was applied as a conditioning method to increase dewaterability and reduce the amount of organic matter. COD, total organic carbon (TOC) and total suspended solids (TSS) were considerably reduced by 85%, 90% and 86%, respectively, after a 2-h treatment under optimized conditions (initial pH of 5, 5:1 H_2O_2/Fe^{2+} dose ratio and 10 mA cm^{-2}). Sludge with good settling and compaction properties was generated, which was easily separated by filtration. In the second step, EF was used to achieve complete mineralization of the remaining organic fraction in the filtrate. 90% of the remaining COD content after ECP was removed following 4 h of EF under optimal conditions (boron doped diamond (BDD)/carbon brush cell configuration at pH 3 and 500 mA), reaching a remarkable COD content only slightly higher than the Singaporean standard limit for discharge into watercourse and recreation purposes (100 mg L^{-1}). In conclusion, electrochemical technology is presented as a potent solution for sludge remediation through this two-step integrated process, in which the sludge is efficiently destabilized and conditioned by the synergistic effects of electrocoagulation and the Fenton's reaction during ECP, while mineralization of the organic contaminants is completed by means of the environmentally-friendly EF process. An overall 99% of COD and TOC removal efficiency was achieved by this sequential system (cf. Fig.1).

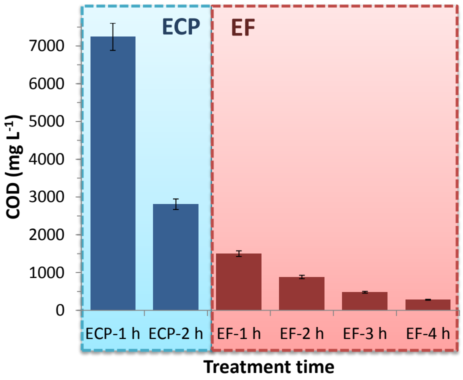

Fig. 1. Overall COD removal during the sequential ECP-EF process. ECP: 400 mL of anaerobic sludge (initial COD=20000 mg L^{-1}), iron electrodes, pH=5, 5:1 H_2O_2/Fe^{2+} dose ratio and 10 mA cm^{-2}. EF: 200 mL of pre-treated solution, BDD/carbon brush electrolytic cell, pH=3 and 500 mA.

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Wastewater treatment using nano-structured activated carbon and its *in-situ* electrochemical regeneration in a novel reactor configuration.

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Industrial contamination of fresh water supplies is a growing problem with serious environmental consequences, both in developed and developing countries. Conventional wastewater treatment relying on biological methods fails to remove recalcitrant compounds from diverse industrial activities, such as mining, microelectronics, refining, pharmaceuticals and chemicals, among others. These contaminants can be removed through adsorption on nano-structured activated carbon (NSAC), which is inexpensive, easy to operate and displays high removal efficiency due to its large surface area[1]. However, adsorption being strictly a separation technology, NSAC is unable to degrade the adsorbed recalcitrant compounds and thus needs to be regenerated upon saturation[2]. To overcome these problems, we propose a novel reactor that makes use of NSAC as adsorbent and as electrode material for electro-Fenton, allowing the *in-situ* regeneration of the spent material.

The electro-Fenton process achieved a regeneration efficiency of 33 ± 2 %, 72 ± 4 % and 87 ± 4 % after 1, 2 and 3 hours of treatment, respectively (Figure 1a). Correspondingly, the energy consumption (E_{consum}) increased with the regeneration efficiency up to 0.0025 kWh per gram of NSAC at the maximum regeneration efficiency of 87 % (Figure 1b). Thus, E_{consum} remained moderate in comparison with conventional thermal methods, which may consume up to 100 times more energy to sustain the high temperature requirements (approx.. 800–900 ºC)[3]. Another advantage of electrochemical over thermal regeneration lied in the improved stability, as demonstrated by the constant efficiency of 85 ± 4 % following 3 cycles of saturation and regeneration. In conclusion, the novel reactor achieved NSAC saturation and *in-situ* regeneration through electro-Fenton with high efficiency, low energy consumption and virtually no structural changes of the NSAC, making it a promising alternative to thermal regeneration for industrial applications.

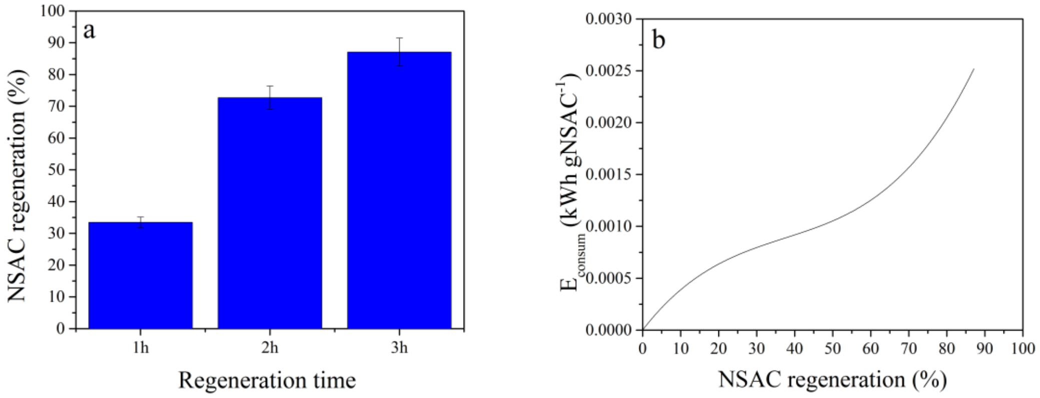

Figure 1. a) Regeneration efficiency of NSAC in time. b) Relation between the energy consumption and regeneration percentage.

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Photoredox Catalyst Based on an Arylimidazole Oxidative Electrochemical Mediator

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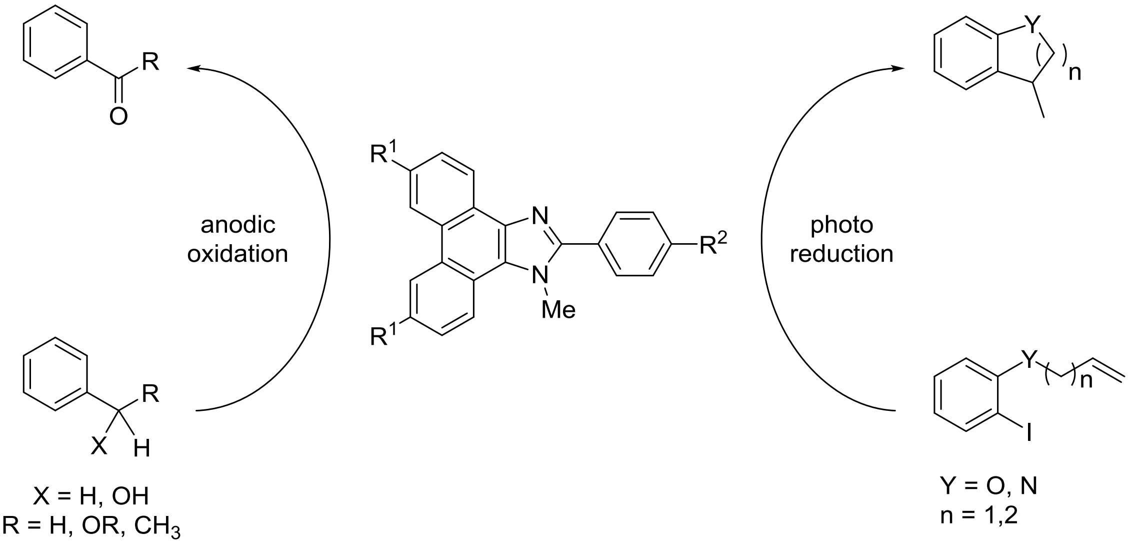
Photocatalysis [1] and electrosynthesis [2] are recognized as environmentally friendly, as they obviate the need for toxic or dangerous reagents. They also allow for unstable reagents and reactive intermediates to be produced in situ, thereby permitting the utilization of mild conditions. A class of oxidative electrochemical mediators based on the triarylimidazole framework have recently been investigated by Little, Zeng and Francke [2-5]. These mediators undergo one electron oxidization at the anode to form a radical cation, and serve as oxidative catalysts. (Scheme 1)

Recently, we have explored the potential of the mediators to serve as photocatalysts in reductive processes. With amines serving as sacrificial oxidants, the excited states, generated using visible light from an LED source, give up an electron thereby reducing the substrate and simultaneously generating the imidazole cation radical. Both dehalogenation of aromatics and reductive cyclization reactions have been investigated and will be discussed

Scheme 1. Dual Catalytic Properties of Arylimidazole/Phenanthroimidazole Mediators



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Optimizing Electrosynthesis of Formic acid from Carbon Dioxide by Immobilized Indium-protoporphyrins

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The ability to produce fuels or fine chemicals from the electrocatalytic reduction of CO_2 is a promising way for a sustainable carbon cycle, when renewable energy sources are used to drive the process. For implementation in the current infrastructure, the formation of liquid products such as methanol, ethanol and formic acid is preferred, as these can directly be employed in fuel cells. Molecular electrocatalysts have been attractive, since they are able to activate CO_2 and mediate CO_2 electroreduction. Metal complexes can provide detailed mechanistic insight relatively easily, by altering e.g. the electronic structure, substituents, metal center. Additionally, immobilization of molecular catalysts is widely undertaken to circumvent mass transport limitations, insolubility in (aqueous) electrolytes and to improve the electron transfer between the catalyst and reactants/intermediates. In a previous study Shen et al. reported low overpotential and high faradaic efficiency for CO_2 reduction to CO in aqueous media on cobalt-protoporphyrin immobilized on pyrolytic graphite (PG) electrodes [1].

In this work we firstly investigate the role of the metal center of immobilized metalloprotoporphyrins (MPP) for the electrocatalytic reduction of CO_2 to formic acid. We prove an interesting influence of the metal center on the selectivity towards formic acid, where In, Sn and Rh metal centers are the most active and Cr, Mn, Co and Fe metal centers are inactive for formic acid formation [2]. We obtain a relatively high faradaic efficiency towards formic acid (FE_{HCOOH} ~70%) on indium-protoporphyrins immobilized on PG. DFT calculations are performed, which explain the experimental observations and discuss the differences in the rate-limiting steps, CO_2 activation and reaction pathways between InPP, RhPP and CoPP [3]. Although the adsorbed porphyrin-substrate interaction is strong, the stability of the immobilized InPP should be improved. We study and give insight in the effects of various important parameters on the activity and stability of immobilized indium-protoporphyrins [4]. It is shown that the adsorbate-substrate interaction plays an important role in the activity and selectivity, as porphyrin immobilization on boron doped diamond and glassy carbon electrodes lead to much lower faradaic efficiencies. Moreover, incorporating the porphyrin in a film of surfactant (didodecyldimethylammonium bromide, DDAB) was expected to improve the selectivity by inhibiting the hydrogen evolution reaction; however, the influence of the surfactant layer is found to be negligible. Additionally, we have investigated the influence of an anodic, cathodic, H_2 - and O_2 plasma treatment of the PG electrode before porphyrin immobilization. The anodic pretreatment proves to be favorable for the stability, while the cathodic pretreatment does not show significant improvement. In the recent literature, the nature of cations is shown to influence the selectivity of CO_2 reduction on Cu [5] and Ag [5,6]. In contrast to metal electrode systems, we report no significant cation effect, which indicates a different behavior between molecular and metal catalysts for CO_2 reduction. Currently, we are performing high pressure CO_2 reduction on this system, from which we can conclude that the immobilized porphyrins are stable under high pressure. The differences in the activity and selectivity as function of pressure are discussed.

Our study demonstrates the importance of various parameters influencing the activity and stability of immobilized metalloprotoporphyrins for the electrocatalytic reduction of CO_2 towards formic acid. The results show optimum conditions for efficient and durable formation of formic acid and suggest directions for designing new immobilized molecular electrocatalysts. The effects are discussed aimed at understanding the underlying aspects of immobilized molecular catalysts, which are often overlooked when using molecular catalysts for electrosynthesis. These findings can be generalized to other immobilized metal complexes for electroreduction of CO_2 and other electrocatalytic reactions.

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"*Inherently Chiral*" Electrode Surfaces and Media: Alternative Approaches to Enantioselective Electrochemistry

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The ability to select among different electroactive molecules, or among different redox centers on a single molecule, in both analytical and synthetic applications, is a typical asset of electrochemistry, based on fine control of the electrode potential, possibly enhanced by the choice of appropriate electrode surfaces and media. An attractive step further, of great fundamental and applicative interest, is represented by *enantio*selective electrochemistry, implying the ability to discriminate the *enantiomers* of chiral molecules in terms of electrode potentials (in electroanalysis), or to selectively activate or achieve a given enantiomer of a chiral molecule through the electrode potential (in electrosynthesis).

Since the enantiomers of a chiral molecule have identical physico-chemical properties and therefore the same electrochemical behaviour except when interacting with some other chiral entity, enantioselective electrochemistry necessarily implies the electron transfer process to take place in asymmetric conditions. This can be achieved by the use of either a *chiral electrode surface* or a *chiral medium*. Among the many approaches so far proposed for this ambitious target along either of the two possible ways, a groundbreaking strategy was recently proposed [1], based on the use of "inherently chiral" molecular materials, either as electrode surfaces [2-5] or as media [6]. The peculiarity of inherently chiral molecular materials is that the same element endows the molecule with both its key functional property and with chirality, coinciding with the main molecular backbone featuring a tailored torsion; this results in outstanding chirality manifestations.

Thus, electrooligomerization of enantiopure inherently chiral electroactive monomers, based either on biheteroaromatic atropoisomeric cores combined with thiophene-based wings or on thiahelicene scaffolds, yields enantiopure *inherently chiral electrode surfaces*, on which impressive peak potential differences are observed in voltammetric experiments for the antipodes of chiral probes, even quite different in structure and electrochemical reactivity.[1-5] At least one of the monomers can even yield self-standing inherently chiral artificial membranes.

Large differences in peak potentials can also be achieved for the enantiomers of different chiral probes working on achiral electrodes, but in suitable *inherently chiral media*. For instance, inherently chiral ionic liquids ICILs have been prepared from atropoisomeric 3,3′-bicollidine, resolved into antipodes without enantioselective HPLC and converted into long-chain dialkyl salts with melting points below room temperature. Both the new ICILs and shorter family terms that are solid at room temperature, employed as *low-concentration additives in achiral ionic liquids*, result in impressive peak potential differences, regularly increasing with additive concentration, for the enantiomers of different probes on achiral electrodes. [6]

Work is in progress along both of the above lines to strengthen and rationalize the first proofs of concept by developing, characterizing and testing a wider variety of inherently chiral inductors (both monomers for electrode surface preparation and ionic liquids/additives), with different chiral probes, particularly of pharmaceutical interest, with more optimized and detailed protocols, and with the support of theoretical computations; other possible applications of the new inductors are also being considered.

A selection of the most interesting recent achievements will be presented and discussed.

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Synthesis of Azanucleosides by Anodic Oxidation in a Lithium Perchlorate--Nitroalkane Electrolyte Solution

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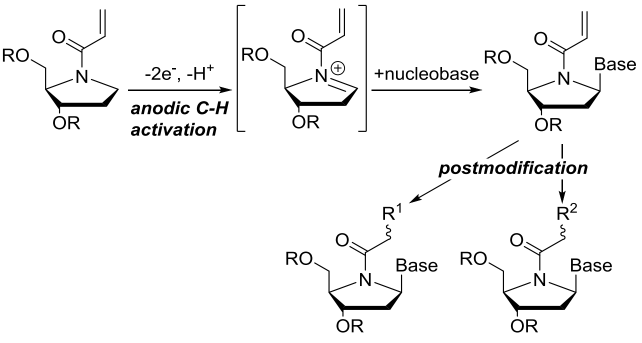
Azanucleosides in which the 4′-oxygen atom is replaced with nitrogen have drawn much attention due to their anticancer and antivirus activity, and tolerance towards nucleases. The traditional synthetic strategy requires, however, multistep reactions and harsh conditions, thereby limiting structural and functional diversity of the products. As a result, it has been difficult to incorporate the desired modification or functional group into the starting material or synthetic intermediate prior to glycosidation, limiting the introduction of functional groups into the azanucleoside product. To address this challenge, we assumed that a straightforward and mild procedure for generating a reactive intermediate, followed by coupling with nucleobase, would allow the conversion of precursors bearing a post-modifiable functional group at the 4′-nitrogen position into azanucleoside derivatives with the 4′-nitrogen functional group intact. Furthermore, the synthesized azanucleoside derivatives would be easily modified at the 4′-nitrogen residue by avoiding cleavage of the 4′-*N*-acyl bond. Herein we describe a short synthetic method for azanucleosides using an electrochemical reaction in lithium per-chlorate-nitroethane medium, followed by post-modification at the 4′-nitrogen position. *N*-acryloyl prolinol derivatives were converted to azanucleosides by anodic activation of the N-α-C-H bond. Moreover, the use of nitroethane lowered the oxidation potential of *N*-acryloyl prolinol in comparison with the use of nitromethane, and increased the Faradic yield. The prepared azanucleosides were efficiently functionalized with lipophilic alkanethiol and fluorescent dye at the 4′-*N*-acryloyl group by conjugate addition and olefin cross-metathesis.

With the optimized conditions of lithium perchlorate/nitroethane electrolyte solution, we embarked on the synthesis of azanucleosides compatible with modification at the 4′-nitrogen position in a later step. The prolinol derivative was oxidized and coupled with N^6-benzolyadenine ($\mathrm{A^{(Bz)}}$), N^2-isobutylguanine ($\mathrm{G^{(Ib)}}$), N^4-benzoylcytosine ($\mathrm{C^{(Bz)}}$) and thymine (T) in one pot. The diastereomers of each azanucleoside were purified by HPLC and their configurations were determined by ^{1}H NMR and NOESY. The introduction of $\mathrm{A^{(Bz)}}$ produced the corresponding *N*-Acr-azadeoxyadenosine derivative in 90% yield without significant side reaction, such as the conjugate addition of a nucleophile at the *N*-acryloyl group. The coupling reaction of $\mathrm{C^{(Bz)}}$ at room temperature produced the desired product in 74% yield and the yield was improved to 83% when the coupling was conducted at 40°C. We also examined post-modification reactions based on the 4′-nitrogen of azanucleoside using conjugate addition and olefin metathesis. The coupling reaction between the β-anomer of aza-d$\mathrm{A^{(Bz)}}$ or aza-dT and 1-dodecanethiol produced the modified azanucleosides in 91% and 93% yield, respectively. These results indicated that the 4′-*N*-Acr group of azanucleoside maintained reactivity towards thiol compounds, allowing post-modification based on the 4′-nitrogen atom.



In conclusion, we have developed a synthetic method for azanucleosides which allows 4′-nitrogen modification in a later step. The activated prolinol substrate was coupled at the 5-position with nucleophiles, including nucleobases, with the *N*-Acr group remaining intact. Moreover, the functionality of the prepared *N*-Acr-azanucleoside was easily increased by conjugate addition with peptide, and olefin metathesis with fluorescent dye.

Electrochemical Acetone Reduction – A Model Reaction for the Electrochemical Refinery of Biological Feedstock

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Bio mass has the potential to serve as a feedstock for the chemical and pharmaceutical industry. However, bio oils obtained from pyrolysis of bio mass is usually rich in oxygen containing compounds that feature predominantly alcohol, carbonyl or carboxylic functions. Reduction of these compounds is required for further processing. Due to reduced electricity prices for industrial consumers in some markets, electrochemical refinery has attracted interest. Furthermore, electrochemical reduction avoids handling of hydrogen at high pressure and temperatures, usually employed in heterogeneous catalysis, which translates into high process costs.

We are going to present the electrochemical reduction of acetone as a model reaction for the reduction of ketones. It was shown before that acetone can be reduced to propane and 2-propanol at polycrystalline platinum [1, 2]. Our own results based on online electrochemical mass spectroscopy (OLEMS) confirm the evolution of propane during acetone reduction from 0.1 M H_2SO_4. However, experiments at single crystal electrodes reveal that propane formation requires the presence of Pt(100)-terraces. No acetone reduction proceeds at Pt(111)-single crystals. However, with increasing density of [110]-steps the current density due to acetone reduction increases at Pt[(n-1)(111)x(110)]-type electrodes. FTIR-experiments and OLEMS-experiments reveal the selective formation of 2-propanol at Pt(110)-electrodes without concomitant hydrogen evolution. Unlike Pt(100), which undergoes rapid deactivation in the course of acetone reduction, the formation of 2-propanol at Pt(110) is not hampered by the presence of even major amounts of 2-propanol.

The reaction order in both acetone and protons was determined. Both reaction orders have approximately the same value, they show a pronounced potential dependent on the reversible hydrogen scale and they remain broken over the entire potential range of acetone reduction. From that and adsorption experiments from very diluted solutions we conclude that acetone reduction proceeds via the reduction of protonated acetone in the adsorbed state. The absence of any bands due to any adsorbate in FTIR-experiments, performed at single crystal electrodes, reveals that acetone is adsorbed in a side-on configuration. Also at Pt(100) no adsorbate is observed, indicating that poisons formed during acetone reduction, are bound in a side-on configuration as well. The expected formation of CO is not observed.

Results obtained for acetone are compared to aliphatic ketones with a larger carbon skeleton. They show the same trend as acetone regarding the influence of the platinum surface structure. In contrast to that the trend regarding the density of [110]-steps is reversed when acetophenone is reduced at platinum single crystals. No reduction takes place at Pt(110) and the highest activity is observed at Pt(111). We understand this as the result of a stronger interaction of the phenyl ring with the platinum surface. The interaction of the phenyl ring with the platinum surface causes at Pt(111) an adsorption geometry required for the reduction of the carbonyl function. The interaction of acetone with the Pt(111) surface is too weak to achieve an adsorption. At Pt(110) the interaction is so strong that hydrogen adsorption is suppressed. We propose that adsorbed hydrogen is required to sustain the reduction of the carbonyl function in a Langmuir-Hinshelwood mechanism, therefore, suppression of H-UPD, suppresses the reduction of acetophenone as well.

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Electrochemically oxidative formation of new chemical bonds mediated by halide ion

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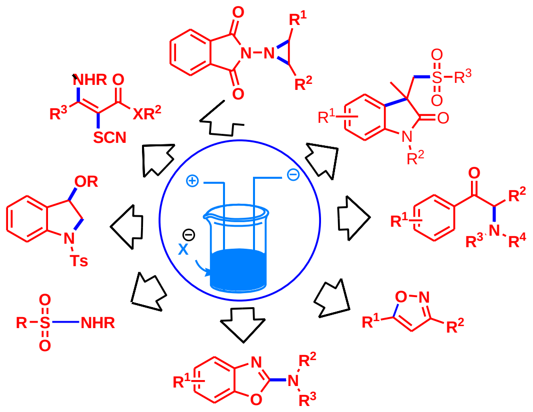
Organic electrochemistry has emerged as a powerful "green and sustainable" approach in the synthesis of organic compounds since electron is used as reagents without stoichiometric amount of chemical redox reagent. Electrosynthesis can be carried out directly or via a redox mediator. Halide ions, especially Br^- and I^-, have been widely employed as mediators in anodic oxidation. In this presentation, we would like to examine recent advance in the electrochemical oxidative functionalization of C-H bonds mediated by halides.



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Electrosynthesis Using a Recyclable Mediator-Electrolyte System Based on the I(I)/I(III) Redox Couple

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The conversion of organic compounds utilizing electric current is considered to be a powerful synthetic tool and an environmental friendly alternative to classic synthetic organic chemistry.[1,2] For instance, it can serve to shorten synthesis pathways or to substitute toxic, carcinogenic or explosive reagents.[1,3] A further improvement of an electrosynthetic process can often be realized by replacing the heterogeneous electrode-centered process by a homogenous one. This substantial change opens the field of redox-mediator driven (indirect) electroorganic synthesis.[4] Redox mediators, either used in catalytic amounts in a one-pot process (in-cell mediators) or in stoichiometric amounts for a sequential process (ex-cell mediators), can often help to overcome a majority of serious drawbacks of electrosynthesis (e.g. improving reaction rates and selectivity, reducing electrode passivation).

In this work, a new mediator was developed, which offers all the advantages of indirect electroorganic chemistry and in addition provides a simplified recovery procedure.[5] This was achieved by tethering a redox-active moiety based on the I(+1)/I(+3) redox couple to a tetraalkylammonium group (see figure below, species **1**). Simultaneously, sufficient ionic conductivity for operation without additional supporting electrolyte is obtained, minimizing the overall waste generation and further simplifying the separation after completed reaction. Studying different solvents for the oxidation of **1**, it became evident that the use of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) is crucial for generating the corresponding I(+3) compound in good Faradaic efficiency at high current densities. For the purpose of proving our mediator-electrolyte concept, we applied it to direct oxidative C-N coupling reactions between various amides and arenes. The reactions turn out to yield the coupling products in good to excellent yields with hydrogen as the only byproduct. With the newly implemented recycling procedure, the mediator can be recovered simply by a solid phase extraction.

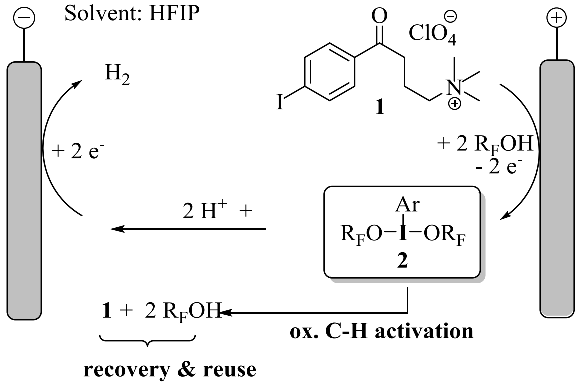

Figure 1: Concept for the electrochemical generation of our iodine(III) species **2** and the subsequent use for chemical transformations.

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Novel Polyelectrolyte Mediators for Indirect Electroorganic Synthesis

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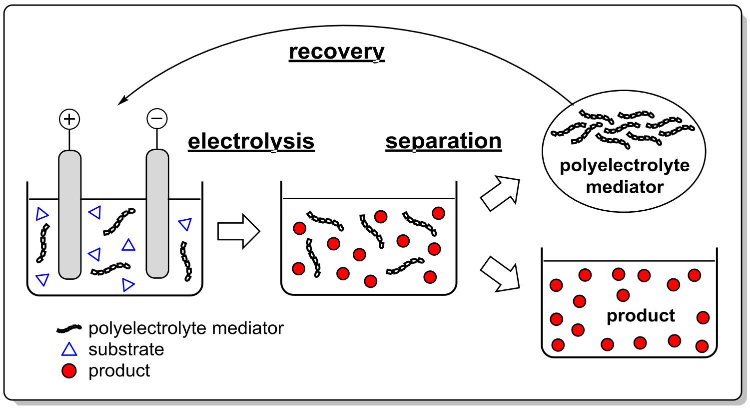
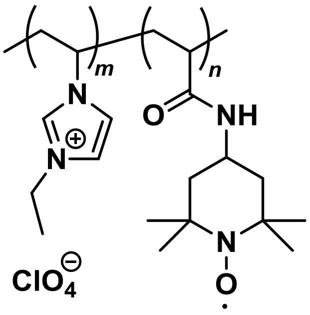
Electroorganic synthesis has been acknowledged as a promising green technology which provides several advantages compared to conventional organic synthesis. These merits include ecologic and economic advantages of using electric current instead of reagents, as well as mild reaction conditions and the possibility for controlling the selectivity via the electrode potential. Despite all the progress which has been made in this field in the last decades, there are still some fundamental challenges which prevent this methodology from application on a broader base, i. e. the necessity for using excess amounts of supporting electrolyte and sometimes, poor kinetics and selectivity associated with the electron transfer between electrode and substrate molecule. Whereas the latter issue is typically addressed with the use of electron transfer mediators,[1] the problem with the supporting electrolyte has been ignored for a very long time.[2]





Considering these challenges, we have developed a system which allows for simultaneous separation and recycling of supporting electrolyte and mediator in a single step. For this purpose, imidazolium and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) groups) were attached to a polymer backbone (see Figure, right), resulting in well-soluble, conducting and redox-active polymers. After completed electrolysis and separation by ultrafiltration, these polyelectrolyte mediators can be reused for several runs.

As proof of principle, we have selected the electrochemical conversion of alcohols as a model reaction. Based on the original electrochemical TEMPO oxidation introduced by Semmelhack et al.,[3] we have developed a procedure which combines high selectivity (Faradaic efficiency: up to 99%) with a convenient separation procedure. Recycling studies reveal that there is no decrease in Faradaic efficiency after several cycles.

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Electrocatalytic Reduction of Carbon Dioxide Using Cyclopentadienone Iron Complexes – New Mechanistic Insights

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Among the possible products of CO_2 reduction, CO is particularly interesting due to a variety of possibilities for utilization as C_1-building block. However, a selective cathodic transformation of CO_2 to CO is not straightforward due to numerous possible side reactions and the high overpotential for electrochemical CO_2 reduction.[1-2] In this regard, substantial progress has been recently made with homogeneous electrocatalysts.[3-5] However, most of the methods reported thus far require precious metals such as Re, Pd or Ru, ligands with limited availability such as porphyrine analogues and/or proton donors such as phenol or trifluoroethanol.

Herein we report an electrolysis protocol for the selective generation of CO from CO_2, catalyzed by robust and easy-to-synthesize (cyclopentadienone)iron-tricarbonyl complexes in the absence of proton donors.[6] The electrocatalytic behavior of the complexes was characterized using cyclic voltammetry (see example in Figure, left), whereby high turnover frequencies and a remarkable influence of ligand substitution and solvent on the catalytic performance were observed. Application in controlled potential electrolysis rendered excellent Faradaic yields for CO generation and good turnover numbers.

Along with the catalytic performance, possible mechanisms are discussed based on voltammetric data, spectroelectrochemical results and DFT calculations. We found that cathodic reduction leads to an intermediate having a hydroxycyclopentadienyl ligand (see Figure, right), which in cooperation with the metal center plays an active role in the catalytic cycle.

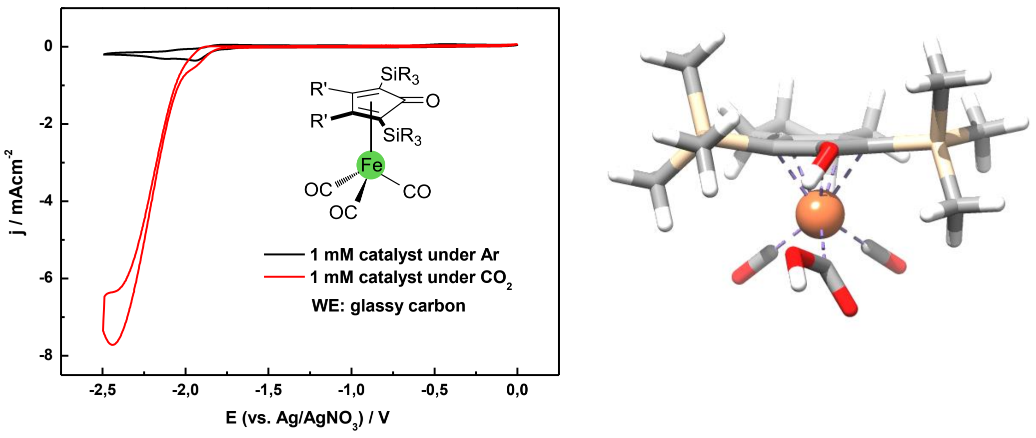

Figure 1. Left: Cyclic voltammetry of the iron cyclopentadienyl catalyst on a glassy carbon electrode under Ar and under CO_2 (0.1 M NBu_4ClO_4 in CH_3CN). Right: Optimized geometry of the adduct between twofold reduced catalyst and CO_2 (B3LYP def2-TZVP(-f) level of theory).

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Amidyl Radicals as Intermediates for the Electrochemical Synthesis of Heterocycles

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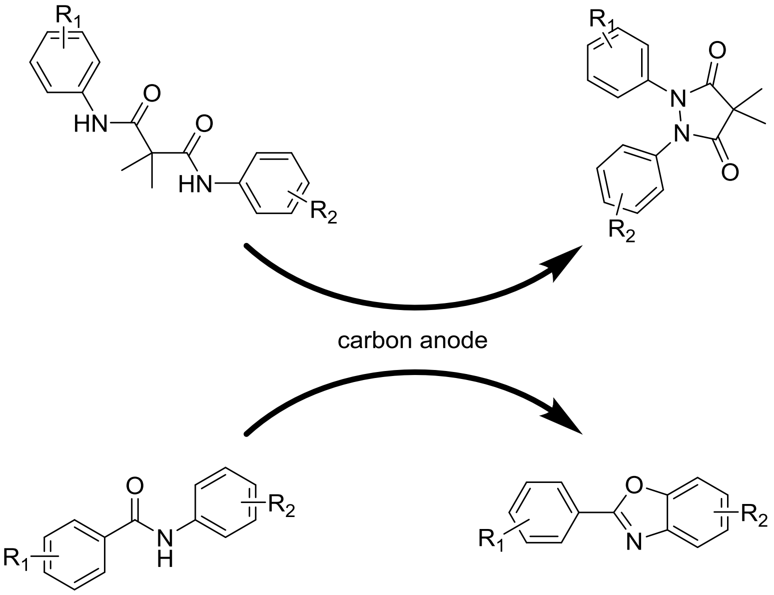
The use of electrochemistry for the generation of reactive intermediates can have major advantages towards conventional synthetic strategies.[1] Less or no reagent waste is produced and new reaction pathways are accessible.[2] In this context, we present a sustainable synthetic approach for the generation of valuable heterocycles like benzoxazoles and pyrazolidin-3,5-diones.[3] Traditional synthesis routes to these compounds often include toxic reagents, catalysts or leaving functionalities.[4]



An amidyl radical serves as reactive intermediate, which is directly generated at the anode. It depends on the components of the amidyl radical, which heterocycle is formed. This approach enables a sustainable access to these heterocycles starting from inexpensive starting materials without any pre-functionalization.

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Electrochemical Dehydrogenative Cyclization Reactions

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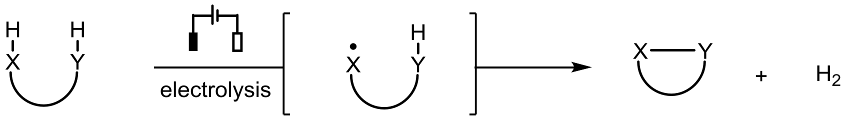
Cross-coupling of C–H and X–H (X = C or heteroatom) bonds is a powerful approach for the construction of carbon–carbon as well as carbon–heteroatom bonds because it offers several advantages including the use of simple and easily available starting materials and the elimination of substrate prefunctionalization.[1] Intramolecularly, these transformations provide convenient access to cyclic structures. Nonetheless, current methods frequently require the use of metal or organic stoichiometric oxidants, which create potential safety hazards for large-scale synthesis and frequently impose considerable amount of waste on the environment. We have developed several electrochemical dehydrogenative cyclization reactions for the synthesis of a variety of cyclic structures.[2] These reactions proceed in a noble-metal- and chemical oxidant-free fashion and produce H_2 as the only theoretical byproduct.



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Electrochemistry in Continuous Flow – Electroorganic Process Development on Lab and Industrial Scale

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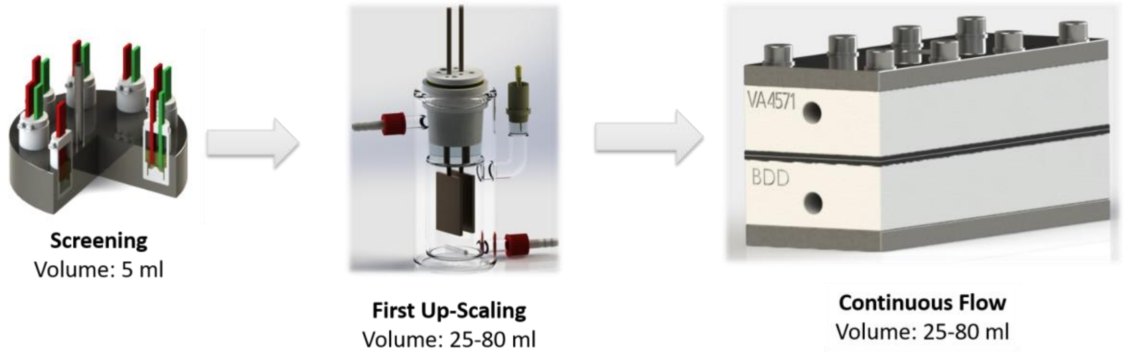
Since renewable energy sources become more and more important, electrosynthesis represents a sustainable and cost efficient "Green Chemistry"-approach with outstanding reactivity and selectivity.[1] In contrast to well applied electroanalytical equipment, the lack of standardized facilities for electrosynthesis hamper research groups and chemical companies to initiate efficient process development. Recently, we presented an initial solution for this problem by an electrochemical screening device with up to eight reactions in parallel for a batch approach on small scale (5-6 ml).[2] This setup facilitates the optimization of first process parameters and up-scaling in larger batch cells.

Nevertheless, electrosynthesis in flow is the only method to produce large amount of substrates efficiently on an industrial scale.[3] We hereby present a highly modular electrochemical flow cell for optimization of process parameter.[4] In this setup every common electrode material can be applied and substituted easily. The gap between the electrodes can be variated and the user can switch between a divided and an undivided cell by using a supplementary membrane. Additionally, an optimized size of the cell guarantees a straightforward up-scaling and helps saving starting material during the development.



To demonstrated the performance of our continuous flow approach, a broad scope of developed electrochemical transformations, like nitrile,[5] isoxoazole[4] or cyclopropane synthesis[6] were demonstrated.

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Indirect Electroreduction on Catalyst-Modified Electrodes as Pretreatment to Enhance Biodegradability

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The treatment of recalcitrant compounds that cannot be eliminated upon conventional biotreatment of wastewater requires physico-chemical methods for their degradation that often suffer from a lack of selectivity and high cost. Recently, integrated processes, combining physico-chemical and biological treatments have received a growing attention for their efficiency in complete mineralization of biorecalcitrant compounds at reduced operating costs.[1] In that case, the aim of the pretreatment is not to mineralize the pollutant but to increase its biodegradability and reduce its toxicity.

Since the role of the pretreatment in coupling process is the enhancement of biodegradability of the molecule at the lowest possible cost, without the formation of toxic by-products, we investigated a coupling method involving an indirect electrochemical process as a pretreatment for the degradation of recalcitrant compounds. The objective is to remedy concentrated effluents on site, before the persistent organic pollutants will be diluted in large volumes of low concentration, more difficult to treat. The expected positive impacts are a selective attack of the targeted functional groups, for a fine control of the compound degradation and an improvement of current efficiency, resulting in saving energy and hence reducing cost. The feasibility of the proposed coupled process was investigated on pollutants containing functional groups that are largely represented among biorecalcitrant pesticides and pharmaceutical compounds and known to be linked to the biorecalcitrance of a molecule.

Indirect electrolyses were carried out in a home-made electrochemical flow cell using a porous electrode of high specific area, allowing a rapid and quantitative transformation of aqueous polluted solutions. Homogenous and heterogeneous catalytic reactions were achieved to selectively reduce/oxidize targeted functional groups of the pollutant.[2] Biodegradability improvement was checked with classical analytical parameters and by biological treatments using activated sludge from treatment plant. We will see among several examples how indirect electrolyses can improve biodegradability and allow the implementation of an electrochemical and biological coupling process.

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Observation of Local Redox Events at Individual Plasmonic Nanoparticles Using Dark Field and Electrogenerated Chemiluminescence Microscopy methods

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Electrogenerated chemiluminescence (ECL) is a process in which light is generated through the relaxation of electrochemically generated excited states. ECL has recently been applied to study individual nanostructures such as single polymer nanoparticles (NPs) to demonstrate the possibility of detecting small light emitting species at the nanometer scale for more accurate and precise quantitative applications. More commonly, small nanostructures can be probed by other optical techniques such as fluorescence and dark field light scattering. Au and Ag NPs are known to have interesting optical properties such as local field enhancement and intense light absorption and scattering under resonance conditions. These particles also support important electrochemical catalytic activities. For example, Au NPs can found to be able to enhance the oxidation of tripropylamine (TrPA) and the generation of electrogenerated chemiluminescence (ECL) from $Ru(bpy)_3^{2+}$ when TrPA is used as a coreactant. Local redox activities of single Au NPs can therefore be investigated using the combined methods of voltammetry and ECL imaging. Our study shows that ECL generation at individual Au NPs increases with particle size (diameters from 30 to 300 nm) and is affected by the local chemical and charge transfer environment of the NPs. Such an ECL detection scheme can allow one to study the local redox activities of single nanoparticles with improved spatial resolution. ECL at single Au NPs shows slight temporal variations in intensity attributed to the oxidation and reconstruction of small clusters on the Au surface during ECL generation. Quantitative agreement between calculations and experiment concerning the effect of particle size and electrode potential on spatial and transient ECL profiles is presented. Single NP collision events can be resolved at nanoelectrode made of a scanning tungsten probe in order to resolve the diffusion and catalytic activities of single Pt nanoparticles using a catalytic amplification method.

Synthesis and Properties of Luminescent Tb-doped Nanoferrites for Anticancer Therapies

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Nowadays medicine demands intelligent drug delivery systems addressing, for example, only tumors. Magnetic nanoparticles seem to meet this requirement, because they can be guided to the specific tissue with an aid of external magnetic field. Currently, modified superparamagnetic iron oxide nanoparticles (SPIONs) are the most promising systems. Modification in their core can broaden their application. For example - doping with lanthanide ions may provide luminescent properties for nanoparticles, making them suitable for monitoring of drug distribution and tissue imaging.

We present synthesis and characteristics of magnetic nanoparticles, doped in their core with terbium ions (TbSPIONs) using the reverse micelle method. The core diameter of SPIONs can be controlled during the synthesis by the adjustment of oil-to-water ratio. Tb-doped nanoparticles were characterized with TEM, PXRD, magnetometry, Moessbauer technique and fluorescence spectroscopy. XPS studies confirmed the presence and stoichiometry of terbium in the magnetic core. Due to the interesting luminescent properties of TbSPIONs, the time resolved fluorescent experiments were also carried out in order to gain an insight into the distribution of Tb^{3+} within the crystal lattice.

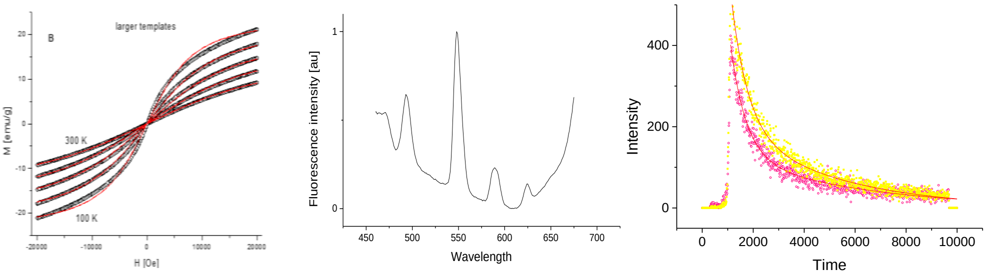

Figure1, from left: Hysteresis loop of dried sample, fluorescence spectrum of nanoparticles suspended in water, fluorescence decay for samples obtained using different oil-to-water ratios.

Such obtained TbSPIONs can provide a unique platform for targeted drug delivery. We subsequently demonstrated and monitored electrochemically the release of cytostatic drug - doxorubicin from the drug/TbSPION systems.

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Detection of Bacteria by Electrochemiluminescence

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Detection of bacteria rapidly and reliably is still a challenge and is critical for global health, for industries (ex: pharmaceuticals, foods and beverages) or even to prevent bio-threats. Most common methods includes identification via PCR amplification of RNA, ELISA, or chemical reactions of dyes in the presence of bacteria cells or their metabolites. Reduction of resazurin to resorufin is one example of a metabolic dye where the color change accompanied with the chemical change is used to detect the presence of live bacteria. In this project, we propose an innovative approach for the detection of bacteria using electrochemiluminescence (ECL). ECL is an electrochemically initiated light emission involving a series of electrochemical and chemical reactions. We aim toward a label-free detection by using the biological metabolism of the bacterium itself to interfere with the redox reactions required to form the excited stage of the electroactive luminophore. Our ECL reagents system for the proof-of-concept consisted of the gold standard in ECL: ruthenium tris(2,2'-bipyridine)(II) as luminophore (emission at ~620 nm) and tripropylamine as a co-reactant. For development purposes, we used the non-pathogenic *E. coli* K12. In the absence of bacteria, intense ECL was emitted. In presence of bacteria, however, the ECL decreased or disappeared completely depending on the amount of bacteria. When using reagents and bacteria at high concentrations, the ECL emission could be detected by the eye and imaged using a simple camera. Higher sensitivity of detection and better characterization is ongoing using photon counters such as photomultiplier tube. ECL is a highly sensitive analytical method and presents low background noise compared to other luminescence techniques; the reverse assay format will further enhance the sensitivity by detecting a small change from a high intensity signal rather than trying to detect a small signal from the noise and allow for a positive control to account for matrix interferences. Our ongoing research focuses on investigating the mechanism of decrease of the ECL and maximizing the analytical sensitivity of the assay.

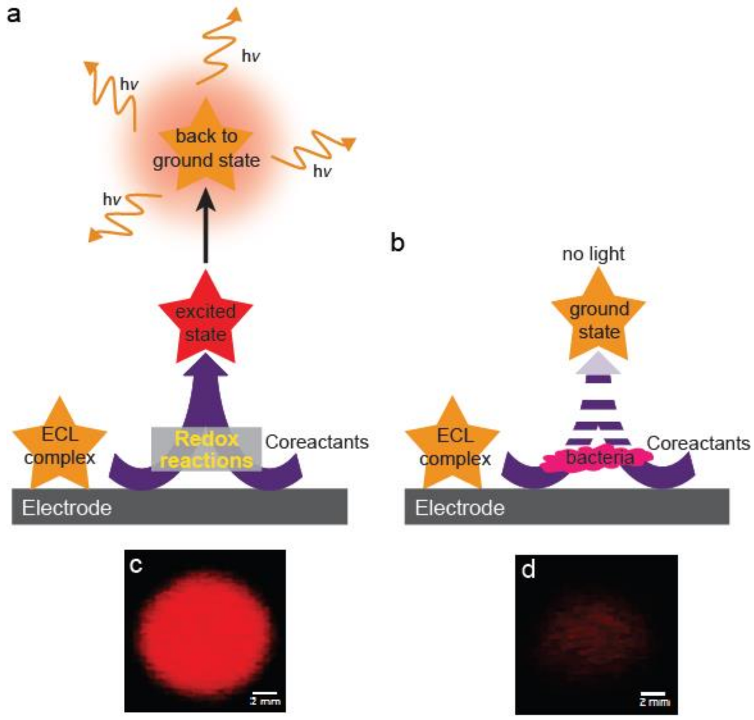

Fig. 1 General scheme of ECL (a) and concept of bacteria interfering with the ECL generation (b); ECL images recorded in the absence (c) and presence (d) of *E. coli* K12.

Carbon nanomaterial for robust and highly sensitive electrochemiluminescent detection of prostate cancer biomarker

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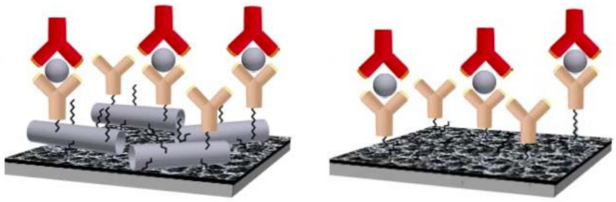
More than 1.1 million cases of prostate cancer were recorded in 2012, accounting for around 8% of all new cancer cases and 15% in men. [1] Efforts to evaluate and discover diagnostic and therapeutic markers for prostate cancer continue. [2] One of these, prostate-specific membrane antigen (PSMA), a transmembrane protein expressed in all types of prostatic tissue, remains a useful diagnostic and possibly a therapeutic target. Recent studies have consistently demonstrated that high levels of PSMA expression have been associated with advanced tumour stage, androgen-independent tumour growth, presence of metastases and early PSA recurrence, which could have implications for treatment decisions. [3]

Our challenge was to design a novel hybrid system for PSMA detection, in which sandwich immunoassay and electrochemiluminescence (ECL) were successfully combined. The unique ability of an antibody to specifically recognize its antigen together with the ECL-based detection approach presents several advantages, such as limited costs, inexpensive equipment, rapidity of analysis, and easy use.

The sensitivity of the immunosensor was enhanced by interfacing the transduction component, an optical transparent electrode (ITO), with functionalized multi walled carbon nanotubes (f-MWCNTs), [4] further modified with an anti-PSMA monoclonal antibody. [5] The sensor was able to produce a concentration-dependent light signal, allowing PSMA quantification in lysate with a limit of detection equal to 0.88 ng/mL. The use of f-MWCNTs has dramatically contributed to enhance the signal intensity produced by the device, in agreement with their renowned conductive and loading properties.



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Plasmon-enhanced electrochemical reaction on nanostructured Ag and Au electrodes in ionic liquids and aqueous solutions

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To describe electrochemical interfacial structures and processes, many theoretical models and calculation methods have been developed. Jellium electron model is widely accepted and utilized to interpret many phenomena related to the electron spillover from the electrified surface to electrolyte. However, the conceptual jellium has not been experimentally measured due to limitations of sensing and resolving the electron in solution on the scale of a few angstroms. We have used surface-enhanced Raman scattering (SERS) to in-situ characterize the electronic jellium at electrode-electrolyte interfaces with molecular/atomic rulers. We also performed DFT calculations on Raman spectra of interfacial water and ionic liquid at negatively charged Ag surfaces related to the jellium model as well as surface plasmon resonance (SPR) distribution under laser illumination. [1,2]

Since the length of the jellium electron spillover from Ag electrode into solution at very negative potentials is over 3 Å, it means that the first layer of adsorbate or solvent molecules are immerged in the jellium electrons. It is special interest to explore a possibility from plasmon spectroscopy to plasmon chemistry to answer a key question on how different types of electrons work jointly at the electrochemical interface. The delocalized electrons driven by both near-field optical filed and electric field may enhance/initiate localized electrochemical reaction. We have perform a systematic study on the effects of nanostructure, temperature, laser power and wavelength, applied potential. Moreover, surface-enhanced Raman spectroscopy was used to characterize the possible products and related mechanism.[3]

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Electrochemiluminescence Resonance Energy Transfer-Based Biosensors

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Electrochemiluminescence resonance energy transfer (ECL-RET) has been considered as a promising approach for the sensitive detection of biomolecules due to the advantage of absence of background light emission, high sensitivity, wide dynamic range, and so on. Although the ECL-RET techniques have been widely used for DNA detection, cytosensing, and immunoassay, the exploration of efficient energy donor/acceptor pairs is still of significant importance. We have reported several sensitive ECL biosensors by using different kinds of nanomaterials as either ECL donor or acceptor.

Gold nanomaterials are one of the most common acceptors since they have high quenching efficiency, tunable and stable optical property, ease of labelling, etc. A sensitive ECL-RET based immunosensor for the detection of tumor markers was developed using energy tunable CdSeTe/CdS/ZnS quantum dots (QDs) and gold nanorods as the donor and acceptor respectively.[1] ECL-RET could occur between $Ru(bpy)_3^{2+}$ and gold nanoparticles/graphene oxide (Au NPs/GO) nanocomposites, resulting in an apparent decrease of ECL signal, and an ECL aptasensor was fabricated and used for the sensitive and selective detection of adenosine triphosphate (ATP).[2] Another ECL-RET system was established with eco-friendly silicon quantum dots (SiQDs) as energy donor and AuNPs as energy acceptor, based on which a novel ECL biosensor was fabricated for sensitive detection of DNA.[3]

As well-known ECL emitters, QDs are also potential acceptors since their optical properties can be tailored to meet specific wavelength requirements by simply changing their chemical composition or size. Benefiting from a short interlayer distance and perfect spectral overlap, highly efficient ECL-RET-based energy funneling was observed in the graded-gap QD bilayers, resulting in a surprising ECL enhancement effect.[4] ECL-RET between luminol as a donor and CdSe@ZnS QDs as an acceptor was reported and used to fabricate a label-free ECL aptasensor for the detection of thrombin.[5] In another work, ECL-RET between luminol and CdS QDs/graphene nanocomposites was investigated and used in the sensitive detection of Cytochrome C which exhibited apparent inhibiting effect on the anodic ECL emission.[6] CdSe QDs were also found as an effective acceptor with lucigenin as ECL donor, and the oxidation product of bromide could further promote this kind of ECL-RET and increase the anodic ECL signal significantly, based on which a sensitive ECL sensor for the detection of cytochrome C was established.[7]

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Bright Multicolor Bandgap Fluorescent Carbon Quantum Dots for Electroluminescent Light-Emitting Diodes

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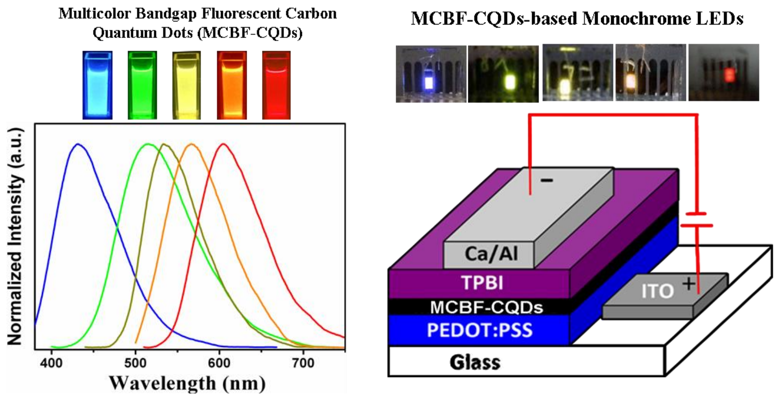
Reported here is the first example of monochrome light-emitting diodes (LEDs) from blue to red that directly use multicolor bandgap fluorescent carbon quantum dots (MCBF-CQDs) as the active emission layer. The MCBF-CQDs were synthesized by a facile solvothermal method and exhibited emission color from blue to red with a quantum yield (QY) up to 75%. Even without using hole transport layer, the maximum luminance (Lmax) of blue LEDs reached about 136 cd/m^2, a record for CQDs-based monochrome electroluminescent LEDs. We further demonstrated the distinctive advantage of such LEDs, the remarkably stable and voltage-independent emission color, which enabled the BF-CQDs great opportunities to achieve high-performance LEDs. Also presented are white LEDs (WLEDs) fabricated by using BF-CQDs blended poly(N-vinyl carbazole) as the emissive layer, which showed a high-performance even comparable to semiconductor QDs-based LEDs.



Bright blue to red fluorescent carbon quantum dots for electroluminescent LED

Acknowledgements

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Electrochemiluminescence Ratiometry for Bioanalysis

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Electrochemiluminescence (ECL) is a luminescence excitation process triggered electrochemically. Combining the advantages of zero optical background and easy reaction control by applying electrode potential, ECL has been proved to be a highly sensitive and enhanced selective method attracted much attention in the areas of biological, environmental and food analysis. Through monitoring the change in ECL intensity, species that directly take part in ECL reaction or indirectly influence the reaction could be quantified. However, other factors such as environmental conditions can interfere with the signal output, especially during trace analysis, which may cause false positive or negative errors.Ratiometric detection is an ideal strategy to limit the interference factors via normalizing environmental variation by self-calibration, which has been widely developed in fluorescence. Inspired by the dual-wavelength ratiometry, one can create ECL ratiometry to make the detection more convincing. The major challenge to carrying out ratiometric ECL measurement is to create ECL report units with two emitting states that have the potential-dependent properties or wavelength-dependent properties upon the substrate concentration. Here, I will report some examples based on ECL ratiometry.

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Electrochemically Sensitized Luminescence from Lanthanides in d–f Heteronuclear Arrays

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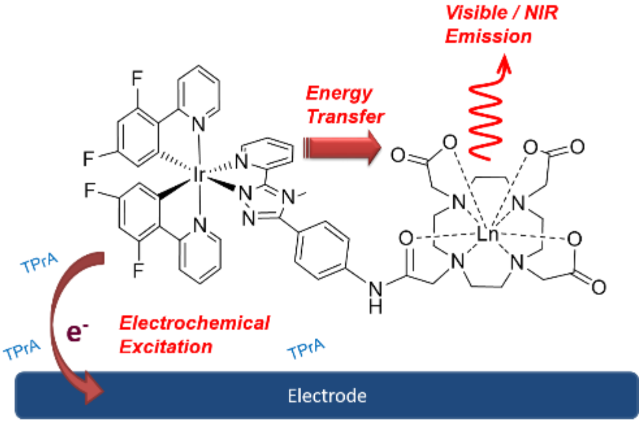

Figure 1 *Electrochemically initiated energy transfer between a cyclometalated iridium complex and a lanthanide ion.*

Electrochemiluminescence (ECL) provides superior sensitivity compared with photoluminescence and facilitates a unique level of control over the luminescent process. For these reasons, it has emerged in recent years as the basis for one of the most important new classes of detection technique in analytical and bioanalytical chemistry. However, progress in this field is hampered by the lack of diversity of ECL-active luminophores, in terms of emission color and other properties. In particular, there is a need for NIR-emitting molecular probes for ECL, which could exploit the transparent NIR window in biological media. As these problems, to a large degree, are related to the difficulty of satisfying electrochemical as well as photophysical requirements in a single emitter, we have sought a new approach where emitters with highly desirable luminescent properties, may be paired with suitable ECL-active sensitizers in a donor-acceptor array.

We report here, a new class of electrochemiluminophore where the emission of a lanthanide ion is sensitized electrochemically rather than optically. A heterobimetallic array is used to facilitate electrochemically initiated lanthanide emission, following energy transfer from an iridium-based electrochemiluminescent (ECL) donor. As this is the first report of such a system, we have coined the term Electrochemically Sensitized Luminescence (ESL) for this process. It is directly analogous to the photosensitization which occurs when a lanthanide ion is excited by a chromophoric antenna. These results open up a myriad of possibilities for new ECL-active species with potentially important bioanalytical application.

Advances in Electrogenerated Chemiluminescence with Iridium(III) Complexes

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Iridium(III) complexes hold great promise for new electrogenerated chemiluminescence (ECL) detection systems,[1,2] as alternatives to the traditional ruthenium(II) bipyridine luminophores. Studies to date of the ECL of iridium complexes, predominantly conducted in organic solvents, have revealed their impressive range of emission colors, excellent luminescence efficiencies, and in some cases, much greater ECL intensities than tris(2,2′-bipyridine)ruthenium(II). However, the translation of these findings into real-world analytical applications has been limited. This presentation describes our explorations of this promising class of ECL luminophore,[3-8] including aspects such as:

(i) Synthesis of highly water soluble iridium(III) complexes (Fig. 1) and their application in ECL.
(ii) A design strategy and conceptual pathway through several barriers that have restricted the application of iridium(III) luminophores as ECL labels in immunoassay and related techniques.
(iii) Multi-color annihilation and co-reactant ECL from mixtures of metal-complex luminophores.
(iv) Potential and spatial resolved multi-color ECL systems.

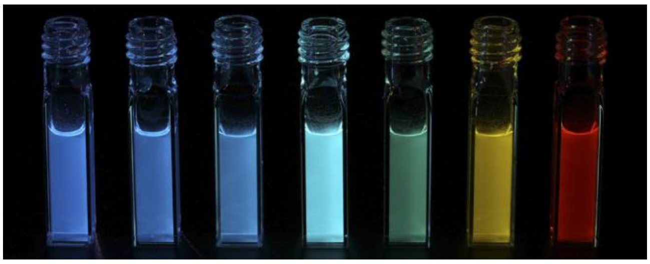

Figure 1. A series of new highly water-soluble iridium(III) complexes

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The First BODIPY-Based Fluorescent Naphthoquinone: Electrochemistry, Cell Studies and Cytotoxicity

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There is a beneficial interface between electrochemistry and life sciences, useful for the design, development and characterization of redox-selective molecules and their molecular mechanism of action [1]. It is wise to continue to investigate the redox activity of bioactive quinones, as well as their use as bioimaging probes. However, fluorescence suppression in quinones'hybrids is a common finding [2]. The strong p-electron acceptor character of the naphthoquinone moiety is able to quench the fluorescence of the hybrid compounds [2]. In this study, a new BODIPY based antitumor naphthoquinone, a fluorescent probe in subcellular localization studies, was synthesized and its electrochemical behavior investigated by cyclic voltammetry (CV). The characterization of the reduction mechanism is fundamental to the understanding of the cytotoxic effects and mechanism of action of this novel hybrid compound. CV experiments were performed in a conventional three- electrode cell. The working electrode was a glassy carbon (GC) BAS (d = 3 mm), the counter electrode was a Pt wire and the reference electrode, an Ag|AgCl, Cl^- (saturated). Compound 1 was composed of two non-conjugated main reducible systems, the *ortho*-dihydrofuran-naphthoquinone (nor-beta-lapachone) and the boron-dipyrromethene, (BODIPY) separated by a methylene spacer. The electrochemical profile of the compound is displayed in figure 1A. The first reduction is represented by two redox systems, the first, well-defined, diffusional and quasi-reversible (Ic/Ia), at potentials of -0.535 V and -0.407 V and the second, ill-defined, better visualized at higher scan rates (1 V s^{-1}) (IIc/IIa). This behavior is representative of the quinone system, where disproportionation occurs, at slow scan rates, leading to the hydroquinone dianion (Fig. 1A and 1C, marked in red). The other reduction wave (IIIc), at -1.901 V (Fig. 1A and 1C, in blue), is related to the reduction of the heterocyclic system and leads to an aromatic ring and a very stabilized radical, which is oxidized at the potential IIIa (-0.009 V), as shown by inversion potentials (Fig.1A). This is a very interesting and complex redox system. The proposed mechanism is proved in figure 1B, through combined CVs of nor-β-lapachone and BODIPY.This molecule constitutes a promising prototype owing to its potential biological activities and imaging capability aimed to performing mechanistic investigations in cells and in vivo, and opens up an interesting avenue of research. Electrochemistry helped to understand the mechanism of biological action. Computational aspects were also explored.

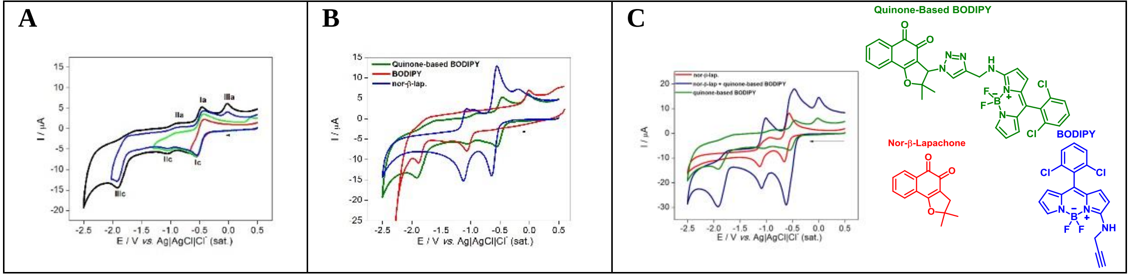

Figure 1. (A) Cyclic voltammetry (CV) of 1 (green) (1 mM), in DMF + $TBAPF_6$ (0.1 M), GCE. (B) Combined CVs of nor-β-lapachone (red), BODIPY (blue) and compound 1 (green). (C) Cyclic voltammetry of the solutions containing all the compounds of interest.

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ECL evaluation of CdTe quantum dots immobilized on screen printed electrodes, characterizations and potential applications

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Electrochemiluminiscence (ECL) has gained interest as a valuable analytical tool in several applications such as chemical sensors and biosensors devices. Comparing with fluorescence techniques, it can be easily miniaturized, portable, and the optical noise can be avoided, making a good candidate as analytical method [1].

There few reports demonstrating the ECL properties of CdTe stabilized with glutathione in literature. As example, Wang *et. al* reported a poor anodic ECL signal of CdTe in solution stabilized with glutathione and proposed that a combination with other less rigid stabilizing agents such as tioglycolic acid. On the other hand, the anodic ECL signal obtained from CdTe quantum dots can be increased, employing indium tin oxide (ITO) electrodes as working electrode[2]. In a similar way, other researchers have employed ITO electrodes in anodic scan because at these potentials the working electrode can be oxidized and be part of the ECL process cooperatively with CdTe quantum dots. Russel at all proposed near infrared quantum dot characterization of co-reactant, and proposed that ECL onset could be a more accurate value for HOMO and LUMO energies [3].

However, it must be denoted at this point, the majority of the literature describes the generation of light from quantum dots for ECL applications by employing photomultiplier as the light detector biased at high potential, requiring high voltage sources, making the equipment difficult for portable applications.This work describes modification of graphite screen printed electrode with APTES electrostatically assembled with CdTe (GSH) quantum dots, in order to study its ECL properties. The corresponding electrode modification steps were characterized by cyclic voltammetry, electrochemical impedance spectroscopy and SEM-EDX.

The electro-chemiluminiscence (ECL) properties in presence of $S_2O_8^{2-}$ and H_2O_2 were evaluated with a commercial portable potentiostast coupled with a photodiode detector. Factors such as scan rate, concentration of co-reactant and pH revealed that the SPE/APTES/CdTe (GSH) system has a more stable ECL signal by employing H_2O_2, between pH 7 and 9.

SPE/APTES/CdTe (GSH) interactions with cationic porphyrins were preliminary studied and demonstrated, in order to evaluate concepts of electrochemical luminescence resonance electron/energy transfer (ECL-RET), observing an increase in the ECL signal. Possible mechanisms for such results are under study, and it can be associated with reactivity of hybrids cationic porphyrins/quantum dots systems for oxygen species[4].

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Fluorescent bioelectrochemistry and hybrid biovoltaics

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Combining bioelectrochemistry with fluorescent microscopy provides a very powerful platform to study of molecular mechanism of redox enzymes. Where electrochemical recordings provide insight into the (electron transfer) kinetics, fluorescent microscopy can supply supplementary information on enzyme conformational states or catalytic processes that are electrochemically silent.

A first example is intramolecular electron transfer of a multicopper nitrite reductase from *Alcaligenes faecalis* S-6, which reduces nitrite to nitric oxide. While electrochemistry informs on the kinetics of the catalytic nitrite reduction as a function of applied potential, fluorescent labelling of the enzyme reports on the steady-state redox states of the two distinct copper sites. The latter is possible because Förster Resonance Energy Transfer (FRET) from the label to one of the copper sites (the 'blue' copper site) is dependent on the redox state of the copper site, thus enabling deconvolution of the interfacial and intramolecular electron transfer steps.[1]

A second example where fluorescence microcopy contributes to bioelectrochemistry is transmembrane proton transport. The heme-copper oxidase from *Escherichia coli*, cytochrome *bo*$_3$, oxidizes a lipid membrane-bound ubiquinol pool concurrent with oxygen reduction and uses the energy generated to transport protons across the lipid membrane. Bioelectrochemical characterization of the cytochrome *bo*$_3$ is possible by electrochemically reducing the ubiquinol pool. By using a pH dependent fluorescent probe, encapsulated in liposomes adsorbed on the electrode surface, both proton transport and ubiquinol oxidation can be monitored.[2]

Finally, fluorescent dyes like $Ru(bpy)_3^{2+}$ can also be used as photosensitizers, creating hybrid biovoltaic systems. Here, the redox proteins will act as an electron conduit, controlling electron transfer between the photosensitizers and underlying anode. A hybrid double layer system was created by forming a densely packed monolayer of the decaheme proteins, MtrC from *Shewanella oneidensis* MR-1, on which TiO_2 particles were adsorbed, dye-sensitized with $Ru(bpy)_3^{2+}$. Using EDTA as a sacrificial electron donor, photocurrents are obtained that are dependent on the redox state of the decaheme protein, confirming that electrons are transferred from the photosensitizer to the anode via the redox protein conduit.[3]

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Facile Tailoring of Chemically Converted Graphenes Using a Water-soluble Pyrene Derivative for Sensitive Electrochemiluminescence-based Analyses

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Here, we report a method to tailor chemically converted graphenes (CCGs) using water-soluble pyrene derivative **1** (3-((pyren-1-yl)methyl)imidazolium-1-propionate) with a zwitterionic arm, which facilitates the integration and functionalization of the CCGs on indium tin oxide (ITO) electrodes for highly sensitive electrochemiluminescence (ECL)-based applications. The compound **1** consisted of a pyrene appended with a 3-(imidazolium)propionate zwitterionic arm, which serves the dual purpose of improving the dispersion of the CCGs in aqueous solutions and further tailoring the catalytic activity of the CCGs with dendrimer-encapsulated catalytic nanoparticles. Specifically, we synthesized the pyrene derivative **1**, and prepared aqueous dispersion of **1**-functionalized CCGs via non-covalent anchoring of the aromatic pyrene moiety of **1** onto the hydrophobic basal planes of the CCGs. The stability of the aqueous dispersion of the **1**-functionalized CCGs was greatly improved due to the hydrophilic zwitterionic arm in **1** anchored onto the CCGs, which thus facilitates the processability for integration of the CCGs onto ITO substrates. In addition, the carboxylic group of the zwitterionic arm in **1** allowed the facile secondary functionalization of the CCGs on the ITOs via the covalent conjugation of amine-terminated dendrimers encapsulating catalytic nanoparticles for highly enhanced ECL emission. As a model system, we conjugated well-defined dendrimer-encapsulated Pt nanoparticles (diameter 1.8 ± 0.2 nm) to the **1**-functionalized CCGs on ITOs. The resulting ITOs exhibited significantly increased ECL emission of the luminol/H_2O_2 ECL system; *i.e.* two orders-of-magnitude enhancement in the ECL compared to that obtained from bare ITOs, which allowed a ~154 times more sensitive ECL-based analysis of cholesterol using the modified ITOs compared with the use of bare ITOs.

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Scanning electrochemical bipolar microscopy (SECBM)

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The combination of scanning electrochemical microscopy (SECM) with bipolar electrochemistry (BPE) is introduced as a new approach to image heterogeneous electrochemical surface processes. The core of the system is a closed bipolar electrochemistry configuration with the bipolar electrode (BE) consisting of a microelectrode as SECM tip (cathodic pole of the BE) connected with a microelectrode tip (anodic pole of the BE) in the second half cell. Reduction and oxidation reactions at the respective BE pole are enabled by a sufficient voltage difference between two feeder electrodes. As the SECM tip is scanned above the sample surface in known distance collecting locally released redox active compounds (sample generation/tip collection mode), the reduction processes are transduced into an optical read-out reaction at the opposite anodic BE pole. Here, $[Ru(bpy)_3]^{2+}$-based electrochemiluminescence, that is detected with a highly sensitive CCD camera, serves as a direct measure of the bipolar current. Analyzing the changes in ECL intensity depending on the analyte concentrations at different positions, ECL-based maps of the locally confined release of electrochemically active molecules, e.g. $[Ru(NH_3)_6]^{3+}$ (Figure 1), are obtained.

Evidently, this configuration can be extended to multi-barrel SECM tips thus being able to simultaneously visualize the release of compounds at multiple locations while positioning the multi-barrel microelectrode above a release site of interest. First results using a heptode as scanned SECM tip are presented.

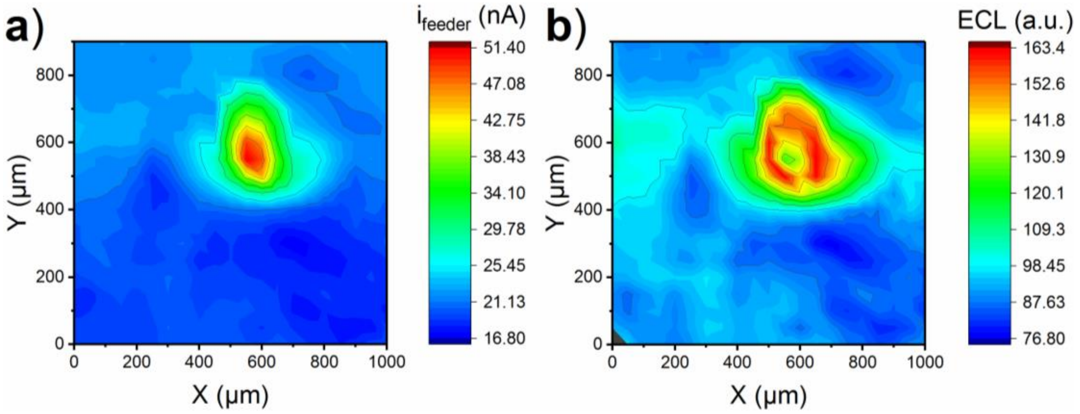

Figure 1 – a) Feeder current and b) ECL map obtained with scanning electrochemical bipolar microscopy and showing the localized release of a redox species (d_{tip} = 50 µm).

From Light-Emitting Bioswimmers to 3D Electrogenerated Chemiluminescence

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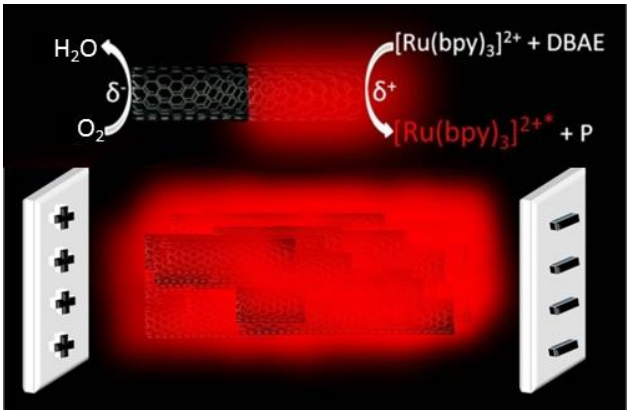
Electrogenerated chemiluminescence (ECL) is the phenomenon of light emission by the excited state of a luminophore produced upon an initial electrochemical activation.[1] The discovery of ECL emission in aqueous media has led to major applications, especially for sensitive immunoassays commercialized for clinical diagnostics.[2] However, ECL emission is only generated at the electrode surface. As a consequence, ECL is by nature a 2D process, which is strictly confined to the surface of the electrode. This appears so far as an intrinsic limitation compared, for example, to chemiluminescence where reagents are mixed and react homogeneously to generate light in the bulk.



Principle of bulk ECL produced by a suspension of CNTs.

Bipolar electrochemistry (BPE) is a powerful wireless method which promotes electrochemical reactions at the extremities of conductive objects placed in solution when applying an electric field. It is an important method for a wide variety of applications.[3] We exploited recently the versatility of BPE and its wireless characteristics to develop ECL-emitting bioelectrochemical swimmers.[4] Indeed, BPE induces simultaneously the production of gas bubbles for propelling the swimmers and enzymatic formation of the activated ECL reagents, which generate light only in the presence of substrate. Due to the wireless capabilities of BPE, we extended this idea from a single to thousands of conductive objects that were simultaneously addressed.[5] Thus we demonstrated the efficient generation of bulk ECL (*i.e.* 3D ECL) at the level of a dispersion of conductive micro- or nano-objects in a capillary.[5] Indeed, each microbead or multi-walled carbon nanotube (MWCNT) is polarized by the electric field and ECL emission is therefore triggered in a wireless manner simultaneously on all objects to generate one or even two different colors.[6] We show here how this process can be applied to multiplexed enzymatic 3D ECL detection.[6]

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Photoinduced Charge Transfer in Quantum Dot Assemblies

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We are exploring nanoparticle-based materials for solar to electrical energy transduction. Nanoparticle devices promise to provide a systematic and modular approach to creating supramolecular assemblies of linked nanoparticles that function as charge transfer elements. I will report on recent work in which we explore how to engineer nanoparticle/nanoparticle interfaces and nanoparticle/conjugated polymer interfaces to enhance charge separation and inhibit charge recombination. Particular foci of our effort are aimed at understanding the importance of energy-level gradients, built-in electrostatic potentials, and symmetry/chirality properties to improve the charge-separation efficiency in inorganic-organic device structures.

Electrochemiluminescence meets nanotechnology, theory and practice of the silica nanoparticles approach

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Electrochemiluminescence (ECL) is a leading technique in bioanalysis.[1] Since the excited species are produced with an electrochemical stimulus rather than with a light excitation source, ECL displays improved signal-to-noise ratio compared to photoluminescence, with minimized effects due to light scattering and luminescence background.[2]

In the quest for ever-increasing sensitivities, ECL can ideally be coupled to nanotechnology and supramolecular chemistry to develop new systems and strategies for analyte determination also in very complex matrices. For instance, we have recently shown a supramolecular approach to detect sarcosine, a potential prostate cancer biomarker, in urines, with good sensitivity and very high selectivity.[3] Dye-doped silica nanoparticles (DDSNs), semiconductor nanocrystals, or polymer dots were also advantageously used as ECL-active systems.[4,5] In particular, DDSNs present many advantages: they can be obtained with accessible synthetic schemes, are intrinsically hydrophilic, and, thanks to silica chemistry, are prone to bioconjugation. Very bright systems can be obtained with this approach since silica is inert from the photophysical point of view, and DDSNs assume the photophysical properties of the dye(s) molecules accumulated within the nanoparticle.[5] In DDSNs, light emission is influenced by the combination of several factors that make DDSNs complex multichromophoric structures, such as the coexistence of dye populations experimenting with slightly different environments and the occurrence of intraparticle energy transfer processes (mainly resonance energy transfer or quenching). When ECL comes into play, the scenario is even more complicated by the presence of the coreactant−NP interactions, since the coreactant needs to approach the NP surface and to react with the dyes buried within the silica at different extent. A scenario of such a complexity was then approached at the theoretical level by developing suitable mechanistic models for ECL generation[6] while, at the same time, the influence of doping level and particle charging on ECL efficiency was evaluated. The results showed that the ECL intensity of a nanosized system cannot be merely incremented acting on doping, since other parameters come into play. These studies provide valuable indications for the design of more efficient ECL nano- and microsized labels for ultrasensitive bioanalysis.

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Conductivity Sensing Based on the Bipolar Electrode

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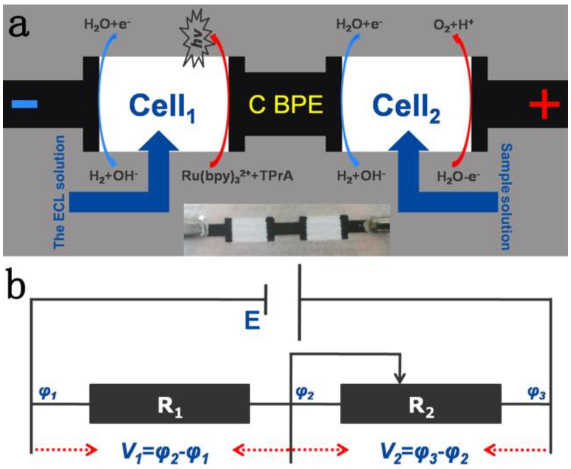
The bipolar electrodes (BPEs) have been widely adopted in transforming the chemical (electrical) signal to optical signal, and thus lead to the emerging of the bipolar analytical chemistry. Due to the quantitative relation between the reactions occurring at both poles of the BPE, the electroactive targets which can be reacted at the two poles can be determined with different optical signals, such as using the electrochemiluminescence (ECL) of $Ru(Bpy)_3^{2+}$ for the determination of oxidant, reductant and ECL probe with the different design of bipolar system[1-4]. However, there are still a number of chemicals, which do influence the electrical signal (to be clear, the conductivity), cannot be detected with this powerful tool.

To resolve it, a new sensing mechanism of the BPE was constructed, with which the conductivity of the solutions can be measured using a closed bipolar system [5]. Thus, chemicals, which are not electroactive materials and do not participate in the ECL process, now can be detected (Scheme 1a) with a BPE, which greatly expands the application range of the BPE and the powerful ECL technique. The sensing principle was based on the influence of potential drop on the reporting channel. As shown in Scheme 1a, with the increase of the conductivity of the supporting channel, the potential drop in the reporting cell will increase and enhanced ECL will be observed.



Scheme 1 (a) Structure and operating principle of the paper-based bipolar conductivity sensing platform; (b) The resistance model of our design.

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Long Range Organization in Room Temperature Ionic Liquids

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We report on the existence of charge-induced long range order (~0.1 mm) in the room temperature ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF_4^-$), supported on a silica surface. The manifestation of this long range order is seen in the rotational diffusion dynamics of a series of charged and neutral oxazine-derivative chromophores that vary with distance from a silica surface. The depth-dependent rotational diffusion behavior is not seen if the IL is replaced with ethylene glycol, nor is it seen if the silica surface is capped with dimethyl dichlorosilane. The data sense the free charge density gradient induced in the IL by the charge present on the silica surface. We understand the functional form and spatial extent of our results based on the IL exhibiting a piezoelectric response with a spatial extent determined by IL fluidity and disorder.

Fine-Tuning of Electrochemiluminescence and Photoluminescence in Bifunctional Organic Dyes

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Organic molecules have been designed and synthesized for ECL purposes,[1] but few systematic studies focused on substituent effects on the ECL emission energy and efficiency.[2] Fluorene- and spirobifluorene-based molecules have been recently considered, including by us,[3] as suitable candidates for electrogenerated chemiluminescence (ECL). Here we describe the ECL properties of a series of compounds formed of two triphenylamines linked by a fluorene or spirobifluorene bridge.[4] The phenylamine moieties were chemically modified at the *para* position by electron-withdrawing or electron-donating substituents. This allowed fine-tuning of the photoluminescence (PL) and ECL emission from blue to green. The ECL spectra show one single band that almost matches the PL band. The ECL process, which was investigated by direct annihilation of the electrogenerated radical anion and radical cation, is easily observable even by naked eye, with quantum yield higher than the standard 9,10-diphenylanthracene. This study shows that effective fine-tuning of the PL and ECL behavior is made possible by chemically assembling luminophore systems that display bifunctional redox features, *i.e.*, systems in which the electroreducible and electrooxidizable moieties are, to a large extent, decoupled.

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White Electrochemiluminescence from a Single Pt Complex

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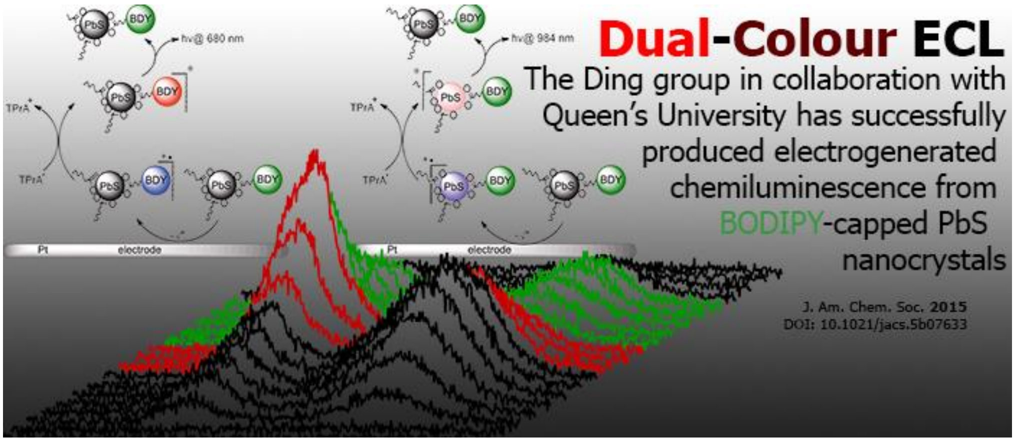
Our research lab at The University of Western Ontario focuses on 4 research themes: scanning electrochemical microscopy of live cells and corrosion processes, ionic liquids as novel electrolytes, electrochemiluminescence or electrogenerated chemiluminescence (ECL) and solar cells. Herein, we demonstrate our progresses on white electrochemiluminescence from a specially designed single Pt complex.

For the first time, we report highly efficient white ECL of a single Pt complex in the presence of persulfate as an oxidative coreactant. Spooling ECL spectroscopy of the complex along with the ECL-voltage curve was used in elucidating the ECL mechanisms. For instance, the strong dual ECL emission peaks of 480 nm and 630 nm (very broad) were attributed to the monomer excited state and excimer, respectively and found to be simultaneous and adjustable with the applied potential during the light evolution and devolution. The ECL of the Pt complex was enhanced maybe due to the collisions with the electrode, and reached an efficiency of 400% relative to that of $Ru(bpy)_3^{2+}$, which is the highest among the Pt complexes.



Selective Electrochemical Bleaching of the Outer Leaflet of Fluorescently labeled Giant Liposomes

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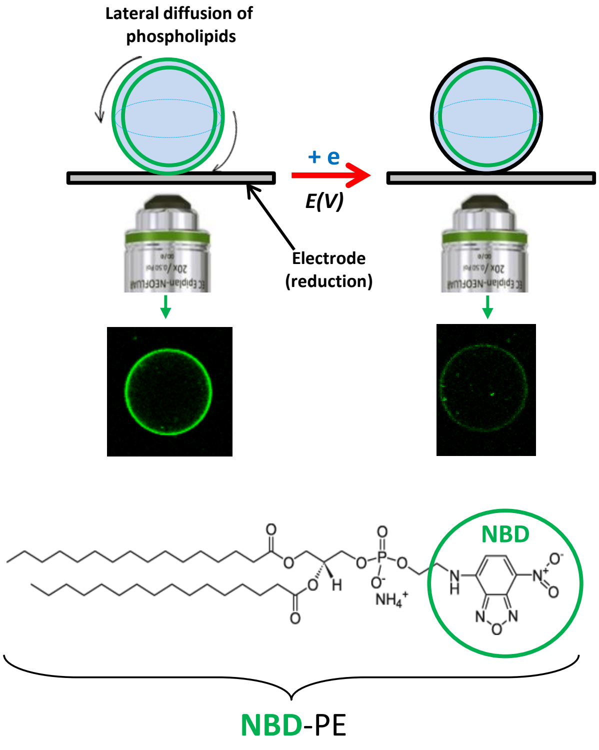
Measuring the dynamic properties of lipid membranes has been previously achieved using a variety of fluorescence-based techniques [1]. Among these techniques is Fluorescence Loss In Photobleaching (FLIP), in which the fluorescence intensity in one region is monitored during the continuous bleaching of another region in the sample. Although photobleaching has been effectively used in biological samples, the high laser intensity needed for bleaching may affect cellular processes. On the other hand, limitations in optics prevent researchers from discriminating between the two leaflets of a bilayer, which are asymmetric in biological samples, and therefore may exhibit different dynamic properties.

In the present work, electrochemistry and confocal fluorescence microscopy were successfully combined to bleach and monitor the fluorescence emitted by NBD-labelled phospholipids diffusing in giant unilamellar liposomes (between 10 and 50 µm in diameter) deposited on a transparent ITO/Au conductive surface [2]. Importantly, electrochemistry could selectively bleach the fluorescence emitted only by NBD fluorophores localized on the outer leaflet of giant liposomes, through the electrochemical reduction of the NBD nitro group (see Scheme).

Compared to photobleaching techniques, the electrochemical bleaching does not affect the fluorescent probes localized on the inner leaflet of giant vesicles thus allowing discrimination between both sides of lipid bilayers. This electrochemical process also discards the use of any chemical reducing/oxidizing agents that may undergo slow internalization within vesicles. Our technique which can be called fluorescence loss in electrochemical bleaching (FLIE) was used to calculate the lateral diffusion coefficient of NBD-PE (4 µm^2/s), which is in agreement with other techniques. This versatile and selective bleaching procedure might make it an invaluable tool in cellular biology and biophysics.



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Electrochemical Modulation of the Fluorescence of Tetrazine grafted monolayers on Au/ITO electrodes

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Tetrazine (Tz) is a molecule whose fluorescence can be controlled via its redox state, a property called electrofluorochromism: in its oxidized state, Tz emits in the yellow range while in its reduced state it does not emit. This is thus a promising material for smart displays based on the emission of light as demonstrated by Audebert et al. [1]. The electrofluorochromic behavior of this molecule in solution was investigated thoroughly [2]. In this study, the possibility for electrochemically controlling the fluorescence of Tz in monolayer amount close to an electrode surface was explored, opening the way to exciting surface-electroflurochromic devices.

Au nanodots were electrodeposited on ITO and the deposition conditions were optimized to obtain Au nano-objects of diameter ~ 50 nm (Fig. 1). Tz derivatized molecules were then grafted either on Au or on ITO via specific anchoring moieties. Electrochemical characterizations (cyclic voltammetry) confirmed the presence of Tz in monolayer amount on each type of surface. The fluorescence of the Tz was then monitored with an epifluorescence microscope coupled to an electrochemical cell. No fluorescence signal was recorded for Tz grafted on Au suggesting an efficient quenching between the excited Tz and the Au islands. For Tz grafted on ITO, a significantly larger fluorescence signal was measured. Moreover the fluorescence of the grafted Tz on ITO could be switched on and off by changing the potential of the electrode (Fig. 2). A clear correlation between the potential of the electrode and the fluorescence response of the Tz was observed, demonstrating the possibility to control electrochemically the fluorescence of molecules near the electrode surface in monolayer amount.

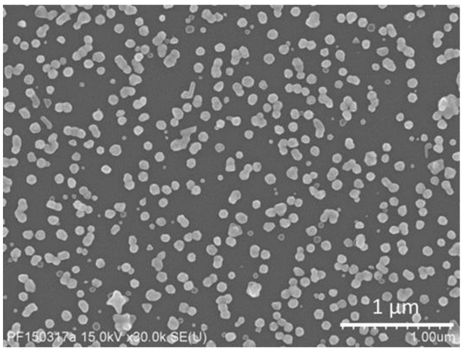

Figure 1. MEB image of an Au/ITO electrode.

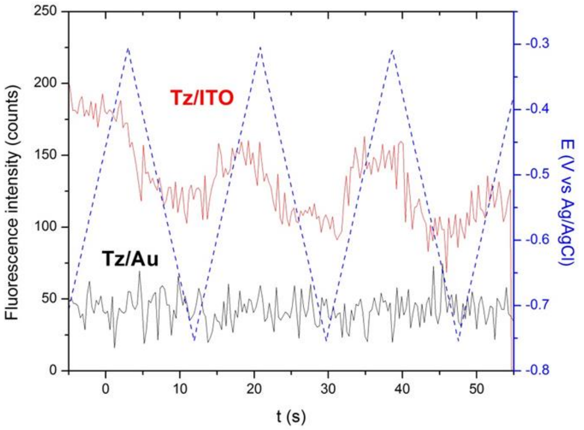

Figure 2. Fluorescence intensity modulation during cycling of the electrode potential for Tz grafted on Au (-) and on ITO (-).

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Highly Electrochemiluminescent Graphene Bilayer Hybrids for 2,4,6-Trinitrotoluene Sensing

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Graphene-based hybrids are of special importance because the multifunctional composites may combine the unique properties of graphene nanomaterials with new properties and functions of other components. They have been proved to be satisfied tunable platforms for sensors because of its good dispersion in water and versatile surface functionalization.[1-2] Herein, novel N-(4-aminobutyl)-N-ethylisoluminol/hemin dual-functionalized graphene hybrids (A-H-GNs)[3] and luminol functionalized silver/graphene oxide composite (luminol-AgNPs-GO)[4] were synthesized and characterized. Their electrochemiluminescence (ECL) behaviors were investigated under cyclic voltammetry and pulse potential. It was found that A-H-GNs and luminol-AgNPs-GO exhibited excellent ECL property.[5] Moreover, highly electrochemiluminescent graphene bilayer hybrids consisting of A-H-GNs and luminol-AgNPs-GO with excellent ECL activity was fabricated for a label-free ECL 2,4,6-trinitrotoluene (TNT) aptasensor. In the presence of TNT, a remarkable decrease in ECL signals was observed. Accordingly, TNT could be detected in the range of 1.0×10^{-12} - 1.0×10^{-9} g/mL with a low detection limit of 6.3×10^{-13} g/mL, which is superior to most previously reported bioassays for TNT. Due to the wide target recognition range of aptamer, this strategy provides a promising way to develop new aptasensor for other analytes.

Acknowledgment

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Marangoni Shutters and Electrovariable Nanoplasmonics

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Control over physical properties of nanoparticle assemblies at a liquid-liquid interface is a key technological advancement to realize a dream about smart electrovariable nanosystems. Electrified interfaces, such as the interface between two immiscible electrolytes solutions (ITIES), are almost an ideal platform to realize this dream.

Previously, the research in the field was focused on "vertical" landing of nanoparticles, driven by an external electric field, from the bulk to ITIES to form mirror-type films.[1,2] However, this approach has the major restriction limiting practical applications: slow diffusion of the nanoparticles from the bulk to the interface. In contrast, the interlayer Marangoni effect has been used to power movements of capsules at a liquid-liquid interface (LLI).[3] By definition, the Marangoni effect is the mass transfer along an interface between two fluids – liquid-liquid or liquid-gas – due to changes in interfacial surface tension. In a classical theory developed by V. G. Levich [4] the concept of capillary motion was derived in the presence of a surface tension imbalance on the free surface of a liquid-liquid interface.

We used Marangoni effect to induce migration of citrate covered gold nanoparticles located close to the ITIES from the middle region of the cell to its periphery with polarizing of the ITIES.[5] Thus, we called such systems "*Marangoni-type shutters*". The necessary difference in surface tension was achieved by using SDS as a surfactant and electric field across the interface. In this work we showed that moving of nanoparticles in-plane of the interface can be performed repeatedly (up to 20 cycles) with significant change of the reflectivity (Fig. 1).

This type of electrovariable plasmonics do not have diffusion limitation in comparison with adsorption/desorption of nanoparticles and the entire movement of nanoparticles assemblies happened almost instantly (within a second). This approach opens a fresh view on electrovariable plasmonics and proposes new opportunities to create smart nanosystems at ITIES driven with electric field.

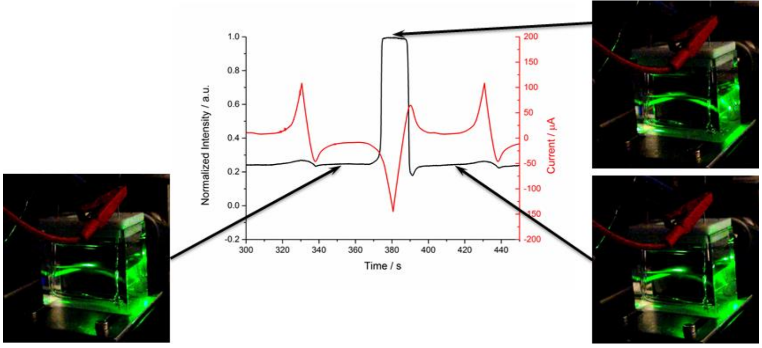

Fig. 1. Marangoni-type shutter in action. A part of cyclic voltammogram with corresponding snapshots taken from the recorded video.

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Amorphous vs crystalline “redox” catalysts for the oxygen evolution reaction – A mechanistic study

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For a long time, the metallic center was believed to be the active site for the oxygen evolution reaction to proceed on the surface of transition metal oxides, following a mechanism derived from the oxygen reduction reaction mechanism decipher for metallic surface. Hence, the reaction was assumed to proceed following four proton-coupled electron transfer (PCET) steps on a single metallic site and oxygen recombination was excluded due to its large activation barrier on metal surfaces with low oxygen coverage. Within this framework, the OER activity is governed by the enthalpy of formation of intermediates (OOH*, O* and OH*). Nevertheless, recent findings on perovskite materials corroborate early work made on binary oxides and demonstrate that surface oxygen can be the active site for the OER to proceed, and can eventually participate to the mechanism.[1,2] Furthermore, triggering the participation of the lattice oxygen to the reaction induces a strong pH dependence for the OER activity that deviates from the classical four PCET steps. Moreover, this mechanism doesn’t apply to the wildly studied amorphous oxy-hydroxides catalysts which can be seen as “redox” catalysts storing charge through their oxidation/deprotonation. Hence, OER catalysts can now be sorted in three main families: 1) the crystalline and dense TMOs for which the OER activity follows the classical 4 PCET steps, ii) the crystalline TMOs for which the surface participate to the OER reaction through the oxidation of oxygen sites, and iii) the amorphous and electrodeposited hydrous films which are porous to the electrolyte and for which active oxygen sites are formed through the oxidation and deprotonation of the film.

In this presentation, we will focus on the different mechanisms pinpointed for these three classes of materials. Through examples, we will emphasize the importance of the surface protonation state that differs between these different electrocatalysts. Eventually, we will discuss the difference in terms of kinetics expected for these different catalysts and discuss the inherent limitations related to each mechanism.

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Structure and Reactivity of Metal-Oxide-Supported Noble Metal Nanoparticles: Electrooxidation of Simple Organic Molecules

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There has been growing interest in utilizing small (simple) organic molecules, as alternative fuels to hydrogen, in electrochemical energy conversion systems. In addition to ethanol (biofuel), that can be ideally oxidized to carbon dioxide thus delivering twelve electrons, recent important systems include dimethyl ether as well. But realistically the respective reaction is rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials.

Platinum has been recognized as the most active catalytic metal towards oxidation of ethanol at low and moderate temperatures. But Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals including ruthenium, tin, molybdenum, tungsten or rhodium are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin monolayer-type films of metal oxo species of tungsten, titanium or zirconium.

We pursue a concept of utilization of mixed metal (e.g. zirconium/tungsten or titanium/tungsten) oxide matrices for supporting and activating noble metal nanoparticles (e.g. PtRu) during electrooxidation of methanol and ethanol. Among important issues is incorporation of Rh nanostructures capable of weakening, or even breaking, the C-C bond in the ethanol molecules. On the other hand, rhodium itself is not directly electrocatalytic toward oxidation of ethanol. The oxides and noble metal nanoparticles have been deposited in a controlled manner using the layer-by-layer method. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account possibility of specific interactions of noble metals with transition metal oxide species as well as existence of active hydroxyl groups in the vicinity of catalytic noble metal sites. In addition, formation of “nanoreactors” where ethanol is partitioned (at Rh) to methanolic residues further oxidized at PtRu cannot be excluded.

Structural effects on the activity, selectivity, and stability of PtSn alcohol oxidation electrocatalysts

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PtSn bimetallic electrocatalysts have been identified as amongst the most active for the oxidation of short chain alcohols as anode electrode materials in direct alcohol fuel cells. For alcohols beyond methanol, cleavage of C-C bonds is required to achieve full oxidation and conversion of the fuel to CO_2. Whilst there is general agreement regarding the effects of Sn on the promotion of oxidation of CO as an adsorbed intermediate via activation of water at lower overpotentials, its effect on selectivity and overall activity are not fully understood. The addition of Sn to Pt changes both the metal-metal bond distance (lattice constant) and the d-band centre (an electronic effect) of the Pt atoms, both of which are influenced by the details of the structure of the PtSn nanoparticles including; alloy composition, extent of alloy formation, presence of unalloyed SnO_2, and surface segregation of a component to form a core-shell structure. We have prepared a range of carbon supported PtSn catalysts and carefully characterised their structures both ex situ (TEM, XRD, XPS, and EXAFS) and in situ (EXAFS) and measured their alcohol oxidation activity (thin film RDE) and selectivity (in situ FTIR) to understand the relative contributions of structural and electronic effects on the overall activity (non-selective oxidation) and selectivity (full oxidation to CO_2) for a range of alcohols (methanol, ethanol, and butanol). Stability of the catalyst nanoparticle structure is of an equal concern for the application of such materials in fuel cells. Thus, we have also subjected the materials to accelerated aging cycles to determine the stability of the structures (in situ EXAFS) and their activities.

Using Potential to Control ~~Thiol-~~ ~~Post-assembly~~the Exchange of Mercaptohexanol Monolayers with ~~Thiolate~~ Thiol-modified ~~-modified~~ DNA

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The structural investigation of ~~T~~thiol-based~~late~~ ~~based s~~self-assembled monolayers (SAMs) ~~manufactured~~ on gold ha~~ve~~s been a research focus for ~~its~~their applications in modifying metal/electrolyte interfacial properties. [1] ~~. [1]~~ To control ~~self-assembled~~ monolayer formation in a tailorable, reproducible way and without significant defects, application of potential during the assembly process ~~of these monolayers~~ has been previously investigated. [2] ~~.~~ Since controlling self-assembly o~~n~~f DNA SAMs on gold is useful for biosensor applications, using potential to control the formation of DNA monolayers is a strategy that would allow for easy variation ~~modification~~ of DNA coverage and for high structural uniformity. ~~reduce defects in the DNA monolayer.~~ [3] ~~To understand a new method which utilises potential control and promotes uniform DNA coverage, a~~For this ~~purspose~~purpose, we have recently developed a two-step process ~~was developed~~, which ~~. This method~~ involves forming a mercaptohexanol (MCH) ~~monolayer~~ SAM on monocrystalline gold and then partially substituting it with fluorescently labelled thiol-modified DNA while applying a potential to the gold surface. ~~A comparison was done between~~~~Particularly w~~We have compared ~~the~~ DNA ~~substitution~~ exchange ~~with~~ using an applied potential (0.4V/SCE) ~~and~~ with DNA exchange ~~that~~ at open circuit potential (OCP) using in-situ spectroelectrochemical fluorescence microscopy ~~imaging~~. This technique images ~~measures~~ the extent of DNA ~~substitution~~ exchange across the gold surface based on fluorescence intensity and its dependence on the surface crystallography. [4] ~~Initial~~ Our results show that applying 0.4 V (vs~~/~~ SCE) to the MCH ~~layer~~ SAM was found to have higher ~~more~~ DNA coverage ~~substitution~~ relative to ~~layers~~that ~~made~~performed at OCP (Figure 1~~Figure 1Figure 1~~). More specifically, low index planes (111,100 & 110) ~~saw~~ observes increased ~~in~~ DNA ~~substitution~~ exchange with applied potential while potential had little effect on higher index planes (311, 210). The resulting DNA ~~SAMs~~monolayers ~~layers~~ from applying more positive or negative potentials ~~as well as negative potentials~~ will also be explored subsequently. Further studies ~~understanding~~ will be ~~provided~~carried out on how potential affects the kinetics of ~~this~~ DNA ~~substitution process~~ exchange and the ~~crystallographic surface preferences~~preference for particular surface crystallography.

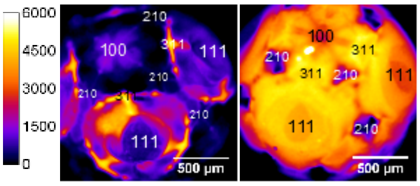

Figure 1 A layer made by ~~substituting~~ exchanging MCH with fluorescently -labelled thiol-modified DNA at OCP (Left) and while applying 0.4 V/SCE (Right)

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Chemical recognition of deprotonated states on the surface of oxygen evolution reaction electrocatalysts

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Water splitting has been envisioned as a promising way to produce clean and renewable hydrogen for energy storage.[1] However, this process is largely hampered by the slow kinetics associated with the oxygen evolution reaction (OER) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. Therefore, numerous researches has been carried out to further push forward the understanding of such complex reaction. Despite many efforts, one major piece of information is still missing, i.e. the proton diffusion and exchange at the interface between the catalyst and the electrolyte during the OER. Owning to the transient feature of the deprotonated oxygen sites, the understanding of how the deprotonation state influences the OER activity is still not clear.

In this work, we tackled this difficulty by proposing the use of a chemical probe that can selectively interact with deprotonated oxygen and allow for the careful analysis of their role in the OER mechanism. By introducing the hydrophobic TMA^+ cations into the system, which 1) specifically interact with deprotonated oxygen and 2) modify the hydrogen bonds network in the double layer region, we demonstrated that the large OER activity observed for iron-containing Ni oxyhydroxides films known for their large OER activity is strongly correlated with the proton diffusion properties at the film/electrolyte interface. We further demonstrate that the use of such hydrophobic TMA^+ cations can selectively modify the reaction mechanism by disturbing the hydrogen bonds network. We also evidence the influence that cations in solution can have on the Lewis basicity of hydroxyl groups. Based on these measurements, we therefore propose that the deprotonation of oxygen sites are critical for the OER reaction to proceed through a two sites mechanisms, which appear to have faster kinetics than the classical "single site" mechanism.

The impact of using chemical probes to capture transient intermediates as demonstrated on the OER catalysts should also be applicable and beneficial for studying other reactions of great importance, such as CO_2 reduction and alcohol oxidation. Moreover, tuning the double layer structure via cation interaction on catalyst interface could be a promising strategy to tune the reaction selectivity.

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Cytosine Adsorption on Gold electrodes as a Function of pH. An in situ Surface-Enhanced Infrared Absorption Spectrocopy and Electrochemistry Study

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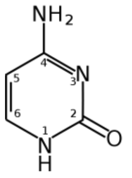
DNA bases are biological relevant molecules playing significant roles in nature, particularly in genetic expression and replication but also in some physiological functions. In this respect, the influence of pH is of particular interest because the bases have different acid-base and tautomeric equilibriums strongly depending on the pH value of the electrolyte. The different acid-base forms and tautomers can conditioned the functions of DNA bases in nature. On the other hand, the studies about adsorption of DNA bases on metal electrodes have, in addition, implications in biotechnological applications. Therefore, this group have been studying the adsorption of the complementary DNA bases adenine and thymine by modern in-situ FTIR techniques that have provided detail information about their different acid-base and tautomeric forms.[1–3] In this communication the study is extended to cytosine adsorption on gold electrodes.

In aqueous solution, cytosine has two acid-base equilibriums with pK_a values of 4.5 and 12.2. At pH values below the first pKa the N3 nitrogen atom is protonated and at pH values higher than the second pKa value the N1 atom can get deprotonated. On the other hand, the theoretical stability of the different tautomeric forms (at least 5 tautomers can be identified) has been study by DFT calculations.[4]



Cytosine

Cytosine adsorption on gold electrodes has been studied by electrochemical STM on Au(111) surfaces[5] and by in-situ FT-IR spectroscopy in acid and neutral media on gold film electrodes[6], and deprotonation of the cationic form was proposed at pH values bellow the first pKa value. In this communication, the adsorption of cytosine on gold thin-film electrodes is studied in a wide pH range (from pH 1 to 11.6) by ATR-SEIRAS. The experimental results are compared with theoretical DFT spectra obtained for adsorbed cytosine on a 19 Au atoms cluster. The experimental spectra obtained at different pH are analysed as a function of the electrode potential.

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New Mechanistic Insights into Solution CO Electro-oxidation on Au Surface in Acidic vs Alkaline Electrolyte by Surface-Enhanced IR Spectroscopy

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The very reason that gold (Au) finds wide spread uses in high-end jewelry and monetary value keeping is its chemical inertness. Therefore, it is a fascinating observation that Au (bulk) electrode can have higher catalytic activity than Pt, the king of the catalytic elements, in terms of electro-oxidation of solution CO, particularly in alkaline electrolyte. In this presentation, we will compare *in situ* surface enhanced IR spectroscopic results obtained during solution CO electro-oxidation in acidic and alkaline electrolyte and discuss our assigning the "weakly-bound" CO as the determinant reaction intermediate responsible for the unusually high solution CO oxidation activity on Au. More specifically, we identified that, in the acidic CO-saturated supporting electrolyte[1], the weakly bound CO interacted mainly with the strongly adsorbed CO on the step-like sites and likely formed a dipolar-coupled weak interacting pair with the latter, as shown schematically in Figure 1. Experimental evidence suggests that this weakly bound CO was the active reaction intermediate and largely responsible for the high COR activity frequently observed on Au electrodes in acidic electrolyte.

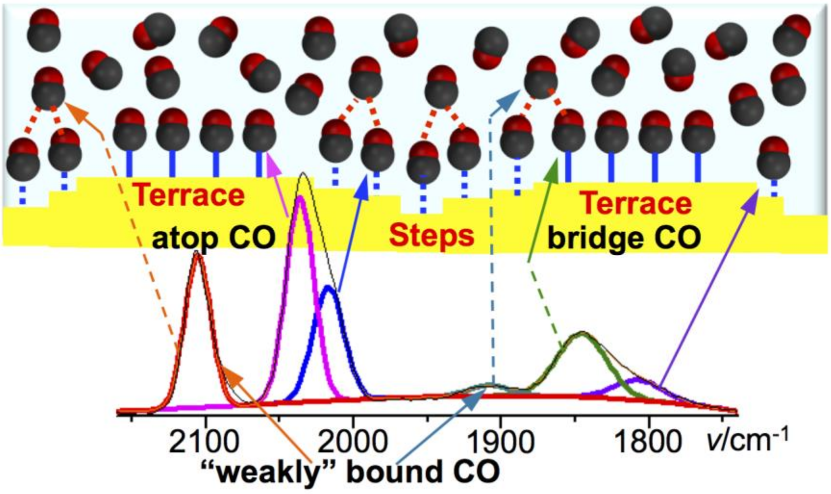

Figure 1. Schematic illustration of the assignments of different types of CO on the Au surface during solution CO electro-oxidation in an acidic electrolyte.

In alkaline electrolyte, we were also able to observe the vibrational band of the weakly adsorbed CO and identify it as the active reaction intermediate for electro-oxidation of solution CO as well. Moreover, using isotope labeling, we were able to confirm spectroscopically the previously proposed CO adsorption-promoted-OH-adsorption hypothesis and proposed a reaction mechanism accordingly that consists of (1) CO-adsorption-promoted OH adsorption, (2) formation of weakly-bound CO from solution CO, and (3) the oxidation of the weakly bound CO by a surface-anchored weakly-hydrogen-bound species. We believe that the synergistic actions of these elemental chemical processes are the reasons for the observed unusual high activity of electro-oxidation of solution CO in an alkaline solution.

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Utilizing Double Layer Capacitance as a General Benchmarking Probe of Electroactive Surface Area

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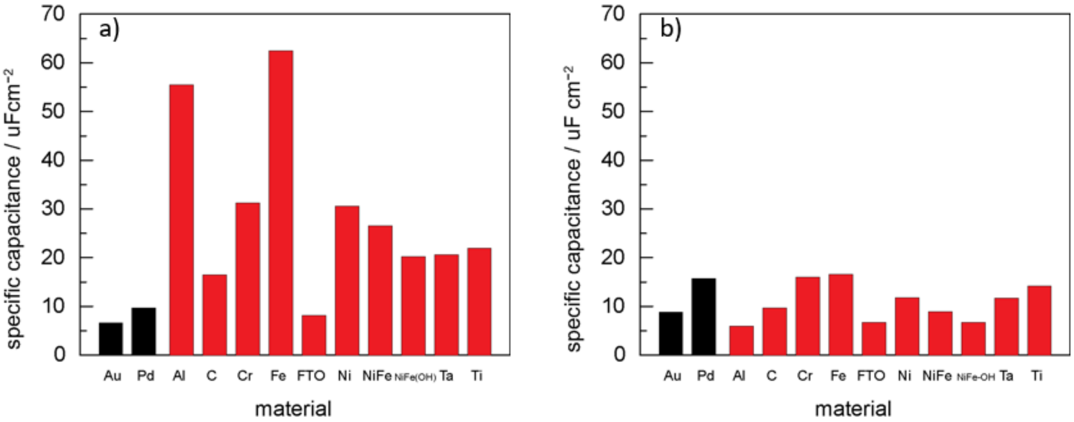

Figure 1. Comparison of specific capacitance of a variety of metals and surface oxidic metals in a) water with 0.15 M NaClO4 and in an organic solvent / electrolyte medium of equal ionic strength. Optimizing the solvent and electrolyte media to have minimal specific adsorption leads to a general value of 11 uF/cm^2 specific capacitance across a wide range of materials allowing for a facile, general, and empirical approximation of surface area for electrode materials.

Electrochemical methods are widely utilized for catalysis, sensing, and charge storage. However, surface area characterization techniques for complex, nanostructured electrodes have largely been overlooked or limited to materials that are amenable to gas phase adsorption techniques, to destructive and limited surface redox processes, and to materials capable of double layer capacitance (DLC) measurements. As such, the appropriate benchmarking, screening, and characterization of materials have been difficult. Herein, we demonstrate that by choosing the appropriate solvent and electrolyte to minimize strong surface adsorption, it is possible to utilize DLC measurements to approximate the surface area of a wide range of metals and surface oxidic metals by mitigating the convolution from so-called pseudocapacitance and sluggish ion rearrangement. In particular, we find that simple DLC measurements at the open circuit potential with a particular solvent / electrolyte mixture empirically produces a specific capacitance value of 11 uF/cm^2 across a wide range of materials.

Role of electrode/electrolyte interface on charged Li-ion cell electrochemical behavior at high temperature

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The improvement of performances, life time and safety of lithium-ion cells is conditioned by the understanding of internal failure mechanisms. Considering all the studies which have combined electrochemical characterization and post-mortem analyses, the internal failure mechanisms concern mainly irreversible lithium ion consumption at the electrode interface with electrolyte due to lithium-plating phenomenon and growth of SEI (*Solid Electrolyte Interface*).

In this work, a combination of electrochemical and spectroscopic analyses has been performed on electrodes, separator and electrolyte from conventional Li-ion cells with ante and post-mortem characterization. It is focused on interfacial reactions at high state of charge and high temperature. The reaction at electrode/electrolyte interface upon storage in such operating conditions is demonstrated. Reaction occurs at electrode/electrolyte interface leading to solid matter deposit with mixture of organic and inorganic species. It can affect separator surface as shown by Atomic Force Microscopy and X-ray Photoelectron Spectrocopy measurements limiting further Li ion diffusion and thus decreasing high rate capability of the Li-ion cell (fig 1a). Such degradation of electrolyte at electrode interface can be also accompanied by gas generation and it was correlated to unexpected lithium deposition on the graphite anodes (fig 1b). A degradation mechanism is proposed based on complementary ex-situ characterization (NMR, GC-MS, XRD and ToF-SIMS) made on fresh and aged electrodes and electrolyte.

Interface evolution has been also monitored by reliable electrochemical measurement using an optimized reference electrode measurement with electrochemical impedance spectroscopy and monitoring of each electrode potential. It allows to characterize the cell at various states of charge and health and determine the state of degradation of both electrodes independently. We have developed an experimental protocol to integrate the reference electrode directly in the commercial cell (3,7V 16Ah, Graphite/NMC) that allows operando characterization of the electrodes and interfaces inside the cell. Resistance of graphite electrode and electrolyte interface is increasing upon aging of the cell at high temperature (fig 1c) in agreement with degradation revealed by physicochemical destructive analyses done after cell dismantling.

The origin of the aging is identified more clearly thanks to the correlation of chemical, structural and electrochemical data collected on Li-ion cell internal components. Our work demonstrates that interfacial undesirable reactions can favor separator properties modification and Li metal deposition and it can lead finally to irreversible capacity loss and safety issue at cell level.

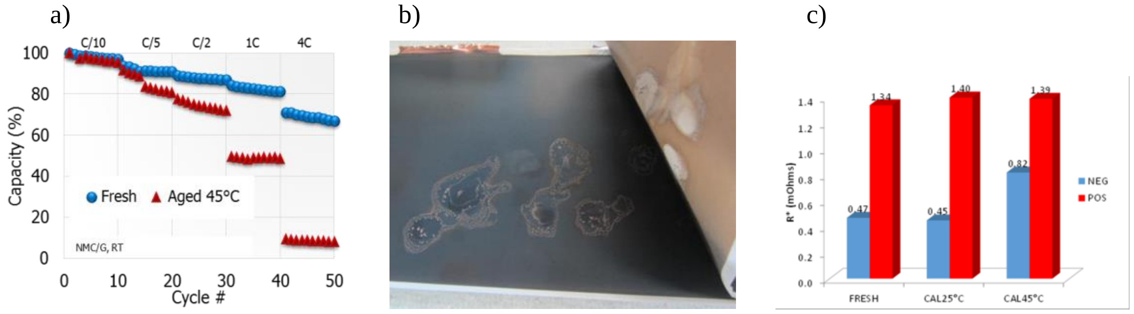

Fig 1. Evidence of internal components degradation in Li-ion batteries after use (a: rate capability with fresh/aged separator; b) deposit on negative electrode after storage at 45°C, c) resistance measurement extracted from EIS measurement on each fresh and aged electrodes

Dynamic Structural and Compositional Characterisation of Thin Metal Films and Bilayers

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Fabrication of a variety of devices involves the deposition and layering of metals onto a substrate. Commonly, the interfaces between these metal layers are subject to metal-metal interdiffusion, formation of brittle intermetallics and corrosion, all of which may compromise device performance and longevity. In the case of printed circuit boards (PCBs), which start from an insulating surface and are completed by insertion of electronic components, we have recently developed environmentally sustainable, non-toxic methodologies for application of metal finishes using Deep Eutectic Solvent (DES) media [1,2].

Here we explore fundamental aspects of the characterisation of metal-metal interfaces in DES media, with the generic goal of quantifying interfacial composition, morphology, structure and thickness. The strategy for accomplishing this involves a range of electrochemical control functions together with novel simultaneous thickness electrochemical potential (STEP) measurements, *in situ* microscopy and neutron reflectivity. Respectively, these provide dynamic speciation during metal deposition/dissolution, external film morphology and spatially resolved internal composition.

Deposition of Ag, Cu and Sn (bi-)layers has been carried out in various configurations onto Au substrates. We will show characteristic STEP traces for each during galvanostatic stripping. The characteristic shape of the potential trace facilitates the identification and quantification of each metal layer at all stages of the dissolution process. Of particular interest is the distinction between dissolution of discrete layers and intermetallics; the degree of mixing between the layers is determined from the *E vs. t* traces.

The morphology of metal layers was characterised by atomic force microscopy (AFM). It was observed that the stripping STEP traces for Cu and Ag bilayers were identical, irrespective of the orientation of the bilayer with respect to the solid-liquid interface. Additionally, STEP data for Au-Cu interfaces showed evidence of intermetallic formation and interdiffusion. Rapid interdiffusion was also observed at the interface between Au and Sn.

While the STEP data are relatively simple to acquire and, with minimal interpretation, are highly diagnostic for interlayer mixing, they necessarily involve sample destruction, i.e. layer dissolution. *In situ* neutron reflectivity (NR) measurements provide a non-destructive probe of the buried metal-metal interface maintained under either static or dynamic (dissolution) conditions. We will present temporally and spatially resolved NR measurements and, through modelling of different scenarios, will show surprisingly diverse behavior for bilayers involving different combinations of Ag, Cu and Sn. A particular strength of the NR technique is that it also permits simultaneous determination of solvent content within porous films or at the outer interface of rough films.

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Connecting adsorption site formation to nanoisland growth during the oxidative roughening of Pt(111)

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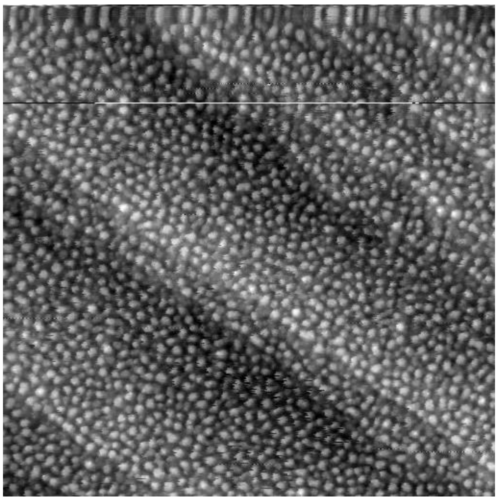
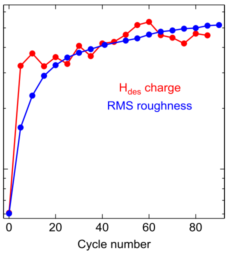
Platinum nanoparticles are used in a wide variety of catalytic processes. In many of these applications, e.g. the anodes of fuel cells, the platinum surface is (partly) oxidized. It is known that by oxidizing and reducing platinum, its surface structure is altered, which plays a role in the degradation of the catalyst. However, even for well-defined single crystal surfaces, over thirty years of research did not yet yield a conclusive description of this process on the atomic level.

To gain insight into the surface evolution during repetitive oxidation and reduction cycles, we obtained real space, high-resolution topography images using a home-built electrochemical scanning tunneling microscope (EC-STM). We observe the formation of nanoscale islands that grow in height with increasing cycle number. Applying a thorough statistical analysis (Height-Difference Correlation Function), we extract the evolution of the local roughness, which is continuously increasing (see figure). As we simultaneously record the cyclic voltammograms, we are also able to quantify the increase in the number of hydrogen adsorption sites for the different types of step edges: [110] and [100]. The evolution of these different sites is in line with literature data and delivers crucial information on the atomic structure of the formed islands. Preliminary analysis that considers both data sources, i.e. we correlate the step length creation with the roughness increase under the constraint of the observed features, leads to a detailed atomic/geometric model describing the roughness evolution.





O_2 Reduction on Glassy Carbon and Au Electrodes in BMP-TFSI with Mg^{2+} Ions: DEMS and ATR-FTIRS Model Study in a Flow Cell

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Room temperature ionic liquids (RTILs) are non-volatile, sufficiently stable, conductive electrolytes, promising, e.g., for applications in metal-air batteries [1,2]. In the Mg-O_2 system, despite of its high theoretical energy density, the Mg anode tends to passivate [3]. *Ex situ* characterization of the passive layer formed at the model electrodes after the oxygen reduction reaction (ORR) in butyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)amide (BMP-TFSI) in the presence of Mg^{2+} ions [4] cannot provide more detailed insights on its formation. The Au electrode/1-butyl-3-methylimidazolium (BMIM)-TFSI interphase was probed by *in situ* infrared spectroscopy in attenuated reflection (ATR-FTIRS) configuration [5], however, not under the reaction conditions and in the static ionic liquid. In the present work we will discuss quantitative DEMS results on the ORR in BMP-TFSI without/with $Mg(TFSI)_2$ on a glassy carbon (GC) electrode, or on a Au thin film electrode. The measurements were performed in a thin layer flow cells [6,7], allowing for differential electrochemical mass spectrometry (DEMS), equipped with a non-porous thin (10 μm) Teflon film [8], or that combined with simultaneous *in situ* ATR-FTIRS.

DEMS measurements on a GC electrode under continuous flow of O_2-saturated BMP-TFSI show two distinct mass transport limited currents at *ca*. -0.4 and -1.2 V (*vs*. Mg), the one at -1.2 V being about twice higher. The O_2 consumption, however, is equal in both cases, indicating a change in the ORR selectivity based on the calculated number of electrons 1 and 2 per O_2 molecule, respectively. The ORR in Mg^{2+} containing BMP-TFSI proceeds *via* two peaks in the first negative-going scan, it is rapidly passivated in the subsequent scans. The ORR in Mg^{2+} containing BMP-TFSI also shows a change from 1 and 2 electrons per O_2 molecule when stepping to -1.2 V. After excursions to -1.4 V, a reversible small O_2 consumption/release appears in the potential range up to -0.6 V likely due to MgO_2 formation/oxidation.

Combined DEMS/ATR-FIRS measurements on the ORR at a Au film electrode similarly show the development of the second current plateau at -1.2 V at about similar consumption of O_2. DEMS measurements of m/z 2 and 44 show no potential dependence during the ORR, although in the N_2 saturated BMP-TFSI a small increase in the H_2 signal can be detected at -1.4 V, which can be attributed to hydrogen release from the trace amounts of water, in agreement with the broad band at around 3600 cm^{-1}, appearing at high potentials. The ORR in Mg^{2+} containing BMP-TFSI proceeds *via* a double peak in the first negative-going scan, afterwards getting passivated. The appearance of the band at around 3740 cm^{-1}, when approaching negative potentials, is characteristic to the OH stretch at MgO exposed to water [9].

The first membrane inlet DEMS results demonstrate potential dependent change in the ORR selectivity. *In situ* ATR-FTIRS show simultaneous changes in the adsorbate population and a passive layer buildup.

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Elucidation of pathways towards multi-carbon products during CO reduction on Cu electrodes

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The implementation of intermittent sustainable energy sources, such as wind and solar power, requires more efficient energy storage technologies. The electrochemical reduction of CO_2 shows promise as a means of CO_2 fixation using renewable electricity, in order to close the anthropogenic carbon cycle. The aim is to produce energy-rich compounds that can be used as fuels, as well as carbon-based chemicals and chemical precursors currently derived from fossil resources.[1] Currently, copper is the only pure metal that can facilitate significant production of hydrocarbons, alcohols and other highly reduced compounds.[2] Due to slow kinetics and complex reactions with numerous electron transfers, however, large overpotentials are currently needed to achieve industrially relevant current densities towards these products. Furthermore, Cu normally produces a mixture of compounds, requiring expensive separation techniques in order to obtain pure chemicals. For commercialisation of CO_2 electroreduction to become realistic, significantly improved catalyst materials are needed.

CO has been identified as an intermediate in the conversion of CO_2 into the further reduced products mentioned above.[3] In addition, CO_2 reduction to CO can already be carried out quite efficiently.[4,5] Because of this, CO electroreduction has received a lot of attention. Li et al. showed that nanostructuring of copper significantly enhances CO reduction selectivity towards C_2 products at very low overpotentials, with Faradaic efficiency as high as 43 % at -0.3 V vs. RHE.[6] In a recent work, we showed that acetaldehyde is also produced from oxide-derived copper under these conditions.[7] We made this finding on the basis of static headspace-gas chromatography, which exhibits high sensitivity to aldehydes,[8] for liquid-phase product analysis. We thus established that acetaldehyde is an intermediate in the reduction of CO into ethanol. We have since extended the scope of our studies to other Cu-based materials, including planar polycrystalline electrodes. We can steer Cu towards the formation of significant amounts of previously unidentified C_3 products at potentials as positive as -0.4 V. Our electrochemical measurements are complemented by X-ray photoelectron spectroscopy and density functional theory calculations.

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On the Mechanisms Underlying Electrolytic Plasma Processes with Vapour Gaseous Envelope

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Plasma-assisted electrochemical processes underpin a range of recent ground-breaking developments in chemistry, biology, medicine, materials science and engineering. Despite high practical significance, electrochemical mechanisms underlying these processes are relatively poorly understood. In particular, for the systems where gaseous products of electrolysis prevail, transition from conventional to the plasma-assisted electrolysis is often treated in terms of bubble to film boiling transition within the framework of Helmholtz-Taylor theory of hydrodynamic heat transfer [1]. However, this does not explain the fact that the transition to the film-boiling mode follows the onset of plasma discharge, not vice versa; neither this helps understanding what governs the charge transfer through the electrode-electrolyte interface under the film-boiling conditions.

We investigated anodic processes that occur during high-voltage polarization of stainless steels in aqueous solutions of ammonium sulphate. These processes currently attract significant interest as environmentally friendly alternatives to conventional acid electro-polishing due to the capability of providing fine surface finish to metal components produced by various methods, including additive layer manufacturing. For the studied system, the transition from conventional to the plasma-assisted regime takes place in the voltage range of 250 to 350 V at electrolyte temperatures of 70 to 90 ^{o}C. This transition was studied by voltammetric and spectroscopic techniques, including impedance, optical and acoustic emission spectroscopies. The impedance spectroscopy was adopted to the conditions of high-voltage electrolysis, with data validated in time domain using originally developed approach [2]. Faradaic yields of the main anodic reactions of metal dissolution and water splitting were investigated using gravimetric methods. To minimise effects of collateral anodic processes, e.g. those involving sulphate species, the samples were polarised before being immersed in the electrolyte.

The optical emission from the anode was observed to commence in the falling part of the current–voltage diagram prior to entering the median region of minimum current density. The optical spectra of discharge borne clear evidence of intermediates and final products of the main anodic reactions, including Fe, H, OH and O species. The impedance spectra revealed presence of three kinetic processes with different time constants which we associate with the interfacial charge transfer and two characteristic responses from different reaction intermediates – one species providing blocking effect by covering about 95% of active sites on the surface and the other unblocking it. The equivalent thickness of the blocking layer was estimated to be in the region of 0.5 to 1 nm, indicating that the current transfer in the system was limited by the adsorbed layer of reaction intermediates rather than by a whole film of gaseous reaction products. The inductive unblocking response coincided with the onset of plasma discharge and a noticeable decrease in the current yield of anodic metal dissolution reaction. This was therefore attributed to the changes in the pathways of the water splitting reaction, which could be catalysed on oxy-hydrated metal surfaces. In particular, it was proposed that this four-electron transfer process has been facilitated by deviation from a two-site terminal oxo-twin route to the single-site early peroxo formation route [3]. Possible reasons and pre-requisites for such change are discussed. Finally, a resonance phenomenon was observed in the acoustic spectrum in the frequency range 800 to 1500 Hz. This could be attributed to the loss of damping capacity in the system due to annihilation of charge transfer resistance by the negative differential resistance related to the blocking response by adsorbed oxo species in this particular frequency range, leading to almost entirely capacitive response of the system.

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Constructive and destructive effects of molecular noise in nanoscale electrochemical systems

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With electrode sizes approaching the nanoscale, it becomes more and more important to understand the impact of molecular noise on the dynamics of electrochemical reactions. In the talk we will consider two examples where molecular noise in nano- and even microscale electrochemical systems has a qualitative impact on the system's behavior. First we will discuss oscillations during hydrogen peroxide reduction on Pt nanoelectrodes. Using the electrochemical master equation, we will demonstrate that (a) steady states and oscillations shift in phase space with decreasing system size, thereby also decreasing considerably the oscillating parameter regions; and (b) the minimal number of molecules necessary to support correlated oscillations is more than 10 times as large as for nanoscale chemical oscillators. Then, we will discuss an experimental study of the impact of noise during CO electrooxidation on Pt microelectrodes. CO electrooxidation is a kinetically bistable reaction, exhibiting the formation of self-organized spatial domains under galvanostatic conditions. For microelectrodes with a size close to the threshold to domain formation, pronounced fluctuations of the electrode potential appear in the system. These potential fluctuations arise from a strong enhancement of molecular or intrinsic noise due to its interaction with the nonlinear reaction kinetics and occur in three manifestations: Spikes towards low potentials with a slow relaxation that are erratic in time, jumps between two potential levels, which occur as well at random points in time and noisy time series without any structure and an increased amplitude. Analysis of all three types of electrochemical noise revealed a $1/f^2$ frequency dependence, whose origins will be discussed. Also features common with neuronal shot noise will be highlighted.

In-Situ Super-Resolution Fluorescence Characterization of DNA SAMs on Gold Surfaces While Under Electrochemical Control

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Preparation of DNA self-assembled monolayer (SAM) on gold surfaces are used in many biosensor approaches. Typically, the thiol modified DNA is allowed to assemble on a clean gold surface first followed by treatment with a small alkyl thiol that is used to remove any DNA that is not specifically bound via the thiol. The assembly of this multi-component SAM depends on many parameters and the resulting surface can have a range of DNA surface coverage that can vary across the surface. In addition, the DNA may be found in a variety of local environments which can co-exist on the same electrode surface. The preparation of DNA SAMs with optimized surface density and uniform local environments is desired, but techniques to assess the molecular organization of the DNA SAM modified gold surface are needed[1]. In particular, a method that can report on the local DNA environment and its variation across the surface will require a imaging method that has molecular scale resolution, but does not perturb the SAM. A high spatial resolution fluorescence analysis of the DNA SAM modified electrode surface in electrolyte and under electrochemical control will be described. Demonstrated is the use of a super-resolution fluorescence imaging approach applied to this modified electrochemical interface. The SMLM (single molecule localization microscopy) method was used to interrogate the fluorophore (Alexa647) modified DNA SAM. The substrate was a gold coated glass surface configured with three electrodes and the electrolyte used contains the required components to enable the blinking of Alexa647[2]. The localization of the individual DNA adsorbates can be realized for low coverage surfaces. The lateral resolution of the custom STORM microscope is 15 nm[3]. The 30 base pair DNA strand used is 10 nm in length when fully extended when hybridized with its complementary strand. Considering that the DNA is not static when adsorbed but is mobile, it would occupy an area that is similar to the resolution of the microscope which enables single molecule resolution of the adsorption site for these individual DNA thiolated molecules. Examples of variation in the DNA assembly on the gold surface will be presented in addition to an approach to estimate the extent of clustering of the adsorbates. The influence of potential on the stability and the imaging conditions is also discussed.

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Seeing Inside a Growing Catalyst

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Characterizing nanocatalysts with atomic precision is key to establish structure-activity-stability relationships, and further improve their (electro)catalytic activity for a given reaction. However, characterization efforts usually focus on the catalyst in its final form (*i.e.* after the synthesis) without any knowledge of how morphology, structure and chemistry organize in its infancy. Despite being experimentally challenging, a step-by-step characterization of the nucleation and growth of a catalyst is fundamental to unravel the effects of the chemical reagents used, the time at which they must be introduced in the synthesis reactor, identify the nucleation and growth kinetics, and determine when the synthesis must be stopped to achieve the desired catalytic design.

Herein, we introduce an experimental approach that is capable of providing atomic-level details on the formation and growth mechanism of a nanocatalyst. Using scanning transmission electron microscopy coupled with X-ray energy dispersive spectroscopy, synchrotron wide angle and small-angle X-ray scattering, X-ray photoelectron spectroscopy and electrochemistry, we captured the various intermediate nanostructures forming during the synthesis of hollow PtNi/C nanoparticles. Our observations (Figure 1) indicate that before reaching its final state, hollow PtNi/C nanoparticles undergo multiple restructuration steps. The synthesis intermediates were isolated, and their electrocatalytic properties were established for the oxygen reduction reaction in both alkaline and acidic electrolytes.

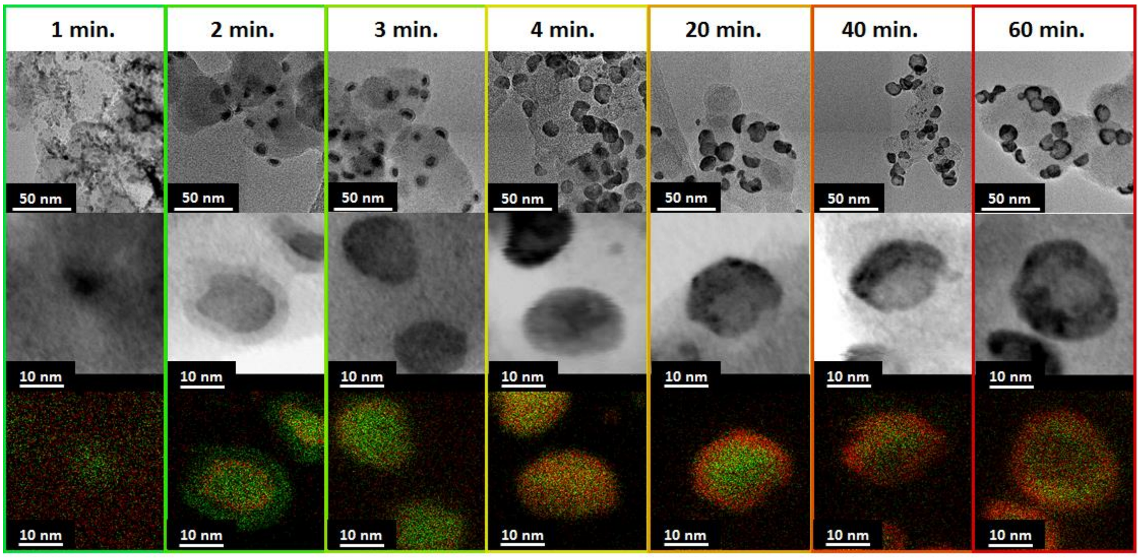

Figure 1. Conventional and scanning transmission electron microscopy images and elemental maps of the different intermediate nanostructures forming during the synthesis of hollow PtNi/C nanoparticles.

What is the trigger for hydrogen evolution reaction?

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Archetype reaction in electrochemistry, hydrogen evolution reaction (HER), was used as a model to analyse can Sabatier principle, as key paradigm of gas-phase heterogeneous catalysis, be transferred to electrocatalysis in straightforward manner, as usually portrayed. More than a century of studies on HER illustrates diversity of approaches introduced into electrochemical research, but also, points out some contradictions and misconceptions which caused that after decades of intensive research still there is no established theory of electrocatalysis. It was previously stated by Trasatti: “A true theory of electrocatalysis will not be available until activity can be calculated a priori from some known properties of the materials.“ Although DFT (density functional theory) calculations gave some contribution in that direction, partial overlap of experimental activity trends and activity trends obtained by DFT calculations should be observed much more critically. While predictive models, based on the optimal adsorption energies of key intermediate(s), so called “volcano” plots, are widely accepted, some researchers stayed persistent with claims that in a case of electrocatalytic reactions Sabatier principle is not sufficient or even misleading in explanation of activity trends. Although Sabatier principle as a concept seems to be intuitive, argumentation shown in this work indicates that electrocatalytic reactions encompass level of complexity which still represents challenge for comprehension even in a case of “simple” reaction like HER. Namely, interaction between electrode material and electrolyte could alter electrode surface in a sense that no bulk or surface property of material could really be directly linked to the rate of electrocatalytic reaction. This suggests, not only that solvent plays very important role in the kinetics of electrocatalytic reactions, but rather suggests importance of interfacial parameters (e.g. potential of zero charge) which are strictly result of interaction between electrode material and solvent. Crucial questions are: 1) what is/are the adequate catalytic descriptor/s for the case of HER b) can we confirm it experimentally and 3) what really triggers HER. Answers on the posed questions was suggested by careful analysis of key contributions about HER up to date, together with new experimental insights obtained in our lab.

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Interplay between electrons and protons at electrochemical interfaces

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At a semiconducting oxide water interface, two double layers (space charge layer and electric double layer) can develop near the interface. The double layer potentials can vary against the voltage and pH because they depend on the density of surface charges that have both electronic and protonic components. While the surface protonic charge density is determined by the acid-base equilibrium between the surface and the solution, electronic charges can also develop owing to the presence of electronic surface states that serve as traps for electrons and holes. A further complication is that the protonation and reduction (or deprotonation and oxidation) can couple at certain surface sites through proton coupled electron transfer (PCET) reactions. This is believed to be the cause of the observed (non-)Nernstian relation between the changes in electrode potentials and the pH, an approximately linear relationship with varying slopes depending on the nature of oxide surfaces.

In contrast, at metal water interfaces electronic charges are all confined on the metal surfaces. The proton in solution, controlled by pH, will be reduced to hydrogen atoms adsorbed on surfaces when applying a negative bias. Usually but not always, the coupling between electrons and protons follows the Nernstian relation.

To understand the potential profiles across electrochemical interfaces, we have performed density functional theory molecular dynamics simulations to calculate the free energies of transfer of an electron, proton, and hydrogen atoms. Our calculations shed new chemical insight into the potential distribution at electrochemical interfaces, and some implication to the photo-electrocatalysis will also be discussed in the talk.

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Hierarchical *“Core-Shell”* Electrocatalysts for the Oxygen Reduction Reaction (ORR) based on Graphene *“Cores”* and Metal Alloy Carbon Nitride *“Shells”*

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The sluggish kinetics of the oxygen reduction reaction (ORR) is one of the most important bottlenecks in the operation of several families of advanced energy conversion and storage devices, such as metal-air batteries and low-temperature fuel cells (*e.g.*, proton-exchange membrane fuel cells, PEMFCs and anion-exchange membrane fuel cells, AEMFCs). Accordingly, the development of efficient ORR electrocatalysts (ECs) capable to address this issue and minimize the high activation ORR overpotentials is one of the most active research areas in this field. It is also to be highlighted that an efficient ORR EC must exhibit several additional features, including: (i) a facile electron transport between the active sites and the external circuit, to minimize the ohmic drops; (ii) a suitable morphology, to ensure that reactants and products are able to easily reach and be removed from the active sites; and (iii) a high durability and a low cost, to comply with the requirements set by the applications.

This work describes the features of a new family of ECs for the ORR that are able to meet all of the above requirements. The ECs exhibit a hierarchical *“core-shell”* morphology; they include a graphene-based nanostructured *“core”* covered by a carbon nitride *“shell”* embedding the ORR active sites in carbon- and nitrogen-based *“coordination nests”*. The nanostructured *“core”* exploits the unique properties of graphene, with a particular reference to its high electron conductivity and low microporosity. The carbon nitride *“shell”* plays a crucial role to stabilize the active sites in its *“coordination nests”*; thus, the resulting ECs exhibit a high durability, significantly improved in comparison with that of state-of-the-art, *“reference”* Pt/C ECs.

The proposed *“core-shell”* ORR ECs are obtained by customizing a unique and extremely flexible preparation protocol [1-3], that allows to fine-tune the morphology and the chemical composition of the ECs. Two main groups of ORR ECs belonging to this family are considered. The former comprises ECs with a low loading of platinum-group metals (L-PGM), optimized for operation in an acid medium at the cathode of PEMFCs; the latter consists of ECs that do not include platinum (N-PGM), intended for application in the alkaline medium in devices such as AEMFCs and metal-air batteries. This work overviews the synthetic strategies used to obtain the ECs comprising the graphene-based nanostructured *“cores”* and discusses the complex correlations existing between the preparation parameters, the physicochemical properties and the electrochemical performance. Finally, the most promising avenues and new directions for the research are indicated, with the aim to obtain ECs comprising graphene-based nanostructured *“cores”* exhibiting an improved ORR performance and durability, and at lower costs, in comparison with state-of-the art *“reference”* ECs.

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Molecular control of interfacial inner-sphere electron transfer via graphite conjugation

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The interconversion of electrical and chemical energy requires catalysts that can efficiently transfer multiple electrons to or from small molecules. Heterogeneous electrocatalysts have extended band structures with high densities of states at the Fermi level, allowing these surfaces to engage in concerted electron transfer and substrate activation; however, metallic surfaces contain a broad distribution of active sites that are difficult to characterize and tune at the molecular level. Recently, we have developed a new class of catalysts that incorporate molecularly well-defined, highly-tunable active sites into heterogeneous graphite electrodes. These graphite-conjugated catalysts (GCCs) feature a unique conjugated linkage between a discrete molecular active site and the delocalized states of graphitic carbons. Edge planes of graphitic materials display high populations of o-quinone moieties that undergo site-selective irreversible condensation with substituted phenylenediamines to form robust, aromatic pyrazine linkages. Here, we probe the electronic structures and charge transfer properties of metal-conjugated GCCs by cyclic voltammetry (CV) and X-ray absorption spectroscopy (XAS). CVs of the dissolved complex tetraamine(phenanthroline)Ru^{2+} ($Ru(NH_3)_4phen^{2+}$) display a reversible Ru(III/II) wave, and the same wave is observed when the molecule is anchored to an electrode surface through an insulating aliphatic linkage. Remarkably, conjugating this Ru center to the graphite surface causes the redox waves to disappear. Consistent with these CVs, in-situ XAS demonstrates that applying oxidizing potentials to an electrode with aliphatically tethered $Ru(NH_3)_4phen^{2+}$ causes a change in oxidation state from Ru(II) to Ru(III), but applying the same potentials to the $Ru(NH_3)_4phen^{2+}$ GCC has no effect on oxidation state. In contrast, when electron transfer is concomitant with bond formation or cleavage at the GCC site, CVs do show waves associated with these bond forming-and breaking steps. These results suggest that the aromatic pyrazine linkage allows for electronic coupling between the Ru center and the graphite electrode, leading to inner-sphere charge transfer at the electrode surface rather than outer-sphere charge transfer. This system provides the first tunable platform with which to probe inner-sphere electron transfer steps at an electrode surface.

Formate Oxidation on Au(111) Electrodes

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The oxidation of formic acid on noble metal electrodes belongs to the simplest reactions in electrocatalysis [1]. However, the reaction mechanism and the influence of various parameters such as pH and coverage of adsorbed species on electrocatalytic activity is not yet fully understood, even for the case of gold surfaces, where the indirect pathway yielding adsorbed carbon monoxide is strongly suppressed [2]. Figure 1 shows that the electrocatalytic activity for formic acid oxidation on an Au(111) single crystal electrode rises with increasing pH until it reaches a plateau around pH 5. This suggests that the formate anion is a main reactant. At the same time, formate adsorbed in a bidentate configuration has been observed by *in–situ* infrared spectroscopy [2] and by *in–situ* scanning tunnelling microscopy [3]. Such strongly adsorbed formate forms stable adlayer structures and therefore is assumed not to be reactive. The dual role of adsorbed formate, either reactive intermediate or blocking spectator species, will be discussed. Characteristic voltammetric potentials also shift systematically with pH (Fig. 1b).

The presence of phosphate species in solution lowers the oxidation currents significantly (not shown). While the use of buffer solutions stabilizes the pH, specific adsorption of phosphates is found to block active sites. Other examples will be given for molecular species, which were found to displace strongly adsorbed formate and thus enhance or lower the overall electrocatalytic activity, strongly depending on the chemical nature of the species.

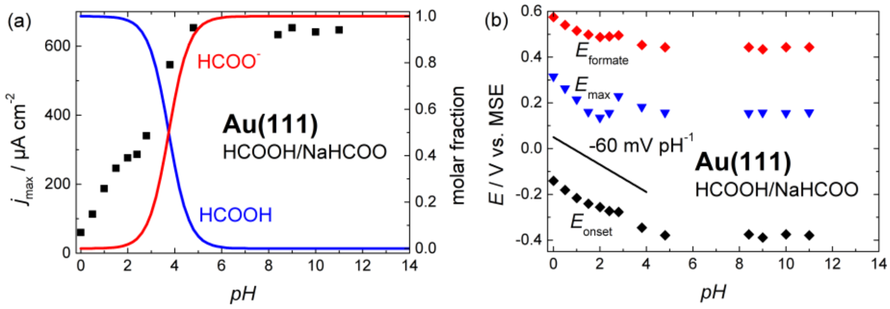

Figure 1: (a) Peak currents for oxidation of 0.1 M $HCOOH/HCOO^-$ on Au(111) as a function of pH together with the molar fractions of $HCOOH_{(aq)}$ and $HCOO^-_{(aq)}$.
(b) pH–dependence of characteristic potentials, *e.g.* for onset of oxidation, E_{onset}, oxidation peak maximum, E_{max}, and phase transition within adsorbed formate, $E_{formate}$.

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DEMS studies using isotope-labeling for unraveling mechanistic details in CO_2/CO electroreduction and O_2 evolution reaction

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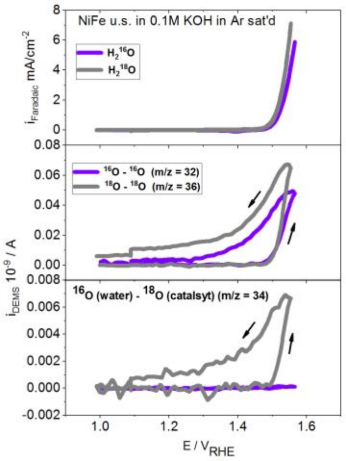
Differential electrochemical mass spectrometry (DEMS) is a powerful tool for following trace amounts of products formed during electrocatalytic reactions. In addition, DEMS combined with isotope-labeling of atoms constituents of reactants or catalyst materials itself, may offer more valuable insights into the reaction mechanisms.

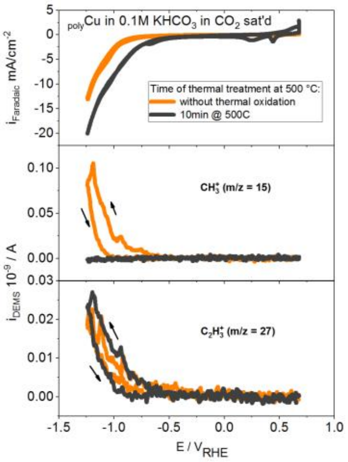
In this work, we examine products of O_2 evolution reaction (OER) and CO_2 and CO reduction reaction (CO2RR and CORR) using isotope-labeling methodology. We present the results obtained using a capillary flow cell that we developed recently with the design featuring a conventional electrochemical cell with a hydrodynamic complementary flow such as rotation disk electrode (RDE).

The fluid dynamic studies of the capillary flow cell will be presented and compared with the modified dual thin-layer flow cell.

The comprehensive studies of the in-situ DEMS on the OER mechanism have already been done for the benchmark catalysts oxides of Ru, Ir, Pt and Au using O18-labeling[1-4]. In these studies, a portion of the evolved oxygen originates from the oxide itself, with exception of Pt oxides[3]. We investigate OER catalysts in presence of isotope-water to gain information on context of the direct coupling versus the acid-based mechanism on Ni-based and NiFe catalysts for alkaline media.

Both CO2RR and CORR involve several multielectron-transfer reactions running in parallel, whereby mechanistic understanding remains a challenge even when most accurate analytical instrumentation is used. Several DEMS studies focusing on CO2RR successfully monitor product formation with remarkable time resolution, however none of them explore using isotope-labeled reactants[5,6]. We set to explore the origin of oxygen atoms in oxygenate-products (i.e. acetaldehyde or ethanol) obtained on oxide-derived copper during CO reduction[7,8].





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Nature, stability and distribution of subsurface oxygen in copper electrodes during the electrochemical CO_2 reduction

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The electrochemical carbon dioxide reduction reaction (CO_2RR) allows the storage of energy in readily available chemicals such as ethylene and other hydrocarbons,[1] while contributing to the abatement of CO_2.[2] Copper is the only pure metal able to perform CO_2RR with appreciable activity and selectivity towards multi-carbon products, due to optimal binding of the key intermediate CO,[3] especially when the electrode is nanostructured and derived from an oxide.[4,5] Oxide-derived copper (OD-Cu) electrodes exhibit activity and ethylene selectivity higher than pristine copper during the carbon dioxide reduction reaction (CO_2RR), and the presence of residual subsurface oxygen in OD-Cu is associated with such improvement.[6] Using *quasi in situ* x-ray photoelectron spectroscopy (XPS), electron energy-loss spectroscopy (EELS) in a transmission electron microscope (TEM) and positron annihilation spectroscopy (PAS), we show that oxygen is primarily concentrated in an amorphous 1-2 nm thick layer on the Cu surface (see Figure 1), it is stable during CO_2RR for up to 1 hour at -1.15 V vs RHE and is associated with a high density of defects in the OD-Cu structure. (S)TEM is able to provide structural and chemical information with high spatial resolution, allowing to identify the local distribution of oxygen in the sample. Positron annihilation coincident Doppler broadening (CDB) spectroscopy yields the chemical surrounding of such defects. Corroborated with density functional theory (DFT) calculations on copper nanoclusters we propose that both the low-coordination of the amorphous OD-Cu surface and the presence of subsurface oxygen that withdraws charge from the copper d-band selectively enhances the binding energy of CO without altering that of other reaction intermediates, therefore breaking the scaling relation between d-band center vs CO binding energy.

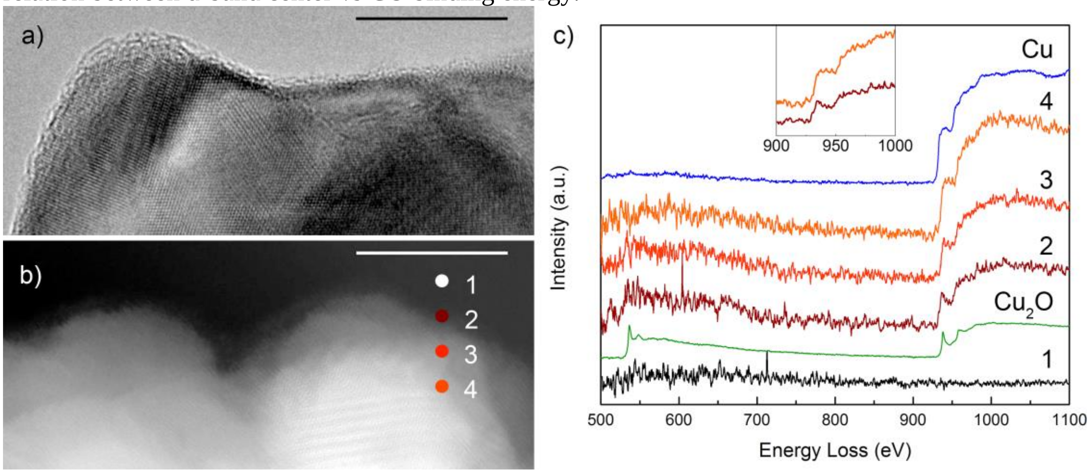

Figure 1. (a) TEM and (b) STEM image of two different OD-Cu nanoparticles. Scale bars are 10 nm. (c) STEM EEL spectra acquired at the points indicated in (b), showing the O-K and Cu-$L_{3,2}$ edges. An increased O content and a more oxidic Cu L edge are observed within a 1-2 nm thick layer under the catalyst surface. Reference spectra for Cu and Cu_2O are shown in blue and green, respectively.

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Oxidation and Surface Restructuring of Pt Electrodes upon Potential Cycling and during Oxygen Reduction Reaction

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ORR is one of the most studied electrochemical reactions due to it’s tremendous fundamental and practical importance. Oxygen is common, readily accessible oxidizing agent and, therefore, Pt ORR cathode is part of many energy conversion devices, e.g. fuel cells. Unfortunately, slow kinetics of ORR negatively affects the performance and it is currently one of the main bottleneck in large scale fuel cells commercialization. It is partly caused by the presence of surface Pt oxides, which slow the reaction rate and trap reaction intermediates on the surface. The oxide formation and dissolution is also known to cause dissolution of Pt catalyst, which further degrades the performance.

Even though the electrochemical formation of surface oxides on platinum surface has been extensively studied in the past, there are still many questions unanswered. Mainly about the detailed structure of the oxide and its growth mechanism [1 and references there-in]. Most of the studies were performed in the absence of O_2, the fuel cell oxidant, and therefore they are less relevant to the fuel cell operation as gaseous O_2 can modify the oxidation potentials and mechanism. Given the above, further fundamental understanding of the Pt oxidation mechanism and its atomistic picture is clearly needed in order to determine the role of surface oxides in ORR and its effect on the fuel cell performance.
Here we show the results of in-situ study of electrochemical oxide formation on Pt(111) and how it is influenced by presence of O_2 during ORR. Furthermore, we show that surface reorganization processes taking place during the oxidation/reduction cycle are governed by the ad-atom surface diffusion dynamics and closely resemble the dynamics found under the vacuum conditions.

The place exchange process associated with the initial stages of oxidation is followed dynamically during cyclic voltammetry (CV) and potential step experiments in the presence and absence of oxygen. Detailed analysis at two potentials shows that the reconstruction is consistent with a place exchange process between Pt and O atoms, in which the exchanged Pt atoms are directly above their original positions in the Pt(111) lattice. The reconstruction initiates with the CV peak at 1.06 V vs RHE, even though repeated cycling to 1.15 V leads to no changes in the CV. Adding O_2 to the electrolyte does not have any significant effect on the oxidation behavior, in contrast to some literature reports, and the O_2 accelerated Pt dissolution is not caused by the negative shift in the oxidation potential. Furthermore, the ORR current decreases before oxidation, implying that the presence of the surface oxide is not the limiting factor in the ORR and the high ORR overpotential is solely due to the slow ORR mechanism on an unreconstructed surface.

The surface restructuring upon electrochemical oxidation/reduction show a characteristic ripening behavior where Pt islands grow and become more prominent and homogeneous in size with increasing number of cycles. Their characteristic lateral dimensions primarily depend on the upper potential limit of the cycle and only slightly increase with cycle number. The structural evolution of the Pt surface morphology strongly resembles that found in studies of Pt(111) homoepitaxial growth and ion erosion in ultrahigh vacuum. This finding shows that the electrolyte does not need to be included in the ab-initio investigations of the Pt surface structure change during ORR.

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Specific Adsorption of Anions from Ionic Liquids: an *in situ* STM and Impedance Study

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Adsorption of particles, such as molecules or ions, is an important basis for many everyday phenomena, such as corrosion inhibition or chromatographic separation. With regard to electrochemical technology, it provides a basis for energy storage in supercapacitors as well as helps to mitigate many important faradic processes via the formation of the electrical double layer (EDL). However, in many cases, the particles themselves adsorb at the surface by chemical bonding interaction, thereby contributing to an effect called specific adsorption, which means that the adsorbed species can no longer be considered as part of the diffuse phase at a solid|liquid interface. Therefore, as part of the solid interface, they contribute strongly to the interfacial properties, such as energy storage, reactivity and interaction with other interfaces. It is of interest to look at such systems whereby there are no neutral particles within the liquid phase, such as ionic liquids (IL). Composed exclusively of ions, ILs constitute a large variety of liquidous electrolyte media that can be specifically tuned for an application in mind. This allows ILs to have a varied range of applications, such as electrolytes for energy storage, separation of ionic or organic species and catalyst media for organic synthesis. Although the formation of the EDL in ILs has been in the scientific focus for over a decade, there is still a lack of understanding with regard to the specific interaction of ions at IL|metal interfaces [1]. This is partially due to the difficulty in describing such interactions from a modelling perspective, as well as the complexity of the systems in electrochemical experiments.

To overcome these problems, both classical electrochemical methods (cyclic voltammetry and electrochemical impedance spectroscopy) as well as *in situ* scanning tunneling microscopy (STM) method have been applied to observe the interfacial structuring at IL interfaces. Single crystal bismuth electrodes have been chosen for the working electrodes due to their variable metallic properties and stable surface structure. Five different IL anions have been chosen for the study consisting of two primary groups. Halide ions, namely chloride, bromide and iodide have been studied as part of a group of strongly adsorbing anions that are known to form dense adlayers in solvent based electrolytes, but whose interfacial adsorption mechanism in ILs is less clear [2]. Triflate (OTf) and bistriflimide (TFSI) anions have been chosen for their potential ability to chemically bond to the surface trough the sulfonyl groups, which has been shown in aqueous solutions but not ILs. These anions have been combined with aliphatic imidazolium cations that are generally thought to not specifically adsorb at metallic electrodes. It is observed that these two groups of anions indeed show a largely different behavior as it pertains to specific adsorption at Bi electrodes. The halide ions adsorb at Bi interfaces forming densely packed monolayer structures that are stable in a wide range of electrochemical potential. Thus it is suggested that the electron transfer coefficient i.e. the number of electrons shared between the ions and the metal changes with potential, rather than the surface coverage of ions. This also results in the fact that considerably more charge can be accumulated at the interface. The second group of anions behaves in a very different manner- the adsorption of the OTf and TFSI anions is a very slow process and the adsorbed layer acts as a dielectric at the surface, therefore considerably lowering the amount of charge that can be stored. It should be noted however, that the systems form two stable polarization areas (electrostatic and dielectric) that can be switched between by varying the applied potential value, possibly contributing to a new electronic memory type system.

Acknowledgements

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In-situ X-Ray Photoelectron Spectroscopic Investigations during Electrochemical Experiments in Ionic Liquids

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Room temperature ionic liquids (RTILs) are a class of ionic compounds that have melting points that are below room temperature. They have decent conductivities and very low vapor pressure. All these attributes not only make them well suited to replace conventional electrolytes for consumer electronics, energy storage and conversion and others but also land them into being well suited for studies inside an ultra-high vacuum chamber that is necessary for X-Ray Photoelectron Spectroscopy (XPS).

Recently, we reported on the reversible cyclic voltammetry of a stable N-heterocyclic carbene inside the XPS chamber. Using the XPS data, we have been able to unequivocally show that the reduction products for the imidazolium species was the relevant carbene [1]. In another study, we showed that constantly anodically polarized gold electrode inside the ionic liquid medium leads to formation of gold nanoparticles through etching of the electrode. We further investigated the charging details of the generated nanoparticles and gained insight into the charging processes therein [2].

On the dynamic side, using squarewave signals of varying frequency, we have been investigating the details of the formation kinetics of the electrochemical double layer. In a recent report we investigated the phenomenon using a simple resistor/capacitor model that explained the behavior near the electrodes, but failed to capture the details of the voltage elsewhere on the system [3]

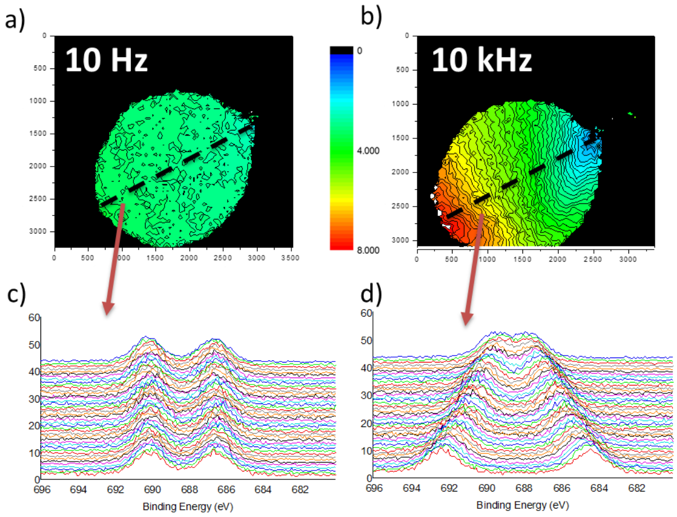

Figure F1s signal shown under DC bias (a) and under AC bias (b). Since the integration time is much larger than the frequency of the Squarewave, both positive and negatively shifted signals are visible. (c) and (d) show the difference in peak positions for the two F1s signals as a function of distance from either electrode under different frequencies.

We will report on new efforts in order to understand the effects of parameters such as mobility of the positive and negative ions, dielectric constant of the medium, the carrier density among others to the observed behavior. These efforts will aid in the understanding of the dynamic behavior of the electrochemical double layer formation. These efforts involve not only experimental work as shown in the Figure, but also numerical simulations using the diffusion and migration of ions within the ionic liquid.

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In Situ Raman Study of Electrochemical Reaction at Single Crystal Electrode Surfaces

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Surface-enhanced Raman scattering (SERS) can be used for in situ investigation of trace chemical species and identification with single-molecule sensitivity. However, the SERS enhancement is limited to a few noble metals such as Ag, Au, or Cu with roughened or nanostructured surfaces, which had limited the breadth of practical applications of SERS in a variety of fields. It also in principle excludes to directly study atomically flat single crystal surfaces that cannot effectively support the strong surface plasmon resonance (SPR). Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) was therefore invented to break the long-standing limitation of SERS. In SHINERS, the Au/Ag core as plasmonic antenna provides high electromagnetic field to enhance the Raman signals of probed molecules at single crystal electrode surfaces, while the ultra-thin, uniform and pinhole-free silica shell separates the Au/Ag cores from the system under study and ensures no interference from processes involving the SERS-active cores.

Shell-isolated nanoparticles (SHINs) can be spread as “smart dusts” over single crystal surfaces with diverse compositions, and it has already been applied to a number of challenging systems, such as hydrogen and CO on Pt(hkl) and Rh(hkl), which can’t be realized by traditional SERS. Combining with electrochemical methods, we have in situ monitored the surface electro-oxidation at Au(hkl) electrodes, and oxygen reduction reaction at Pt(hkl) surfaces. Hydroxyl, peroxide and superoxide were directly observed as intermediates which proved the long-standing speculation in electrochemistry. These results demonstrate that the in-situ EC-SHINERS technique offers an effective and reliable way for real-time investigation of catalytic processes at the atomic and molecular level. SHINERS method has also been used to probe structure and processes on materials of different composition and morphology, from metal single-crystals to semiconductors and from food samples to living cells.

The concept of shell-isolated nanoparticle-enhancement is being applied to other spectroscopies such as infrared absorption and sum frequency generation. For instance, the shell-isolated mode was applied to fluorescence spectroscopy with thousands fold enhancement on fluorescent signals. The concept was also extended to second-harmonic generation (SHG) to build up a gap-mode nanoruler. New scanning probe microscopy tip structures inspired by SHINERS, such as shell-isolated tip-enhanced spectroscopy (SITERS) with nanoscale spatial resolution, are under development. The shell-isolated mode is extremely flexible and of use in surface analysis.

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Electrochemical Oxygen Reduction on Zinc Oxide
A Combined DFT and ATR-IR Study of the Detailed Mechanism

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Zinc coatings play an important role in corrosion protection of steel structures. Besides the galvanic protection, the significantly lower rates of the oxygen reduction reaction (ORR) in the presence of zinc corrosion products contribute to the corrosion protection.[1]

Using *in-situ* ATR-IR spectroscopy, we have detected several intermediates of the electrochemical oxygen reduction reaction on the Ge(100) model semiconductor surface. DFT calculations allowed an assignment as superoxide and peroxide intermediates covalently attached to the germanium surface.[2,3] Furthermore, the detailed reaction mechanism in terms of electron transfer and proton transfer steps and hence including charged intermediates was derived, based on DFT calculations. The model is based on small clusters representing the surface and solvated ORR intermediates. The combination of a first solvation shell of explicit water molecules to treat H-bonding effects and a self-consistent reaction field approach for the long-range electrostatic effects was developed. A grand canonical approach based on calculated chemical potentials for protons in solution and for electrons in the standard hydrogen electrode results in a semi-quantitative evaluation of the relative stabilities of educts, intermediates and products including charged states. This allows to derive a step-by-step mechanism of ORR as function of the electrode potential and pH.

This method will be applied to the electrochemical oxygen reduction on zinc oxide to identify the catalytically active surface site and propose a detailed catalytic cycle. The mechanism is validated by experimental observation of key intermediates using ATR-IR.

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In situ electrochemical AFM Investigation of Pt Surface during Potential Cycling

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Understanding the electrochemical behavior of platinum at solid/liquid interface is of great importance to the development of efficient electrochemical devices, such as fuel cells and water electrolyzers. In this work, the evolution of the surface morphology of a polycrystalline platinum under potential cycling condition was investigated by in situ AFM. The applied upper potential limit plays an important role. After 50 cycles between 0.05-1.8 V_{RHE} in 0.1 M H_2SO_4, the Pt surface is coarsened and nanoparticles of several nanometers appear on the surface, which might due to the dissolution-redeposition process of Pt. Increasing the upper potential to 2.0 V, both the roughness of the surface and the number of the nanoparticles increases. Further sweeping to a potential range of 0.05-2.5 V results in violent oxygen evolution reaction as well as the formation of nanoparticles within the size of 20 nm which covers the whole surface. More work is underway to illustrate the phenomenon on the Pt surface.

ATR-SEIRAS study of CO_2 electroreduction on Ag and Pt in an imidazolium-based ionic liquid

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The electrochemical reduction of CO_2 is being widely studied as a fossil fuel free method to produce hydrocarbon fuels. In aqueous media the reaction is inefficient due to the competing hydrogen evolution reaction, which proceeds faster on most metals[1]. Reports have claimed that imidazolium-based cations co-catalyze CO_2 reduction to CO, a key intermediate to hydrocarbons, with high faradaic efficiency at Ag electrodes[2,3]. However, the mechanism by which this happens is still poorly understood.

Surface-enhanced infrared absorption spectroscopy in the attenuated total reflectance mode (ATR-SEIRAS) is a surface sensitive technique used to study electrochemical interfaces[4]. It utilizes the enhanced IR absorption from molecules adsorbed on thin metal films to detect species at the interface with little interference from the bulk signal and no mass transport limitations. ATR-SEIRA spectra using a Ag thin film electrode in N_2- and CO_2- saturated 18 mol% 1-ethyl,3-methylimidazolium tetrafluoroborate (EMIM BF_4) at -1.5 V vs. Pt are shown in Figure 1. In the presence of CO_2, a negative peak at 2343 cm^{-1} confirmed the reduction of solvated CO_2, producing adsorbed CO (1936 cm^{-1}). An intense peak at 1316 cm^{-1}, absent in N_2-purged electrolyte, must correspond to either a reaction intermediate or an additional product of CO_2 reduction. Its frequency is typical for the symmetric stretching of a carboxylate. The absence of the corresponding asymmetric stretching suggests that it must correspond to a bridge-bonded adsorbed carboxylate. The spectral features between 1750 cm^{-1} and 1400 cm^{-1} in both experiments were assigned to potential-driven reorientations of the ionic liquid. Similar experiments were performed with Pt, but in this case only bands corresponding to adsorbed CO could be observed, and the band corresponding to an adsorbed carboxylate was absent.

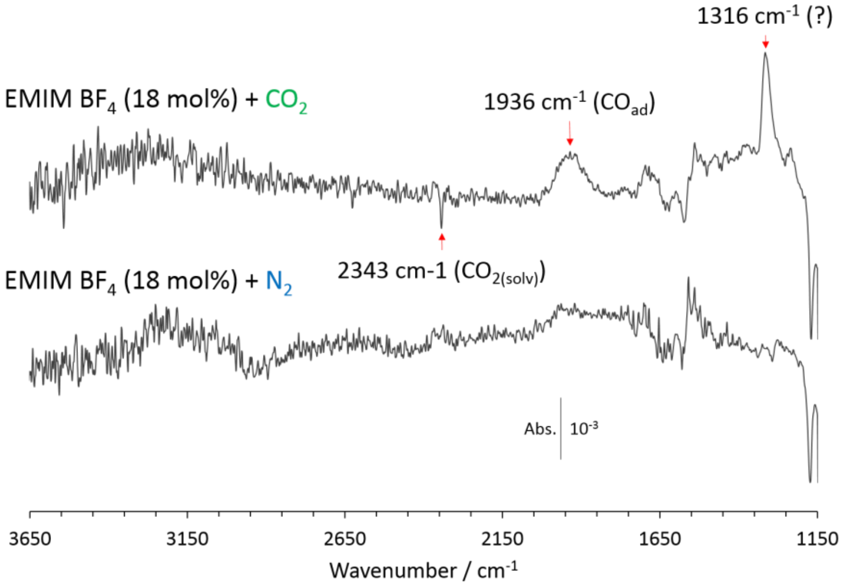

Figure 1. ATR-SEIRAS absorbance spectra of an Ag thin film electrode in N_2- and CO_2- saturated 18 mol% EMIM BF_4 at -1.5 V vs Pt wire.

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Model Electrocatalyst to Study the Anchoring of Pt on Carbon for PEFCs

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It is well known that catalysts in fuel cells undergo degradation, which limits the lifetime of the cell [1]. Many degradation mechanisms have been shown to take place, of which the two biggest contributors are Ostwald ripening and carbon oxidation [2]. In order to explain these degradation mechanisms, the anchoring of Pt with its carbon support needs to be better understood.

To study the above, a suitable systematic approach is required to investigate the mechanism by which Pt is anchored onto its carbon support. This can be achieved by indirectly studying anchor sites by monitoring the mechanism of degradation, as well as durability. In this study, highly ordered pyrolytic graphite (HOPG) was employed as a model substrate, which was further functionalized with different oxygen containing groups, viz. –OH and –COOH [3-6] to isolate potential anchor groups.

The 2-D HOPG system was treated with Fenton's reagent ($H_2O_2/FeSO_4$) or HNO_3/H_2SO_4 as chemical oxidants, to create vacancies within the sp^2 carbon structure, which are terminated with the relevant functional groups. Pt was sputtered at a loading of 20 – 150 $\mu g.cm^{-2}$ onto the modified HOPG substrate by DC magnetron sputtering. The system was then characterized by x-ray photoemission spectroscopy to confirm surface functionality, x-ray diffractometry to determine average Pt particle size and the phase of the surface layers, x-ray reflectometry to determine the thickness of the layer stack, Raman spectroscopy to confirm surface structure, and SEM-EDS mapping to visualize Pt agglomeration before and after cyclic voltammetry scans.

The system was then tested electrochemically, by running accelerated durability tests (ADT) [7] on the Pt/HOPG samples, as well as running Fe^{2+}/Fe^{3+} cyclic voltammograms to study the electrochemical changes of the surface modified HOPG substrates.

Surface measurements indicate an arrangement of Pt around islands of –OH groups on HOPG. This is further supported by the Fe^{2+}/Fe^{3+} redox couple exhibiting a reduced peak-to-peak separation for the -OH terminated HOPG compared to the other HOPG structures. This suggests an increase in the density of state of HOPG near the Fermi level [8], thus allowing for inner-sphere electron transfer and hence a greater affinity for Pt. Furthermore, ADTs show good agreement with the DFT work published by Matsutsu *et al.* [9] whereby Pt affinity follows the trend of –OH > –COOH > pristine.

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Bromate reduction at rotating disk electrode via autocatalytic redox-cycle mechanism: predictions vs. experimental data

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Because of a very high solubility of bromates and their 6-electron reduction to Br^- their concentrated solutions possess very high energy densities. In view of non-electroactivity of BrO_3^- anion within a large potential range its electroreduction can only take place via a mediator redox cycle. Our theoretical study [1-5] has demonstrated a surprising possibility to avoid additions of an external redox couple for its transformation. It has turned out that even a tracer amount of Br_2 inside an acidized concentrated BrO_3^- solution is able to catalyze efficiently its reduction.

Fig. 1 shows theoretical predictions for this system (EC" line) for the maximal current density, j^{max}, vs. the revolution frequency of the rotating disk electrode (RDE), f, in comparison with predictions for the conventional EC' system where the reduction is performed by an added redox couple, Ox/Red (EC' line). Unlike the latter which shows a monotonous change of j^{max} (the weaker the agitation, the lower is the current), the EC" line for the BrO_3^- + Br_2 system demonstrates an ***anomalous*** behavior within an intermediate range of frequencies where j^{max} ***grows drastically*** with ***diminution*** of the frequency.

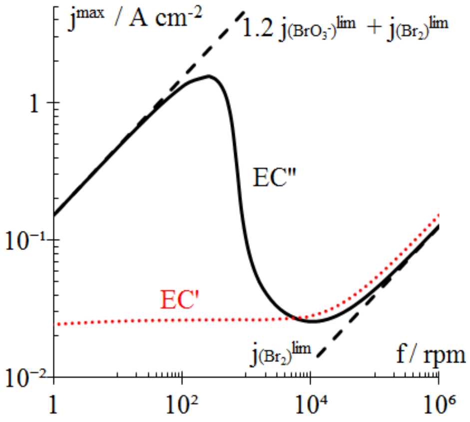

Fig. 1

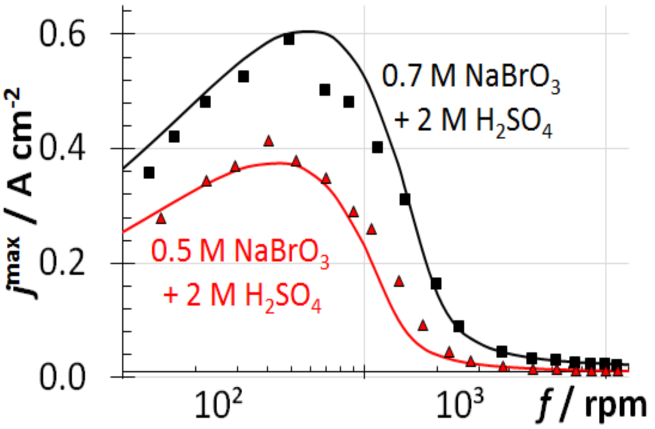

Fig.2

This astonishing feature is a direct consequence of the ***autocatalytic*** character of the process since BrO_3^- is transformed into components of the mediating redox couple, Br_2/Br^-, with their enormous accumulation inside the kinetic layer near the electrode surface.

Fig. 2 presents comparison of such unusual predictions with experimental data for two bromate solutions. The latter confirm both the existence of the anomalous behavior inside the expected range of rotation frequencies and a high intensity of the current near the maximum of each curve where it can even exceed the diffusion-limited current for BRO_3^- ion.

These results make this system prospective as oxidant for electric energy sources.

Acknowledgement: This work is supported by the Russian Science Foundation (grant № 15-13-20038).

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In situ Infrared Spectroscopic Study on Electrocatalysis of Ethylene Glycol Oxidation on Bare and Bi-Modified Pd Concave Nanocubes in Alkaline Solution

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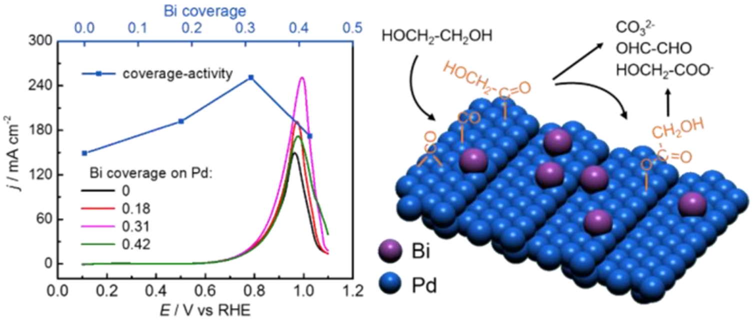
Anion exchange membrane fuel cells (AEMFCs) have gained extensive attention because of their ability to operate with catalysts composed of non-Pt materials in comparison with their acid counterparts[1-3]. Ethylene glycol (EG) as a fuel for AEMFCs is very attractive in considering its biomass nature, safety and high theoretical energy density. The electro-oxidation of EG in alkaline media on Pd nanocatalysts is directly relavant to the anode reaction of direct alkaline EG fuel cells. Also notable is that this anode reaction can work along with energy-saving hydrogen production by means of electroreforming EG in alkaline media. Therefore, it is very important to develop efficient Pd-based anode catalysts based on mechanistic understanding of interfacial chemistry of EG oxidation (EGO) occuring at Pd surfaces. High-indexed Pd nanocrystals provide a good platform for this purpose in considering their normally higher electrocatalytic activities in oxidizing small organic molecules.

Herein we report an in situ infrared spectroscopic study of electrocatalytic EGO in alkaline media on surface-cleaned high-index Pd concave nanocubes (Pd CNCs) with and without surface Bi modification. CO-adsorption displacement effectively removes the surfactants on as-synthesized Pd CNCs, facilitating controlled Bi adatoms formation. EGO on the Pd CNCs is notably enhanced as a result of Bi modification, with the activity peak at a Bi coverage of ca. 0.31 in terms of apparent and specific oxidation current densities. Internal (ATR-SEIRAS) and external (IRRAS) reflection modes of in situ infrared spectroscopy have been used to probe the EGO process at molecular level. High surface sensitivity ATR-SEIRAS enables to identify readily the formation and removal of CO and 2-hydroxyacetyl surface species during EGO on Pd CNCs and Bi-modified Pd (Bi/Pd) CNCs. Compared to that on bare Pd CNCs, the CO_{ad} band is significantly stronger on Bi/Pd CNCs, suggestive of a promoted C-C bond cleavage. IRRAS results further reveal that glycolate and glyoxal are the main products of EGO on both pristine and Bi/Pd CNCs. In addition, formations of glyoxal, CO and CO_2 on Bi/Pd CNCs are relatively enhanced, as compared to those on bare Pd CNCs. Based on the comprehensive spectral results and literature reports, relevant reaction pathways are proposed for EGO at Pd CNCs in alkaline media. Our work indicates that high-index Pd nanocrystals modified with a Bi adlayer may serve as a promising catalyst for EGO in alkaline media once their sizes are scaled down to a few nanometers.



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Cations at the Interface during CO_2-to-Fuels Catalysis: Spectators, Inhibitors, or Activators?

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While planar electrified metal surfaces mediate the synthesis of fuel products from CO_2, including methane, ethylene, and various alcohols, these processes suffer from moderate current densities and Faradaic efficiencies [1]. Introduction of high surface area and/or defect-rich electrodes enhance both the rate and efficiency of desired CO_2 reduction transformations [2]. In addition to changes in the ex-situ preparation of the electrode, CO_2 reduction rates also benefit from the presence of larger cations in the aqueous electrolyte. For example, exchanging CO_2-saturated $CsHCO_3$ for CO_2-saturated $LiHCO_3$ increases CO production Faradaic efficiency by 20% on Ag surfaces and ethylene Faradaic efficiency by 30% on Cu surfaces [3]. However, the detailed picture of the cations near or at the electroactive surface remains unclear; do they actively participate in the steps leading up to and including the rate-limiting step of CO_2 reduction catalysis? Efforts to determine the role of cations suffer from the lack of a spectroscopic signature corresponding to the hydrated cation under catalytically relevant conditions [4].

In this talk, we uncover the kinetic role of cations on polycrystalline Ag surfaces during catalysis and determine that the cations are active participants in the catalytic cycle using electrokinetic investigations, in-line gas chromatography, impedance spectroscopy, and in-situ Surface Enhanced Infrared Absorption Spectroscopy. The concentration-dependence of cations on both the desired reaction, CO evolution, and the parasitic side reaction, H_2 evolution, are studied for the first time. Under conditions of CO_2 reduction catalysis, we identify that increasing cation concentration at fixed electrolyte strength enhances the rate of CO_2 reduction catalysis regardless of the identity of the cation, **Figure 1**. Conversely, we find that the simultaneously occurring H_2 evolution is inhibited by increases in the concentration of cations. We also find that the capacitive behavior of the Ag surfaces changes drastically as a function of cation concentration regardless of identity. The consequences for all these observations in terms of interfacial structure, CO_2 reduction mechanism, and catalyst design will be discussed.

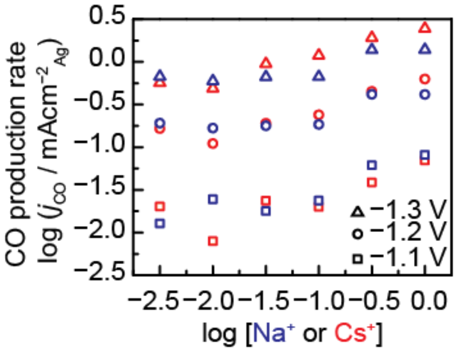

Figure 1. CO production rate from CO_2 increases as a function of the concentration of Na^+ (blue) or Cs^+ (red) in fixed total 1.1 M electrolyte strength at applied potentials of –1.1 V (squares), –1.2 V (circles), and –1.3 V (triangles) vs SHE on Ag surfaces.

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Chromocene Redox Reaction at Ag(111)-Ionic Liquid Interfaces

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Room temperature ionic liquids are an important type of solvent in electrochemistry because of their wide electrochemical windows, reasonably good conductivity and non-volatility. Combined characterizations on single crystal electrode-ionic liquid interfaces by microscopic and spectroscopic techniques have revealed that the anisotropic cations of the ionic liquid molecules can form ordered adsorption at surface and arrange along the surface normal to form layered structure [1, 2]. The size and orientation of the cations further modify the fine structure of the electric double layer structure of the interface. These distinctive features may have profound influence on the kinetics of charge transfer process taking place at the interface. Investigations on electrochemical reactions in ionic liquid media have been carried out to testify the validity of conventional electrochemical kinetics theory[3, 4] or predict influence of the double layer structure on the reaction kinetics[5] in ionic liquids. However, the structural correlation of reaction kinetics is hindered by the lack of experiments for kinetics studies using well-defined electrode-ionic liquid interface. Almost all of the reported works were carried out using polycrystalline or amorphous electrodes, which loose the distinctive features of ordered adsorption and layered structure and cause complexity for analysis on the basis of theoretical model.

In this paper, we report a study on the reaction kinetics of chromocene (Cc) at interfaces of Ag(111) electrode and imidazolium-based ionic liquids with different length of the side chains. The Ag(111) electrode undergoes no surface reconstruction and is stable upon immidazolium adsorption, allowing the kinetic investigation at well-defined interfaces. By employing fast cyclic voltammetry, electrochemical impedance spectroscopy and classical electrochemical kinetic formulas, standard rate constant as well as symmetry factor are measured with dependency on the length of the imidazolium. Based on the understanding of the detailed structure of the electric double layer of the interface, possible structural influences on the measured kinetic parameters are discussed.

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At the Electrode/Electrolyte Interface of Aqueous Solar Cells: a Photoelectrochemical and Chemometric Investigation

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In recent years, with the idea of creating efficient, safe, and low-cost dye-sensitized solar cells (DSSCs), the research moved the attention towards alternative solvent-based electrolytes. Above all, DSSCs with water-based electrolytes have been proposed as one of the possible solution, providing reduced costs, non-flammability and environmental compatibility [1]. Recently, we demonstrated that stability issues can be properly addressed by choosing the appropriate dye [2,3]. Moreover, the possibility of gelling the liquid solvent into a polymeric matrix can reduce the electrolyte leakage outside the device, increasing the long-term stability [4].

In this contribution, the investigation on a series of iodine and cobalt-based 100% aqueous electrolytes is presented to improve the photoanode/electrolyte interface in the emerging solar energy converters. Thanks to our previous experience and to a multivariate approach (design of experiment, DoE), the effects of the change in redox mediator concentrations and in photoanode preparation on DSSCs performances have been evaluated. Finally, the gelation of the best aqueous electrolytes with bio-derived polymers has been performed. Photovoltaic performances and stabilities will be discussed by comparing liquid and gel electrolytes. In lab-scale solar cells interesting photovoltaic performances superior to 4% were achieved.

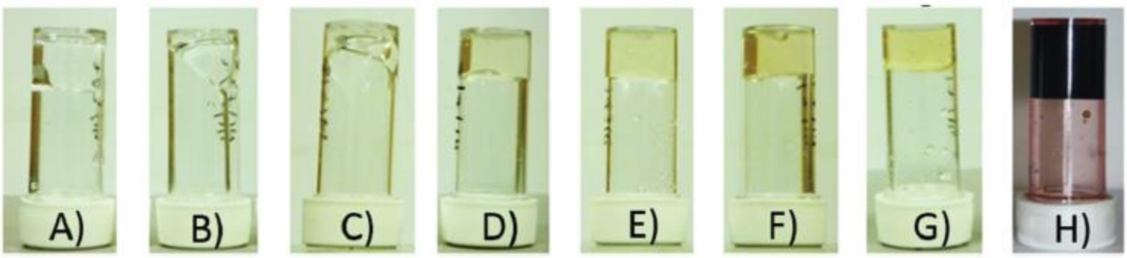

Fig. 1 - Gel electrolytes containing 0.5 M aqueous NaI and 3.5 (A), 5 (B), 7.5 (C), 10 (D), 12.5 (E), 15 (F) and 20 wt% (G) of carboxymethyl_cellulose sodium salt. The image of a gel electrolyte containing 0.5 M aqueous NaI, 30 mM I_2 and 10 wt% CMC is also shown (H).

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Bromate reduction at rotating disk electrode via autocatalytic redox-cycle mechanism

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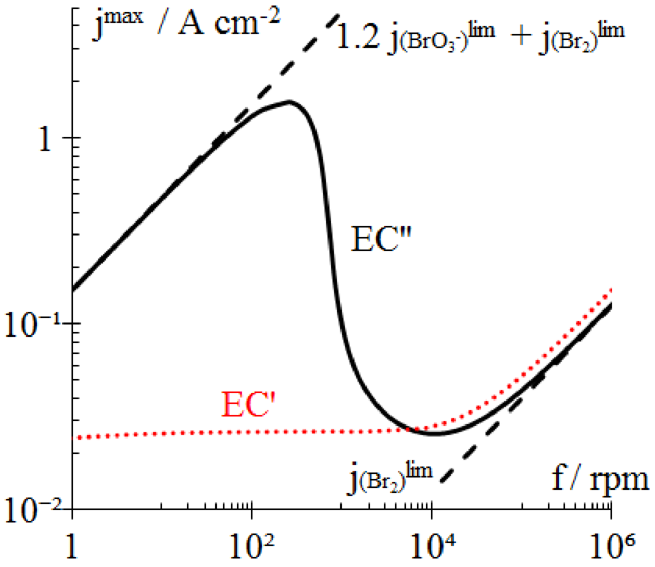
In view of non-electroactivity of BrO_3^- anion within a large potential range its electroreduction can only take place via a mediator redox cycle. In this study it has been analyzed on whether the Br_2/Br^- couple can play this role efficiently for a very low Br_2 concentration in bulk solution. Under strongly acidic conditions Br^- ions produced at the electrode from Br_2 react with BrO_3^- ions inside the solution phase, with regeneration of Br_2 which can participate again in the electrode reaction [1].

Theoretical analysis of this process has been carried out for the steady-state one-dimensional system corresponding to this reaction at rotating disk electrode (RDE) [2-5]. The set of convective-diffusion equations for all components of the system (BrO_3^-, Br^-, Br_2', H^+) coupled with nonlinear chemical-reaction terms has been solved both numerically and analytically [6,7]. The results obtained are radically different from predictions of the conventional redox-mediator catalysis (EC' mechanism) where the current is proportional to the bulk concentration of the mediator component, i.e. it vanishes for its very low concentration. On the contrary, our analysis has proven that under certain conditions the current can reach very high values (comparable with the diffusion-limited current for BrO_3^-) even for ***tracer*** amounts of Br_2 in the bulk solution (lines in figure show predictions for the "maximal current" j^{max} for each rotation frequency f). Besides, contrary to predictions for the other mechanisms (including the EC' one) the current for the bromate system ***increases drastically*** for ***less intensive agitation*** (i.e. for ***lower*** RDE frequency) within a certain range of frequencies (EC'' and EC' lines in figure).

These unique features are originated from the ***autocatalytic*** character of the process, i.e. owing to transformation of Br atom of bromate anion into components of the catalytic Br_2/Br^- couple so that passage of the comproportionation reaction leads to progressive accumulation of these species, with autocatalytic increase of the current up to the maximal limit of 1.2 $j_{(BrO3-)}^{lim}$ + $j_{(Br2)}^{lim}$, where $j_{(BrO3-)}^{lim}$ and $j_{(Br2)}^{lim}$ are diffusion limited currents for BrO_3^- and Br_2 (see figure).



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Double layer effects on CO adsorption and oxidation on Pt(111)

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Adsorption and reaction at the electrode-electrolyte interface take place in an interfacial region known as the electrical double layer (EDL). Traditionally, the EDL is divided into two separate spatial regions, an inner or Helmholtz layer, and an outer diffuse or Gouy-Chapman layer [1]. The electrode surface charge is effectively screened by the counter charge in the EDL, and hence the potential drop between (metal) electrode and the electrolyte effectively occurs within this EDL [1,2]. The thickness of the diffuse layer is expected to increase with the concentration of ionic species on the electrolyte and vicinity of the electrode, and as consequence the potential drop (and the electric field) will be different for different electrolyte concentrations[2]. Understanding how the EDL structure and properties will affect the electrochemical reactions is an aspect of sum importance in electrochemistry. However, the main research done in this subject is normally devoted to electron transfer reactions [3,4,5] and there are only few studies concerning electrocatalytic reactions [6].

The most frequently used model reaction in electrocatalysis is, without doubt, CO adsorption/electro-oxidation on Pt electrodes. CO adsorption and oxidation is well described in literature for Pt electrodes [7] and moreover, the reaction can be followed by spectroscopic methods allowing the in-situ observation of the CO/Pt interactions when changing the structure of the double layer.

In this work, by means of Fourier Transformed Infrared Spectroscopy (FTIR) and cyclic voltammetry (CV) we studied the influence of the diffuse double layer structure on the CO adsorption and oxidation on Pt(111) electrodes, in aqueous media, by changing the supporting electrolyte concentration. Interestingly, we find that both CO adsorption (in terms of its C-O vibrational Stark tuning rate) and CO monolayer oxidation exhibit no diffuse double layer effect, similarly to the effects observed for organic solvents in previous works by Weaver et al []. According with our interpretation, the existence of a monolayer of CO adsorbed on the Pt(111) surface totally changes the EDL structure and the potential (electric field) drop is dominated by the CO forming a Helmholtz like structure independent on the diffuse layer thickness [9].

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Surface force versus carrier concentration measurements of glyme lithium electrolytes

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In “soggy sand” electrolytes (insulating oxide nanoparticles dispersed in typically organic lithium salt solution), lithium conductivity is enhanced (and anion conduction depressed) in the space charge zones due to the coupled effects of anionic adsorption and association-dissociation equilibrium.[1-2] This study elucidates the interfacial layering and long-range electrostatic forces in pure and Li-salt (lithium triflate, LiTf) containing glyme (poly(ethylene glycol) dimethyl ether, PEGDME, Mw = 150 g mol^{-1}) electrolyte on cleaved mica.

Surface force apparatus measurements of pure PEGDME on mica initially show no layering or surface interaction. However, pronounced interfacial structuring occurs in time (after 30 minutes) with compression profiles indicating immobilized polymeric brush like structures (up to 10 nm in size as calculated from de Gennes theory), most probably a consequence of complexation of surface K^+. Upon addition of LiTf, the interfacial structure appears to drastically change with the molecularly structured electrical double layer below 15 nm.

The presence of different ionic species and their concentration (free ions, ion pairs, dimers) in the electrolyte bulk are determined from the infrared stretching band of triflate.[3] Addition of mica to LiTf+PEGDME-150 enhances the ion pair dissociation resulting in higher concentrations of free ions in agreement with the “soggy sand” theory. Preferential anion adsorption is additionally confirmed by negative Zeta potential values at all mica vol%.

Information on the electric double layer obtained by surface force measurements is compared to infrared spectroscopy. The discrepancy obtained in terms of effective screening length is discussed.

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Effect of Selective Adatom Decoration at Steps of Pt Model Surfaces on the Oxygen Reduction Reaction

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Oxygen reduction reaction (ORR) is arguably the most important reaction in electrocatalysis. However, its reaction mechanism still remains unclear, since it involves the participation of several intermediates which are difficult to detect by using the currently available experimental techniques. The detailed investigation of the mechanism on model surfaces in singular potential ranges can shed light about this topic.

In this work, the ORR in 0.1 M $HClO_4$ is studied at Pt(S)[(n-1)[(111)x(110)] stepped surfaces in order to analyze the effect of the role of the steps. On Pt(111), at potentials below 0.3 V, oxygen only can be reduced to hydrogen peroxide, since hydrogen adsorption hinders the O-O bond scission by blocking the active surface sites [1]. This current drop takes place in two steps. However, the limiting current density corresponding to the complete reduction of oxygen to water is almost recovered for a terrace length of 5 rows of atoms (Fig. 1A). It could be proposed that for shorter terraces, almost all the produced H_2O_2 molecules can travel to the steps, where they can be reduced to water, while for longer terraces not all the H_2O_2 molecules can reach the steps before diffusing away to the solution.

To check this hypothesis we use selective decoration of the step sites by Bi or Te adatoms [2]. If the adatom blocks the step site, which is the active site for H_2O_2 reduction at these potential values, a diminution in current should be observed, as figure Fig. 1B demonstrates. By comparing the measured current at potentials before and after the second current drop, it could be observed that for terraces longer than 7-8 atomic rows, the decorated stepped surfaces show an inhibition similar to that measured on Pt(111) electrodes (Fig. 1C). Remarkably, this inhibition diminishes progressively for shorter terraces. This is because Bi does not deactivate totally the steps toward H_2O_2 reduction, giving rise to the volcano-type behavior shown on Fig. 1D. Experiments in the presence of hydrogen peroxide confirm these observations. This study points out the surface mobility of H_2O_2 intermediate generated at the {111} terraces, an aspect that has not been considered yet, which can travel through the terraces to the {110} steps or diffuse away to the solution, as a function of the terrace length.

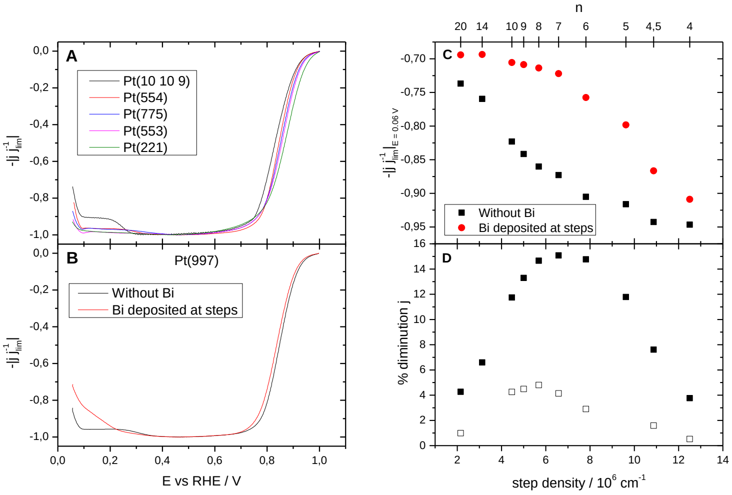

Figure 1. Polarization curves for the ORR on different Pt(S)[(n-1)(111)x(110)] stepped surfaces in 0.1 M $HClO_4$; 50 mV s^{-1}, 2500 rpm (A); ORR for Pt(997) without Bi and with Bi deposited at steps (B); normalized current densities at E = 0.06 V as a function of the step density (C); % of current density diminution by using Bi step decoration for E = 0.06 V (solid squares) and E = 0.15 V (open squares) (D)

Acknowledgments

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Shooting the Next Films: Focus on Preferentially-oriented Metal Alloy Electrocatalysts Prepared with Pulsed Laser Deposition.

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The simultaneous control of surface crystal orientation and composition of metal alloys represents both a formidable challenge and a vital prerequisite to designing tailored electrocatalysts. Selecting a preferential orientation can dramatically enhance surface-sensitive reactions, while strain and ligand effects in alloyed films can unlock surprising catalytic properties. Adopting a bottom-up approach, pulsed laser deposition (PLD) enables the epitaxial growth of metallic films on well-ordered substrates, thus leading to the formation of preferentially-oriented surfaces. As an additional advantage, the experimental conditions typical of PLD allow obtaining kinetically stable alloys even in the “miscibility gap” of the phase diagram [1,2], thus opening up a promising avenue for metal electrocatalysis.

In this work, PLD was employed to deposit thin-film alloys onto well-ordered MgO(100) substrates; Pt was combined with a second metal (Rh, Ru or Ir), and the experimental conditions during PLD were optimized to obtain an alloy having a preferential (100) orientation, as confirmed by structural characterization (XPS, XRD and AFM) [3]. These alloys were investigated with electrochemical probes (H adsorption, CO stripping, NO_2^- reduction), referring to pure metal films as benchmarks to rationalize the voltammetric features of bimetallic systems. In the case of Pt, these experiments highlighted the presence of short terraces and step sites of (100) orientation, while higher deposition temperatures and an increased film thickness favored the growth of longer (100) terraces [4]. Similarly, H and OH adsorption at Ir evidenced the extensive presence of (100) surface domains. Instead, PtIr alloys featured voltammetric signals combining the shape and the position typical of both pure metals [3].

Such “hybridization” of the two alloyed metals was also observed with respect to the electrocatalytic activity, resulting in an unexpected, enhanced response of $Ir_{75}Pt_{25}$ towards nitrate reduction in H_2SO_4. The introduction of Pt minimizes the severe poisoning affecting nitrate reduction at pure Ir, while preserving the remarkable catalytic activity of Ir and the high onset potential recorded for Pt(100). Additionally, CO stripping can effectively reactivate $Ir_{75}Pt_{25}$ surfaces poisoned by repeated cycles, while this method did not allow the recovery of the activity of the Ir electrode. These properties were rationalized in terms of a mutual shifting of the electronic levels of the two metals induced by alloying (ligand effect). Finally, thin-film Pt-M alloys were tested for their activity towards the oxidation of dimethylether, a reaction of potential interest for fuel cell applications that is strongly promoted on defect-free Pt(100) terraces.

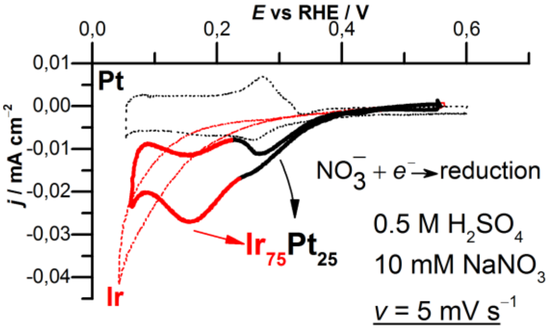

Figure 1: The voltammetric response of an epitaxially-grown $Ir_{75}Pt_{25}$ alloy towards nitrate reduction in H_2SO_4 (bold line), compared to the voltammograms recorded for the pure metals (red dashed line, Ir; black dashed line, Pt).

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[4] M Duca *et al.*, Thin-Film (100)-Alloy Electrocatalysts Prepared by Pulsed Laser Deposition: the Nitrate Reduction Activity of PtRh and PtIr, *in preparation*

Understanding and Tailoring the Performance of Transition Metal Oxides for the Oxygen Evolution Reaction

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The oxygen evolution reaction (OER) is a bottleneck in direct solar and electrocatalytic water splitting cells, and rechargeable aqueous metal-air batteries. Improving the cost-efficiency of these devices requires development of efficient and cheap oxygen evolving catalysts. A good catalyst material should fulfil several important criteria: the composition and structure should be stable at conditions of interest, it should be able to conduct electrons from the active site, and it should be sufficiently active to catalyze water oxidation to oxygen. Furthermore, the catalyst should be cheap and non-toxic.

We explore two different oxide classes: pristine and doped perovskite oxides (ABO_3, where A is the alkaline earth or lanthanide metal and B the 1st row transition metal) and several MnO_2 polymorphs.
Stability and the electronic conductivity of doped materials are assessed and compared to pristine catalysts by computing formation energies and analyzing the electronic structure of bulk crystals, respectively. After selecting stable dopants, we calculate the relevant surface termination and deduce the reaction overpotential from the energetically most favorable reaction mechanism.

For the perovskite oxides, we observe an inverse correlation between the OER activity and stability such that the most catalytically active $LaCrO_3$ and $CaFeO_3$ oxides are not sufficiently stable and will readily dissolve under operating conditions. We identify Fe^{4+}, Co^{3+}(IS), Ni^{3+} and Mn^{3+}/Mn^{4+} pairs as electronically conductive species and distinguish among three different electron conduction types: intrinsic conductance (Fe^{4+} and Ni^{3+}), electron polaron hoping along the Metal-Oxygen-Metal chains (Mn^{3+}/Mn^{4+}) and conduction via oxygen holes in the valence band. Although, the intrinsic stabilities of La perovskites are rather low, they are likely to be the most stable catalysts in open systems because they do not form carbonates that occur readily for alkaline earth metal oxides. From a combinatorial analysis on La perovskites, we identify Cu doped $LaMnO_3$, Mn doped $LaCuO_3$ and $LaCoO_3$ and Ni doped $LaCoO_3$ as the most promising oxygen evolving catalysts.

We find that the oxygen evolution activity of MnO_2 polymorphs reduces in the $\alpha MnO_2 > \beta MnO_2 > \gamma MnO_2$ sequence. We pinpoint αMnO_2 as the most active catalyst and subsequently investigate whether its performance can be improved by doping. The electronic conductance is greatly improved by creating Mn^{3+} sites, i.e. Mn^{3+}/Mn^{4+} pairs, which is accomplished by intercalating electrolyte ions (e.g. Na^+ or K^+) inside αMnO_2 holes. From the catalytic analysis, we identify Pd doped αMnO_2 as the most active catalyst for oxygen evolution.

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Production of Reactive Oxygen Species during ORR.
SECM and Spectroscopic Investigations.

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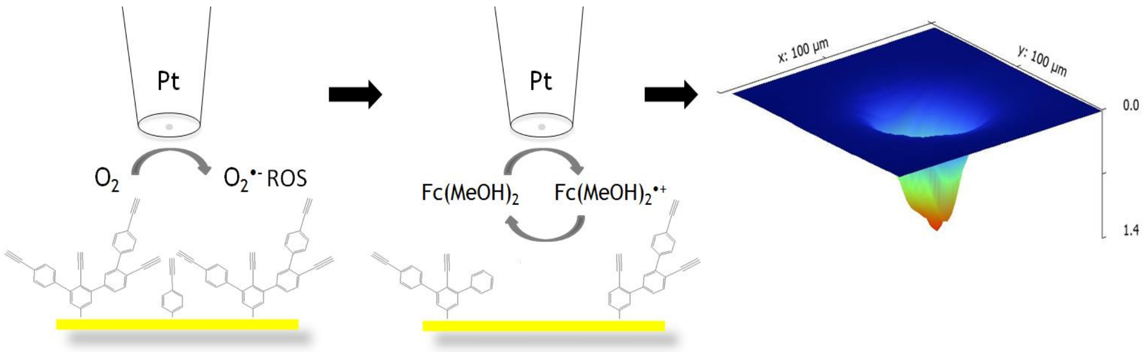
Multi-electronic O_2 reduction reaction (ORR) and its catalysis are of general importance in natural and industrial processes. ORR could involve the concomitant production of different intermediates corresponding to the different redox states of O_2. Among them, some intermediates are especially aggressive like OH radical and must be avoided in practical applications. Recent literature has also shown that in some conditions, ORR on a Pt electrode could be accompanied by the electrochemical dissolution of the Pt electrode when O_2 is reduced. [1,2]

To get more insights about ORR and associated reactions, we used a “footprinting” strategy based on the use of a sensitive surface and feedback mode SECM to evidence the formation of reactive oxygen species during the ORR.[3] The principle of the method is depicted on the following scheme: O_2 is reduced at a tip electrode that is localized in the vicinity of a test substrate composed of a conducting substrate (glassy carbon) covered by a sensitive organic layer. In a second step, the local transformation of the layer is read with an indifferent redox mediator providing a view of the reactivity of the produced intermediates.



ORR was investigated in different solvents (Water, DMF) as function of different experimental parameters (pH, potential, additives…). Surface Raman studies (SERS) have been performed to identify a possible relation between ROS production and Pt dissolution.

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Anatase and amorphous TiO_2 Nanotube Anodes for Li-Ion Batteries: XPS and Impedance Study of Lithiation and Delithiation

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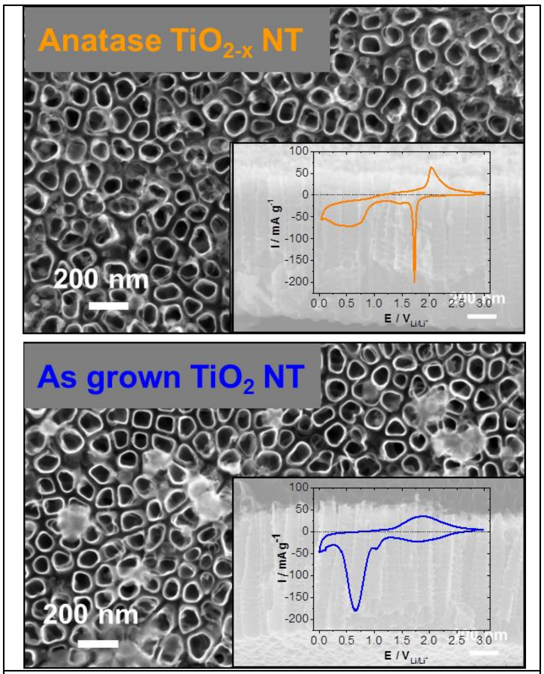

Figure 1: SEM images of anatase and as-grown TiO_2 NTs with the corresponding CVs in EC/DMC electrolyte with $LiPF_6$.

Lithium (Li) ion batteries have been used in a wide variety of portable electric devices due to their high energy densities. Since several years, research for anode materials is addressed to titanium dioxide (TiO_2), which offers important advantages in terms of cost effectiveness, safety and environmental compatibility. The Li insertion potential of TiO_2 is between 1.2 V and 2.0 V vs. Li and lies within the stability window of common organic electrolytes, which leads to superior safety. TiO_2 shows a very low volume change during cycling, which leads to high cycling stability, high rate, low-temperature charge/discharge capability and high thermal stability in both the charged and discharged state. Therefore, self-organized anodic TiO_2 nanotubes (NTs) are a promising anode material which, in addition to the above mentioned advantages, allows one-dimensional electronic and ionic conductivity, short pathways for Li-ion diffusion and high tolerance to structural changes.[1]

In this work, the surface chemistry during lithiation and delithiation is monitored using X-ray photoelectron spectroscopy (XPS). Based on the XPS results a model for electrochemical impedance spectroscopy (EIS) analysis is developed to investigate intrinsic kinetic and thermodynamic electrochemical properties of the lithiation/delithiation reaction.

It is confirmed with cyclovoltammetry and galvanostatic cycling that amorphous TiO_2 NTs demonstrate an enhanced performance in Li-ion batteries compared to anatase TiO_2 NTs which is a known phenomenon.[2] The present work shows that the reason for this enhanced performance can be understood with the help of EIS and XPS studies performed under quasi-stationary conditions where both thermodynamic and kinetic properties of the nanotubular materials during lithiation and delithiation can be separately extracted. For amorphous TiO_2 NTs, in a potential range between 3.0 and 1.1 V_{Li}, more adsorbates (mainly $LiCO_3$ and LiF) from the electrolyte are formed at the surface when compared to anatase TiO_2 NTs. The conductivity of the surface films thereby increases due to the presence of large amounts of LiF at potentials of $\leq 2.0\ V_{Li}$, most likely through Li-ion transfer from LiF into the space charge zones of TiO_2.[3] The charge transfer resistance is found to be much lower and more reversible during cycling, and the solid-state diffusion of Li-ions is faster in amorphous TiO_2 NTs.

The use of XPS and EIS has been shown to be a powerful combination for fundamental understanding of lithiation/delithiation characteristics of nanotubular TiO_2 anode materials for Li-ion batteries.

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Spectroscopic Evidence of Cation-Dependent Potential-Induced pH Changes during CO_2 Electroreduction

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One of the major challenges in the electrochemical reduction of CO_2 in aqueous solvent is the competing hydrogen evolution reaction which occurs at about the same potential at which CO_2 is reduced. This process not only competes with the CO_2 reduction process but increases the local pH at the cathode, due to the loss of protons to which CO_2 reduction itself also contributes. The optimal pH for CO_2 reduction has been found to be about 7, however, as the overpotential increases, increasing H^+ depletion causes the pH to increase to as much as 9 or 10. Carbon dioxide is consequently then converted first to bicarbonate and then to carbonate, thereby reducing the amount of CO_2 available for reduction and hence the efficiency of the process [1].

The nature of the electrolyte cation has been found to affect the faradaic efficiency and selectivity of the CO_2 reduction process [2–6], and attempts have been made at explaining this effect. Singh et al. recently attributed it to the cation size [7]. According to them the pK_a of the hydrated metal cation decreases close to the cathode. This decrease is larger the larger the cation, and results in a buffering effect close to the electrode surface. The buffering ability would decrease, hence, in the order of $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

We have tested this hypothesis by probing the local pH of the cathode in-situ using ATR-SEIRAS. The ratio between the integrated intensity of the CO_2 and HCO_3^- bands, which has to be directly proportional to the pH, provided a means of determining the change in the interfacial pH during CO_2 eletroreduction. Our results confirm that the magnitude of the pH increase at the interface follows the trend $Li^+ > Na^+ > K^+ > Cs^+$, adding strong experimental support to Singh et al.'s hypothesis.

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Following ion content within charged micropores of bimodal carbide-derived carbons using small angle neutron scattering

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Given that the kinetics of ion insertion into and adsorption within micropores are two foundational phenomena in charging and discharging of electrochemical double layer capacitors, methods must be developed to characterize ions within micropores of charged porous materials. Here we will discuss the use of electrochemical small angle neutron scattering (ecSANS) to characterize ion insertion into micropores of Mo_2C and SiC derived carbons from imidazolium based-salts in acetonitrile using the Extended-Q SANS instrument at the Spallation Neutron Source (SNS-ORNL). Effects of ion insertion into micropores were also followed as a function of alkyl chain length of the imidazolium cation, e.g. EMIM vs HMIM (ethyl vs hexyl).

The scattering within the micropores was found to be sensitive to the applied potential as shown in Figure 1. The changes in scattering intensity suggest that ions of the opposing charge do not simply enter and displace the solvent, rather there is a convolution of effects. EMIM was shown carry more of the charge than the anion (TFSI) by the increase in the scatter length density (SLD) difference between the electrolyte within the pores and the carbon walls. The larger cation (HMIM) was found to enter into the micropores at large negative potentials ($E < -1$V). At potentials less negative than -1V, the anion seems to preferentially carry the charge balance.

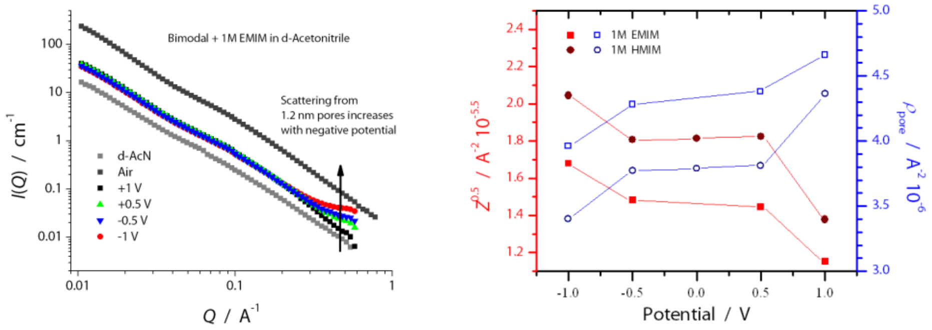

Figure 1: a) SANS of the Mo2C CDC empty, filled with d-Aceonitrile, and electrolyte at different states of charge; b) Scattering invariant along with estimated SLD of the electrolyte within the micropores.

Understanding Methanol Electro-Oxidation Mechanisms on RuO_2(100) Surface at Atomic and Molecular Level by Combined Studies of *in-situ* FTIR Spectroscopy and DFT Atomistic Modelling

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Direct methanol fuel cell (DMFC) has been regarded as a promising alternative for the power supply for portable, automotive and stationary applications, and has attracted increasing interests recently. To date, platinum still remains the central catalyst in fuel cells, although the CO_{ads} poisoning issue affects its efficiency seriously. Ruthenium is a critical additive for enhancing the activity. Binary PtRu catalysts have shown the highest activity towards methanol oxidation. A general bi-functional mechanism was proposed for interpreting the promoting roles of Ru because it can provide oxygen-containing species derived from water dissociation at remarkably lower potentials than pure platinum, and thus facilitates CO_{ads} oxidation to CO_2. Reactivity of Ru towards electrooxidation of CO and other C_1 molecules has also been reported, however the mechanisms of the surface reactions are still unclear.

Ru is a versatile catalyst in heterogeneous catalysis and electrocatalysis. The electrochemical behaviour of the well-defined Ru single crystal surfaces and the reactivity of the Ru surfaces towards small organic molecules have been studied systematically. It has been found that low coverage surface (hydro-)oxide (2 x 2)-O(H) is inactive towards CO_{ads} oxidation, whilst higher coverage surface (hydro-)oxide (1 x 1)-O(H) is active towards CO_{ads} oxidation, but still inactive towards methanol oxidation. However, it is very interesting to find out that the RuO_2(100) phase formed at higher potential is active towards CO and methanol oxidation. In-situ FTIR data showed that methanol was oxidized to CO_2 via direct pathway without CO_{ads} formation. High level density functional theory (DFT) calculations and ab initio molecular dynamics (MD) simulations were performed to gain an insight into the methanol oxidation mechanisms. The overall mechanisms have been identified as: $CH_3OH^* \rightarrow CH_3O^* \rightarrow HCHO^* \rightarrow HCH(OH)_2^* \rightarrow HCHOOH^* \rightarrow HCOOH^* \rightarrow \text{mono-}HCOO^* \rightarrow CO_2^*$, which are very different from those on metal surfaces where CO formation is inevitable. The coupling between $HCHO^*$ and one water molecule forming $HCH(OH)_2^*$ is the key step for the following reactions. Aqueous environment is found to stabilize mono-$HCOO^*$ effectively via hydrogen bonding between the dangling O atom and water molecules, making the higher stability and activity of mono-$HCOO^*$ than bi-$HCOO^*$ for CO_2 formation. This theoretical understanding of surface oxidation mechanisms of C1 molecules would help understand the more complex electro-catalytic processes of other small organic molecules on metal oxide surfaces.

Insight in the Formic Acid Oxidation Mechanism on Platinum from Computational and Experimental Results

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The formic acid oxidation is a very relevant reaction, especially in connection with the fuel cell technology. Formic acid can be used as a fuel, and also its oxidation process can be used as a model reaction to understand the oxidation of more complex fuels, such as methanol or ethanol. Despite the apparent simplicity of the considered reaction, because only 2 electrons are exchanged, a detailed mechanism explaining all the available evidences on platinum has not yet been described. Under the accepted mechanism, two parallel pathways, which are sensitive to the surface structure, have been confirmed. One of them involves adsorbed CO as poisoning intermediate and the second one goes through an active intermediate, which readily evolves to yield CO_2. In this communication, we shed light in to the oxidation mechanism using experimental and computational results. In the first place, the mechanism for CO formation will be studied. Using the potential and surface structure dependence of the reaction giving rise to the formation of CO in combination with DFT calculations, we will propose a detailed mechanism for this step. It will be shown that this step requires the simultaneous adsorption of OH and H on the surface, explaining the experimental observation that CO is only formed in a potential region centered on the potential of zero free charge [1].

On the other hand, the identification of the active intermediate has been difficult and elusive. Adsorbed formate was detected by in situ surface-enhanced IR absorption spectroscopy (SEIRAS), and for that reason was proposed as the active intermediate [2]. However, other experimental results suggest that adsorbed formate would not be an active intermediate, but a mere spectator. Additionally, the surface structure dependence and pH effects [3-5] have not been sufficiently addressed. The combination of DFT and new experimental results will serve to establish the role of adsorbed formate and also the identification of the active intermediate.

Acknowledgments

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Computational Ag/AgCl reference electrode from density functional theory-based molecular dynamics

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A DFTMD method has been recently developed[1-3] for calculating redox potentials, and direct comparison with experiment is enabled by a computational design of standard hydrogen electrode (SHE) potential. Although SHE is a common choice for potential reference in aqueous solution, its use in non-aqueous solutions including ionic liquids[4] is often limited. For the latter case, the Ag/AgCl reference electrode appears more widely used. Therefore, there is a need to develop an alternative reference electrode for calculating redox potentials in non-aqueous system.

We develop a reversible scheme to compute the insertion free energy of a chloride ion in solution using DFTMD, which can be converted into a potential reference of the Ag/AgCl electrode, similar to the computational SHE. As a starting point, this reference electrode is calculated and validated in the aqueous solution by comparing with the previously developed computational SHE. We find a small error of less than 0.1 V. Figure 1 below shows the thermodynamic cycle used to calculate the potential of the Ag/AgCl (1 M Cl^-) reference electrode with respect to SHE.

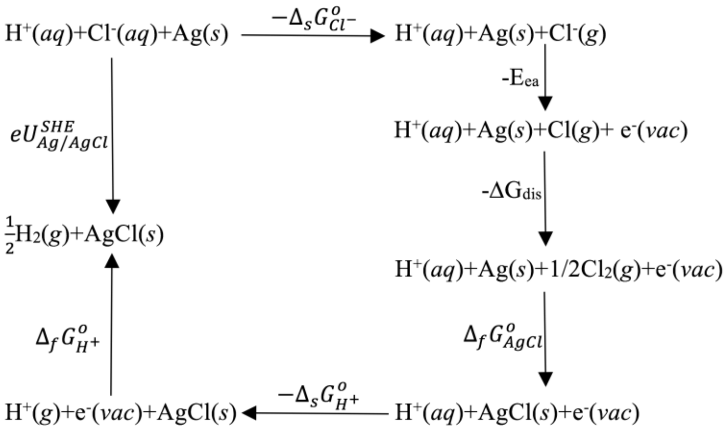

Figure 1. Schematic representation of the thermodynamic cycle of the redox potential, $eU^{SHE}_{Ag/AgCl}$, of Ag/AgCl (1 M Cl^-) with respect to SHE. E_{ea} is the electron affinity of Cl, ΔG_{dis} is the dissociation energy of Cl_2 in gas phase, $\Delta_f G^o_{AgCl}$ and $\Delta_f G^o_{H^+}$ are standard energies of formation of AgCl and proton, respectively. The notation of solvation energies of Cl^- and H^+ are $\Delta_s G^o_{Cl^-}$ and $\Delta_s G^o_{H^+}$, and they were calculated by using the DFTMD method.

This Ag/AgCl reference electrode will be applied to non-aqueous solvents in the future. The calculated redox potential will be used to validate the experimental results and predict redox potentials in non-aqueous systems.

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Dynamics of Surface Phases - the Nuts and Bolts of Rational Design of Binary Alloy Catalysts

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Power generation in fuel-cell-based devices is among the most pressing issues stimulating electrocatalytic research in recent decades. Both experimental and theoretical approaches have clearly outlined the potential of nanoparticulate metal alloys to effectively catalyze the underlying electrode processes. Indeed, the coexistence of different transition metals in an alloy allows for the convenient adjustment of the catalyst's reactivity in order to tune the binding strength of the key reaction intermediate to achieve optimal catalytic performance.

However, the design of alloy-based catalysts is currently limited by the inability of computational pre-screening strategies to account for environmentally induced changes in the surface composition and structure of prospective catalysts *in operando*. The role of adsorbate-induced changes in surface structure changes is particularly accentuated in in the case of multifunctional catalysts which are prevalent in the oxidation of organic molecules.

The multifunctional nature of these catalysts results from the synergetic co-operation of the individual alloy components and their differing abilities to co-adsorb CO and OH. The nobler metal component in the alloy readily adsorbs CO while the more oxophilic metal prefers OH. Thus, the overall oxidation process can be regulated by controlling the co-adsorption of OH and CO.

The paper will present a new systematic theoretical approach for identifying thermodynamically realizable catalyst surface phases for the further investigation of their catalytic properties. Surface free energies derived from density functional theory (DFT) are used to construct surface phase diagrams based upon relative stability of different surface structures which may form at the catalysts surface under a variety of potential *in-operando* conditions. The predictive power of the theoretical approach will be demonstrated for the oxidation of formic acid on Pt-Ru catalysts in acid media. Adsorbed CO and O induce *in operando* reordering of the metal alloy at the surface, making it particularly sensitive to the catalyst composition and external conditions. Our theoretical model predicts that a Ru-rich Pt-Ru surface stabilizes the mixed CO-O adsorbate phase that we expect to be most conducive to stable, efficient bifunctionality.
The validity of the theoretical predictions can be assessed by X-ray absorption spectra (XAS) which is sensitive to the local structure as well to the composition of the adsorbate layer. The comparison of the EXAFS functions of anodically polarized PtRu alloy in presence and absence of the formic acid allows to reproduce the local chemical composition and its time evolution. The combination of the XANES and EXAFS parts of the X-ray absorption spectra then prove both qualitatively and quantitatively the composition of the adsorbate layer. The results of the spectroelectrochemical experiments is in quantitative agreement with the predictions of the DFT based model confirming the suitability of the theoretical model for bifunctional catalyst rational design.

Confinement Effects on an Electron Transfer Reaction in Nanoporous Carbon Electrodes

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Nanoconfinement effects strongly impact on many liquid properties, such as transport, diffusion coefficients, phase transitions, and solvation structures.[1,2] They are particularly important for supercapacitors, which have emerged as a complimentary energy stroage solution to batteries.[3] The effects has been observed to have a significant influence on the performance of supercapacitors, as has been demonstrated by experiment[4] and simulation[5], where it was shown that the use of materials with sub nanometric pores as electrodes greatly increase the capacitance of these devices.

Within the realm of electrochemical applications, room temperature ionic liquids (RTILs) have attracted a considerable attention. Here we investigate how the electrochemical reactivity in such media may be impacted inside nanoporous carbon electrodes. We perform a molecular dynamics study of Fe^{3+}/Fe^{2+} electron transfer (ET) reaction. The redox couple is dissolved in the 1-ethyl-3methylimidazolium tetrafluoroborate (EMIM-BF_4) RTIL, which is put in contact with carbide-derived carbon (CDC) nanoporous electrodes. The electrodes are held at constant electric potential by allowing the atomic charges on the carbon atoms to fluctuate. From the theoretical point of view, ET reactions in solution are usually studied in the framework of Marcus theory, which aims at accounting for the influence of solvent fluctuations on the rate of ET.[6] We show that the Fe^{3+}/Fe^{2+} couple dissolved in EMIM-BF_4 exhibits a deviation with respect to the standard Marcus theory. This behavior is rationalized by the stabilization of a solvation state of the Fe^{3+} cation in the disordered nanoporous electrode that is not observed in the bulk. The Fe^{3+} cation, which is tetracoordinated in the bulk, admits two stable solvation states in the nanoporous material: tetracoordinated and hexacoordinated. To account for this deviation we use the two-Gaussian solvation model,[7] from which the free energy curves for all the redox species in their various solvation states were extracted. This allows us to qualitatively analyze the effect of the confinement on the ET reaction. The fluctuations in the structure of the solvation shell of Fe^{3+} are shown to have a negligible effect from a thermodynamic point of view. In addition, it is shown that the activation energy of the associated ET process is much higher for the hexacoordinated form. It is therefore likely that the stabilization of this solvation state will result in a slow down of the ET reaction kinetic. This work is a first step towards a deeper understanding of the influence of the confinement on the ET in redox supercapacitor devices, which will be extended in the future to promising systems such as biredox RTILs.[8] The techniques developed in this work could also provide useful information for the development of ionic liquids-based thermo-electrochemical cells.

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Morphological Structure of Cathode for Enhancing Electrodeposit Adhesion Strength

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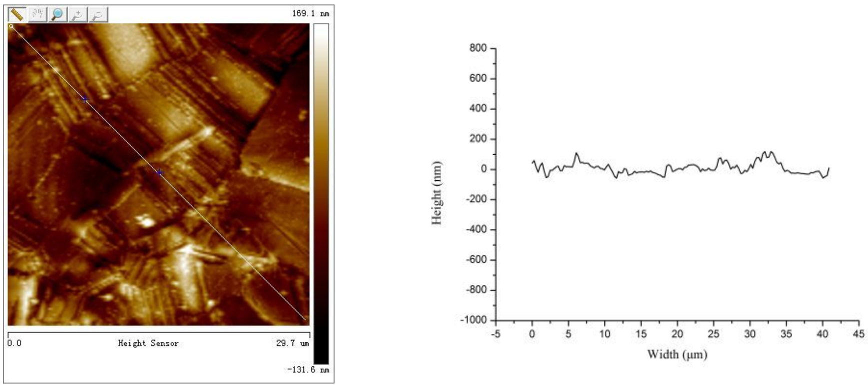
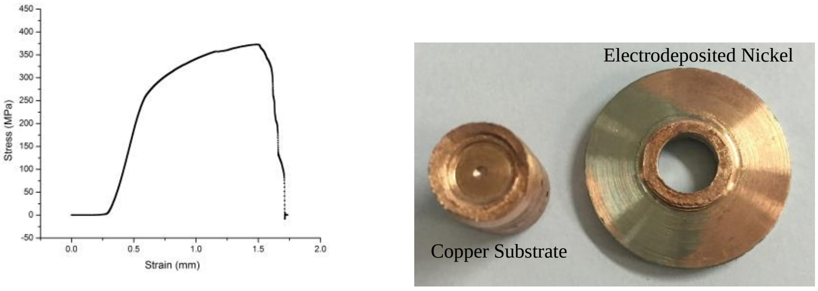
Abstract:

To improve the adhesion strength of nickel deposit on the copper alloy substrate as cathode in electrodepositing process, a series experiments on substrate pretreatment have been carried out. Among the experimental results the highest adhesion strength of about 380 MPa, which is near the tensile strength of the copper substrate, was achieved by using a mechanical property testing machine. The micro-morphologies of the pretreated substrates have been carefully observed and analyzed by using AFM, SEM and XPS. The results showed that the morphological structure of the copper substrate was the critical factor influencing the adhesion strength of the nickel deposits. A typical morphological structure with clear grain boundaries and smooth grain surface contributed to the high adhesion strength. A hypothesis was proposed based on the theories of step preferential electro-crystallization and metallic bonds formation.



(a) (b)

Fig.1 The micro-morphology of the pretreated copper substrate attributed to high adhesion strength for nickel electrodeposit: (a) AFM 2D photograph, (b) contour line at the white line in (a)



(a) (b)

Fig.2 The adsorption strength test for the electrodeposited nickel layer on the copper substrate: (a) stress-strain curve, (b) the sample after testing

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Role of the adsorbed oxygen species in the selective electrochemical reduction of CO_2 to alcohols on copper single-crystal electrodes

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To date, copper and copper oxide-derived surfaces are the only catalysts that could electrochemically convert CO_2 to high-value and energy-dense products such as methane ethylene, formic acid, methanol and ethanol, among others.[1-3] However, the efficiency and the selectivity of this process are far from optimal and the parameters controlling these factors are not-fully understood. Until now, such differences in reactivity and selectivity have been attributed to the surface area, surface structure and roughness as well as to the history of the electrode.[1,3-5] Recently the different selectivities of Cu oxide catalysts have also been attributed to a number of factors, including the oxidation state of the Cu, the oxygen content on the films and the roughness of the electrode.[3,6,7]

We have recently used Cu(100) and Cu(111) electrodes and have pulsed voltammetry to control the surface structure and the oxygen content at the surface. The pulse sequence was programmed to guarantee reproducible initial conditions for the reaction (Figure 1A) at every fraction of time and at any given frequency without compromising the surface structure.

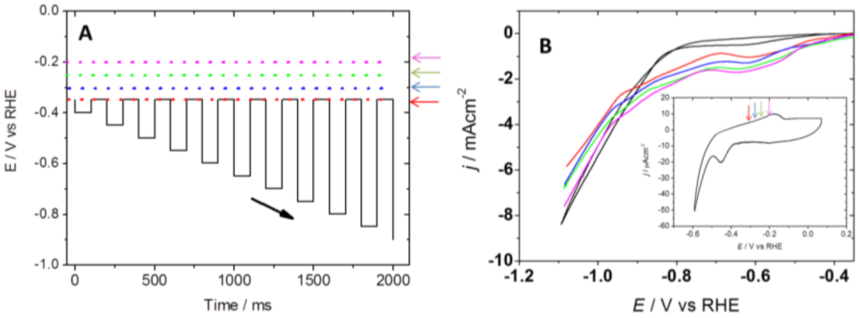

Figure 1: (A) Pulse program for the pulsed voltammetry. (B) Pulse voltammetry's of Cu(111) electrodes in phosphate buffer solution in presence of CO_2. The black curves correspond to the cyclic voltammetry's at (υ=10 mV/s). Inset: cyclic voltammetry's in absence of CO2 of the Cu(111) and Cu(100) (υ=50 mV/s). The arrows indicate the e positive potential steps during the pulse voltammetry's.

We have found that oxygenated hydrocarbon species – formaldehyde, formate, methanol, ethanol, acetone and acetaldehyde – were only observed under pulse potential conditions Using On-line electrochemical mass spectrometry , we found that under pulse potential conditions, the selectivity toward of the oxygenated species appears to be in detriment of hydrogen evolution and formation of CH_4 and C_2H_4. This may be associated to the adsorption of OH species to the surface when the potential is stepped up to the upper potential. The product selectivity would be associated to the OH coverage, which is surface structure and potential dependent. In the reduction of CO_2 to methanol in the gas phase, the promotion of CO_2 chemisorbed on oxygen-modified Cu surfaces and CO_2's subsequent hydrogenation is a key feature of the mechanism.[8,9]

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Employing Surface Specific Vibrational Spectroscopy to Study Adsorbate Structure at Electrochemical Interfaces

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Vibrational spectroscopies, such as surface enhanced Raman spectroscopy (SERS) and surface-enhanced infrared absorption spectroscopy (SEIRAS), have proven to be important tools for the identification of intermediates and products in electrochemical reactions. The combination of conventional electrochemistry methods and these molecular spectroscopies can allow for full analysis of charge transfer processes and complicated redox reactions. However, when the reaction intermediates or products have similar spectral response as the reactants or solvent of the electrolyte, the identification of these surface species becomes difficult. Vibrational sum frequency spectroscopy (VSFS), based on a second order nonlinear optical process, is intrinsically interface specific due to its symmetry selection rule,[1] and can in principle distinguish the interfacial species from those in the solution bulk. In this contribution I demonstrate two successful application of VSFS for this purpose: (1), probing sub-population of hydrophobic water molecules at the gold electrode/water interface (Fig.1);[2] (2), probing weakly adsorbed formic acid molecules at the Pt(100) electrode during the electrochemical oxidation process (Fig.2).[3]

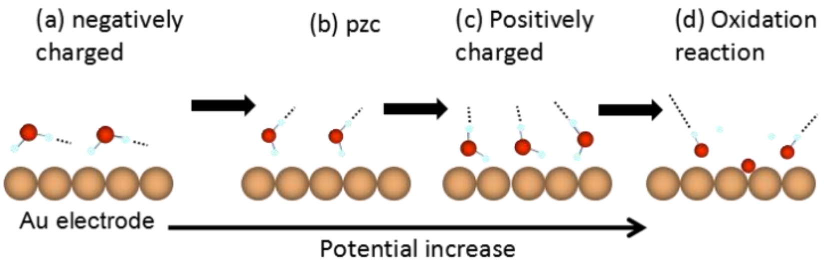

Fig. 1, hydrophobic water molecules were probed experimently as sub-population of interfacial water at the gold electrode under electrochemical conditions.[2]

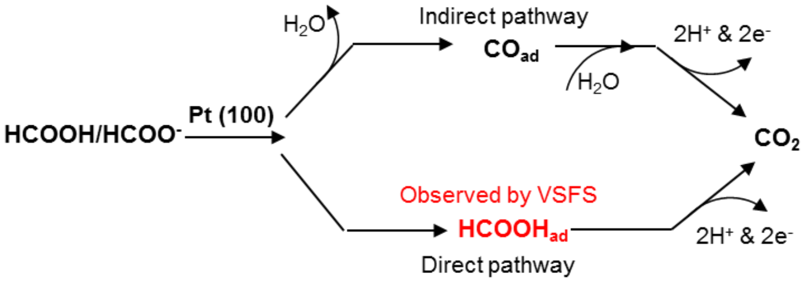

Fig. 2, weakly adsorbed formic acid molecules were detected during formic acid electrochemical oxidation on Pt(100) electrode. [3]

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Improved electrochemical properties of $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode material via Li-reactive coating with metal phosphates: First-principles based screening and experimental verification

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Nickel-rich nickel-cobalt-manganese oxide (Ni-rich NCM) is a promising cathode material which can fulfill a large capacity with low manufacturing cost, but they suffer from several types of degradation behaviors such as lattice instability, cation disordering, phase transformation, and gas generation. [1,2]

For mitigation of degradation behaviors, the surface modification method (surface coating) has been suggested by providing the physical barrier at the surface of the cathode. However, this approach potentially has drawbacks; 1) Li ion diffusion during electrochemical cycling can be impeded. 2) Residual Li, which is a source of gas generation, needs to be washed during synthesis and it can degrade the battery performance. Hence, another method has been suggested to eliminate above concerns simultaneously; *i.e.*, finding coating materials which can directly react to residual Li, so that they can be transformed to Li-containing phases and in parallel, the amount of Li residues are reduced.

In this study, combined with simulation and experiment, we propose the optimal metal phosphate coating materials for the purpose of removing residual Li on the surface of Ni-rich layered oxide cathode material of $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. First-principles based screening process for 16 metal phosphates is performed first to search an ideal coating material which is highly reactive to Li_2O. (Figure 1(a)) By constructing the phase diagram, we find the equilibrium phases between coating materials and Li residue based on database of DFT hybrid functional. Then among them, experimental verification for $Mn_3(PO_4)_2$, $Co_3(PO_4)_2$, $Fe_3(PO_4)_2$, and $TiPO_4$ is accomplished. (Figure 1) It demonstrates that the Li-removing capabilities of proposed materials are in general comparable to results from calculations. In addition, electrochemical properties up to 50 cycles of charge/discharge process exhibit that Mn-, Co-, Fe-phosphate materials are superior to uncoated sample for prevention of capacity fading behavior while $TiPO_4$ shows very poor initial capacity and rapid reduction of capacity during cycling. Finally, Li-containing equilibrium phases examined from XRD analysis are confirmed with simulation results.

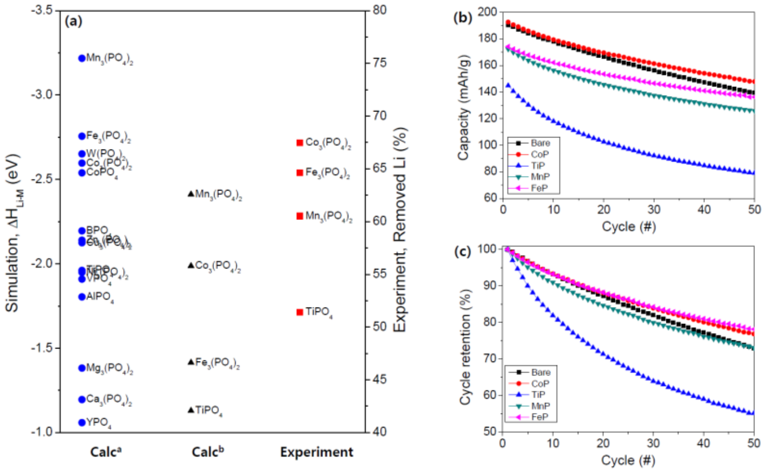

Fig. 1. (a) Comparison of Li-removal reactivity between calculations and experiment. Calc[a] and Calc[b] denote the most reactive reactions and the corresponding molar ratio from the experiment, respectively. (b) The variation of the initial capacity and (c) the capacity retention rate during 50 cycles for NCM and NCM coated with Co-, Ti-, Mn-, and Fe-P.

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Electrochemical Surface-enhanced Raman Microscopy (EC-SERM)

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The pursuit of techniques that can provide electrochemical response with high temporal and spatial resolution has never stopped in order to monitor and understand the complex electrochemical process. Conventional electrochemical methods cannot fulfill the increasing request to detect the local electrochemical information, which can only obtain the total current response of analytes on the electrode. Scanning electrochemical microscopy is the most widely used electrochemical imaging technique to obtain the heterogeneous electrochemical information of electrode surfaces. However, its spatial resolution and detection sensitivity is still limited by the probe and the point-scan mode limits its imaging rate. Recently, the combination of high resolution optical imaging techniques such as surface plasmon resonance, fluorescence and dark field scattering with electrochemical methods are receiving increasing interest. However, all these optical methods lack molecular signature, which can hardly be used in a complex system containing multiple electrochemical active components due to the poor chemical identification and low selectivity.

To address the aforementioned challenges, we developed an electrochemical surface-enhanced Raman microscopy (EC-SERM), which allows us to simultaneously monitor the local electrochemical redox process of a mixture, nile blue and viologen, on a Ag NPs electrode. We successfully reconstructed the independent local Faradaic electrochemical current of these two molecules from the SERS signal without the interference from the double layer charging process and dissolved O_2. We can further sensitively measure the electrochemical information of trace species which is covered by massive interfering components in the complex environment. Those advantages are quite useful in practical systems that always exist unwanted molecules or impurities.

In addition, we developed a wide-field Raman imaging system with high imaging speed that is able to monitor the spatiotemporal change at every point across the whole electrode simultaneously. We employed this wide-field imaging system to reveal the heterogeneity of redox process of nile blue on a microelectrode, as shown in Fig 1. This wide-field EC-SERM successfully offers the spatially correlate between electrochemical behavior and the particular surface sites at where the reaction happens. The simultaneously detection of distinct electrochemical behavior across the electrode surface without any scanning process demonstrates the power of wide-field EC-SERM for probing nanoscale electrochemical processes, which is especially important for those irreversible reactions. We believe that EC-SERM could serve as a powerful platform for imaging surface heterogeneity under a complex molecular environment, and sensitively and selectively provide the local electrochemical information of molecule of interest.

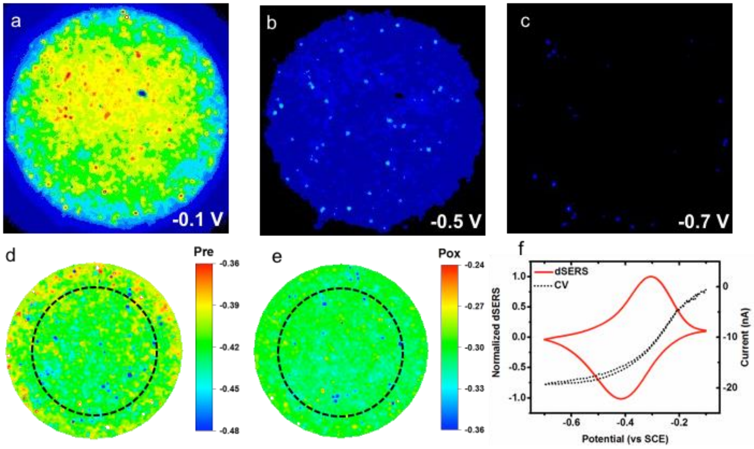

Fig 1. The potential depended wide-field imaging of nile blue adsorbed on a Ag microelectrode (a,b,c). The pseudo color images of cathodic (d) and anodic (e) peak potential obtained by EC-SERM. The conventional CV and the simultaneously recorded curve of the derivative of SERS intensity over the whole microelectrode (f).

Electrochemistry at 50 MHz: Probing Beyond the Electrical Double Layer

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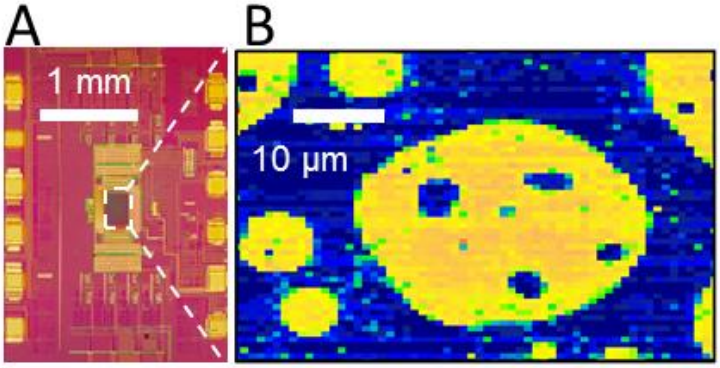

Figure 1. (A) Optical micrograph of the CMOS chip used for the high-frequency measurements. Inside the dashed white rectangle lays an array of 256 x 256 nanoelectrodes (180 nm diameter). (B) Capacitance image of micro-droplets of *o*-dichlorobenzene (yellow color) with water (blue color) inclusions.

The electrical double layer (EDL) formed at the interface between an electrode and a solution plays a major role in the response of biosensors based on field effect and capacitance variation. Because the thickness of the EDL is about a nanometer under physiological conditions, the response of these sensors is drastically impacted by the presence of small molecules that can adsorb on the electrode. While such a feature is desirable for the detection of analytes having the same dimension than the EDL it becomes a major source of noise when targets larger than the EDL (such as proteins, nanoparticles and microbeads) are in a complex matrix (e.g. serum, urine etc...). Here, we show that capacitance measurements at 50 MHz enable probing well beyond the EDL, few microns deep in solution. We will explain the fundamental physical phenomenon governing the capacitance response at high frequencies and present experimental results obtained with a CMOS-based microchip comprising an array of 65,536 individually addressable 180 nm diameter electrodes **(Figure 1A)**. [1,2] The analytical capabilities of this platform will be illustrated with the analysis of oil microdroplets (**Figure 1B**) and gold/polystyrene microbeads in water.

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Promoting Role of Bismuth on Pt Single Crystals for the Selective Oxidation of Glycerol to Dihydroxyacetone

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The selective oxidation of alcohols to carbonyl compounds catalyzed by noble metals has received growing attention because of its environmentally friendly form to produce high value-added chemicals. Promoters, such as Bi, Pb, Sb, Ag, Te and Sn, have significant impact on the activity and selectivity of these catalysts. Glycerol, a surplus by-product from the production of biodiesel can be oxidized to functionalized feedstock such as dihydroxyacetone (DHA), glyceric acid (GEA) and tartronic acid (TA), all commercially useful compounds. DHA, a product of secondary alcohol oxidation, is especially interesting because it is widely used in the cosmetic industry as self-tanning agent. The selective electro-oxidation of glycerol to 1,3-dihydroxyacetone (DHA) has been extensively studied using Pt or Pd promoted by bismuth.

Our recent work on Pt single-crystal electrodes showed that the selectivity of the electrochemical oxidation of glycerol to DHA is sensitive to the surface structure and that this sensitivity is related to the initial mode through which glycerol binds to the surface [1]. Previous results have shown that the electro-oxidation of glycerol to DHA can be achieved with almost 100% selectivity by making use of adatom species on a Pt/C electrode [2]. It was observed that in the absence of promoters, the primary alcohol oxidation is dominant; however, with bismuth or antimony in solution, the oxidation of secondary hydroxyl groups is preferred.

This work discusses the effect of irreversibly adsorbed bismuth (Bi_{ir}) on the activity and selectivity of glycerol oxidation on Pt single-crystal electrodes by using a combined detailed spectro-electrochemical experiments [3].

Our results show that the presence of bismuth on the Pt(111) electrode improves both the activity of the reaction and the selectivity to dihydroxyacetone, while on Pt (100) electrode the presence of bismuth causes a decrease in the activity and does not change the tendency of the Pt(100) surface to produce only glyceraldehyde [3, 1]. The role of Bi in the oxidation of glycerol is at least twofold. On Pt(111), Bi blocks sites preventing the adsorption of poisoning intermediates such as carbon monoxide, leading to a higher activity. On Pt(100) the presence of Bi reduces only partially the amount of poison formed during the reaction, as our stripping experiments and in situ FTIR results show the presence of a strongly bound glycerol-related adsorbate and a small amount of linearly bonded carbon monoxide. Secondly, and more importantly, we attribute the increase in the selectivity to DHA on Pt(111)/Bi_{ir} to the interaction of the Bi adatom with the enediol intermediate, an adsorbed intermediate that exists on Pt (111) but not on Pt(100) [1]. The enediol is the key intermediate in the isomerization reaction between glyceraldehyde and dihydroxyacetone, and the stabilization of this intermediate by the interaction with the bismuth enhances the rate of the isomerization reaction toward the thermodynamically most stable isomer, namely dihydroxyacetone [3].

The results presented in this work give insight into how Bi adatoms on the Pt surface enhance the secondary alcohol oxidation in glycerol. However, we note that the presence of a low coverage of Bi on Pt(111) does not lead to an almost complete shift in the selectivity from glyceraldehyde to dihydroxyacetone, which is the influence that (dissolved) Bi has on the electrocatalytic oxidation of glycerol on a carbon-supported nanoparticulate platinum catalyst.

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Computational Modeling of Solid Electrolyte Interphase Formation in Lithium-Ion Batteries.

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Solid electrolyte interphase, SEI, is a layer of organic compound which is formed on the negative electrodes of lithium ion batteries (LIB) during their first charging cycle. The formation, structure, and deformation of SEI is one of the main factors that determines the life time and performance of LIBs. However, our knowledge on their structure, formation, and working mechanism is far from complete.

Here we represent the computational lithium electrode model, based of computational hydrogen electrode model of catalysts community, which enables us to calculate the formation free energy of reactions on top of electrodes.

We then apply the method to study the formation of one of the most observed SEI compounds, namely dilithium ethylene glycol dicarbonate, $(CH_2OCO_2Li)_2$:LiEDC , on Li, Li_2O, and Li_2CO_3 surfaces. We demonstrate that the formation of LiEDC is much more favorable on Li_2CO_3 than other two surfaces and support our founding with experimentally observed data.

Salt-on-a-chip: Microcontact Printing of Ionic Liquids for “Membrane-less” and “Spill-less” Gas Sensors

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Lab-on-a-chip systems have gained significant interest for both chemical synthesize and assays at the micro-to-nano-scale with a unique set of benefits. However, solvent volatility represents one of the major hurdles to the reliability and reproducibility of the lab-on-a-chip devices for large scale applications. Here we demonstrate a strategy of combining non-volatile and functionalized ionic liquids with microcontact printing for fabrication of “wall-less” microreactors and microfluidics with high reproducibility and high throughput.[1-2] A range of thiol-functionalized ionic liquids have been synthesized and used as inks for microcontact printing of ionic liquid microdroplets arrays onto gold chips. The covalent bonds formed between the thiol-functionalized ionic liquids and the gold substrate offer enhanced stability of the ionic liquid microdroplets, compared to conventional non-functionalised ionic liquids, and these microdroplets remain stable in a range of non-polar and polar solvents, including water. We then demonstrate the use of these open ionic liquid microarrays for fabrication of “membrane-less” and “spill-less” electrochemical gas sensors with enhanced reproducibility and robustness.

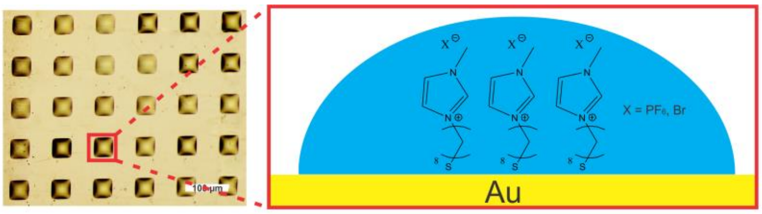

Figure 1. Micrograph of Thiol-functionalized ionic liquid micropatterned with the size of 50 µm fabricated via microcontact printing. The inset shows the illustration of the thiol-functionalised ionic liquid microdroplets.

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Redox reactions in < 20 nm thick electrochemical cells

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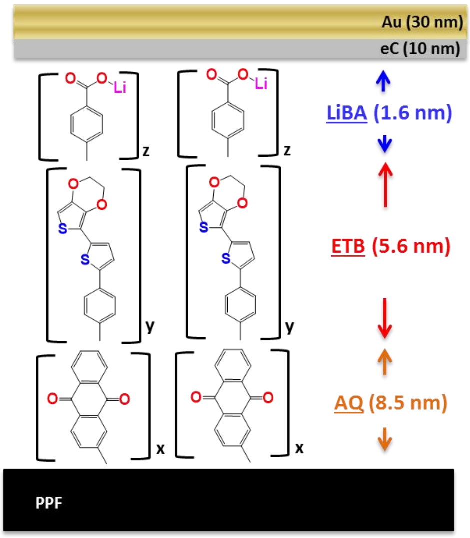
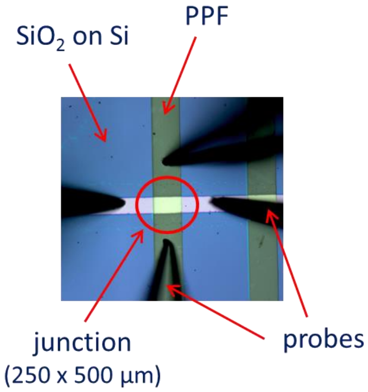
Much of the motivation for developing molecular electronic devices is the prospect of achieving novel electronic functions by varying molecular structure. We describe a "building block" approach for molecular junctions resulting in one, two or three nanometer-thick molecular layers in a commercially proven junction design. Layer growth and multilayer structures were monitored with UV-Vis absorption and Raman spectroscopy, in some cases enhanced by embedded Ag particles. A single layer of anthraquinone between carbon electrodes provides a tunnel device with applications in electronic music, and a second layer of a thiophene derivative yields a molecular rectifier with quite different audio characteristics. A third layer of lithium benzoate produces a redox-active device analogous to a 16- nm thick battery with possible applications in non-volatile memory devices or on-chip energy storage. The building block approach forms a basis for "rational design" of electronic functions, in which layers of varying structure produce distinct and desirable electronic behaviours.





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Spectroscopic Observation of a Hydrogenated CO Dimer Intermediate During CO Reduction on Cu(100) Electrodes

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Copper has the extraordinary ability to electrochemically reduce carbon dioxide and carbon monoxide to useful products such as methane and ethylene[1]. The exact mechanism and the corresponding reaction intermediates are currently under debate or unknown. A considerable number of experimental observations as well as density functional theory (DFT) calculations have established that CO_2 and CO reduction on copper electrodes forms C_1 and C_2 products through different reaction pathways.[2-6] Hori et al[1] showed that the reduction of CO to CH_4 follows a concerted proton-electron transfer mechanism, in stark contrast with C_2H_4 production, the rate-limiting step of which is not sensitive to pH and only involves an electron transfer.

Experiments performed in our group showed that C_2H_4 formation takes place preferentially at Cu(100) electrodes without simultaneous CH_4 formation, which indicates that the reaction paths towards CH_4 and C_2H_4 must bifurcate in the early stages of CO reduction[7]. Specifically, a C_2 intermediate that requires only electron transfer to be formed, namely a negatively charged CO dimer, has been proposed as the first C-C coupled intermediate[2, 8, 9]. Various recent computational works have studied the structural sensitivity of this intermediate, and concluded that the formation of the dimer is indeed favored both thermodynamically and kinetically on Cu(100) sites compared to Cu(111)[9-11]. However, there is still no direct experimental evidence that proves CO dimerization in aqueous solution during CO reduction on copper electrodes, and the existence of the dimer is mostly a logical deduction from experimental and computational results.

In this presentation, we will provide for the first time experimental evidence for the formation of a hydrogenated CO dimer (OCCOH) at low overpotentials during CO reduction on Cu(100) electrodes in LiOH solution, employing in situ Fourier transform infrared spectroscopy (FTIR). Our observations are supported by detailed DFT calculations. Furthermore, the formation of this intermediate is structure sensitive, as it is observed only during CO reduction on Cu(100) and not on Cu(111), in agreement with previous experimental and computational observations.

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Investigation of nanoparticle impacts at liquid|liquid, soft interfaces using ferrocene-assisted oxygen reduction reaction

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The oxygen reduction reaction (ORR) is a key chemical pathway towards the generation of solar fuels. Among the different strategies proposed to improve the ORR, its activation at the liquid|liquid interface shows some promise [1]. Moreover, the introduction of nanoparticles, NPs has been shown to provide a significant catalytic enhancement [2]. Recent electroanalytical techniques, based on the detection of the electrochemical contribution of individual NPs, can be of great interest for mechanistic inspection [2, 3]. Herein, we propose to exploit this concept of single NP electrochemistry detection at a micro liquid|liquid, or soft interface between two immiscible electrolyte solutions (ITIES) through the catalysis of the ORR. This strategy has several advantages in that the ITIES is defect free and thus reproducible. Typical cyclic voltammograms (CVs) obtained at a micro-ITIES between water|1,2-dichloroethane (w|DCE), are shown in Figure 1A with (red trace) and without (black curve) ferrocene added to the DCE phase. The former demonstrates the facilitated ion transfer (FIT) of protons across the interface through the formation of ferrocene-hydride at potentials >–0.1 V. After addition of Pt-NPs to the aqueous phase chronoamperograms were recorded at –0.3 and 0 V. Spikes in the current signal could then be detected when the FIT/ferrocene-hydride formation was triggered at $\Delta_o^w\phi$ = 0 V. Moreover, increase in the concentration of Pt-NPs results in a concomitant increase in the frequency of impacts, as shown in Figure 1B; the frequency is in good agreement with the calculated flux of NPs to the liquid|liquid interface. These stochastic features are reminiscent of electrochemical nanoimpact experiments at microelectrodes and suggest that the current spikes detected here are related to catalytic NP impacts at the liquid|liquid interface. The absence of current spikes at lower potential indicates the necessity of metallocene-hydride formation before Pt-NP catalysis of O_2 reduction can take place as well as the possibility of a nanofilm developing. A mechanism explaining the observed phenomena is drawn in Figure 1C. This works demonstrates that the concept of NP electrocatalytic impact can be transposed to soft interfaces and that this strategy can provide valuable insight into the mechanism of NP-catalyzed reactions at liquid|liquid interfaces (here demonstrated for the case of O_2 reduction).

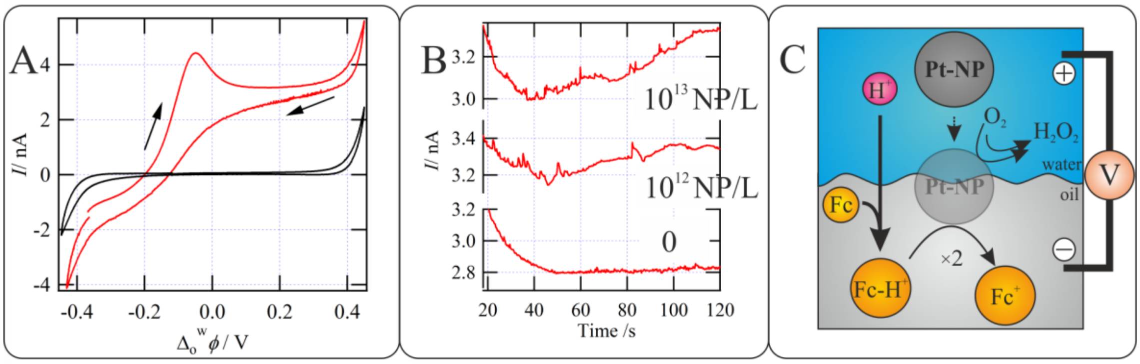

Figure 1: **[A]** Cyclic voltammograms obtained at a 25 μm diameter w|DCE interface with (red trace) and without (black trace) 5 mM of ferrocene added to the DCE phase; 5 mM of H_2SO_4 was used as the analyte(proton source)/supporting electrolyte in the aqueous phase. **[B]** Proposed mechanism of ferrocene-hydride formation and Pt-NP catalyzed O_2 reduction. **[C]** Chronoamperograms obtained at 0 V and varying NP concentrations as indicated inset.

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Optical Imaging of Phase Transition and Li-Ion Diffusion Kinetics of Single $LiCoO_2$ Nanoparticles during Electrochemical Cycling

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Understanding the phase transition and Li-ion diffusion kinetics of Li-ion storage nanomaterials holds promising keys to further improve the cycle life and charge rate of Li-ion battery. Traditional electrochemical studies were often based on bulk electrode consisting of billions of electro-active nanoparticles, which washed out the intrinsic heterogeneity among individuals. Here, we report a surface plasmon resonance microscopy (SPRM) approach to image Li-ion insertion/extraction rate of single $LiCoO_2$ nanoparticles during electrochemical lithiation/de-lithiation processes, from which the phase transition and Li-ion diffusion kinetics can be quantitatively resolved in a single nanoparticle, in operando and high throughput manner. SPRM is an optical microscopy that maps the refractive index (RI) of single $LiCoO_2$ nanoparticles, which gradually decreases with the gradual extraction of Li-ions, enabling the optical read-out of single nanoparticle electrochemistry. As RI is an intrinsic property of any material, the present approach is also anticipated to be applicable for versatile kinds of anode and cathode materials, facilitating their rational design and optimization towards durable and fast-charging electrode materials.

The present work was the first attempt to optically image the Li-ion extraction and insertion kinetics of single $LiCoO_2$ nanoparticles, which exhibited several advantages associated with SPRM. Firstly, it measured the RI of electrode materials, making it a promising technique for studying various kinds of anode and cathode materials, because RI is an intrinsic property of materials and it is known to be sensitive to the chemical composition and electronic structure of nanomaterials. Secondly, it exhibited a fast temporal resolution up to microseconds, thus suitable for studying fast dynamical processes. Third, SPRM is a wide-field imaging technique and is capable of simultaneously monitoring tens of nanoparticles. The combination of SPRM with SEM and other in situ characterization techniques provides a unique capability to efficiently and appropriately establish the structural-activity relationship.

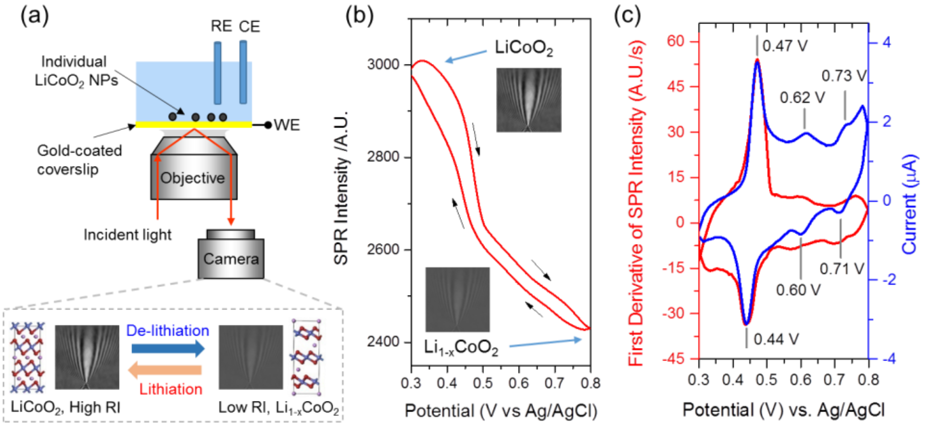

Fig. 1. (a) Schematic illustration of monitoring the electrochemical lithiation of single LiCoO2 nanoparticles. De-lithiation decreases the refractive index (RI) of individual nanoparticle, leading to a decreased optical contrast in SPRM image. (b) SPR intensity curve of a single $LiCoO_2$ nanoparticle when applying a cyclic voltammetry sweep between 0.3 to 0.8 V at a scan rate of 10 mV/s. SPR intensity gradually decreases with increasing electrode potential (de-lithiation), which was followed by a complete recovery when the potential scans back to the original value (lithiation). (c) The first order derivative of SPR intensity curve (red curve) represents the cyclic voltammogram of single nanoparticle, which is in good agreement with the average electrochemical current contributed by all LiCoO2 nanoparticles on the gold film (blue curve).

Ultrasmall Au Nanocatalysts Supported on Nitrided Carbon Supports for CO_2 Electrochemical Reduction

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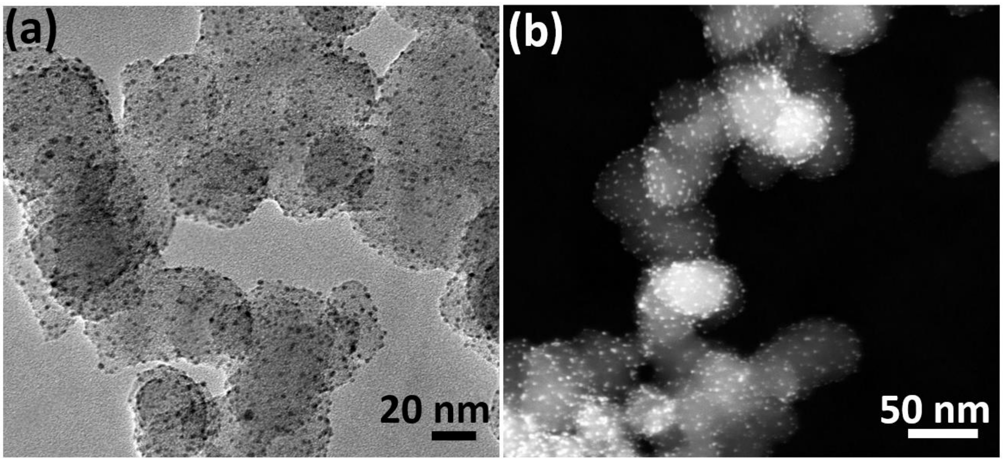
Au is known to be catalytically active for CO_2 reduction. The catalytic activity of Au is highly size-dependent as confirmed by numerous previous studies. In particular, ultrasmall Au nanocatalysts (< 2 nm), referred to Au nanoclusters with a few to hundreds of atoms, have received substantial attention recently, since they hold a high surface-to-volume ratio and a large proportion of surface (edge and corner particularly) atoms. However, all current synthetic approaches of ultrasmall Au nanocatalysts require excess surface ligands to prevent the overgrowth and stabilize the nanoclusters, due to the high surface energy. We show a robust and universal "soft" nitriding method to *in situ* grow ligand-free ultrasmall Au nanocatalysts onto carbon supports. Through a low-temperature urea-annealing pretreatment (300 ^oC), "soft" nitriding that enriches the nitrogen-containing species on the surface of carbon supports, can enhance the affinity of Au precursors and/or its nanocatalysts to carbon supports. Sub 2 nm, ligand-free Au can grow *in situ* on 7 different types of nitrided carbons in the absence of any organic capping agents *via* chemical reduction or thermolysis. Ligand-free Au supported on nitrided carbon is found to be electrocatalytically very active for CO_2 reduction, compared to their counterparts with surface capping agents and/or larger nanocrystals. We demonstrate, the activity and selectivity of supported Au nanocatalysts are highly dependent on the surface N sites that act as Lewis base to tune the binding affinity of CO_2 to Au.



Electrochemical glucose sensor based on gold-doped nano-perovskite-clusters – New strategy for non-enzymatic sensing application

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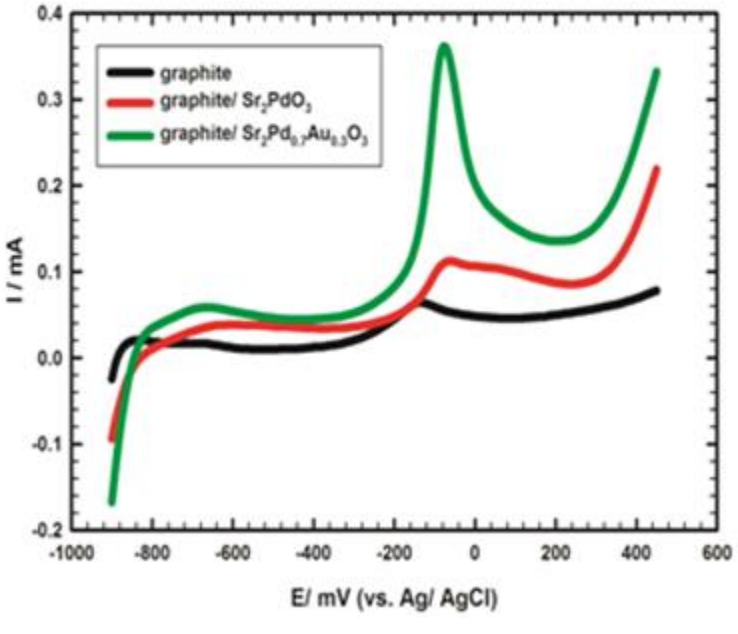
Herein, we prepared gold-doped nano-perovskite-clusters of the type $Sr_2Pd_{1-y}Au_yO_3$. Glycine-nitrate combustion method was used to prepare the perovskites. The prepared material is administered as surface modifier for non-enzymatic catalytic sensing of glucose. The structure, morphology and electrochemical properties of the prepared nano-perovskites were studied using voltammetry, electrochemical impedance spectroscopy (EIS), field emission scanning and high resolution transmission electron microscopies (FE-SEM/EDAX and HR-TEM), X-ray diffraction (XRD), differential thermal analysis (DTG), X-ray photoelectron spectroscopy (XPS) and particle size analyzer. The XRD patterns of the perovskite catalysts showed well-defined crystalline orthorhombic Sr_2PdO_3 as the main phase and particles size in the nanometer range. The partial doping of Pd^{2+} by Au^{3+} significantly enhanced the elecrocatalytic activity towards non-enzymatic glucose sensing in 0.1 mol L^{-1} NaOH showing the highest elecrocatalytic activity for $Sr_2Pd_{0.7}Au_{0.3}O_3$. Oxygen vacancies in the lattice via charge compensation are assumed to alter the electrocatalytic activity at the interface. In addition, this sensor showed a good response toward other saccharides like fructose and sucrose. Figures of merit for the performance of the non-enzymatic glucose sensor are reported including stability, sensitivity, selectivity, linearity, detection limit and applicability in real sample analysis. The limit of detection, limit of quantification, linear dynamic range and sensitivity for the proposed senor are 2.11 nmol L^{-1}, 7.05 nmol L^{-1}., 0.4 µmol L^{-1} to 100 µmol L^{-1} and 14.4 $mA.L.mmol^{-1}.cm^{-2}$, respectively.

Cyclic voltammetry of different electrodes towards glucose in basic medium. The highest current signal is obtained at the gold-doped perovskite nano-cluster.



Stability of monometallic nanoparticles in organic solvents

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In recent years a lot of attention has been devoted to the synthesis of nanoparticles for several electrochemical applications such as carbon-carbon bond formation reactions [1]. On this topic, a multitude of studies have been carried out to investigate the synthesis of tailor-made nanoparticles with an optimal activity [1].

A measure not yet investigated is the long-term stability of these electrocatalytic materials in organic solvents. In aqueous solutions it is known that one of the predominant electrocatalysts stability issues is the growth of particles, which is accompanied by unvented decrease in electrochemical active surface area. Identified degradation mechanisms are agglomeration/coalescence/coarsening, Oswald Ripening and also reshaping [2]. However, this knowledge is still unknown in organic solvents. Accurate understanding of the degradation processes will open new directions towards the synthesis of long-term, stable nanoparticles in organic electrocatalysis.

In this work we will for the first time report a stability study of metal nanoparticles towards an organic reduction reaction (reduction of C-X). To give an in-depth description of the stability our approach will be threefold and show the (1) electrochemical, (2) microscopical and (3) analytical approximations. The electrochemical investigation will be carried out using cyclic voltammetry (CV) and linear sweep voltammetry in combination with a rotating disk electrode (LSV-RDE) as primary techniques. Morphological variation will be studied with Identical location Scanning Electron Microscopy (IL-SEM) and In Situ Transmission Electron Microscopy (IS-TEM). This enables the morphological study of the same particles at nanoscale level. Finally, the analytical investigation will be carried out by coupling an electrochemical flow cell with ICP-MS. The online approach of ICP-MS in organic solvent has never been performed before and will give accurate analytical knowledge of the degradation mechanism of nanoparticles occurring in organic solvents.

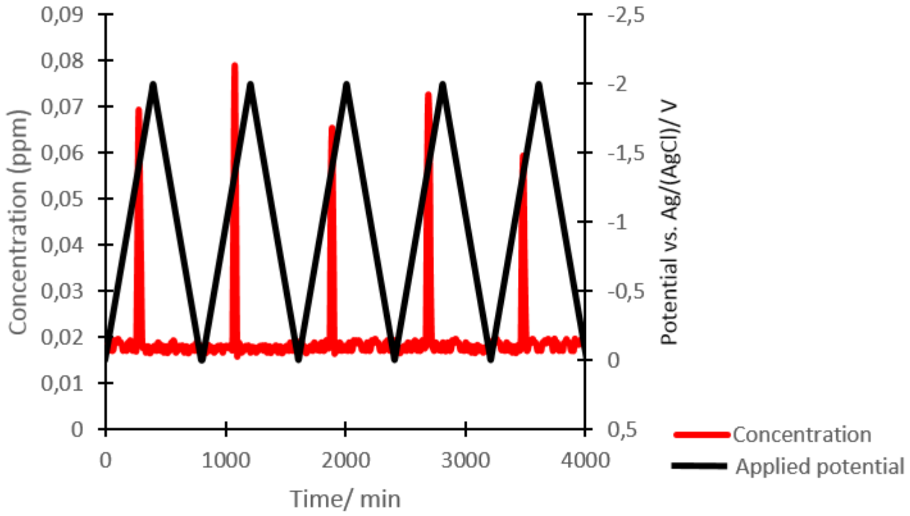

Figure 1: Online ICP-MS coupled with an electrochemical flow cell in organic solvents (MeOH) for the degradation of Ag nanoparticles

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Pulsed Potential Atomic Layer Deposition (PP-ALD)

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Atomic Layer Deposition (ALD) is a method for the formation of nanofilms of materials. It is based on the use of surface limited reactions to form deposits and atomic layer at a time. In electrochemistry, the most well known form of surface limited reactions are underpotential deposition (UPD). UPD is where an atomic layer of one element is deposited on a second, the electrode, at a potential prior to, under, that needed to form bulk deposits of the material. The combination of ALD with UPD is referred to as Electrochemical ALD (E-ALD, EC-ALD, EC-ALE…). Historically the technique consisted of UPD of one element followed by UPD of a second, completing one deposition cycle. By repeating the cycle, a sufficient number of times, a film of the desired thickness is formed. E-ALD has been performed in the author's group using an electrochemical flow cell, where the solutions are exchanged each cycle. Each cycle resulted in the deposition of an atomic layer of each of the constituent elements. For films less than 100 nm in thickness, using an automated flow cell system, films are produced in a reasonable amount of time. However, for deposition of micron thick films, exchanging the solution each cycle make the process slow.

This talk will describe the basic E-ALD process, as well as the recent extension (PP-ALD), where the solutions are not alternated each cycle. That is, instead of changing the solution and potential each cycle, a solution containing precursors for both element is used, and the cycle consists of alternating from a reduction potential, where both elements are deposited, to an anodic potential, where any excess of one of the elements is stripped. By controlling the cycle parameters, each potential cycle results in the deposition of a single monolayer or less of the desired compound. By keeping the amounts deposited each cycle to a fraction of a monolayer, the buildup of an elemental excess is prevented. By simply controlling the potential and not changing the solution each cycle, it is possible to increase deposition rates by several orders of magnitude.

Work on the PP-ALD cycle chemistry for a number of compounds has been underway in the author's group and will be discussed.

Electrocatalytic Reduction of Oxygen on Metal Nanoparticles in the Presence and Absence of Interactions with Metal-Oxide Supports

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Here we report the development of catalysts for the oxygen reduction reaction (ORR) based on the interactions between metal nanoparticles (MNPs) and passivating metal-oxide supports. Specifically, platinum and gold dendrimer-encapsulated nanoparticles (Pt DENs or Au DENs), consisting of up to 147 atoms, were shown to entirely recover Al_2O_3 or SnO_2-hindered electron transfer between pyrolyzed photoresist film (PPF) electrodes and outer-sphere redox molecules. More importantly, although not in direct contact with the underlying oxide thin films, DENs proved to be electrocatalytically active for the ORR. To study the ORR in the presence and absence of the MNP/support interactions, we used a UV-ozone treatment to decompose the dendrimer template, leaving behind naked metal NPs. The UV-ozone treatment did not affect the surface composition, size, or shape of the MNPs, as confirmed by XPS and STEM analysis. Therefore, this is a near-perfect system for the analysis of MNPs/metal-oxide effects on the electrocatalytic reactions because the same electrode can be studied with MNP/metal-oxide effects turned on or off.

We also fabricated a dual-electrode flow cell with over 50% collection efficiency and mass transfer rate up to 0.01 cm/s to study both kinetics and mechanism of the ORR. The study was done using Pt DENs/PPF, Pt DENs/Al_2O_3/PPF, Au DENs/PPF, Au DENs/Al_2O_3/PPF, and Au DENs/SnO_2 /PPF catalysts with MNPs/metal-oxide interactions turned on or off. After removal of the dendrimers from the DENs confined on Al_2O_3, we did not observe significant changes in the kinetics or mechanism of the ORR. This is expected because Al_2O_3 is a non-reducible oxide and it serves as a control support. However, after turning on the interactions between Au NPs and SnO_2, the improvement in activity for the ORR was observed.

Electron Transfer Properties of $Au_{25}(SR)_{18}$ in Film and Solution

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In applications of molecular monolayer-protected gold clusters in solution or solid state, assessing the dynamic behavior of the capping monolayer is crucial, as this determines the cluster's effective size and electron transfer (ET) properties. Here we describe a systematic study on the effect of the monolayer thickness on the ET between molecular $Au_{25}(SR)_{18}^0$ nanoclusters in films and its relation to the ET behavior of the same clusters in solution. The length of the ligands protecting the Au core was varied by using a series of structurally related thiols. Conductivity measurements were carried out on dry films obtained by drop casting $Au_{25}(SR)_{18}^0$ solutions onto interdigitated gold electrodes, whereas ET in dichloromethane solution was studied by cyclic voltammetry with a glassy carbon electrode. Comparative analysis of observed distance effects (determined by the value of *n*) on the rate of ET in the two physical states reveals that in films the monolayer fluidity is substantially less pronounced and, therefore, the effective monolayer thickness in $Au_{25}(SR)_{18}^0$ is larger than in solution.

Gold Superatoms and Superatomic Molecules Protected by Ligands

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Icosahedral Au_{13} clusters and deformed icosahedral Au_{11} clusters can be found as ubiquitous cores in ligand-protected Au clusters as evidenced by single-crystal X-ray diffraction (SCXRD) studies [1]. The high stability of these Au cores is explained in terms of the closure of geometric and electronic structures. The $Au_{11/13}$ cores are fully protected by the ligands via Au-P, Au-Cl, Au-C, and Au-S bonds. A simple electron counting scheme predicts that the electronic structures of the $Au_{11/13}$ cores are closed with the electron configuration of $(1S)^2(1P)^6$. In this regard, the Au_{13}(8e) and Au_{11}(8e) cores in the ligand-protected Au clusters can be viewed as spherical Au superatoms with rare-gas-like electron configuration. Synthesis of Au superatoms with non-rare-gas electron configuration is an interesting challenge toward the establishment of a periodic table of artificial elements on a nanoscale. Recent SCXRD studies demonstrated formation of a variety of dimeric structures of Au_{13} via different bonding modes: a vertex-sharing Au_{25}(16e), face-sharing Au_{23}(14e) and non-sharing Au_{26}(16e). These examples suggest that a new class of artificial molecules (superatomic molecules) can be made using superatoms as building blocks [2].

The talk will cover the following topics on ligand-protected superatoms and superatomic molecules: (1) new spectroscopic characterization of Au superatoms [3–5]; (2) synthesis of Au-based superatoms with non-rare-gas electronic configurations [6–8]; (3) synthesis and characterization of Au superatomic molecules [9–12].

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Monolayer Protected Nanoparticles as SECM Mediators

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Our goal is to understand and control the electron transfer in nanoscale systems, specifically in monolayer protected clusters (MPCs) as redox mediators. My approach focuses on the use of scanning electrochemical microscopy (SECM) and other advanced electroanalytical techniques to study the molecular wiring of nanoscale capacitors in the form of monolayer protected clusters, and take advantage of the metal core for controlling catalytic functions of future nanocircuits. We have shown varied electrochemical behaviors based on monolayer compositions of the monolayers. Included in these electron transfer studies are the barrier effect of fixed electrostatic charges within the thiol monolayer, the dependency of pH on electron transfer rate through monolayers with carboxylate groups, and the role of three dimensional versus two dimensional thiol flexibility in monolayers. Recent achievements in this work is the creation of mixed thiolate MPCs that use molecular wires for enhanced electron transfer kinetics. Using the SECM, we can image chemical catalysis reactions as one method for determining the successful "wiring" of our nanoparticle assemblies.

Directional Migration of Pt Size-Selected Nanoclusters During ORR Under High Mass Transport Conditions

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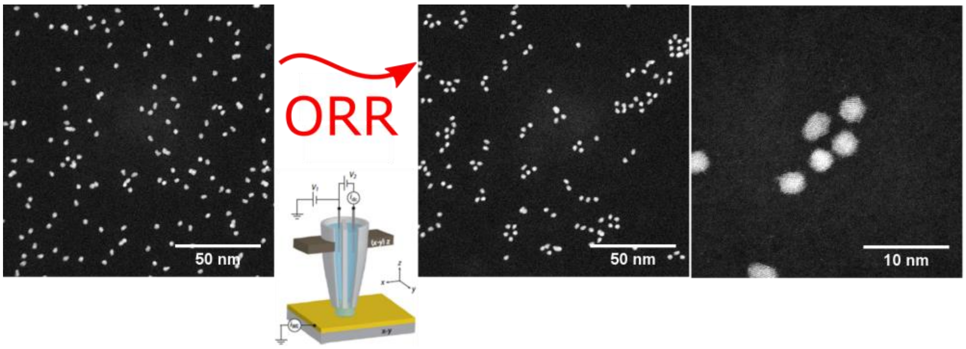
Although extensive research has been directed over the last decade to the oxygen reduction reaction (ORR), the structure-activity-stability relationship of the most efficient (Pt and Pt alloy) catalysts is still not fully understood. Here, we present a novel approach that allows the electrochemical measurement of a small number of well-defined and characterized bare (ligand-free) nanoclusters (NCs) under high mass transport rates, combined with aberration-corrected, high resolution HAADF-STEM imaging of (almost) the totality of the nanoclusters measured electrochemically.

This is achieved by depositing Pt size-selected clusters, produced in a magnetron-sputtering, gas-aggregation cluster beam source with a lateral time-of-flight mass filter on carbon-coated TEM grids, which are mounted on an inverted optical microscope equipped with a dual-barrel SECCM setup. We show how the recorded electrochemical data combined with statistical analysis of STEM images provides major new insights into the effects of NC surface coverage and diffusional overlap on the ORR activity as well as on the catalyst degradation processes.



Whereas particle detachment occurs in some cases, only about 10-20% of the activity losses can be associated with it. More importantly, we find irrefutable evidence that Pt NCs migrate during the ORR measurements and arrange themselves, without physically merging, in groups of up to 15-20 NCs. Although it is accepted that, upon a variety of electrochemical processes, metal NCs supported on carbon substrates can be propelled out from the surface [1,2], and are able to migrate along the surface during electrodeposition [3] or ORR measurements [4], we show for the first time that such movement is not entirely stochastic, but directional. With the support of FEM simulations, we postulate that such directional NC migration is caused by an uneven distribution of flux around individual NPs caused by partial overlap of O_2 diffusion zones during the ORR measurements.

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Variation of the Fermi level of the Nanoparticle: Effect of the Collision with an Electrode and the Contact Electrification

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When a metallic nanoparticle (NP) comes in close contact with an electrode, its Fermi level equilibrates with that of the electrode. In the absence of chemical reactions in solution, the charge on the metallic nanoparticle is constant outside the cut-off distance for electron tunneling before or after the collision. However, the double layer capacitances of both the electrode and the NP are influenced by each other, varying as the function of distance [1]. Because the charge on the nanoparticle is constant, the outer potential of the metallic NP and hence its Fermi level varies as the capacitance changes. This effect is more pronounced for small particles (< 10 nm) in diluted supporting electrolyte solutions, especially if the metallic nanoparticle and the electrode have different potentials of zero charge (pzc), as shown in Fig. 1. NPs were found to be more electrochemically active in the vicinity of the electrode [1]. The force between the equilibrated NP and the electrode is always repulsive when they have the same pzc. Otherwise there can be an attraction even when the NP and the electrode carry charges of the same sign, due to the redistribution of surface charge density at both the NP and electrode surface [1]. These effects have not been considered before in the impact electrochemistry of NPs on the electrodes.

Additionally, we have recently proposed that another phenomenon affecting the charge state and potential of bimetallic systems, namely the contact electrification, can be quantitatively understood by simply considering the bimetallic segregated systems as a nanocapacitor, where a thin vacuum layer separates the two metals (Fig. 1). The potential difference between the two metals is directly given by the work function difference (or in solution by the pzc difference), and the amount of transferred charge can be calculated simply from electrostatics [2,3].

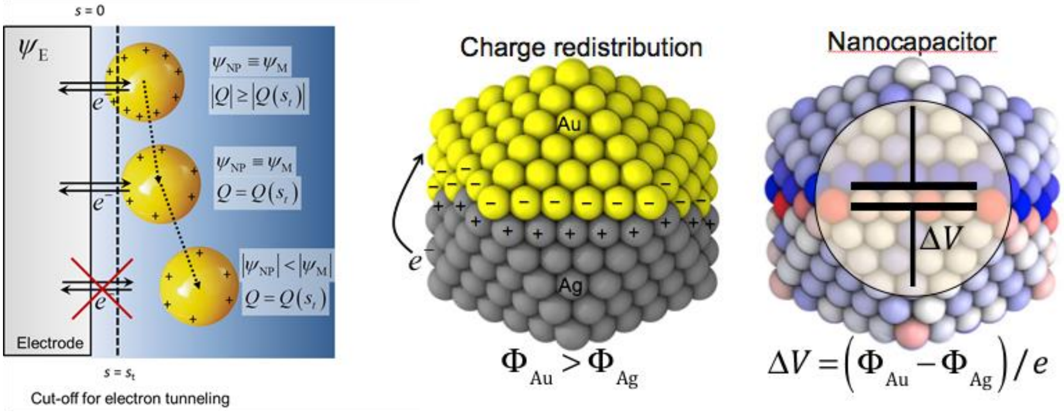

Figure 1. Charge redistribution due to contact electrification, leading to formation of electrostatic dipoles with an electric double layer when immersed in electrolyte solutions.

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Ligand Exchange Reactions in Thiolate-Protected Au_{25} Nanoclusters with Selenolates or Tellurolates: Preferential Exchange Sites and Effects on Electronic Structure

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Thiolate-protected gold clusters ($Au_n(SR)_m$) with small metal cores have a geometrical/electronic structure different from that of the corresponding bulk metal. Regarding the geometric structure of $Au_n(SR)_m$ clusters, a special atomic arrangement with restrained surface energy for a given volume, such as an icosahedral structure, appears in addition to the close-packed structure of bulk gold. Furthermore, $Au_n(SR)_m$ clusters possess a discrete electronic structure instead of a continuous bulk structure. Because of these differences from bulk gold, small $Au_n(SR)_m$ clusters exhibit size-specific physical and chemical properties, such as photoluminescence, redox behavior, and catalytic activity. In addition, these properties and functions vary considerably depending on the number of constituent metal atoms and geometrical structure of the metal core. $Au_n(SR)_m$ clusters with these characteristic features have attracted much attention as new functional nanomaterials in a variety of fields ranging from basic research to applications. Ligand exchange reactions have also been extensively studied for the exchange site. These reactions can introduce new ligands onto $Au_n(SR)_m$ clusters to afford new physical/chemical properties and functions. Many studies on the ligand exchange reactions of $Au_n(SR)_m$ clusters using other chalcogenates (i.e., selenolates or tellurolates) as exchange ligands have been conducted in recent years. However, there is limited information on the preferential exchange sites and electronic structure of the exchanged products. In this presentation, we introduce the geometric and electronic structures of the products obtained by reacting $[Au_{25}(SC_2H_4Ph)_{18}]^-$ with PhSeH or $(PhTe)_2$. Single-crystal X-ray structural analysis revealed that these exchange reactions preferentially produce products containing substituted ligands close to the gold core (Figure 1). In addition, we quantitatively determined the changes in the redox potentials and optical transition energies induced by continuous ligand exchange (Figure 2). This systematic investigation revealed that exchange with SePh induces nonlinear changes in the electronic structure of the clusters with the number of exchanged ligands (Figure 2). These findings are expected to lead to the improved design guidelines to produce clusters with new functions by ligand exchange with other chalcogenates.[1]

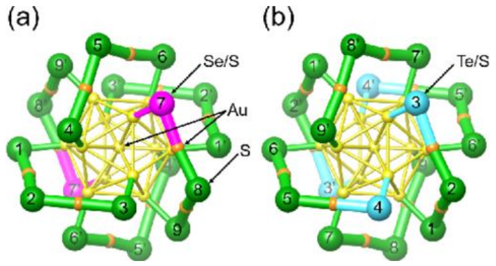

Figure 1. Framework structures of clusters obtained by reacting $[Au_{25}(SC_2H_4Ph)_{18}]^-$ with (a) PhSeH and (b) $(PhTe)_2$.

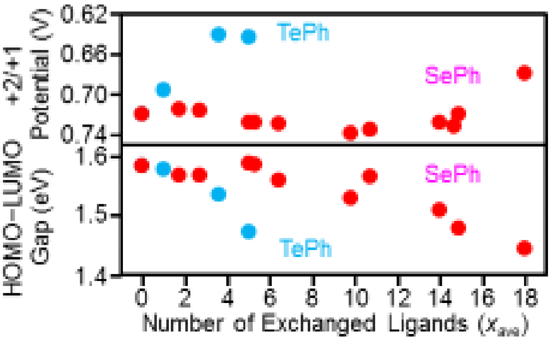

Figure 2. Correlations between the number of exchanged ligands and electronic structure.

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Metal-Support Interactions of Pt Nanoparticles supported on Boron Carbide Composites

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Fundamental research into PEFC is focused on the kinetic activity, stability and cost of the cathode catalysts[1]. Considerable efforts have been made on improving Oxygen Reduction Reaction (ORR) activity via nanoparticulate Pt and Pt alloys supported on high surface area carbon[2,3]. The relationship between the rate of the cathode reaction and the oxygen adsorption energy shows a volcano-shaped trend, with platinum closest to the peak, in agreement with d-Band theory[4], which provided the leading design principle for advanced ORR catalysts over the last decade. Substantial research was made to identify alloy partners for Pt that shift the d-band centre to sufficiently destabilise oxygen intermediates with substantial success at the lab scale[5]. An alternative method of improving platinum ORR activity is by utilisation of strong metal support interactions (SMSI's).

A recently developed technique by Zalitis *et al.* (2013)[6] was tailored to incorporate the advantages of both the *ex-situ* RDE method and *in-situ* PEFC measurements by an *ex-situ* procedure conducted under high mass transport and low catalyst loading conditions. This technique performed on a commercial Pt/C catalyst are comparable to kinetic activities for ORR reported for *in-situ* PEFC[6]. This high mass transport technique, therefore, allows for *ex-situ* fundamental studies on ORR catalysts to be carried out, while remaining comparable PEFC.

We will present our work on boron carbide composites as electrocatalyst support materials for ORR. This study investigated the kinetic ORR activity of Pt/BC and Pt/C catalysts under high mass transport and low catalyst loading conditions, and compared these results to traditional RDE measurements. The role of SMSI's on kinetic catalytic activity for the ORR due to species adsorption to the platinum surface is investigated in acidic media. Advanced surface characterisation was conducted via *in-situ* X-ray Absorption Spectroscopy (XAS) to investigate the d-band vacancy changes at a range of potentials.

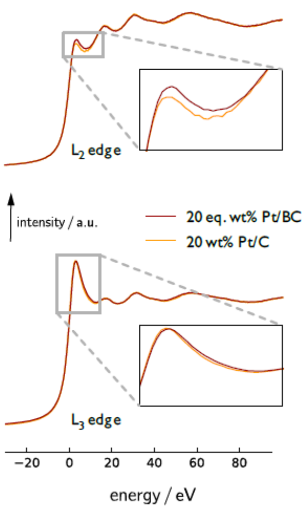

Figure 1: *in-situ* XANES L_2 and L_3 edge measured at 744 mV vs. NHE.

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Metal Nanoclusters: Synthesis, Structures and applications in Electroanalysis and Electrocatalysis

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Coinage metal nanoclusters consisting of several to hundreds of atoms have attracted intensive attention due to their size-dependent unique physical and chemical properties resulting from the discrete energy levels and band-gap energy structures, and their widely potential application in biosensors, nanodevices, data storage, and catalysis etc. In recent years, compared to silver and gold, the reports on the synthesis and properties of copper nanoclusters are relatively limited for its susceptible to oxygen that render poor stability. However, the abundance, low-cost of copper and its properties distinctly different from silver and gold motivate us to find a new and efficient strategy for the preparation of copper clusters and explore their application in analysis. We report here the synthesis of metal nanoclusters, especially copper clusters with controlled composition through chemical reduction processes and the determination of their structures. By loading the as-synthesized metal clusters on different substrates, the nanoclusters were successfully applied to the electroanalysis including the detection of glucose, hydrogen peroxide. Compared to large metal nanoparticles, the nanoclusters exhibited higher detection sensitivity and wider linear range. Meanwhile, metal nanoclusters showed high electrocatalytic activities for hydrogen evolution reaction etc. [1-6]

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Electrocatalytic Hydrogen Production Using Molecular-like Metal Nanoclusters

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The next generation and renewable energy, hydrogen, has received great attention due to its possibility for efficient energy production and solving problems for the depletion of fossil fuel. Hydrogen evolution reaction (HER) has been studied with various catalysts such as bulk metals and metal complexes represented by Pt metal and hydrogenase. Molecular-like gold nanoclusters, especially ultrasmall Au_{25} nanocluster that has similar characteristic with both bulk metals and metal complexes has distinctive catalytic activity for renewable energy production. Furthermore, the activity and selectivity for the catalytic reactions can be easily modified by introducing a foreign metal such as Pt into the Au_{25} platform. In this presentation, we report synthesis of ultrasmall Au nanoclusters; namely, $Au_{25}(SR)_{18}$, and bimetallic $PtAu_{24}(SR)_{18}$ clusters, where SR is thiolate, and their electronic structures and catalytic properties. Unlike Au_{25} nanocluster that shows high catalytic activity for CO_2 reduction reaction, mono Pt doped $PtAu_{24}$ nanocluster exhibits remarkable HER activities with very low onsetpotential (E_{onset}=70mV vs. RHE) that is comparable to that of natural hydrogenase (~100 mV) enzymes and high TOF value of 34 mol H_2 $(molcat)^{-1}s^{-1}$ (at $\eta = 0.6$ V). This can be ascribed to the positive shift of the reduction potential that matches well with the reduction potential of proton and its thermodynamically neutral binding energy for proton adsorption. The outstanding HER activity of $PtAu_{24}(SR)_{18}$ was clearly manifested when comparing with the benchmarking Pt/C catalyst.

Zeolitic Imidazolate Framework-Derived ZnSe/Porous Carbon/ PEDOT:PSS as the Counter Electrode for Dye-Sensitized Solar Cells

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Recently, metal-organic frameworks (MOFs) have received extensive attention as a class of porous crystalline materials, which are composed of metal ions/clusters and coordinated organic ligands. These materials possess unique structural topology and tunable functionalities that are useful for gas absorption, separation, catalysis, sensors, dye-sensitized solar cells (DSSCs), and so on. Zeolitic imidazolate frameworks (ZIFs), which are composed of tetrahedrally-coordinate transition metal ions (*e.g.* Co, Cu, Zn *etc.*) connected by imidazolate linkers, are a class of MOFs that are topologically isomorphic with zeolites.

In this study, we synthesized zinc selenide (ZnSe) derived from ZIF-7 as the counter electrode (CE) material in DSSCs. The as-prepared ZIF-7 was annealed in a furnace at 900 ˚C holding for 1 h in N_2. After that, the sample was selenized at 450 ˚C holding for 30 min in N_2 to get the product, ZIF-7 C-Se (ZnSe-C). Subsequently, the product was mixed with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) in ethanol and the solution was drop-coated on 1 cm^2 controlled FTO substrate at 50 ˚C on a hot-plate. The ZIF-7 C-Se/PEDOT:PSS (ZnSe-C-P) thin film was obtained.

As shown in Fig. 1(a), the scanning electron microscopy (SEM) image shows that the bare ZnSe-C materials exhibit a popcorn-like structure. Fig. 1(b) shows that the morphology of PEDOT:PSS is pretty flat. Fig. 1(c), reveals that PEDOT:PSS uniformly covers on ZnSe-C, suggesting that it is beneficial for the charge transfer. The photocurrent density-voltage (J-V) curves of the DSSCs with the CEs of the bare ZnSe-C, bare PEDOT:PSS, optimized ZnSe-C-P and Pt are given in Fig. 2. ZnSe-C-P exhibits an attractive photovoltaic conversion efficiency of 8.69%, which is higher than that of Pt (8.26%), suggesting that ZnSe-C-P has an excellent electrical conductivity and good electro-catalytic ability toward I_3^- reduction. Fig. 3 shows cyclic voltammograms (CV) of various electro-catalytic films. Among these CEs, ZnSe-C-P has the highest value of the peak current density among the CEs, once again confirms that it has good electro-catalytic ability toward I_3^- reduction. Moreover, the peak-to-peak separation (ΔE_p) of ZnSe-C-P is smaller than those of bare ZnSe-C and bare PEDOT:PSS, showing that it is easier to trigger the redox reaction. This study concludes that CE based on ZnSe-C-P is a prospective substitute to Pt and could provide new opportunities for advancing high-efficiency DSSCs.

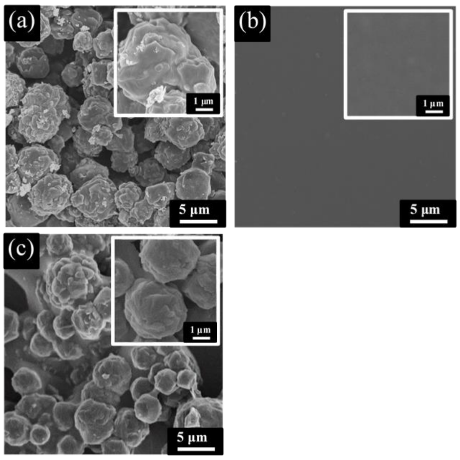

Fig. 1 FE-SEM image of (a) bare ZnSe-C, (b) bare PEDOT:PSS, and (c) optimized ZnSe-C-P.

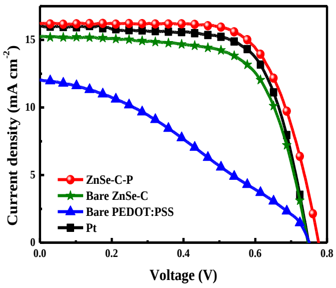

Fig. 2 Photocurrent density−voltage (J−V) curves of the DSSCs with the CEs of the bare ZnSe-C, bare PEDOT:PSS, optimized ZnSe-C-P, and Pt.

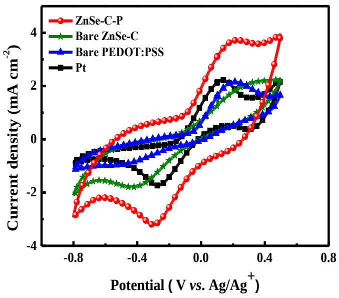

Fig. 3 Cyclic voltammograms of I^-/I_3^- redox couple on the CEs of the bare ZnSe-C, bare PEDOT:PSS, optimized ZnSe-C-P, and Pt.

Electrocatalytic Reduction of Carbon Dioxide on Metal Nanoclusters

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Metal nanoclusters containing a few to a few hundreds of atoms have been the focus of recent investigations because of their novel electronic, optical, and catalytic properties. They appear to represent the bulk-to-molecule transition region where electronic band energetics yield to quantum confinement effects and discrete electronic states emerge. In this presentation, we report efficient and selective electrocatalytic conversion of CO_2 based on atomically precise metal nanoclusters. Gold, silver and bimetallic nanoclusters, such as $Au_{25}(SR)_{18}$, $Ag_{25}(SR)_{18}$, and $PtAu_{24}(SR)_{18}$, where SR is alkanethiolate, were synthesized and cast on glassy carbon electrode. Electrocatalytic activities of these clusters for the reduction of CO_2 were compared in an H-type cell. Product analysis using gas chromatography has shown that CO was predominantly produced on $Au_{25}(SR)_{18}$ and $Ag_{25}(SR)_{18}$ while H_2 was favorably produced on $PtAu_{24}(SR)_{18}$.

Insight in the electrochemistry of earth-abundant, magnetron sputtered molybdenum sulfide nanoclusters

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Metallic clusters have gathered significant attention in the past years in the catalysis community due to their well-defined properties. In particular, cluster preparation by magnetron sputtering and gas condensation techniques permit the tailoring of crucial parameters in catalysis such as composition and loading. In conjunction with a lateral time-of-flight mass filter, nanoclusters can be obtained with a highly accurate size control.[1] Magnetron-sputtered nanoclusters have been extensively prepared with precious metals[2] and their alloys,[3] but earth-abundant materials are scarcely explored. Transition metal dichalcogenides (TMDs), and specifically molybdenum disulfide (MoS_2), have been incrementally investigated as earth-abundant substitutes of precious metal catalysts for the hydrogen evolution reaction (HER) in photoelectrochemical and PEM electrolyser devices.[4] Previous investigations in our group lead to the successful fabrication of size-selected lamellar MoS_x nanoclusters with masses in the 50-2000 MoS_2 units range, and Mo:S ratio 1:1.6±0.1.[5] This work expands the application of magnetron sputtered MoS_2 nanoclusters by analyzing their inherent electrochemistry and electrocatalytic performance to the HER. Two routes were explored to maximize their HER activity: the activation of the catalytically inactive S-edge sites by transition metal doping,[6] and sulphur incorporation to increase the content of bridging S_2^{2-} and terminal S^{2-} ligands responsible for proton adsorption/desorption.[7] The first was carried out with a one-step, dual target (Ni and MoS_2) magnetron sputtering and gas condensation technique. The resulting Ni-MoS_2 hybrid nanoclusters (average diameter= 5.0 nm, Mo:S ratio = 1:1.8±0.1) showed enhanced activities compared to the undoped $MoS_{0.9}$ nanoclusters: 100 mV onset potential shift and 3-fold increase in exchange current density.[8] Additional anodic stripping experiments proved that undoped and doped Mo- or S-edge sites are electrochemically distinguishable according to their thermodynamic stability and relative abundance. The second was undertaken by exposing size-selected MoS_2 nanoclusters to a sulphur gas under UHV conditions. Aberration-corrected STEM studies revealed minor size modifications (5.5 to 6 nm) as well as higher crystallinities in the nanoclusters after sulphur evaporation and annealing.[9] Subsequent electrochemical tests revealed an almost 200 mV HER onset potential upward shift of sulphur-modified MoSx nanoclusters with respect to the unmodified counterparts. We believe these results provide invaluable information for the preparation of novel nanostructured TMDs with higher activities and stabilities.

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Ligand-Protected, Au/Cu Nanoparticles for the Electrochemical CO_2 Reduction Reaction

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Converting waste CO_2 emissions into value added chemicals and fuels is an appealing carbon mitigation strategy because the products can generate revenue. The electrochemical CO2 reduction reaction (CO_2RR) is a leading CO_2 conversion approach because it can operate at high reaction rates and excellent efficiency at ambient conditions using environmentally friendly aqueous electrolytes and carbon-free electricity sources (wind, solar, etc.). We've combined experimental and computational techniques to understand the electronic structure and CO_2RR activity of thiol-capped, 2±1 nm, bimetallic gold-copper nanoparticles (Au/Cu NPs). The Au/Cu NPs contained between 0 and 64% Cu. X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and extended x-ray absorption fine structure (EXAFS) to determine the oxidation state and likely location of copper atoms within the Au/Cu NPs. Cu atoms adopted a +1 charge state and preferentially occupied oligomer structures within the ligand shell, rather than the nanoparticle "core". This observation confirms the experimental and computational work by the Tsukuda,[1] Millstone,[2] and Hakkinen groups.[3] A combination of near infrared photoluminescence (NIR PL) and soft X-ray absorption spectra at the Sulfur L edge also indicated that composition-dependent shifts in PL energy often observed for small, thiol-capped bimetallic NPs stems from perturbation of emissive S states in the ligand shell. Realistic Au/Cu NP models were constructed with density functional theory (DFT) based on the predicted crystal structure of $Au_{144-x}Cu_x(SR)_{60}$ nanoclusters.[3] The resulting nanocluster models showed excellent structural agreement with experimentally-measured Cu K-edge EXAFS data, and we analyzed the composition-dependent CO_2RR energetics at the NP surface. The predicted CO_2RR reaction pathway also agreed with experimentally-determined Tafel slopes and we determined the initial electron transfer to CO_2 as a rate limiting step for all Au/Cu NP compositions. The Au/Cu NPs showed composition-dependent CO_2RR rates that exceeded pure Au NPs. Interestingly, the bimetallic NPs produced only CO and H_2, whereas bulk, polycrystalline copper produced a mixture of H_2, CO, CH_4 and C_2H_4. Electrocatalytic activity studies identified 49% Cu NPs as the most active composition with reaction turnover frequencies exceeding 60 s^{-1} and Faradaic Efficiencies approaching 100% at -1.0V *vs.* RHE. This study shows that atomic composition can be used to tune the electronic structure and chemical reactivity of small bimetallic NPs.

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Platinum-modified Titanium Electrode for Electrochemical Ozone Generation Prepared by the Multiple Electrostrike Method

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There are some electrodes for electrochemical ozone generation. For example, boron-doped diamond (BDD) electrode [1] and tantalum oxide–platinum composite electrode [2]. However, these electrodes cannot be prepared with low cost, large area, and simple methods. In this work, electrochemical ozone generation at an easily prepared platinum-modified titanium (Pt/Ti) electrode was investigated in comparison with a BDD or a Pt electrodes. The Pt/Ti electrode was prepared by our original method, multiple electrostrike (ME) method as follows. A vibrating Pt wire (cathode) was rubbing over the titanium plate (anode) surface with 7.5 V of potential. Molten Pt metal particles ranging from several nanometers to submicrometers were sprayed onto Ti plate (Fig. 1, bright spots). Ozone generation activity of the electrodes was evaluated in acryl sealed 36 L box (Fig. 2 left). Ozone gas has been generated potentiostatically (5 V) in 3 mL of 0.5 M H_2SO_4 and dispersed by the fan. Ozone generation activity of the Pt/Ti electrode was found to be much higher than that of a BDD or a Pt electrodes (Fig. 2 right). The superiority of the Pt/Ti electrode over simple preparation method, in terms of the flexibility, durability, and ozone generation activity were demonstrated with the conventional methods and conditions. This research is attractive to develop a practical unit for inexpensive and effective ozone generators.

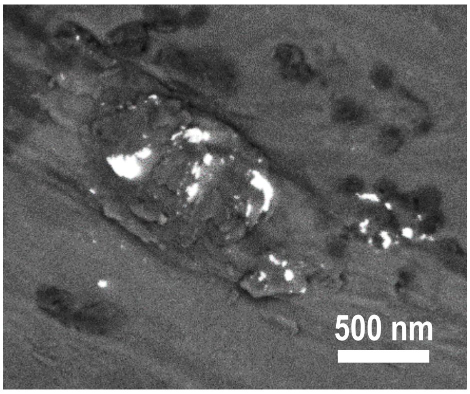

Figure 1. Back scattered electron image of the Pt/Ti electrode.

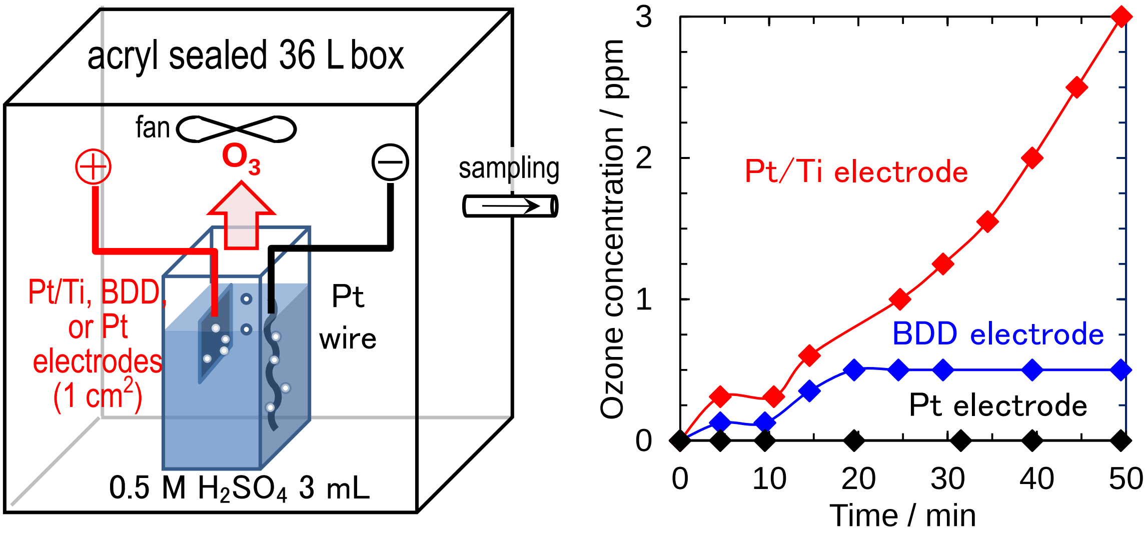

Figure 2. Schematic illustration of the evaluation method (left) and ozone generation activity (right) of the electrodes.

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Does geometry matter in nanoparticle's reactivity towards glucose sensing?

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Developments in controlled nanoparticles synthesis of different metals, has reached the point where the most varied geometries and sizes of a large number of materials have been obtained[1]. By controlling the geometry, it is also possible to obtain different catalytic, photochemical[2] and electrochemical responses[3]. In the present work, cuprous oxide nanoparticles (Cu_2O-NPs) were synthesized obtaining different geometries such as cubes (crystallography type (100)), octahedra (crystallography type (111)) and spheres presenting a mixture of both to crystallographic phases. The average size of all nanoparticles was between 200 – 250 nm.

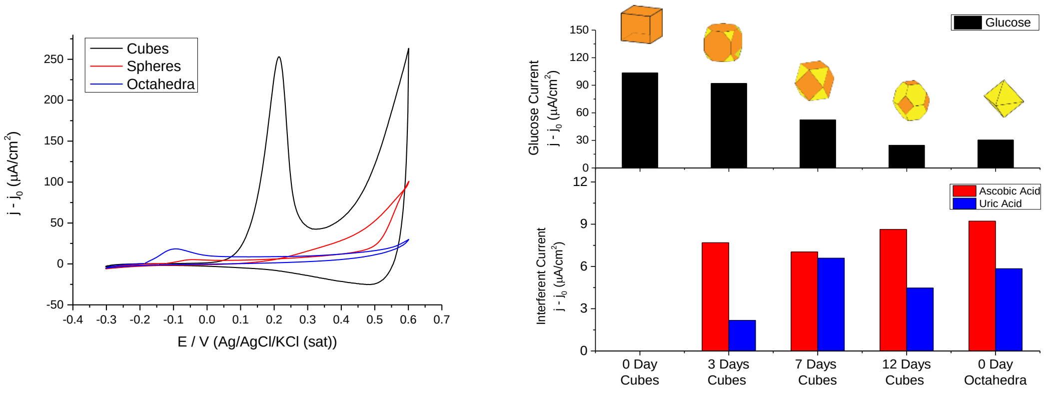

Figure 1. j/E Profiles of different Cu_2O-NPs in NaOH 0.1 mol L^{-1}, v = 10 mV s^{-1}. Current densities for glucose (top panel) and interferents (bottom panel) for cubic Cu_2O-NPs as a function of time after their synthesis. The last point in the curve displays the current densities obtained for freshly prepared octahedral Cu_2O-NPs .

Figure 1 shows different electrochemical responses for each type of geometry. Reactivity tests were accompanied by a chronoamperometric analysis for glucose detection, obtaining different behaviors for each type of Cu_2O-NPs, as well as the analysis of some interferents like Ascorbic Acid (A.A.) and Uric Acid (U.A.). Very high selectivity can be observed for the cubic Cu_2O-NPs . It was established a relationship between structural stability and shelf time, which was accompanied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The importance of the structure and crystallography stability for each Cu_2O-NPs was demonstrated for obtaining high catalytic currents and selectivity for chosen analytes.

Acknowledgments

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Electrocatalytic Oxidation of Organic Molecules and DNA by Ligand-Free Gold Nanoclusters on Nitrided Carbon

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Electrocatalytic properties of ligand-free gold nanoclusters (AuNCs, < 2 nm) grown on nitrided carbon supports (denoted as AuNCs@N-C) were evaluated for the oxidation of representative organic molecules including alcohols, an amine, and deoxyguanosine in oligonucleotides and DNA. AuNCs@N-C catalysts were incorporated into films of architecture {PDDA/AuNCs@N-C}$_n$ using layer-by-layer (LbL) assembly with oppositely charged poly(diallyldimethylammonium) (PDDA) onto pyrolytic graphite (PG) electrodes. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to survey the electrocatalytic properties of these AuNCs@N-C films. Ligand-free AuNCs in these films demonstrated excellent electrocatalytic oxidation activity with maximum peak currents and lowest potentials for oxidizing ethanol, propanol, and tripropylamine (TprA) compared to controls with Au-surface capping agents or to larger sized Au nanocrystals on the nitrided carbon supports. Kinetic studies by EIS showed that ligand-free AuNCs films gave the smallest charge transfer resistance, largest electrochemical active surface area and largest apparent standard rate constants, compared to the control films for all compounds examined. DNA films on AuNCs@N-C were oxidized at deoxyguanosine moieties with good catalytic activity that depended on charge transport within the films. More recently, we have found that embedding the AuNCs@N-C particles in Nafion films on PG electrodes provided very good voltammetric signals for oxidized DNA and DNA that had bee reacted with styrene metabolite styrene oxide. Results suggest that these electrodes can be used as sensors for screening DNA damage and oxidations by metabolites of genotoxic chemicals.

Electrochemical Synthesis and Tribological Properties of Flower-like and Sheets MoS_2 in LiCl-KCl-(NH4)$_6$Mo$_7$O$_{24}$-KSCN Melt

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Abstract:

MoS_2 has attracted increasing attention due to the fascinating chemical, physical and mechanical properties, which was used in many applications such as lubricants, energy-storage devices, capacitors and sensing platforms [1,2]. This work presented the electrochemical synthesis of three-dimensional flower-like and sheets molybdenum disulfide structures by co-reduction of Mo(IV) and S(II) ions on a Mo electrode in molten LiCl-KCl-$(NH_4)_6Mo_7O_{24}$-KSCN. The influence of temperature and current density on the formation of MoS_2 was studied, and the controllability of MoS_2 structure and the high purity of the sample were realized. Afterward, all the MoS_2 were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), high-resolution TEM (HRTEM) and pin-on-disc friction and wear machine. Fig. 1 illustrated the SEM (a), SAED (b) and HRTEM (c) images of MoS_2. As shown in Fig. 1a, three-dimensional flower-like molybdenum disulfide hierarchical structures were revealed. The selected-area electron diffraction patterns (Figure. 1b) confirmed that crystal was single-crystal characteristics. The selected-area electron diffraction (SAED) pattern can be indexed as a hexagonal MoS_2 single crystal, recorded from the [111] zone axis. The typical flower-like structure of MoS_2 was confirmed by the ordered lattice fringes of 0.34 nm, which correspond to the interlayer spacings of the (002) planes (see the HRTEM image in Figure 1c). Pin-on-disc friction and wear machine MoS_2 as a solid lubricant had the low friction coefficient and good wear resistance.

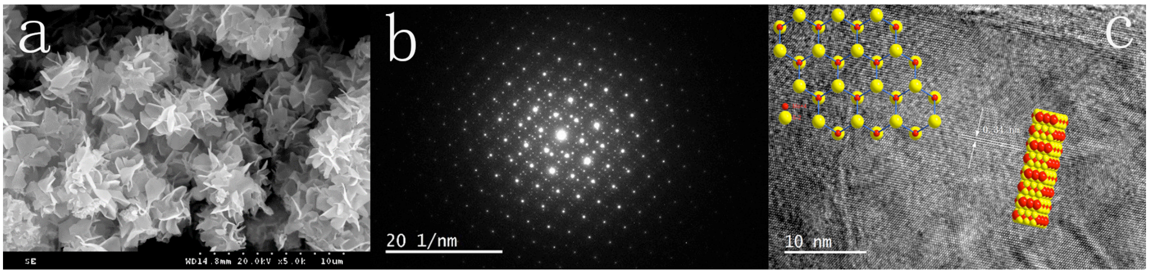

Fig. 1 SEM image (a), SAED (b) and HRTEM image (c) of MoS_2

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Consistent Models for Electrochemical/Mechanical Coupling in Solid Ion Conductors

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Our group has recently dedicated substantial effort to the production of thermodynamically consistent transport theories to describe concentrated electrolytes, with the aim of accounting for transport effects that arise from the thermodynamics of solution volume. We have found that so-called 'excluded-volume effects' can be substantial for non-aqueous liquid electrolytic solutions, in which dissolved ions typically occupy a substantial volume fraction. In simulations of the one-dimensional experimental geometries typically used to establish transport properties for lithium-ion-conducting electrolytes, we find that the neglect of these effects leads to appreciable errors in measured properties.

For system geometries with spatial dimensionality greater than 1, it is found that models are not closed if they carry a volume-explicit equation of state for the electrolyte alongside the typical concentrated-solution theory. We have addressed this issue and achieved model closure by carrying a momentum balance alongside the typical governing equations for transport theory.

The addition of a momentum balance to concentrated-solution transport theory begs a number of theoretical questions. A particularly significant set of problems arises when considering the interaction between electrochemical transport and mechanical stress for elastic solid electrolytes, such as the recently popular class of solid superionic lithium conductors. This talk will focus on our recent progress toward developing a theoretical model that allows for general treatment of ion transport and mechanics in these ceramic, ionically conductive materials. We will describe a variety of new thermodynamic measurements that may be needed to characterize elastic solid electrolytes, describe the modifications of familiar transport laws that are needed to account rigorously for the energetic impact of electrolyte elasticity, and examine the impact of electrochemical/mechanical coupling on practical data such as impedance spectra.

Simulation Study of Ion Diffusion in Charged Nanopores with Anchored Terminal Groups

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We present coarse-grained simulation results for the enhanced ion diffusion in a charged nanopore grafted with ionomer sidechains. The pore surface is hydrophobic and its diameter is varied from 2.0 nm to 3.7 nm. The sidechains have from 2 to 16 monomers (united atom units) and contain sulfonate terminal groups. Our simulation results indicate a strong dependence of the ion diffusion along the pore axis on the pore parameters. In the case of short sidechains and large pores the ions mostly occupy the pore wall area, where they are strongly associated with their host sulfonates. In the case of short sidechains and narrow pores, the electrostatic delocalization of the ions stemming from their loose association with the sulfonates is outweighed by the structuring and polarization effects of the water molecules. In the case of long sidechains, and when the sidechain sulfonates reach the pore center, a radial charge separation occurs in the pore. Such charge separation suppresses the ion diffusion along the pore axis. An enhanced ion diffusion was found in the pores grafted with medium-size sidechains provided that the ions do not enter the central pore area, and the water is less structured around the ions and sulfonates. In this case, the 3D density of the ions has a hollow-cylinder type shape with a smooth and uninterrupted surface. We found that the maximal ion diffusion has a linear dependence on the number of sidechain monomers. It is suggested that the maximal ion diffusion along the pore axis is attained if the effective length of the sidechain extension into the pore center (measured as the doubled gyration radius of the sidechain with the Flory exponent 1/4) is about 30% of the pore radius.

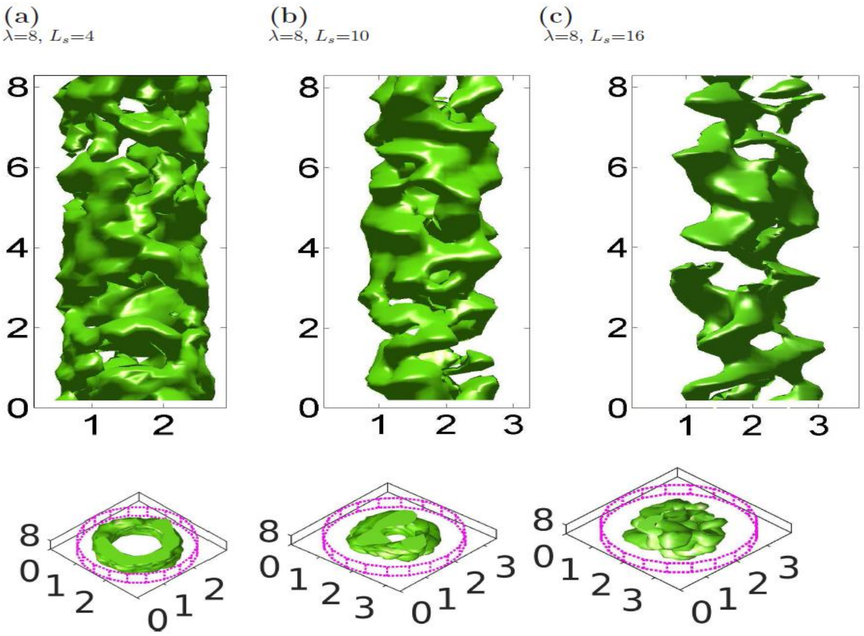

Figure. 3D ion density distribution $\rho_H(r)$ for sidechain length L_S=4 and pore diameter d=2.9nm (a), L_S=10 and d=3.3nm (b), and L_S=16 and d=3.6nm (c) for the water content λ=8. The figures on the upper row correspond to the projection of $\rho_H(r)$ on the *xz*-plane (only a section of the pore along *x*-axis is shown). The figures on the bottom row correspond to the projection of $\rho_H(r)$ on the *yz*-plane with a slight angular tilt for showing the internal surface of the density distribution. The pink-colored circles and lines in the bottom row figures represent the position of the pore surface. The ion diffusion for the intermediate case (b) is maximal.

E. Allahyarov, P. L. Taylor, H. Löwen, *Enhanced ionic diffusion in ionomer-filled nanopores*, J. Chem. Phys. **143**, 243126 (2015).

Analytical Theoretical Treatment of Interfacial Charge-Transfer Mechanisms at Microinterfaces

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The redox/ionic species involved in interfacial electron/ion transfer processes often show some kind of reactivity in solution: isomerization, complexations, ion pairing, (de)protonation, etc. This makes the interpretation of experimental data more challenging, though it also opens the possibility of applying electrochemical techniques to the study of homogeneous chemical reactions. For the accurate modelling of such situations and the determination of the corresponding chemical kinetics and thermodynamics, in this communication a very general and simple theoretical approach is presented, applicable to any (pseudo)first-order reaction mechanism. Special attention will be paid to the use of microelectrodes and liquid|liquid microinterfaces given the benefits these offer for experimental quantitative studies.

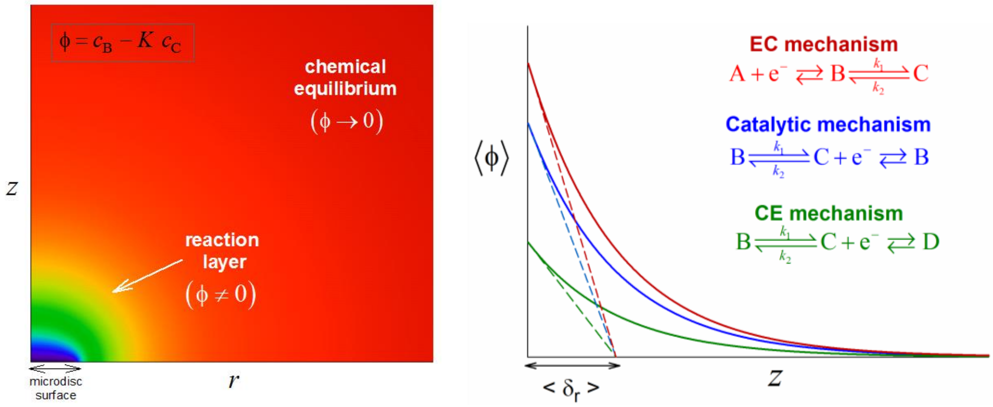

Figure 1. Linear reaction layer (δ_r) at a microdisc electrode as an estimation of the region of the solution where chemical equilibrium conditions are perturbed by the interfacial process. Three electrode mechanisms are considered as examples.

The theoretical treatment is based on a suitable and physically-sound definition of the so-called linear reaction layer, δ_r (see Figure 1) [1], which takes into account the influence of the mass transport conditions. Hence, the δ_r-value will depend, not only on the chemical kinetics, but also on the size and shape of the interface when its characteristic length(s) lies in the micrometer scale. Accordingly, analytical expressions for δ_r are obtained for the most common geometries of microelectrodes and liquid|liquid microinterfaces [2].

Once the mathematical form of δ_r is established appropriately, and by making use of the so-called diffusive-kinetic steady state approximation [3], simple closed-form expressions are derived for the transient current-potential response of a number of mechanisms of electron transfer (catalytic, CE, EC, ECE, open square, CEC, square schemes) and ion transfer (facilitated transfer, inhibited transfer, ACDT) at microelectrodes (microdiscs, microbands, etc.) and liquid|liquid microinterfaces. The expressions derived yield accurate results in very reduced calculation times compared to numerical simulations. Also, the steady-state and the total chemical equilibrium responses can be derived as limiting cases.

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Beyond Newman's Model: Microstructurally-Resolved Simulations of the Dynamic Responses of Lithium Ion Batteries upon Cycling

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The so-called Newman's mathematical model [1] has nowadays a tremendous impact on the understanding and optimization of Lithium Ion Battery (LIB) cells. This model is supported on the porous electrode theory, where lithium ion transport is explicitly described in both the electrolyte and the active material, and where closure Butler-Volmer equations allow linking the calculated electrostatic potentials at both liquid and solid. However, at the active material level, it does not consistently link the lithium transport mechanism at the atomistic scale with the macroscopic diffusion properties: indeed, solid transport is modelled as a Fickean diffusion process. Fickean models have the advantage that they can be parameterize with a single parameter (the diffusion coefficient) measurable with techniques such as the galvanostatic intermittent titration technique (GITT), potentiostatic intermittent titration technique (PITT), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV), but which lead to a significant discrepancy in the reported values [2] [3]. This discrepancy among the reported studies probably results from the fact that these models used to fit experimental data neglect the microstructure details inside the active material. Therefore, refining the description of the transport mechanisms at the active material level is of crucial importance for a correct evaluation of the cell performance and for its optimization.

In this work we report a novel bottom-up multiscale cell model built on the basis of irreversible thermodynamics principles [4] [5]. In particular, the model describes the lithium transport in the active material by capturing the influence of the microstructural details at the particle level, and allows linking atomistic level calculations (lithium hopping between sites) and the macroscopic mathematical formulation of the diffusion process. We apply our model to graphite and metal oxide (such as Li_yCoO_2) LIB active materials. Results obtained are compared to the ones obtained with the Newman's model and from in house extracted electrochemical experimental data. Practical implications of using our model to extract diffusion coefficients from GITT, PITT and EIS experiments are discussed.

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Acceleration of Saddle-Point Searches Assisted by Machine Learning

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The general aspect of electrocatalysis is to rationalize the relationship between electricity and chemical change[1]. For a mechanistic understanding of electrocatalytic reactions, one normally requires the calculation of reaction energies and activation energy barriers[2]. This is a computationally demanding task because the needed potential energy surface (PES) is a non-convex function built by solving the electronic structure problem several hundreds of times. At present, there exist methods designed to facilitate the finding of saddle-points such as nudged elastic band[3] (NEB), dimer method[4], and conjugate peak refinement method[5]. However, they may still be time-consuming processes especially for those cases when the gradient is computed.

In recent years, machine learning (ML) has emerged as an alternative way to predict energies and atomic forces. Artificial neural networks (NN), together with adequate local chemical environments in an atom-centered model[6], have demonstrated to be a powerful supervised ML algorithm to fit and mimic complex functions such as the PES. The methodology to perform ML predictions is based on three steps: 1) building a training set, 2) training the model, and 3) doing predictions.

In this contribution, we will show how ML can decrease by orders of magnitudes the computational time needed by the aforementioned saddle-point search methods without losing accuracy[7]. To accomplish this, we will employ the Atomistic Machine Learning Package[8] (Amp) together with density functional theory calculations to achieve predictions at *ab initio* level.

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Flight Path Fuel Cell: Theory and Modeling Setting the Course for Future Aviation

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The global transition to a clean and sustainable energy infrastructure does not stop at aviation. Since air traffic accounts for ~6% of the global energy consumption, the European Commission defined a set of environmental goals for the "Flight Path 2050": 75% CO_2 reduction, 90% NO_x reduction and 65% perceived noise reduction. Using hydrogen as an energy carrier cannot only fulfill these needs, it would also offer a tenable and flexible solution for intermittent, large scale energy storage for renewable energy networks [Bockris 1980]. For aircrafts, hydrogen has the advantage of a 3 times higher gravimetric energy density (33.3 kJ/kg) compared to hydrocarbons. Although the 4 times lower volumetric energy density gives some grievance, early aircraft design studies found a benefit for hydrogen in large, long range passenger airplanes in which the fuel accounts for a large weight fraction [Bockris 1980].

Once hydrogen is used as an energy carrier, there is no better device than a fuel cell to convert its stored chemical energy. With the spike of polymer electrolyte fuel cells (PEFC) in the 90s, aircraft design studies during the early 2000s revealed that PEFC's gravimetric power density is at least a factor of 3 too low for use in airplanes [NASA 2004]. However, since then the performance of electrocatalysts, which are the "heart" of a fuel cell, has increased by a factor of 10, with a doubling in performance about every 5.4 years [Eslamibidgoli 2016]. To unlock PEFC's potential, advances made on the materials level have to be transferred upwards the multiscale hierarchy over the cell and stack levels towards the systems level. Fuel cell system (FCS) modeling can direct this transfer and guide future research and development on the sublevels.

This talk discusses the feasibility of "all fuel cell" passenger aircrafts from a fuel cell modeling perspective. In aircrafts, FCS are exposed to unconventional and rapidly changing environmental conditions: from sea level pressure and temperatures >50°C on the tarmac of Kuwait to low pressure at -50°C a few minutes later in 10,000 m cruising altitude. Whether a FCS can be used in such an environment is assessed using the concept of feasibility envelopes. From the analysis of these feasibility envelopes, design strategies for FCS, components and materials are developed, as shown exemplary in Fig. 1.

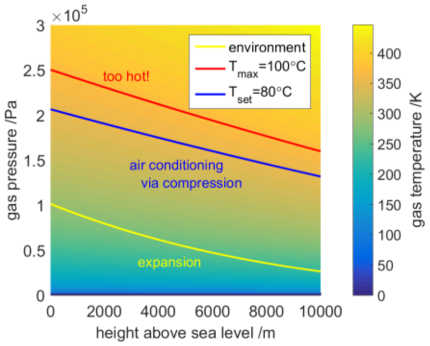

Figure 1: Feasibility envelope of an air compressor for a PEM fuel cell system. Yellow: ambient pressure and temperature. Red: pressure at which the compressed air reaches destructive temperatures. Blue: target pressure for a desired air temperature of 80°C.

Strategies for FCS design based on steady-state as well as dynamic considerations are introduced. In the dynamics-based design, hybridization strategies of fuel cells (high energy capability) with batteries or supercapacitors (high power capability) are discussed. Furthermore, model-based analyses on the FCS level can identify enabling key factors on the component and material levels and can direct future research and development efforts. Finally, the integration of FCS design into a holistic aircraft design framework and scenario-based analysis of the future of passenger aviation is sketched out.

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Local and Global Electric Driving Forces for Proton Discharge from Aqueous Solutions on Charged Electrodes. MD Trajectory Simulations

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An established reactive trajectory approach for proton discharge from aqueous solutions at charged metal surfaces is based on an extension of a minimalistic empirical valence bond (EVB) model to study proton transfer in the bulk. It relies on a parameterization of quantum mechanical density functional calculations [1] and allows the study of clean surfaces and those with charged or uncharged defects in the presence or absence of bulk electrolytes [2-4]. The model philosophy is to be minimalistic. Trajectory simulations exhibit substantial variations of characteristic quantities, e.g., discharge times and location, number and frequency of Grotthuss hops, with system composition and setup. These variations can be understood in terms of site blocking on the surface, changes in interfacial water structure and hydrogen bond network, and electrostatic screening in the liquid.

We analyze approximately 20,000 proton discharge events in aqueous NaCl solutions for different surface charge densities of the electrode and different compositions of the electrolyte solution (different number of cations and anions). Static and dynamic average electric fields acting on the proton transfer complex in directions perpendicular and parallel to the electrode surface are calculated. The time evolution of electric fields and of hydrogen bonding just before the discharge events provide a statistical view of the discharge mechanism. Given that in force field models of water and aqueous solutions the description of hydrogen bonding is an essentially electrostatic one, the relative importance of global (’electrochemical’) and local (’hydrogen bonding’and 'solvation') electric fields on the reaction mechanism can be assessed in a statistical manner.

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Modelling of the Electrochemical Impedance of Acceptor Doped Cerium Oxide

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Oxygen ion conductors, like yttrium stabilized zirconia (YSZ) or doped ceria, are currently the most suitable electrolytes for solid oxide fuel cells due to their mechanical and chemical stability and compatibility with the employed electrode materials. Their ionic conductivity is strongly influenced by dopant concentration, temperature, atmosphere and microstructure of the material. While theory and experiments generally agree on the influence of the first three parameters, the influence of the microstructure remains a hot topic. Nanocrystalline samples could display superior conductivity through enhanced grain boundary diffusion or through the effects of space charge overlap. However, accepted theories all predict a lower conductivity for nanocrystalline materials [1] – a point of view that is backed up by many experimental studies [2] but opposed by some [3].

Experimentally, it is possible to separate the bulk and grain boundary conductivities using Electrochemical Impedance Spectroscopy (EIS), but the interpretation of the obtained impedance spectra is not straightforward. Currently the measurement data is interpreted using the dilute solution model with the Mott-Schottky approximation. However, we know from measurements and atomistic simulations that these assumptions are simply not accurate at realistic doping percentages. This implies that currently, EIS can only provide a qualitative comparison of these materials but not a quantitative assessment of the underlying physical processes. Modelling can help us to gain insight in those underlying physics.

Oxygen ion conductivity is a prime example of a material property that cannot be completely understood or studied on a single length scale. Fundamental parameters, like interaction energies or diffusion barriers, are determined on the atomic scale. Dopants and vacancies cluster together to influence the transport properties on the mesoscopic scale [4]. And finally, the influence of grain-size, grain boundaries and interfaces is best studied using a continuum model [5].

We propose a multiscale model, linking Monte Carlo simulations to calculate the local crystal structure, with transport processes on a continuum scale, based on the Cahn-Hilliard description of solid electrolytes. We use this model to calculate impedance spectra and ionic conductivities and to show how parameters such as interaction energies, diffusion barriers and grain boundary orientations influence these results.

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Control of Phase Separation by Electro-autocatalysis

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Motivated by the possibility of electrochemical control of phase separation, a variational theory of thermodynamic stability is developed for driven reactive mixtures [1], based on a nonlinear generalization of the Cahn-Hilliard and Allen-Cahn equations [2]. The Glansdorff-Prigogine stability criterion is extended for driving chemical work, based on variations of nonequilibrium Gibbs free energy. Linear stability is generally determined by the competition of chemical diffusion and driven autocatalysis. Novel features arise for electrochemical systems, related to controlled total current (galvanostatic operation), concentration-dependent exchange current (Butler-Volmer kinetics), and negative differential reaction resistance (Marcus kinetics). The theory shows how spinodal decomposition can be controlled by solo-autocatalytic charge transfer, with only a single Faradaic reaction. Experimental evidence is presented for intercalation [3] and electrodeposition in rechargeable batteries, and further applications are discussed in solid state ionics, electrovariable optics, electrochemical precipitation, and biological pattern formation.

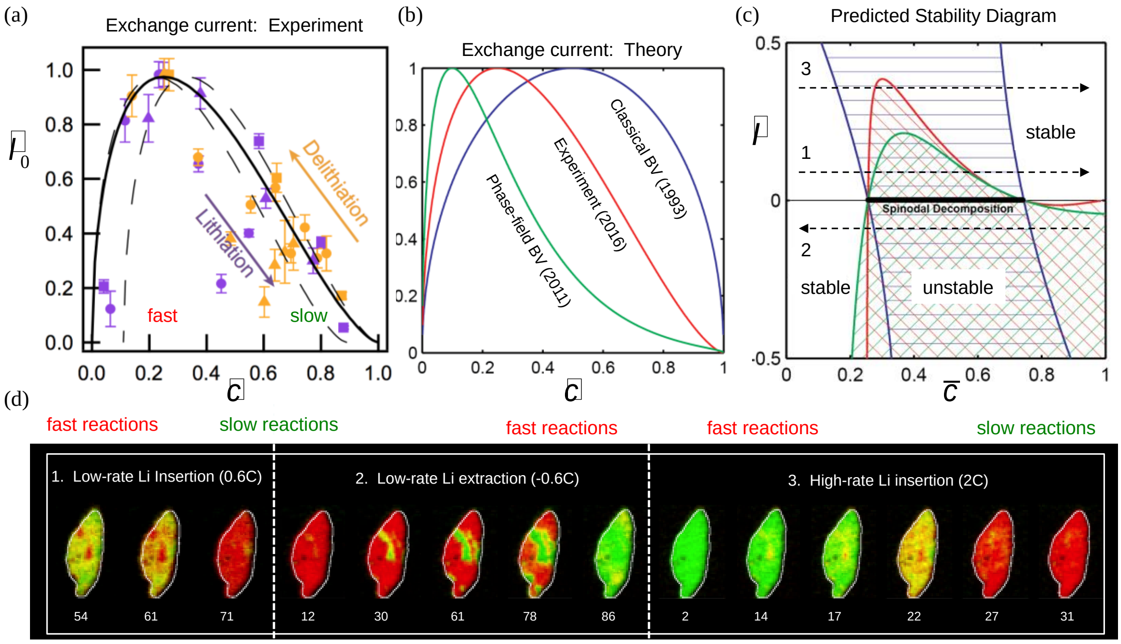

Figure. Experimental evidence for the control of phase separation by electro-autocatalysisd in single nanoparticles of lithium iron phosphate, obtained by *in operando* scanning transmission x-ray microscopy (STXM). (a) Measured exchange current versus local surface concentration, (b) compared with Butler-Volmer kinetics from our original phase-field model and traditional porous electrode theory. (c) Predicted linear stability diagram versus current and composition for the exchange current curves in (b) from models and experiment. (d) STXM images showing lithium evolution (X=0, 0.5, 1.0 in Li_XFePO_4 for green, yellow, red) during cycling at different rates. At a moderate insertion rate (0.6C) some phase separation occurs, which is enhanced significantly during extraction at the same rate (-0.6C). Next, at a high current (2C) above the critical insertion rate, phase separation is suppressed. [Adapted from Ref. 3.]

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How Accurate are OER Activity Predictions from DFT?

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It is well accepted that RuO_2 and IrO_2 are amongst the best catalysts for the oxygen evolution reaction (OER), by providing the lowest anodic overpotential. Although both materials have similar activity for the reaction, it has been experimentally shown that RuO_2 has a lower overpotential than IrO_2 in both acidic and alkaline media.[1] Yet, recent theoretical investigations, using a thermodynamic model to predict the OER activity,[2] reported a high overpotential for the RuO_2 (110) surfaces (Fig. 1).[3] In this study[4] we show that DFT, using both RPBE and PBE functionals and a range of pseudopotentials consistently predicts overpotentials that are significantly larger on RuO_2 than on IrO_2. We have developed a new methodology, based on scaling relations, that shows that the inaccurate RuO_2 activity prediction originates from anomalous oxygen/oxygenates adsorption energies. The inaccuracy is lifted by the addition of explicit water solvation and by including van der Waals corrections to the DFT scheme. The oxygenate adsorption energies are then corrected and both IrO_2 and RuO_2 are predicted to have low overpotential by the thermodynamic model.

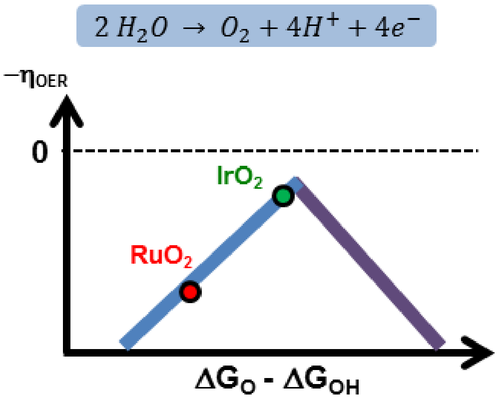

Fig. 1: DFT wrongly predicts RuO_2 as less active than IrO_2 for the oxygen evolution reaction.

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Model-based Uncertainty Quantification for the Product Properties of Lithium-Ion Batteries

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In Lithium-ion Batteries, influences of the manufacturing process steps on the product performance are often not fully understood and non-intuitive. Due to this lack of knowledge, the application of uncertainty quantification (UQ) methods to the manufacturing process of LIBs is gaining interest [1, 2]. As part of a model-based analysis it can reveal interactions between uncertain parameters and processes and enables an interpretation of their effect on the cell performance.

In this work, a highly efficient model-based UQ approach is introduced to the manufacturing process of LIBs to investigate cell-to-cell deviations and the impact of sub-cell level variation of material and electrode properties on the cell performance. Therefore an electrochemical battery model of the Doyle-Newman type [3, 4] is extended. This model is integrated in a sampling-based UQ framework. A nested point estimate method (PEM) [5] is applied for a large number of independent normal distributed parameters. In addition to the reduction of the computational cost, this method supplies a highly efficient global sensitivity analysis (SA).

The simulation study considers two consecutive non-ideal manufacturing process steps: coating and calendering represented by the resulting liquid phase volume fraction, the electrode thickness, and the effective solid phase conductivity. In addition, a distribution of active material properties (deviations in particle size, specific capacity, and electrical conductivity) is analyzed. Considering cell-to-cell variation, in a first step the UQ framework is used to determine the battery's discharge curve and its confidence interval. In parallel, global sensitivities are evaluated to the investigated parameters. In a second step, the influence of the sub-cell level deviation of the most sensitive parameters is investigated using the model introduced before.

The cell-to-cell variation of parameters leads to uncertainties in cell voltage and capacity while a significant non-linearity of the investigated electrochemical system is observed. The sensitivity analysis reveals a C-rate dependent transition of limitation between the electrodes. Eventually, the sub-cell level variation of parameters provokes additional kinetic losses and in some cases an earlier onset of the diffusion limitation compared to a homogeneous electrode. These losses are mainly related to the current distribution in different cell areas with their respective deviating properties which leads to locally higher overpotentials.

The results of this work show that a model-based approach is feasible to quantify the relation between uncertain properties and cell performance. The proposed UQ framework enables a further understanding of phenomena of the analyzed non-linear electrochemical system. The introduced model reveals the electrochemical response of the Lithium-ion Battery to spatial variations of cell properties on a sub-cell level and their effect on the cell performance. As it turned out, highly efficient concepts for uncertainty quantification and sensitivity analysis are mandatory for these kind of studies.

Acknowledgment:
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Predicting SEI Morphology from Transport and Reaction Kinetics

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Lithium-ion batteries are the technology of choice for a broad range of applications due to their good performance and long-term stability. The structure and composition of the solid electrolyte interphase (SEI) is the key for the long time stability of low-voltage anodes such as graphite in combination with high performance liquid electrolytes. Direct contact between these phases results in continuous reduction of electrolyte solvent and salt. Thus, during the first charge of a pristine graphite electrode, a protective layer of connected solid SEI particles is formed which separates electrode and electrolyte, reducing the rate of electrolyte reduction considerably. However, the reaction is never absolutely suppressed and long-term SEI growth remains the biggest contributor to capacity fade in lithium-ion batteries.

Our model describes the long-term evolution of a porous SEI [1,2], considering the interplay of structure, reaction kinetics and transport mechanisms. It extends the approach of previous models [3,4] which describe SEI thickness evolution using only a single rate-limiting transport mechanism. We consider all potentially rate-limiting transport mechanisms, as e.g. electron conduction, solvent diffusion and lithium interstitial diffusion. The emergence of a spatially structured SEI as well as details of the structure is the consequence of coupling these transport mechanism with different SEI formation reactions.

The first model considers a single representative SEI formation reaction and predicts continuous growth of a porous SEI. Electron conduction drives film growth and thickness evolves with the square-root of time. We can show that the emerging structure is not specific for electron conduction but could also be observed with diffusion of neutral lithium interstitials through the SEI as main transport mechanism. The predicted porosity of the layer can influence the rate limiting transport mechanism, as we show in parameters studies. Adding a second SEI formation reaction leads to the formation of a dual-layer SEI. The properties of the additional layer depend on the type of the second reaction, i.e., solvent reduction or reduction of SEI compounds. Furthermore, we predict an equilibrium relation between the thickness of the inner layer and the total SEI thickness. Different SEI profiles generated in our model are studied with impedance simulations of graphite anodes. The impact of the rate limiting transport mechanism on possible inhomogeneities of the SEI thickness on the scale of the microstructure of the electrode is demonstrated in structure resolved 3D cell simulations. All predictions above are observable with suitable experimental techniques, such as neutron reflectometry, and can be used for model validation.

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Multi-Scale Simulation of Surface Film Growth Mechanisms in Lithium-Ion Batteries

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The formation and degradation of solid films on negative electrodes in lithium-ion batteries, known as the solid electrolyte interface (SEI), has been studied extensively by experimental and model-based methods during the last decades. Nevertheless, the complex chemical and electrochemical reaction networks and the resulting surface film growth mechanism are not yet well understood [1]. The growth of the formed film is determined by lateral interaction of species on the atomistic scale and macroscopic properties such as applied current and electrode design. These interactions result in a highly heterogeneous multi-component structure of the SEI. On the one hand this long time- and length-scale problem cannot be simulated by pure atomistic models and, on the other hand, continuum models are not able to consider lateral interaction of species and film heterogeneity.

With these considerations in mind, we have developed a modeling methodology for simulation of such surface film growth in lithium-ion batteries, which directly couples continuum and atomistic models by application of multi-scale modeling techniques [2]. Heterogeneity is introduced in a full order continuum battery model of the P2D type [3], by applying kinetic Monte Carlo simulations for heterogeneous film growth processes as illustrated in Figure 1 (left). The model is applied to solvent decomposition problems on graphite electrodes. Results illustrate how this modeling approach extends commonly used pure continuum models and demonstrates the multi-scale nature of this surface film growth problem. Spatial distribution of system states, e.g. electric potentials and concentrations, can lead to considerably deviating surface film structures, as can be seen for instance in Figure 1 (right). Further, the simulated electrode potentials are shown to be in very good agreement with experimental data.

This methodology provides the most advanced simulations of the frequently stated multi-scale nature [4] of the SEI formation in lithium-ion batteries. As such, this methodology enables a more detailed study of this highly complex but important problem in the development of lithium-ion batteries, by providing a computational tool for the testing of hypothesized mechanisms that can be compared with experimental data, which can facilitate the generation of deeper understanding of the exact mechanisms.

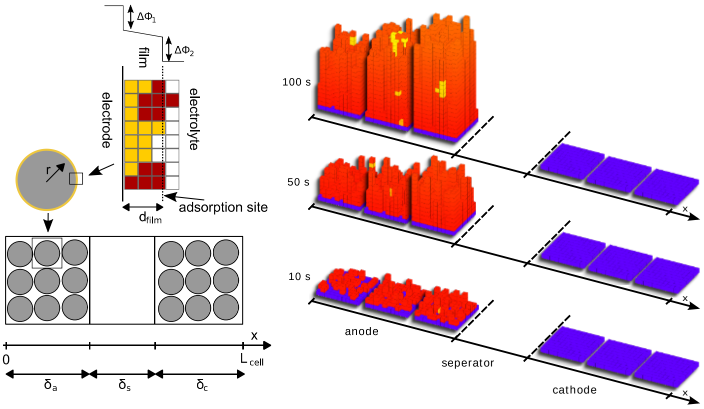

Figure 1: Multi-Scale Model (left) Effect of Multi-scale Nature (right)

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Generalized Diffusion Impedance and Its Inversion to Diagnose Microstructure of Electrodes

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In pursuit of higher energy and power density, as well as longer lifetime, modern electrochemical energy systems commonly employ nanostructured materials[1,2]: battery electrodes consist of nanoparticles; capacitor electrodes are full of nanopores; and in fuel cells and flow batteries electrolytes flow through nano-porous electrodes[3,4]. Short diffusion length in the nanostructures renders the transition behavior of finite diffusion impedance (either bounded or transmissive) now accessible to impedance measurement. However, in many cases, conventional finite diffusion models (*e.g.* finite-length Warburg) are not able to fully explain experimental impedance spectra of the nanostructured systems. One of the main factors causing such deviation is presumably the inherent randomness of the nanostructures, such as particle size distribution in batteries[5,6], pore size distribution in capacitors[7], and distribution of boundary layer thickness in flow batteries. Such randomness of nanostructures commonly introduces a distribution of diffusion time (DDT) in the systems. Here we present a diffusion impedance model generalized by a distribution of diffusion time, instead of a single value of diffusion time constant. The model can explain a range of common deviations from the traditional diffusion models, including the constant-phase-element (CPE) behavior. Furthermore, it suggests a nondestructive, global characterization method of the electrode nanostructure by inversely solving the model for the distribution function. Such a characterization method is particularly essential for diagnosing state-of-health or degradation of electrochemical energy systems. This method has been applied to experimental data of a battery, a capacitor, and a flow battery, and their preliminary results will be presented as well (Figure 1).

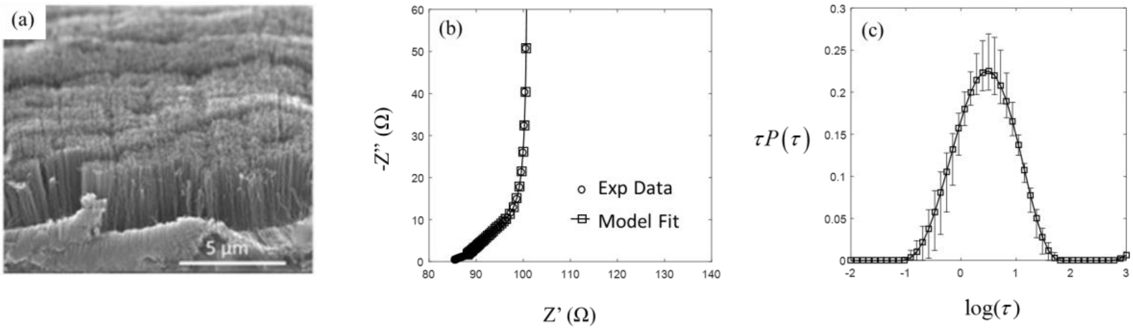

Figure 1. (a) SEM image of a carbon nanotube (CNT) capacitor electrode[8], (b) its impedance spectra [9] and the model fit curve, and (b) the corresponding distribution of diffusion time

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~~First Principles Modelling of Metal-Electrolyte Interfaces with Density Functional Theory based Molecular Dynamics~~Modelling metal electrolyte interfaces from density functional theory based molecular dynamics

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Metal-electrolyte interfaces are of great importance for electrochemical devices, in which many processes occur. Due to the level of complexity, experiment alone is difficult to reveal the microscopic structures and properties of interfaces. Ab initio modelling, on the other hand, can offer a complementary tool to help gain atomic level understanding of interfaces. ~~Experimental measurements normally can only reveal the macroscopic properties of the electrochemical cells, such as the response of current to voltage. In order to design cells with better performance, we need to deepen our understanding of the microscopic structures at the electrochemical interfaces and theoretical modelling has natural advantages to do this.~~

~~This project aims~~We aim at investigating the properties of transition metal-electrolyte interfaces with density functional theory based molecular dynamics (DFTMD) simulations. Firstly, based on ~~the idea of hydrogen insertion~~the recently developed DFTMD standard hydrogen electrode (SHE) [1], we've ~~developed~~ proposed a new ~~method~~ computationally efficient scheme for determining the electrode potential of the metal-electrolyte interfaces on the SHE scale.[2] The reliability of this new ~~method~~ scheme has been verified by estimating the potential of zero charge (PZC) for several metal surfaces, namely Pt(111), Au(111), Pd(111) and Ag(111). We've also found that there is an apparent charge transfer between the surface water molecules and the metal electrode, which is the dominant factor for the energy difference between the PZC of a metal surface and its work function.

We then constructed an electric double layer by bringing in counter ions into the Helmholtz layer. The model is shown below. The estimated double layer capacitance from our calculations is ~30 μF/cm², which is close to the experimental value of 20 μF/cm². We've found that the surface water ~~will~~ reaches dielectric saturation at a very negative potential and its preferred orientation is with one H atom pointing down. Moreover, we provided evidence that the stretch vibration of υ(OH…M) in H-down water is located at 3200~3500 cm^{-1}, not the previously reported[3,4] mode at ~2900 cm^{-1}, which we ~~claimed~~ believe originates from the chemically adsorbed surface water.

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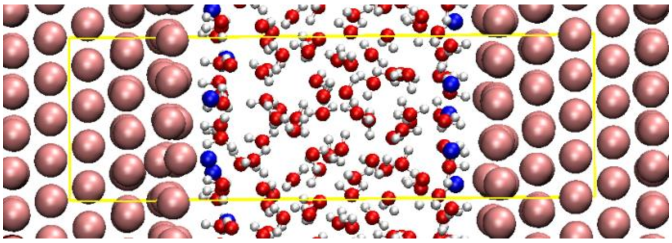

The metal-electrolyte interfaces were modelled using a periodic supercell slab of several atomic layers and a vacuum which was filled with water molecules. To simulate charged surfaces Na^+ counter ions were added. Born Oppenheimer DFTMD simulations were carried out using the CP2K/Quickstep package, ~~employing the Perdew Burke Ernzerhof (PBE) functional to describe the exchange correlation effects~~and PBE functional was used ~~. The dispersion effect is included using~~with the Grimme's D3 correction.

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Towards a first-principles simulation of constant-potential reactions in electrochemistry

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Most common techniques for the experimental investigation of electrochemical processes are performed under conditions where the applied electrode potential is directly controlled by an external circuit, the simplest being a constant electrode potential. However, in *ab initio* simulations of such reactions based on density functional theory (DFT), a constant potential for the involved electrode is not guaranteed. This is especially severe for dynamic simulations involving a direct charge transfer from the electrode to an adsorbed species. The most fundamental, but still not fully understood, example including such a behavior is the Volmer reaction (proton reduction), a part of the hydrogen evolution reaction (HER).

In this contribution, we present a new way to simulate the dynamics of the Volmer reaction, setting the groundwork for the study of potential-dependent reactions. While the standard usage of electronic structure methods deals with canonical ensembles, we extended the methodology by allowing a varying number of electrons in the unit cell. Changing into such a grand canonical ensemble leads to the need for the addition of a balancing charge in the simulation cell, which we implemented as a counter electrode immersed in an implicit solvent. The method on one side guarantees overall charge neutrality and at the same time gives control over the local charging in the unit cell.

Due to its numerical efficiency we are also able to combine the methodology with routines for the description of the kinetics of the reaction, such as the nudged elastic band (NEB) method. By varying the number of electrons added to the electrode surface in the course of the simulation, a constant electrode potential in the evaluation of minimum energy pathways (MEP) can be achieved and, therefore, more realistic potential-dependent transition state barriers can be calculated.

Characterization of the Nano-Porosity of Silicon Nitride Thin Layers: Impedance Modeling of Nanopores

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Silicon nitride (SiN_x) is commonly used as a dielectric thin film (10 to 100 nm) within stacks deposited by magnetron sputtering in the glass industry. The porosity of such thin films can be detrimental to the product durability and performances upon ageing [1].

The nanostructural characterization of silicon nitride thin films has been investigated by Transmission Electronic Microscopy (TEM). Several microscopy techniques such as TEM, Scanning Transmission Electronic Microscopy in High Angle Annular Dark Field mode (STEM HAADF) revealed pores from 1 to 3 nm in diameter with heterogeneous distribution in the thickness direction. Electron Energy Loss Spectroscopy (EELS) were employed to get information concerning local composition inside the pores, especially oxygen. [2]

Complementary to the nanometric approach, Electrochemical Impedance Spectroscopy (EIS) measurements were conducted on these layers. [3] A first model composed of well-described elements (Young model, power-law model) was used to describe the impedance behavior in nanopores. Quantitative physical parameters were obtained such as the through-porosity total fraction or the resistivity profiles in the thickness direction of the layers. [4]

In order to give a more precise description of the nanopores distribution in the layer, new models were built relying on the microstructural informations obtained from TEM observations. Combining TEM and SIE allowed us to draw these new models and to extract quantitative information on the diameters, the morphology and the local density of nanopores. The effect of the high confinement of the ions of the electrolyte in nanometric pores has also been investigated. The variation of the layer nanostructure (pores diameters, density and thickness of the layer) is allowed by changes in the deposition parameters of the reactive magnetron sputtering (plasma composition, deposition pressure, and sputtering rate). The decrease of the pores diameters implies to adapt the SIE model to fit peculiar low frequency behaviors.

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Understanding Selectivities During CO_2 Reduction on Metalloporphyrin Catalysts

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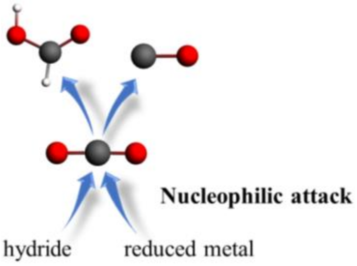
The efficient and selective reduction of CO_2 in fuels is a necessity in view of the achievement of a closed anthropogenic carbon-cycle.[1] The ubiquitous metalloporhyrin complexes (MP) and their derivatives are promising catalysts for the electrochemical reduction of CO_2.[2] As expected, it was experimentally observed that the change of the metal can completely change the selectivity and the activity of these catalysts.[3] Yet, the relation between the metallic center and the activity is still unclear. This work, performed with density functional theory calculations, provides valuable insight for the understanding of this relation for a large set of metals (first-row and second-row transition metals Cr-Zn and Ru-Cd, and main-group metals Ga, In and Sn) with a simplified model porphine ligand.

We first evaluated a widely-used methodology, especially in the heterogeneous catalysis community, where the selectivity between CO and further reduced species on the one hand, and formic acid on the other, is qualitatively predicted by computing the thermodynamics of the formation of the carboxylate (*-COOH) and formate intermediates (*-OCHO) assuming a concerted proton-coupled electron transfer. The predictions obtained are in general not in agreement with the experiment.[4] In a second phase, the exploration of other reduction mechanisms for the formation of formic acid, while considering the same mechanism for the formation of CO, allowed us to propose a mechanistic picture that is much more consistent with the experiment. The crucial event, shared by all the proposed mechanisms, is a nucleophilic attack of the carbon of the CO_2 which allows its activation (cf scheme 1). The nature of the nucleophile, the metal or a hydride, is determinant for the selectivity during the reduction.



Scheme 1. Depiction of the relation between the nature of the nucleophile and the selectivity during the CO_2 reduction by MP.

We were then able to identify two subgroups within MP catalysts. First, MP for which the reduction takes place at the metal (metal-electroactive) that may activate the CO_2 by its coordination on the metal (C-bonded CO_2), hence possibly forming CO or further reduced species, but no formic acid. It encompasses the transition metals Cr, Mn, Fe, Co and Ru. Second, MP for which the reduction takes place at the porphyrin ligand (π-electroactive) and which, after the possible protonation of the ligand (phlorin intermediate) and transfer of the hydride from the macrocycle to the carbon of CO_2, selectively produce formic acid. All other considered metals (late transition metals group 10, 11 and 12, and p-metals Ga, In and Sn) are likely to be concerned. Interestingly, the particularly high activity experimentally observed for In and Sn is explained by the ability of these metals to fix the CO_2 in the vicinity of the hydride. Other metals cannot, and thus, only produce trace amount of formic acid. The rhodium MP, which is metal-electroactive, is an exception that produces formic acid because of the initial formation of a nucleophilic hydride on the metal in a two-electron and one-proton transfer step.

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First-Principles Studies of the Structural Properties of Nickel (Oxy)hydroxide as Oxygen Evolution Reaction Electrocatalysts

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Nickel oxide (NiO_x)-based electrocatalysts are among the most promising materials for oxygen/hydrogen evolution reactions in alkaline conditions. In the late 1960s, X-ray diffraction studies revealed four main phases of Ni (oxy)hydroxide materials [1], involving two phases of nickel hydroxide, α- and β-$Ni(OH)_2$, and two phases for the oxidized materials, β- and γ-NiOOH. In this contribution, we present results of first-principles calculations of bulk properties, surface configuration, electronic structure, charging effects and catalytic properties of various phases and surface terminations of Ni (oxy)hydroxide. Using the spin-polarized DFT + U approach, we first focused on understanding the structure and orientational order of interfacial water on the (001) surfaces. Thereafter, we explored the mechanisms of the oxygen evolution reaction at the surface accounting for implicit and explicit solvent.

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Electrokinetic Fingering: A Problem in Vector Laplacian Growth

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Pattern formation is ubiquitous in various physical and chemical processes and has fascinated scientists over the past couple of decades. Perhaps two of the most well-known examples are the dendrite formation during metal electrodeposition and viscous fingering in Hele-Shaw and porous media flows. In both cases, interfacial instabilities play a major role in controlling the growth rate and the resulting pattern. In many applications, however, these interfacial instabilities are undesired. For instance, dendrite formation is a major safety concern and barrier to using metal anodes in rechargeable batteries. Similarly, in enhanced oil recovery, viscous fingering results in non-uniform displacement and trapping of oil which limits extraction efficiency.

Theoretically, many interfacial instabilities are understood in the context of Laplacian growth phenomena, where the growth rate is related to the gradient of a harmonic function, e.g. concentration field in metal electrodeposition or pressure field in viscous fingering. However, the growth rate could in principle depend on multiple driving forces in a coupled way that is not described by classical theory. In this talk, we will consider a class of problems, which we term “Vector Laplacian Growth”. In these problems, the growth rate is determined by the gradient of a vector-valued harmonic function that represents the coupling between different physical driving forces.

Based on our theory, we will revisit the classical Saffman-Taylor instability in the presence of electrokinetic phenomena, i.e. electro-osmotic (EO) flow and streaming current, using both analytical and numerical techniques. Interestingly, we find that in this case, the instability growth rate depends on both the viscosity ratio of two fluids, as well as the ratio of the electric current to flow injection rate. Remarkably, our theory predicts that the instability could be suppressed if the right physical conditions are met, or otherwise enhanced leading to greater mixing of the two fluids. We believe that our findings have important implications in electrically enhanced oil recovery application and might help with understanding other similar multi-field driven instabilities.

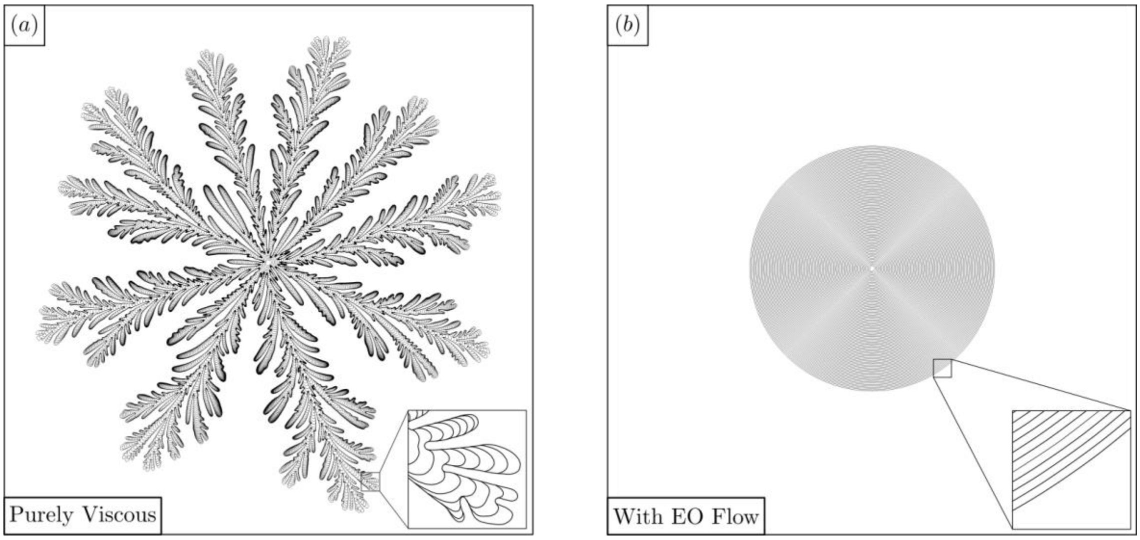

Figure 1- Numerical simulation of classical and electrokinetic (EK) fingering. (a) As explained by Saffman and Taylor, viscous fingering occurs when a low-viscosity fluid, e.g. water, is used to push a high-viscosity fluid, e.g. oil. (b) Our theory of Vector Laplacian Growth predicts that, in certain cases, electrokinetic phenomena can suppress the fingering, resulting in a uniform displacement.

Computational Design of Efficient Photoelectrode for Water Oxidation

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The design of highly efficient electrodes for photoelectrochemical (PEC) water splitting is of both fundamental and practical importance.[1-3] By simulating the oxygen evolution reaction (OER), we can identify the most electrochemically active structures and surfaces for water splitting and can design materials with strongly enhanced activity.[4-5] This method allows identifying the rate limiting reactions at the electrochemical interface. In this study, we choose hematite as a model system. We will discuss the effects of surface orientation, active surface sites, presence of surface steps, lateral interaction, and oxygen vacancies on the OER activity. Particularly, the presence of oxygen vacancies is found to be efficient to control the OER. Figure 1 shows the free energies of intermediate species calculated for the (110) surface with/without oxygen vacancies (a), and the comparison of the calculated overpotentials with the literature (b). An OER overpotential of as low as 0.47 V was obtained for an optimal oxygen vacancy concentration of 1.26/nm^2. These results are used to calculate the rate constants of the OER steps which will serve as input for state-space modeling[1, 6] to simulate electrochemical impedance data that can be directly compared to experiments. The computational design of highly efficient photoelectrode can then be proofed by experiments.

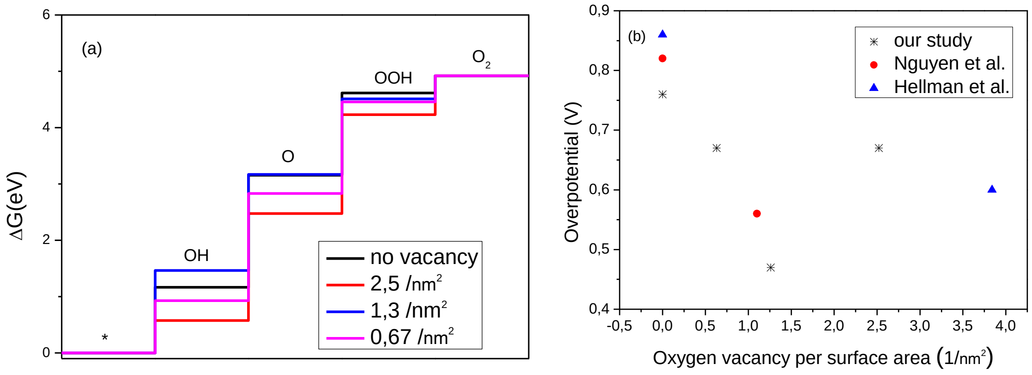

Figure 1 (a) Free energy versus reaction step of the OER as a function of the oxygen vacancy concentration of the (110) surface. (b) The effect of oxygen vacancy on oxygen evolution reaction overpotential. The data are compared with similar calculations on the hematite (0001) surface by Nguyen et al.[7] and Hellman et al.[8]

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Structural, Electronic, and Chemical Properties of β-NiOOH from First Principles

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Abstract

NiO_x, long studied for its use in nickel-based secondary batteries, has been the subject of much interest recently due to its efficacy as an oxygen evolution reaction (OER) catalyst. Despite extensive study over the course of a century, however, many outstanding questions remain surrounding both the structure and activity of NiO_x. Further compounding this ambiguity is the finding that much of the previous experimental work on NiO_x may have been influenced by incidental doping. In the first part of this talk, we focus on the simplest members of the NiO_x family, β-$Ni(OH)_2$ and β-NiOOH. With density functional theory (DFT)+U calculations, we identify a β-NiOOH structure that has a staggered arrangement of intercalated protons more consistent with experimental crystal structures of β-NiOOH than previously proposed geometries. Next, by conducting a thorough study of various initial spin configurations of this β-NiOOH structure, we found that a low-spin d^7 Ni^{3+} configuration is always favored. This finding suggests that a Jahn-Teller distortion, rather than disproportionation, explains the different Ni-O bond distances found in experiment. G_0W_0 calculations performed on both β-$Ni(OH)_2$ and β-NiOOH reveal electronic structures consistent with previous experimental results. Lastly, calculations of various low-index surface energies of both β-$Ni(OH)_2$ and β-NiOOH demonstrate that the (0 0 1) surface is the most thermodynamically stable surface, in keeping with numerous experimental results but in contrast to recent computational models. In the second part of the talk, we discuss the chemical reactivity of β-NiOOH. We first compare several surfaces of β-NiOOH studied for the OER and determine that, unlike some earlier models selected, the (001) surface is the most stable surface under electrochemical conditions. Next, we compare the energies of this material's several possible magnetic states and predict that, unlike bulk β-NiOOH, (001)-β-NiOOH manifests a slight preference for a ferromagnetic state. Finally, we compare four different postulated OER mechanisms on the resulting structural model. In addition to excluding a proposed mechanism involving hydrogen peroxide formation, we identify two binuclear mechanisms with slightly lower overpotentials than the commonly studied associative mechanism. All three overpotentials are in excellent agreement with measured values; the similarity in calculated overpotentials for these three mechanisms thus highlights the fact that several mechanisms are likely to be operative under electrochemical conditions on β-NiOOH. This finding suggests that much of the complexity in studying the OER on NiOOH is due to multiple competing mechanisms occurring under a given set of conditions, which therefore should be considered in subsequent analyses.

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Use of Modeling for Diagnostics of Polymer Electrolyte Fuel Cells

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Diagnostic methods are important to understand the phenomena controlling the polymer electrolyte fuel cell (PEFC) performance. The aim of this work is to identify performance limiting characteristics of a fuel cell by polarization curve analysis. A two-dimensional multiphase numerical model has been developed for Polymer electrolyte fuel cells (PEFCs). The model accounts for multicomponent diffusion, gas and liquid convection, electronic and protonic conduction, and water transport in membrane. A novel agglomerate model with non-first order double trap kinetics has been implemented in the numerical model for cathode oxygen reduction reaction (ORR). The model is used to delineate the effects of different performance limiting mechanisms. Cell simulations are carried out for different limiting cases conditions, e.g., performance limited by only membrane conductivity, or performance limited by oxygen diffusion in agglomerate. The aim is to identify unique signature of each performance limiting mechanism on the polarization curve, which can help in rapid diagnostics of a cell.

The model is used to generate polarization curves of a cell for different limiting cases and at varying oxygen concentrations. Two parameters are analyzed from the polarization curves: i) the Tafel slope, and ii) the reaction order. Figure 1 shows the Tafel slope changes and reaction order for some of the limiting cases. At higher current densities, the Tafel slope increases compared to the kinetic region. It can be observed from Fig. 1(a) that the Tafel slopes can differentiate between some limiting mechanisms, but cannot pinpoint a single limiting factor, as some of the mechanisms have similar slopes. To further separate the limiting behaviors, pol curves at different oxygen concentrations are obtained to analyze the apparent oxygen reaction order. Figure 1(b) shows the reaction order for a cell limited by bulk diffusion in porous layers. The order changes from half to one with increasing current density, providing a unique behavior. Similarly, all mechanisms can be uniquely identified. For experimental validation, a lab scale fuel cell is used for obtaining pol curves at beginning and end of life. Using the different limiting cases, the performance degradation can be modeled and limiting mechanisms identified.

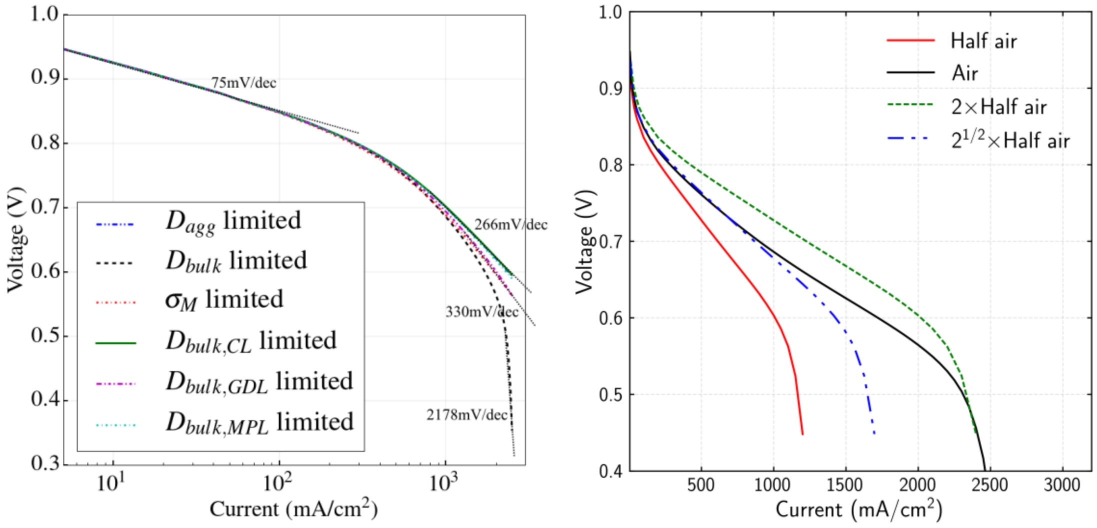

Figure 1. (a) Change in Tafel slopes for different limiting mechanisms, (b) Reaction order analysis for a bulk diffusion limited cell. Solid lines are simulated results, and dashed lines are half order and first order multiples of Half-Air

Acknowledgements:

This work was funded by the Assistant Secretary for Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office, of the U. S. Department of Energy under contract number DE-AC02-05CH11231.

Importance of Stochastic Limitations in Electrochemistry at Arrays of Nanoelectrodes Functionalized by Redox Self-Assembled Monolayers

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Arrays of nanoelectrodes become nowadays more and more accessible and widely used for fundamental studies as well as an analytical tool. In this work we consider arrays of active nanosites modified with self-assembled monolayers (SAM) functionalized with redox moieties. Since the size of the active site is nanoscopic, a number of attached redox moieties is finite. It is well-known that if the number of redox molecules is too small (from few tens to few hundreds) the electrochemical response will feature stochastic behaviour and cannot be described by the classical 'continuous' laws like Fick's law, Nernst equation etc. based on the statistical behaviour of large amount of molecules [1]. To emphasize this we performed stochastic simulations for the case of Nernstian electron transfer (ET) between the SAM's redox heads and the electrode. The obtained results showed that number of redox heads staying in a given redox state is fluctuating, which if converted to potential values will result in SAM's highly fluctuating potential [2].

Such non-classical behavior of the SAM will have even more important implications for the case of mediated ET, i.e. when solution contains freely diffusing redox probe capable to exchange the electron with monolayer redox heads with the following ET between the redox heads and the electrode. The electrochemical response under these conditions will also be influenced by the competition between the mass transport of the redox probe towards the SAM and kinetics of the homogeneous and heterogenous ETs [3]. Results of the simulations together with the possible experimental implications will be discussed.

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Ab initio modelling of the electrochemical interface: applications to CO_2 Reduction

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The electrochemical reduction of CO_2 has the potential to store energy from intermittent renewable sources and to produce carbon-neutral fuels and chemicals[1]. In recent years, theoretical studies of CO_2 reduction have usually applied the computational hydrogen electrode model, which allows for the determination of the energies of reaction intermediates without explicitly treating the potential and the ions in solution[2]. This thermochemical approach has been shown to correlate well with experimental onset potentials [3, 4] and applied to computational screening of new catalysts [5, 6]. However, an understanding of charge transfer barriers, kinetics, selectivity, and pH effects all require explicit consideration of solvent and charge. In this talk, I will discuss new developments in the explicit treatment of the electrochemical interface, which is based on a simple capacitor model that uses the interfacial charge to obtain barriers at constant potential (Fig. 1a and b)[7, 8]. I will then discuss the application of such a scheme to CO_2 reduction: the determination of reaction pathways on transition metals (Fig. 1c) field and solvation effects[9, 10], the resultant kinetics, and the implications for catalyst design.

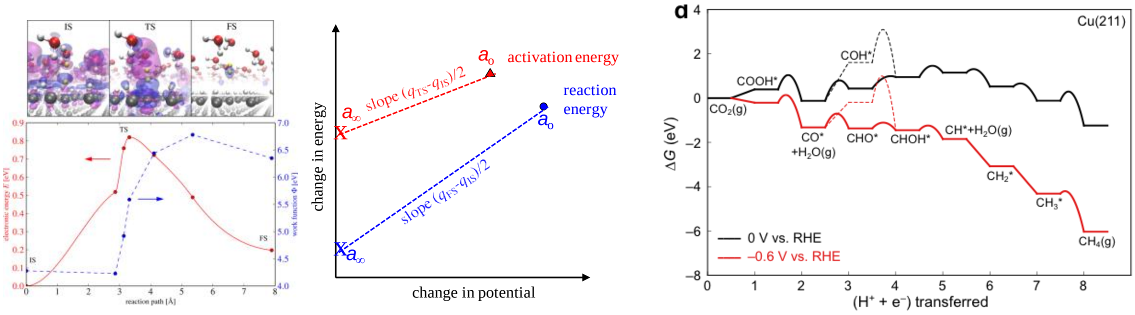

Fig 1. Left: Heyrovsky proton-electron transfer barrier calculated in a 3x4x3 Pt slab – charge density isosurfaces, work function, and energy along the reaction pathway. A dramatic 2-3eV shift in work function (and therefore the absolute electrode potential) is observed in the calculation. Centre: schematic of the charge extrapolation scheme, whereby the constant potential energetics using the change in charge density along the reaction pathway. From Ref. [7]. Right: Reaction pathway on Cu(211) determined with explicit barrier calculations. From Ref. [11]

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“Overpotentials Always Reflect Kinetics: The Need for Rigorous Teaching of Electrochemical Phenomena”

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The recent increased interest in electrochemical energy generation and storage related research and technologies, including fuel cells, batteries, supercapacitors, redox flow batteries and others, has given rise to a new generation of practitioners of electrochemistry. However, our ability to train electrochemists has not kept pace with such a dramatic increase in demand. As a community we need to revisit our approach to teaching electrochemistry while ensuring and maintaining a rigorous approach to the teaching of electrochemical phenomena. In this lecture I will try to provide some lessons, based on my 30+ years of experience as to what approaches have been most effective.

Graduate Education in Corrosion Science and Engineering at the University of Virginia

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The goals and methodology of graduate education in corrosion science and engineering at the Center for Electrochemical Science and Engineering at The University of Virginia are reviewed. These include establishment of both core competencies and advanced understanding(s) in materials science, electrochemistry applied to corrosive degradation in aqueous solutions, surface science and engineering, solution chemistry and/or fracture mechanics through a plan of study typically involving 13 graduate classes in Engineering, Chemistry and/or Physics. In addition a key aspect of our educational goal, beyond the classroom, is a significant and in-depth Master of Science and Doctor of Philosophy research experience culminating in a written thesis or dissertation and oral defense. This research experience is designed to provide an excellent training ground for development of individuals capable of not only performing multi-disciplinary research in the corrosion field, but also with the capability of surveying the literature, identifying research gaps and opportunities and developing strategies for addressing such needs. Corrosion science and engineering students perform focused research in the areas of aqueous corrosion, high temperature corrosion, environmentally assisted cracking. Interactions with other faculty and students providing education and performing research in other electrochemical technical areas (e.g., electrodeposition, photoelectrochemistry, batteries) provide critical enhancements to the students' experience. At the end of this experience, students are capable of either performing as competent corrosion engineers or as scientist making both technological and scientific contributions to our field with good written and oral communication skills. The course curricula, research philosophies and the assessments used to achieve these goals are presented.

Integrating Applied Electrochemistry into an Undergraduate Curriculum

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Electron transfer reactions are a fundamental component of the undergraduate curriculum. Students are typically exposed to at least the basics of redox chemistry in introductory general chemistry courses. The inclusion of applied electrochemistry in upper-level lecture and laboratory courses, however, is much more variable and often minimal. Importantly, electrochemical methods are readily accessible to undergraduate students and they complement many other commonly learned theories and techniques. The ways in which electrochemical topics have been integrated into both teaching and research laboratories in the Chemistry and Biochemistry curriculum at Barnard College will be discussed. Particular emphasis will be given to the design and execution of electrochemical research projects in the undergraduate setting.

Computational Electrochemical Engineering

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I will describe an introductory graduate course in electrochemistry and electrochemical engineering, emphasizing thermodynamics, electrode kinetics, and ionic mass transport. Drawing on examples from industrial, energy, and environmental applications, we apply electrochemical theory for the purposes of design and analysis, with an emphasis on scaling phenomena. Course projects require computer simulations. The course is intended to aid graduate students in quantitative analysis of their research involving electrochemical technologies.

Teaching Electrochemistry Surreptitiously: Instrumental Analysis

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Most students graduating from college with a degree in chemistry have very little exposure to electrochemistry beyond the text book notation of galvanic and electrolytic cells and some equilibrium chemistry in general chemistry. This gap persists up to and through their senior year. The author teaches an instrumental class billed as the chemistry capstone for graduating senior in their second semester. In this class the first ¼ of the semester is on noise and data analysis; the second ¼ on molecular spectroscopy; the third on atomic spectroscopy AND electrochemistry; and the final ¼ on mass spectrometry. The lab follows this sequence, for the most part, with the final section devoted to a community based research project.

In order to introduce electrochemistry which is coupled to atomic spectroscopies a section billed as “Solutions and interfaces” introduces concepts like the Debye length, solution mobilities, diffusion coefficients, and hydrodynamic radii. This allows problems of differential mobility to be introduced into issues related to atomic gas production in flames to be handled within the same conceptual framework. The differential mobility also relates to electrospray “coulombic fissure”. From this chapter students ideally move into a section on electrochemistry which begins with conductivity detectors used in the IC lab, followed by the conceptually similar membrane electrodes. Finally we end with ASV and CV.

In this talk the author will illustrate the topic sequence with student derived data for the various laboratories covered over the years.

If time permits the author will outline the topic sequence for an advanced undergraduate/graduate topic sequence in electrochemistry that begins with compounds with minimal bond rearrangement and works up to complicated nature derived electron transfer chains. In the second half applications of those concepts to technical problems is illustrated. This set of materials is developed in collaboration with faculty at other institutions and is under contract for book publication with Wiely.

Jumpstarting Young Scientists into Advanced Electrochemical Concepts for Emerging Energy Challenges

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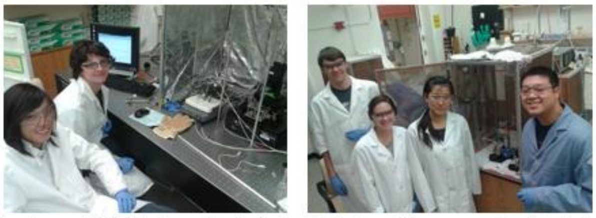
Solving energy challenges requires a highly educated and creative generation of young scientists. My research program has embraced the opportunity to empower high school, undergraduate and graduate students to make energy sciences an essential component of their profession through hands-on activities. In this session, I will describe the most useful concepts, as well as successful and unsuccessful activities [1] we have deployed for swiftly engaging students in advanced topics in electrochemical energy. We will discuss:

The Electrochemical Bootcamp- Scheme 1. We aim to transform our laboratory into an education and discovery "hub" for electrochemistry. For this purpose, we have developed over the past three years (and continuing), an efficient on-hands teaching experience in which we hold experimentally guided sessions for learning about electron transfer theory, photo- and electrocatalysis for renewable fuels, energy storage, nano-electrochemistry, and simulations. The wider reach of this program in comparison to conventional laboratory training, is that the bootcamp has been traditionally open freely to interested undergraduate, graduate and post-doctoral participants from all interested groups in the university.



Bootcamp 2015: Undergraduate students Zack and Hyun, as well as Graduate students from the Moore, Jain and Rodriguez-Lopez lab learn about energy storage

Outreach with ACSSM: Through our collaboration, undergraduate students prepare demonstration videos, and attend a lab demonstration in Urbana High School

Scheme 1. "Bootcamp" and Outreach activities in the Rodriguez-Lopez laboratory.

Outreach through the ACS Undergraduate Chapter. Young chemists should realize that energy sciences are central to their life and profession. As the faculty advisor to the undergraduate ACS chapter we have collaborated with the student group to execute local outreach activities for high-school students focusing on energy sciences.

Integrating active learning in the classroom. My courses break passive learning and engage students in providing solutions to big challenges. In a graduate course students do not deliver papers, instead they create products focused on group work and sharing. Examples include a protocol for analyzing operating Li-ion batteries, a group-written book on instrumental artifacts, and a technical brochure for an instrument.

I will explicitly discuss how these activities contribute to our research and introduce students with no background in electrochemistry into advanced research.

[1] JRL Laboratory – Teaching and Outreach. http://www.scs.illinois.edu/rodriguez-lopez/Misc.html [Accessed March 22 2017]

Teaching Electrochemical Impedance Spectroscopy, 2nd Edition

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Impedance spectroscopy is a popular electrochemical measurement technique, but successful implementation requires specialized training that is not easily available. At the 2013 ISE annual meeting in Querétaro, we described our philosophy for teaching electrochemical impedance spectroscopy, embodied in our textbook on the subject, published in 2008[1]. The object of this presentation is to describe our current approach to the subject, reflected in our second edition [2].

This communication will describe an approach towards teaching impedance spectroscopy in which students are encouraged to modify experimental parameters in accordance with the experimental system, to use a variety of graphical representations to develop preliminary estimates for physical properties, to develop models from proposed chemical, electrochemical, and physical mechanisms, and to perform regression analyses which account for the error structure of the measurement. In our second edition, a greater emphasis is placed on examples, homework problems, and the use of graphical methods to differentiate between frequency dispersion associated with resistivity distributions in films and geometry effects. As impedance spectroscopy is not a “stand-alone” technique, students are encouraged to seek independent observations that can be used to support or disprove the models developed.

[1] M.E. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy*, John Wiley & Sons, Hoboken, New Jersey, 2008.
[2] M.E. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy, 2nd Edition*, John Wiley & Sons, Hoboken, New Jersey, 2017.

Charge Propagation in Electroactive Materials: Diagnosis with Microelectrodes

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Historically, electrochemistry in the absence of a bulk liquid phase has focused on the problems of energy storage and production. Recently, it has become possible to apply conventional electrochemical methods to characterize solid-state type redox electrolytes with respect to analytical characterization of materials, measurement of electron transfer rates, and determination of analytes using amperometric sensing. The characterization of materials by solid-state voltammetry primarily has focused on mixed-valence, ionically conducting compounds and on diverse organic ionomers hosting identifiable molecular (redox) sites.

We are going to address practical issues related to the principles and analytical aspects of electrochemical studies (typically done at room temperature) of solid, rigid or semi-rigid (nonfluid) systems in the absence of a liquid solution phase. Representative examples include redox and conducting organic polymers, melts and solid solutions of redox centers in solid ionic conductors, mixed-valence polynuclear inorganic materials, transition metal salts, oxides, and zeolites. The emphasis is on the elements of dynamics for the efficient delivery of charge and on reactivity of the 'redox conducting' materials. The effective (apparent) diffusional mechanism is critical to the success of most analytical measurements in solid-state.

The potential materials for solid-state electrochemical measurements are expected to contain three-dimensionally distributed highly concentrated redox centers between which fast electron self-exchange (hopping) is feasible. These redox centers are fixed and, although they may have short range mobility about an equilibrium position, they classically are macroscopically immobile. The applicable materials also must host mobile counter-ions that are capable of providing charge balance during electron transfers, thereby serving the same purpose as the supporting electrolytes in conventional electrochemistry. The population of these ions must be sufficient to support diffusive mass transport of electrons and to minimize ohmic effects.

We will describe typical electrochemical cells and experimental tactics to overcome the relatively slow dynamics of transport in solid (non-fluid) systems. Application of microdimensional electrodes leads to an improvement in the quality of solid-state electrochemical data and provides new diagnostic and analytical possibilities. Basic concepts of mechanistic studies, which are relevant to the development of novel analytical methods, together with trends towards possible future applications will also be addressed.

Engaging Undergraduate Students in Learning Electrochemistry through Analytical Chemistry Courses

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Learning the fundamentals of electrochemistry and especially electrochemical techniques of analysis can be tremendously challenging for undergraduate students. The basic concepts of atomic structure, oxidation, reduction, balancing electrochemical reactions, let alone the more advanced notions of thermodynamics, kinetics, mass transfer, and heterogeneous chemical systems are spread out over different courses, often taught in different departments, and across four years in a traditional education toward a B.S. degree in Chemistry at a university in the United States. This presentation will discuss several examples that have been used to overcome this challenge through student engagement by providing opportunities for behavioral and emotional investment, in addition to the cognitive involvement. Approaches will be discussed that create a motivating environment where students eagerly combine the breadth of concepts and fill in gaps in their knowledge autonomously. Analytical chemistry provides an ideal venue for this educational methodology, because it focuses on real-world applications and their personal significance to the student. Activities will be described that have been successfully implemented at the freshman/sophomore level in the Quantitative Analysis course and at the junior/senior (and sometimes graduate) level in the Instrumental Methods of Analysis course. For instance, the drinking water disaster in Flint, Michigan has been used in Quantitative Analysis to illustrate oxidation/reduction, half reactions, thermodynamics, heterogeneous distribution of chemical events, mass transfer, and an incredibly complex set of chemical equilibria. In Instrumental Methods of Analysis, students work in teams to address analysis problems of their own choosing and of personal interest, followed by teaching and engaging other students in what they have learned. Examples have included breath analyzers based on the ethanol fuel cell principle (of interest to students eligible to drink alcohol and must exert a decision whether to drive), continuous glucose monitoring (involving a student who is a Type I diabetic and who could speak from personal experience), and coulter counting of blood cells (where students were interested in cancer treatment and monitoring). These examples and approach incorporate many important characteristics supported by educational research on how to engage students in learning [1]. The features include making the topic meaningful, fostering a sense of competence, providing an environment of self-sufficiency, collaboration with other students, good interactions between students and teacher, and mechanisms that establish mastery of the material.

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[1] See article and educational research cited within Nicolás Pino-James, “Golden Rules for Engaging Students in Learning Activities”, in George Lucas Educational Foundation’s Edutopia, https://www.edutopia.org/blog/golden-rules-for-engaging-students-nicolas-pino-james, published December 8, 2014; updated December 11, 2015, accessed 2017.

Electrochemistry in the undergraduate curriculum in the UK

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In contrast to the USA, where electrochemistry is often considered a part of Analytical Chemistry, in the UK electrochemistry is taught as part of the Physical Chemistry curriculum. Physical chemistry itself is taught as an identified component, usually as one third of the required core Chemistry modules taken by undergraduate students, in each of their three years of study for a BSc degree, before students select from more specialist modules in their final terms of study for either the BSc or MChem degrees. Electrochemistry is typically first introduced in thermodynamics as part of the core modules in the first year, where the poor presentation of Galvanic cells at the pre-University (A-level or International Baccalaureate) must be overcome. Deeper understanding of the kinetic aspects of Electrochemistry and its applications tends to be developed further through laboratory classes and in specialist modules in the third and fourth years. Whilst the thermodynamics approach to Electrochemistry doesn’t inspire many students to select Electrochemistry for their final year projects, the more applications-led approach in the practical classes and our third year module reverses this trend.

Integrating Hands-on Battery Design into a Chemical Engineering Unit Operations Laboratory

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Though electrochemistry and electrochemical engineering play significant roles in the behavior of many engineered systems – either through their fundamental operation (i.e. batteries) or secondary effects (i.e. corrosion) – engineering undergraduates typically do not graduate with appreciable fundamental knowledge in these area. It is important for our community to reach out to these students and develop coursework modules that build both fundamental and applied knowledge related to electrochemical systems. In this talk, integration of electrochemical science and engineering principles into the Junior Laboratory course (CHEG 3128) at the University of Connecticut will be discussed. The battery module in this course has been offered for the past two years.

In this laboratory, teams of four students are provided with a problem statement: Design a battery pack that can seamlessly REPLACE the AA batteries in a child’s toy. Students are allowed to choose their own platform. They must determine the power requirements for the toy under various operational conditions. Of course, on day 1, undergraduates do not know almost anything about how to design a battery. Therefore, we systematically step them through a series of tasks and lectures to build their knowledge and competency – covering thermodynamics, polarization (kinetics and mass transfer), cell design, etc. The details around these will be discussed in the talk.

The course culminates with a demonstration day where teams show off their home-made batteries, operating a wide range of toys.

Bridging the gap between disciplines in the electrochemical education of scientists and engineers

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Electrochemistry is an interdisciplinary subject, advances, especially in energy conversion applications, depending highly on the combined effort of chemists, physicists, materials scientists and engineers. Yet, a course on electrochemistry is hardly found in the curriculum outside chemistry or chemical engineering departments. Moreover, successful and smooth collaboration and communication between graduate students of different disciplines within a common project is often hampered by different languages used in the individual fields of specialization. In this contribution, I will discuss how a course on ‚Electrochemical Sciences’ could be structured for physics students, highlighting how to link the different aspects of electrochemistry to the general physics background of the students. Furthermore, I will compile a list of topics where, for historical reasons, electrochemical language differs from the one of physicists, illustrating the necessity to find a common language. With this I also hope to initiate a discussion how we could achieve this goal.

Teaching Electrochemistry and Electrochemical Engineering: Curriculum for a Technical Elective and a Graduate Course

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Building a course in a technical discipline requires fitting its canonic constituencies into the practice of the actual contact hours allowed, the frequency of meeting and the length of the class period. This is indeed becoming complex when such class is to be cross-listed with several programs run by different colleges/schools, or across colleges (a.k.a. "interdisciplinary") and across the entire university (a.k.a. (cross-disciplinary"). At the University of New Mexico the author have been teaching "*Electrochemistry & Electrochemical Engineering*" since the Fall Semester of 2000. It was preceded by a "*Biosensors: Fundamentals and Applications*" gradate course (1996-2000) thought as a Spring Semester course for 5 years. The electrochemistry class became rapidly popular and was cross-listed (gradually) with all the programs listed above as academic affiliations of the author: *Chemical & Biological Engineering (CBE)* – traditional chemical engineering program, core constituent of the School of Engineering (SOE), with specializations in energy, materials and bio-engineering; *Chemistry and Chemical Biology (CCB)* – large chemistry program a major player in College of Arts & Sciences, with critical service across campus and a feeder to the "pre-med" programs for the School of Medicine (SOM); university-wide *Graduate Program in Nano-Science & Micro-Systems Engineering (NSME)* established with a series of NSF sponsored projects in interdisciplinary education and the *Graduate Program in Biomedical Engineering (BME),* which is a bridge between SOE and SOM. Given the fact that all these programs draw some students with interest in electrochemistry, the resulting graduate student base becomes quite diverse.

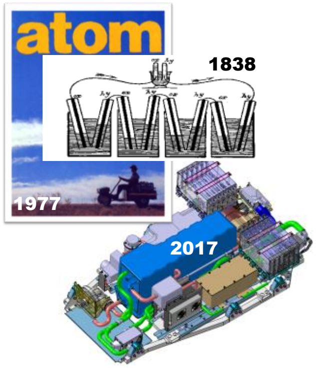

Fig: This class usually covers the basics of electrochemistry and electrochemical engineering and uses fuel cell technology as a means of illustrating the major principles of electrochemistry.

Additional complexity arises from the practice of smaller universities (in the US) to offer such classes as *technical electives* to the seniors (theoretically 4th year college undergraduate, if all things were going well the previous years), as the number of students in any given specialization may not be enough to have a separate undergraduate classes outside the mandated core class (upon which the ABET bestows the accreditation). As a result, such introductory graduate classes (in the US) are taken by both, terminal (professional) masters in engineering (ME); and in masters in science (MS) students; and by the PhD students, as in those colleges that allow direct PhD programs for scientists and engineers (all described in above). And just to make sure this situation is not complex enough, several of these programs offer a "combination degrees" like BS+MS in either 3+2 or 4+1 yearly schemes, and in some universities both schemes at the same time (for different degrees). All of it is present in the University of New Mexico - the case study for this talk. A text that is rather general and comprehensive was adopted since day one for this course. Its second edition presents even more opportunities for diversification.

We will discuss building a curriculum that (hopefully) satisfy all constituencies, based on book that that is European as origin (ref.) and with a flexibility of the assignments and class deliverables that will satisfy the educational outcome criteria of various schools and colleagues. The symposium audience will be asked to take a *quiz* - a short surprise test, for which you are not supposed to know about to be prepared.

Text: Carl H. Hamann, Andrew Hamnett & Wolf Vielstich, *Electrochemistry*, Wiley-VCH, 2nd Edition, 2007, ISBN: 978-3-527-31069-2 (can be found for as low as $50 @ Texbooks.com)

Low Cost, Small Scale Environmental Electrochemistry Experiments

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Electrochemistry has much to offer in the area of environmental remediation and preservation. This relatively new field requires that simple yet highly educational and motivational experiments be developed for students. Therefore we have developed the following experiments: 1) Indirect electrochemical destruction of organic pollutants. 2) Electrocoagulation of oil suspensions. 3) Electrocoagulation of dyes. 4) Metal ion recovery with the electrodeposition of a fractal. 5) Gas remediation in household syringes with elemental recovery. 6) Electrochemical production of chlorine dioxide at both electrodes. 7) Electromigration, electroosmosis and pH-front movement during electrokinetic soil remediation. 8) Soil remediation and extractant recovery. 9) Selective removal of Cs in a surrogate nuclear waste solution. 10) Experimental transitions in a Pourbaix diagram. 11) The production of ozone. 12) The production of ferrate for water treatment. 13) The production of solvated electrons. 14) The simultaneous reduction of metal ions and oxidation of organics at an illuminated semiconductor. 15) A one-penny photovoltaic cell.

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Cheap and accessible electrochemistry: modern fabrication tools towards electrochemistry instrumentation.

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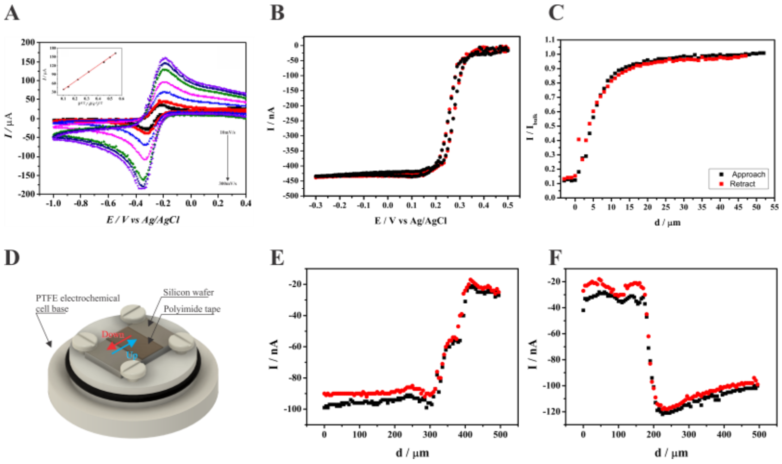
Microcontrollers and 3D printers are versatile prototyping platforms that once were exclusive to big companies. With the rise of the "Do It Yourself" (DIY) community those tools are now accessible to the final consumer and are finding space not only among the DIY community but also on chemistry laboratories. The uses of such techniques for developing accessible instrumentation is of special interest for teaching facilities as they not only cost less than commercial equipment and are more flexible but also require a more profound understand of the basics of the technique been used by the operator/student. This is highly desirable as it breaks down the equipment from its "black box" construction and allows the student to proper understand the principle of operations and the limitation of the equipment in hand.

Herein we present the application of those prototyping tools on the fabrication of low cost electrochemical instrumentation suitable for educational proposes. The design and application of a basic potentiostat, capable of resolving currents in the range of nA and a low cost alternative for acquiring space-resolved electrochemical information (Scanning electrochemical microscope, SECM) that use the microcontroller based potentiostat and 3D printed parts is presented. A commercial Arduino Uno (Arduino, Italy) microcontroller board is used as a potentiostat [1], position controller for the z-stage and x-stage (perpendicular and parallel to the sample plane) and data acquisition system/user interface unit. The z and x stages were built using an ISO metric 5 mm diameter threaded rod encased in a linear stage printed out of PLA on a Cliever (Cliever, Brazil) FDM 3D printer. The threaded rod is attached, with a 3D printed coupler, to a stepper motor that is controlled by the microcontroller in order to move the stages. The microcontroller runs a custom built program to control both the stages and the potentiostat. The proposed potentiostat was able to perform basic cyclic voltammetry experiments with both regular electrodes and microelectrodes (UME) (Figure A and B respectively). The SECM was used to characterize the UME through cyclic voltammetry to determine the tip-substrate separation/current dependence and to perform a constant high SECM line scan experiment over an insulator substrate (silicon wafer) on a potassium ferricyanide solution. The resulting approach curves and line scans (Figure C, E and F, respectively) demonstrate the capability of acquiring space-resolved information by the proposed system. Further improvements are being made to allow for electrochemical images to be acquired through array scans.



(A) cyclic voltammetry experiments performed on a platinum electrode at different scan rates. Insert Randles–Sevcik plot. (B) cyclic voltammetry experiments performed on a platinum UME. (C) Approach curve over an insulator substrate. (D) Representation of the insulating substrate showing the topographic step. Line scans along the step. (E) Going up the step and (F) going down the step.

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Electrochemistry Education for an Undergraduate Audience

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In this presentation a discussion of current topics related to teaching undergraduates will be presented. Methods used to teach to at the sophomore and junior level with differing academic backgrounds will be covered. In addition topics related to types of labs that can be used to cover cyclic voltammetry, reductive desorption as well as building a basic biosensor will be examined. Teaching electrochemistry is vital at the undergraduate level to get students excited about a seemingly vague area of chemistry. This presentation will hopefully provide new ideas of how to get students engaged in this area of research.

Teaching Electrochemistry for Chemistry and Material Sciences Degrees

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Electrochemical education in actual Chemistry or Materials Sciences curricula, in which the number of credits that can be used with this purpose is very low, requires a tight selection of subjects and special strategies. In addition, the student background concerning essential maters needed to follow complex derivations is usually low. Thus, for instance the math level in Chemistry Degree is not sufficient and the knowledge of chemistry of some of the Material Sciences students is almost lacking.

In this communication, the program of one obligatory annual course of Physical Chemistry for Chemistry students in which the fundaments of Electrochemistry are included is presented and discussed, on one hand. On the other hand, the program of an optional course named “Fundamental Electrochemistry for Material Sciences” is also presented.

The Physical Chemistry course consists of 6 credits (60 hours) of theoretical lessons and problems resolution seminars and 2 credits of practical laboratory training, which are homogeneously developed along the whole academic year. The students’ background includes some previous knowledge of chemical thermodynamics and of chemical kinetics. Proposals are made to integrate the main thermodynamic and kinetic aspects of Electrochemistry into the general Physical Chemistry knowledge but pointing out their especial characteristics. The fundaments of actual electrochemical applications are emphasized

The Electrochemical course for Material Sciences is organized in 4 credits, including 1.5 credits for practical training and was developed during the second semester of the last academic year. In this case te students do not have much background on the kinetics and thermodynamic bases used in Electrochemistry. Therefore, the program includes the thermodynamic, kinetic and structural bases of electrified interfaces necessary to understand nowadays state of applied Electrochemistry such as energy conversion and storage, corrosion and electrochemical engineering. [1–4]

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What Your Students Ought to Know about Electrochemistry (But Ask Us Instead)

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"Have you made sure your reference electrode is connected to your potentiostat? Are you even using a reference electrode?"

Electrochemistry equipment manufacturers frequently find themselves in the position where they are providing guidance and troubleshooting advice to graduate students and industry technicians. In addition to these expected services, the role we find ourselves often playing is auxiliary academic advisor. Over the years, our electrochemists have collected numerous anecdotes about a variety of apparent research catastrophes, and graduate advisors may be personally surprised to learn the kinds of stories we have heard. While there are certainly instances when reported problems are valid and require in-depth technical assistance with the instrument, it is not uncommon for the problem to be traced to a gap in fundamental or practical electrochemical knowledge.

When an issue is encountered in an electrochemical experiment, the underlying problem is either the fault of the chemistry or the instrument. This creates tension between the student or technician and the electrochemical equipment manufacturer, and we find that blame is often reflexively passed onto us during a phone call or email exchange. However, the simplicity, and sometimes unintentional comedy, of many of these issues may suggest the heart of the problem is fear of asking one's advisor, or of damaging equipment from improper use.

In this presentation, we will share some of the recurring problems we encounter from bewildered students and technicians across the world, and use these stories to alert lab directors about some common deficiencies we have observed. While we are sympathetic to the varying methods, busy schedules, and tight deadlines of the average academic advisor (or industry supervisor), our experience of repeatedly filling in basic knowledge gaps suggests there may some simple, practical steps that can be taken with those who are beginning electrochemical research to build a strong foundation for future success.

Teaching Electrochemistry to other Scientists -The Tricky Parts

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The fundamentals of electrochemical science have been thoroughly established, including most of the mathematical descriptions required for quantitative work. Yet electrochemistry remains somewhat elusive and perhaps even mysterious to many scientists. Still, experts in various and diverse fields frequently encounter electrochemical phenomena and identify a need to acquire some understanding of electrochemistry, or they recognize that the utility, sensitivity, and selectivity of certain electroanalytical methods could be employed to great advantage even in non-electrochemical studies. This talk explores some of the difficulties, barriers, and misconceptions that can inhibit people without a formal training in electrochemistry from accessing the wealth of electrochemical knowledge that exists and the wide range of electroanalytical techniques that have been developed.

Typically, only a few concepts of electrochemistry are introduced in high school and undergraduate level university courses, and generally these are treated superficially, often with instruction of dubious quality. Moreover, the use of electrochemical jargon, the choice of seemingly random and even contradictory sign conventions, the practice of using various reference electrodes of convenience, and other cultural traits of electrochemists tend to make the field difficult to access for “outsiders”. This presentation discusses efforts and experiences in teaching electrochemical concepts to both those who are just learning science in general and those who are expert scientists in another field, with the emphasis on the latter. A variety of common misconceptions and tricky concepts will be identified and addressed, including “potential”, relationships between energy scales, reference electrodes, equilibrium, standard potentials, coupled reactions, potentiostats, electrodes, and electrochemical cells.

Raising Interest in Electrochemistry Through Forensic Science: Visualisation of Latent Fingerprints on Metal Surfaces

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In the last two decades, two significant research themes in electrochemistry have been chemical modification of electrodes and surface imaging. Another area of science that has been prominent in educational, research and practitioner circles is forensic science. This presentation uses the link between these two fields of endeavor as an educational motivator.

Invariably, a major issue in a criminal investigation is establishing the identity of an individual - whether suspect or victim - and the most common means of accomplishing this is via fingermarks on an object or at the scene of a crime. In most instances, this is a *latent* (non-visible) fingermark, that must be rendered visible by a suitable chemical or physical treatment. Despite over a century of research in this field, the surprising fact is that the success rate for developing a latent fingermark to a standard permitting a legally acceptable identification is only ca. 10%; there is considerable motivation for new technologies.

We have been developing a new approach to the visualisation of latent fingermarks on metal surfaces, which are prevalent in both violent crime (bullet casings, knives) and volume crime (tools, handles at points of entry). The concept is that the fingerprint residue acts as an insulating mask, such that electrochemical processes can only occur on areas of bare metal surface [1-3]. Electrodeposition of a visually contrasting material on the bare surface between the fingerprint residue generates a negative image of the fingerprint. Implementation of this strategy is given a further dimension by using a conducting polymer as the deposited reagent [1-3], since their electrochromic properties permit reversible adjustment of colour and/or contrast to optimize image quality.

This presentation will describe translation of this research topic to the educational arena. The technique has been developed as an undergraduate teaching laboratory experiment for students undertaking a *Chemistry with Forensic Science* degree programme. In overview, the inclusion of material science and spectroscopic techniques in these studies makes them educationally attractive as a means of demonstrating the inter-disciplinarity of contemporary scientific research. Educationally, the experiment offers an opportunity to discuss fundamental electrochemical concepts, starting from electron transfer itself, then extending to coupled chemical processes (EC-type processes exemplified by proton transfers in polyaniline films [1]), electrodeposition, nucleation and growth, redox-driven ion-exchange, and the development of a band structure (in the polymer) from the molecular orbital structure (in the monomer). Distinction between thermodynamic issues (governing film redox state and thence colour) and kinetic issues (relating to the rate of colour variation) is a common problem for students new to electrochemistry. Consideration will be given to this and other challenges experienced by students.

Electrochromic polymer enhancement of latent fingermarks is an experiment that offers a number of options, according to the requirements of the course or the backgrounds of the students. It can be delivered in a relatively closed manner based on relatively proscriptive instructions, or it can be extended in various directions. In the latter instance, one can vary the polymer or the substrate, can incorporate spectroscopic/imaging techniques of varying levels of sophistication [3], and can explore the more applied aspects such as exposure of the “exhibits” to different environments that mimic a crime scene. This last point provides an opportunity to demonstrate that, quite frequently, electrochemistry is part of a larger process and one must take a holistic view. In the present context, this involves consideration of evidence collection, use of sequential fingermark treatments and surface analytical or imaging methods.

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Beyond Talking about Stress and Mental Health

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During the past few years, there has been nationwide an increased interest in stress and mental health in education, unfortunately, sometimes triggered by tragic events. It has been estimated that roughly one third of all students request at some point during their undergraduate career some type of stress or mental health counseling. There is no reason to believe that the numbers are all that different at the graduate student level, but few data are currently available.

The Department of Chemistry, University of Minnesota, has made over the past five years stress and mental health a focus topic for its graduate program. Its approach is not to lower the bar for its students to get the PhD degree; we don't want our students to work less hard or make fewer substantial achievements. Instead, we want to create conditions in which students feel comfortable working hard and feel engaged and empowered to help shape their own future.

Back in 2012, we called mental health specialists from the university health services into the chemistry department to give a workshop for everyone to increase the knowledge and skills of faculty and students to recognize signs of distress and address stress and mental health issues with advice and referral. That workshop inspired many of the chemistry graduate students to create the Community of Chemistry Graduate Students (CCGS), a group that has since then been working in close collaboration with chemistry's director of graduate studies. The CCGS's chief aim is to create a social support network for the department's graduate students and to address and reduce student stress. As a result, students have organized workshops on physical health, stress management, and mental health, and organized social activities to prevent isolation, including biweekly coffee hours and jogging groups.

The CCGS representatives and chemistry's director of graduate studies have also worked with university health services to develop and administer two surveys over the last three years about stress and the support system of chemistry graduate students. When results became available, we organized a department-wide event attended by both faculty and students in which representatives from university health services presented the survey results and led a discussion on possible improvements of how things are done in the department. This has led to an atmosphere in which stress and mental health are openly talked about, and everyone has a better understanding of available resources.

The survey taught us a lot about our students and within a relatively short time allowed faculty to improve procedures. For example, following the first survey, the form for annual reviews of graduate students was rewritten, putting more emphasis on student self-evaluation, and forcing faculty to comment on the students' self evaluation. Surprisingly, some students are much harsher on themselves than the faculty are on them. A properly filled out evaluation also gives students a better idea whether they are on the right track to the degree. We also introduced a new fifth year milestone to ease the transition to post-graduate job life.

Communicating Electrochemistry and the Language of Electrochemistry

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The teaching of electrochemistry usually begins with oxidation-reduction reactions and electrolyte solutions, moving on to phenomena at the solid-liquid, usually electrode-solution, interface. A proper understanding of interfacial properties and of electrode reactions requires knowledge of the solid state, solid surfaces, the liquid (electrolyte) phase and of charge separation and transfer, a lack of which can lead to learning difficulties. For these reasons, communication of the key concepts in a clear way and with a common language, using the same expressions and the same conventions, is of paramount importance. This common language and development of internationally-respected conventions, as well as making the bridge with other areas of chemistry, with physics and with biology, is crucial for education and for demonstrating the importance and role of electrochemistry in many fields of application. Issues related to conventions have been and are being addressed by IUPAC, but the full adoption of recommendations is still a goal to be achieved at the worldwide level. Speaking a common language also aids communication and enables dissemination and scientific progress to be achieved more readily and rapidly. All this is particularly relevant at the present time when the applications of electrochemistry are attracting increased interest from scientists and from engineers in many different disciplines.

Examples from the energy area and in alternative energy sources, from new and more efficient electrocatalytic materials, in corrosion and in electrochemically-based sensors and biosensors, will be used as illustrations.

Advancing Electrochemical Education Through FACETS

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Electrochemical Science and Engineering education is particularly challenging, as comprehensive learning requires prerequisite knowledge in general and physical chemistry, thermodynamics, mass transport and kinetics, electrostatics, fields, potentials, electrical circuits, differential and integral calculus. Practical working experience in electrochemical experimentation and industrial processes also greatly facilitates comprehension. Interested students are therefore rarely sufficiently prepared to develop a deep understanding of electrochemistry. A lack of knowledge in any of the aforementioned prerequisite areas can pose significant barriers to advanced learning. Often a student will pass a prerequisite course but may have missed a key concept that is needed for comprehending electrochemical theory and practice. A modular approach to education, particularly micro-credentials in the form of digital badges, may offer a better way to ensure that students have the appropriate background knowledge to fully grasp electrochemistry and electrochemical engineering at an advanced level. The students will be introduced to key physical and chemical concepts in a modular format with digital verification and certification of their competency. It may also provide a means to credential competence in the many diverse subject areas of electrochemistry.

The Department of Chemical and Biological Engineering (CBE) at the University of New Mexico is engaged in a program to revolutionize engineering education by launching FACETS: Formation of Accomplished Chemical Engineers for Transforming Society. FACETS will revolutionize CBE by: (1) introducing "CIRE" design challenges in the core curriculum that are Community-, Industry-, Research-, and/or Entrepreneurship-based; (2) conducting professional development institutes that will train and mentor faculty and graduate students; workshops will be led by experts from industry and national laboratories, from the learning sciences, from engineering education and multicultural studies, for example the directors of UNM Native American Studies and Chicano/a Studies, and (3) create a digital badging system that will help students take ownership of their competencies and develop engineering identities and enable faculty to monitor and assess student outcomes and to engage in research on their teaching. We believe that this comprehensive approach towards modular learning and digital validation will improve our teaching of Electrochemistry and Electrochemical Engineering and heighten our student’s understanding of the subject material. Core modules and digital credentials are being prepared in the subject areas of:

- Electrochemical Cell Types
- Ionic Transport and Conductivity
- Electrostatics, Fields and Potentials
- Double Layers
- Electrochemical Thermodynamics
- Electrolytes; Aqueous, Non-Aqueous, Ionic Liquid and Molten Salt, Solid and Polymer
- Batteries: Primary and Secondary
- Fuel Cells
- Electrolysis
- Electrodeposition
- Electroanalysis and Electrochemical Sensors

Combining Multiscale Computational Modeling and Interactive Virtual Reality for Teaching Electrochemical Energy Storage

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Computational modeling and numerical simulation are recognized to be important disciplines to foster the progress at the rechargeable batteries R&D [1-2]. Computational modeling can nowadays address the resolution of complex mathematical equations describing the physicochemical mechanisms under different geometrical assumptions, including three-dimensional representations of the electrodes. However battery computational models used in the state of the art are not interactive, thus, the system being simulated cannot be modified during the simulation, and the modeled geometries (e.g. three-dimensional porous electrodes) are usually represented as one dimensional or bi-dimensional projections. Such an approach of visualization of results and the lack of interactivity of them leads to inaccurate representations. Teaching the batteries operational principles and approaches for modeling them become an even more difficult task in view of the inherent multi-disciplinarity and complex operation conditions expected in real applications.

Here, we report an innovative tool which combines multiscale simulations of electrochemical reactions and transport mechanisms in electrodes of rechargeable batteries [3-5] with an interactive Virtual Reality (VR) environment [6]. The tool permits simulating a battery operation under application conditions within a three-dimensionally-resolved game context, and has been used for teaching electrochemical energy storage and conversion within the Erasmus Master Programme M.E.S.C. [7]. The VR environment provides to the user immersive and interactive features which enhance the understanding of batteries operation principles. Furthermore, we discuss the feedback from students and new opportunities for teaching electrochemistry.

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The Role of Independent Projects within a Graduate Electrochemistry Course

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Electrochemistry as a discipline is taught comprehensively as a graduate course throughout the United States. With the increasing movement towards active learning environments in classrooms, this talk will highlighted several past and current models of including laboratory and computational components to augment the classical lecture format in the graduate electrochemistry course. Significant challenges occur in “flipping the classroom” or other in vogue “SCALEUP” course models when a working knowledge of the field is very difficult to obtain from reading even the most accepted texts. Hybrid models incorporating out of class projects have been adapted to increase the relevance of the field to particular students while building up a working knowledge and experimental experience. The nature of these projects has shifted over the years to specific assignments to independently designed projects to team projects.

Theoretical Analysis of Microelectrode Arrays Under Forced Convection

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Numerical solutions to the equation that governs steady-state mass transport to a hexagonal array of small redox-active disks embedded in an inert rotating disk electrode, RDE, under both diffusion-limited and mixed, first order kinetic control were obtained using COMSOL. Analytical expressions were found, which accurately reproduced the simulations, yielding, for limiting cases, a behavior in agreement with that reported in the literature. This formalism was applied to the analysis of thin films of nanoparticles dispersed in inert high area supports attached to the surface of an inactive RDE. To this end, calculations were performed, wherein the total normal flux of reactant to the disk electrode was assumed to be controlled by the kinetics of a first-order reaction. The results obtained could be represented to a very good degree of accuracy by the expression for the dimensionless current under kinetic control, ρ_K:

$$\frac{1}{\rho_K} = \frac{K_o}{(1-\theta)K} + \frac{\pi R_1}{4\Delta(1-\theta)} + 1 \qquad [1]$$

which, as shown in Figure 1, reproduces the numerical simulations to within 5% even up to a value of R_1 as large as 0.002 and 1-θ as low as 0.05. Rather unexpectedly, Eq. 1 is identical to that proposed by Zoski et al.[1] once the dimensionless quantities are expressed in terms of their dimensioned counterparts, i.e.

$$\frac{1}{I^{array}} = \frac{1}{nFA_{disk}(1-\theta)c_{bulk}}\left\{\frac{\pi r_1}{4D} + \frac{\delta}{D}(1-\theta) + \frac{1}{k}\right\} \qquad [2]$$

where I^{array} is the current of the whole array and A_{disk} is the cross-sectional area of the entire disk electrode. As noted by these authors, the first two terms in parenthesis are attributed to mass transport to the individual nanoparticles under quiescent conditions and to convection, respectively, and the last term accounts for the kinetics. Moreover, in the absence of convection, Eq. 2 reduces to that proposed recently by Kim and Bard[2] in their analysis of Koutecky-Levich plots for microelectrodes. Hence, contributions to mass transport to the nanoparticles other than those derived from convection are indeed negligible and the equation can be used with confidence.

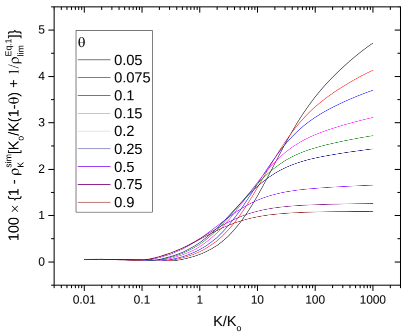

Figure 1. Plots of the absolute value of the $\% \, error = 100\left\{1-\rho_K^{sim}\left(\frac{K_o/K}{(1-\theta)} + \frac{1}{\rho_{\lim}^{Eq.\,1}}\right)\right\}$ at $R_1 = 0.002$, as a function of K/K_o for values of 1 - θ shown in the legend, where $\rho_{\lim}^{Eq.1}$ represents the dimensionless limiting current specified in the equation above.

Acknowledgements

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Title Key Concepts in Electrochemical Education: Flux, Potential Axes, and Dimensionless Parameters

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Electrochemistry is about the system; its study is divided into thermodynamics and dynamics. Understanding the distinction between thermodynamics and dynamics is important.

Thermodynamics describes the best case scenario, the 100 % efficient system. Understanding relationships between multiple species and potentials is key to appreciating possible states of the system and the equilibrium condition.

Dynamics includes transport and kinetics. It is dynamics that limits the behavior of the system. Gradients drive transport. Flux characterizes gradients and sets current. Although the idea of flux is critical to understanding transport, flux is not commonly part of the chemistry curriculum.

Kinetics imposed on thermodynamics and transport alters the rates and efficiencies of electrochemical systems. The extent of kinetic impacts is dependent on the relative magnitudes of the kinetics and the transport. Dimensionless parameters characterize relative effects and provide important metrics in efficient system modeling.

In undergraduate classes where electrochemistry is introduced and in graduate electrochemistry classes, mastery of thermodynamics, transport, and kinetics is enhanced by introduction of potential axes, simulations, and dimensionless parameters. Tools include paper, spreadsheet, and simple coding.

Similar to the potential axis in sweep voltammetry, potential axes first map standard potentials and then reflect effects of concentration. Potential axes identify species that react spontaneously and can identify the sequences of species electrolyzed at the anode and cathode. A spreadsheet template of potential axes readily demonstrates impacts of concentration and pH.

Flux emphasized as number per cross sectional area per time is critical to understanding transport and current. In graduate courses, implementation of explicit finite difference simulations clearly demonstrates the role of flux and flux gradients in establishing current and concentrations. For those unfamiliar with coding, a simple compile such as Visual Basic® within Excel® provides rapid implementation of Fick's first and second laws and direct graphical representations. Once a student has implemented a simulation, flux is well appreciated.

Simulation of a heterogeneous or homogeneous mechanism introduces kinetics. Simulation implemented dimensionlessly increases the generality of the simulations and reduces the number of simulations. Simulations that embed dimensionless parameters can be exploited to evaluate relative impacts of transport and kinetics through ratios of system parameters that include diffusion coefficients, lengths, concentrations, and rate constants.

Armed with thermodynamic appreciation through potential axes, notions of transport driven by flux reinforced by simulations, and impacts of reactions characterized by dimensionless parameters that ratio kinetic and transport rates, students of electrochemistry have preliminary tools to assess, appreciate, and design electrochemical systems.

Electrochemistry in the Undergraduate Curriculum – Exciting the Next Generation of Electrochemists and Electrochemical Engineers

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Electrochemistry and electrochemical methods in the general chemistry sequence, analytical and instrumental analysis as well as undergraduate research seems to induce student trepidation if not outright fear.

By using an approach that follows directly from their understanding of equilibrium and which relies on how electrochemical processes impact their everyday life, it has been possible to increase the students' interest and commitment both in the classroom and in the research laboratory.

A number of approaches to engage students with electrochemical concepts and applications in lecture, laboratory, and undergraduate research projects will be used to illustrate the successes to date. In addition, suggestions for how some of these might be adapted for the future will also be discussed.

The Importance of Fundamental Electrochemistry and Methods for Educational Corrosion Courses in the Field of Civil Engineering

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To date, there is no solution for simultaneously affecting a reinforced concrete system as a global, which is otherwise a prerequisite for successful and durable corrosion control. The reason is the commonly fragmented approach i.e. civil- or corrosion-engineering oriented only, and hence the restriction of the applied methods and technology to either steel or concrete. However, within the present challenges of climate change, health and safety risks, it is now evident that a proactive and multidisciplinary approach to solve corrosion-related issues in our built environment is required. This holds not only for research and practical applications, but logically, also for providing education to young specialists and professionals in the relevant fields. Therefore, civil engineers and material scientists in the field of in-depth investigation of corrosion phenomena and/or corrosion control, need to be educated in fundamental electrochemical principals in view of corrosion assessment. A proper experimental design, the right choice of corrosion experiments, electrochemical methods and knowledge of electrochemistry are prerequisites for the right approach in corrosion assessment, data interpretation and corrosion control of civil structures.

Well known is that steel corrosion in reinforced concrete is of great concern with respect to structures durability. The assessment of the condition of reinforced concrete structures in terms of: time to corrosion initiation, the level of damage, the performance of the system related to mechanical properties, etc. is always related to estimating corrosion rates i.e. to determination of electrochemical parameters for the steel reinforcement in certain technical and environmental conditions. Further, electrochemical techniques for corrosion prevention and/or protection (e.g. cathodic protection), in terms of assessing their efficiency, is also based on recording electrochemical parameters. Since steel corrosion in reinforced concrete is an electrochemical process with high complexity, its investigation and proper interpretation is only possible via knowledge and adequate implementation of electrochemical techniques. To this end, the paper will discuss the design of a corrosion course for civil structures, where fundamental electrochemistry is covered as theory and practice, together with main aspects of concrete material science. The integration of these fields of science – both in theory and hands-on practical sessions, illustrates the multidisciplinary approach, required for corrosion assessment of civil structures. The course is to the authors' best knowledge not available in its' form and content in other current educational programs and is a step forward towards bridging gaps in education for specialists in the field. General and more sophisticated electrochemical techniques will be illustrated (e.g. linear polarization resistance, potentio-dynamic polarisation, electrochemical impedance spectroscopy) in their demonstration together with approaches employed for cement-based materials only (e.g. electrical resistivity measurements, microstructural properties evaluation, etc.). An example of both lab and field practical sessions will be discussed in view of the application and data interpretation of fundamental electrochemistry in civil engineering.

Building a Research Career in Electrochemical Technology: The Benefits of a Postdoctoral Experience in Industry

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For many, a postdoctoral position is the next major career step after obtaining a Ph.D. In 2012, nearly 35% of fresh engineering doctorates and 55% of physical chemistry doctorates trained in the United States had a definite commitment to go on to a postdoc position. A large majority of these postdocs, 89%, will be in academic labs. The rest receive their training in industry, national laboratories or other government entities. While industrial postdocs are relatively rare, the experience offers a variety of benefits, including higher compensation, the opportunity to be part of and manage a teams, and access to industry contacts and resources. There are additional benefits to gaining experience in small businesses, including the opportunity to write proposals, and understand business structure. Industry also benefits from hosting postdocs who can help bring fresh technical approaches, offer an expanded network of collaborations and stimulate innovation. While many of these experiences can happen in academia, postdoctoral positions in industry are often an overlooked option. This may be because there is a lack of understanding of the benefits on both sides. Here, we specifically discuss the benefits of industrial postdocs in electrochemical technology and explore strategies to encourage more postdoctoral participation in industry.

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Use of KISSA-1D© Electrochemical Reaction Mechanisms Simulation Software for Teaching

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The use of simulation software is a valuable tool for teaching electrochemistry. Cyclic voltammograms (CV) of a heterogeneous-electron-transfer reaction, associated (or not) to fast homogeneous and/or heterogeneous kinetics, provides the fundamental understanding of the factors that influence the shape of the curve such as area, concentration, diffusion coefficients, temperature, standard rate constant, transfer coefficient, kinetic and equilibrium constants, and scan rate. The available species' concentrations vs distance from electrode plots throughout the voltammogram are a powerful visual aid in understanding the influence of diffusional mass transport on the current response. Accurate treatment of the various and simultaneously acting scales is one of the main difficulties in simulations of electrochemical problems. KISSA-1D©, the user-friendly software developed in KISSA-group [1], provides a general framework to treat such situations. It requires from a user only to set up an electrochemical problem (by providing mechanism, rate constant, diffusion coefficients, etc.) in a user-friendly environment and returns the simulations results without any intervention into numerical part from the user side. The accuracy of the numerical solution is guaranteed in KISSA-1D© by employment of a non-uniform and adaptive grid. The latter is constructed on the basis of a kinetic criterion (rather than on a gradient-based one as in other programs) and provides a high dynamic resolution at the acute reaction fronts which are automatically detected and tracked by the program at each time step [2-5]. The efficiency of this strategy was proved by addressing such sophisticated problems like electropolymerization [5], competitive reactive adsorption of the benzyl halides at silver electrodes [6] and dynamic adsorption [7], investigation of reaction mechanisms leading to the electrogenerated chemiluminescence (ECL) [8, 9], etc. A couple examples of real data imported to KISSA-1D© for comparison to simulations for elucidation of mechanism and determination of the parameters are presented.

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COMSOL Finite Element Simulation for Electrochemistry Education and Research

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Numerical simulation is a powerful approach not only for electrochemical research and development, but also for education of future electrochemists. Recently, the finite element simulation of electrochemical systems was dramatically facilitated by a commercial package, COMSOL Multiphysics. In this presentation, I will discuss about my experiences of introducing COMSOL to solve electrochemical problems in laboratory and classroom. For instance, first-year graduate students with little background of electrochemistry can use COMSOL with a simple handout to simulate a time-dependent current response at an ultramicroelectrode in a two-dimensional space, which can be readily extended to the simulation of scanning electrochemical microscopy. For research, COMSOL can simulate highly complicated systems with three dimensions, Marcus-type electron-transfer kinetics, coupled chemical reactions, surface processes, and multiple phases. Pitfalls of COMSOL simulation found in the literature will be also discussed.

Strategies for Sustainable Electrochemical Engineering Education

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One of the most recent trends in education within the last two decades have to do with Education for Sustainability (EfS). EfS is defined as "a transformative learning process that equips students, teachers, and school systems with the new knowledge and ways of thinking we need to achieve economic prosperity and responsible citizenship while restoring the health of the living systems upon which our lives depend. [1]" Education for Sustainability presents a great opportunity for Electrochemical Engineering but it raises the question how could programs in Electrochemical Engineering Education (EEE) become sustainable? Attracting the next generation of scientists and engineers who will contribute to the solution of global problems is critical not only for humanity well being but also for sustainability of knowledge and education.

This talk will discuss experiences in developing sustainable electrochemical engineering education programs that involve: course curricula, independent design projects, outreach programs implemented through universities and professional societies [2-4], and curricula development for educating science teachers.

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Teaching Instrument Design and Construction with 3D Printers

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Education in electrochemical sciences often includes instrumentation and interfacing hardware with the external world. We have developed laboratories for undergraduate students that are essentially open labs that integrate building 3D printers, where students learn basic concepts in electronics. Combining this with instrument design and application of the 3D printers to build ancillary parts for additional experiments has proven fruitful, and very energizing to the student participants. Details of these projects will be given and future plans to expand the project will be discussed.

Superconformal Film Growth: Challenges and Opportunities

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State of the art manufacturing of semiconductor devices involves electrodeposition of copper for device wiring and more recently through-silicon-vias (TSVs) for chip stacking . The process depends on the use of electrolyte additives that affect the local deposition rate thereby resulting in superconformal, or bottom–up "superfilling" of trenches and vias. In the case of on-chip Damascene processing of submicron features the deposition process is explained by the recently developed curvature enhanced accelerator coverage (CEAC) mechanism. The model stipulates that 1.) the growth velocity is proportional to the local accelerator, or catalyst, surface coverage and 2.) the catalyst remains segregated at the metal/electrolyte interface during copper deposition. For growth on non-planar geometries this leads to enrichment of the catalyst on advancing concave surfaces and dilution on advancing convex sections; thereby giving rise to bottom-up superfilling of recessed surface features such as trenches and vias.

In the case of larger features, such as through-silicon-vias (TSV), additional physics become important. Specifically, mass and electrical transport limitations combine with metal deposition induced breakdown of the suppressor layer with the resulting positive feedback leading to an extreme form of bottom-up feature filling.

Despite the success of these superconformal growth processes much remains to be known concerning the detailed molecular nature of the competitive co-adsorption processes involved in both the suppression and acceleration of the metal deposition reaction. The application of in situ surface science tools such as in situ STM and SEIRAS towards a better understanding of the additive interaction will also be detailed.

Curriculum Development Focused on Experimental and Simulation Skills in Electrochemistry

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In the United States undergraduate curriculum, electrochemistry concepts are introduced in General Chemistry during the students' first year as an undergraduate, but standard electrochemical techniques are not covered in the laboratory. In the Analytical Chemisty curriculum, the students are introduced to potentiometry techniques and usually a broad overview of coulometry, amperometry, and voltammetry, but minimal experimental work is done to prepare the student for actually doing electrochemistry experiments in the laboratory. Over the last decade, there has been increasing interest in electrochemical devices (electrolyzers, fuel cells, batteries, solar cells, electrofuels, etc.), so many graduate students are finding themselves trying to do electrochemical experiments without practical knowledge on the techniques. Last year, the University of Utah revamped their electrochemistry course sequence to include more practical techniques and applications to the second half of the graduate course sequence in electrochemistry. This included the students coming to lab and doing a cyclic voltammetry experiment and then learning to simulate the results using Comsol Multiphysics. In the laboratory portion, they learned the importance of proper electrode polishing, electrolyte/solvent choices, issues with oxygen and water in their electrochemical cell, and the effects of changing concentration, scan rate, potential window, etc. In the computer lab portion of the course, they learned to use Comsol and to simulate voltammetric experiments with microelectrodes and macroelectrodes, as well as the incorporation of mechanisms (EC, CE, ECE, etc.) into the simulation. These hands-on experience helped them get the necessary skills to utilize electrochemistry in the research laboratory, but also helped them conceptually understand the lecture material.

Electrochemistry Training Program in São Paulo: From a local experience to an International Program

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Currently the vast majority of equipment used in electrochemical laboratories are automated and data acquisition is made using a computer. These systems facilitate the experimental work and increase the speed of data acquisition, but do not facilitate the understanding of the operator against the benefits and difficulties of each electrochemical technique. Moreover, often the researcher has difficulty in choosing the technique best suited to address a particular situation. This fact is emphasized in the last decade, due to the fact that electrochemistry and its fundamentals were subjects eliminated from chemistry undergraduate programs. On the other side, it is a matter of fact that electrochemistry is each time more used as a characterization tool in many laboratories involving material science, biomedical studies, environmental, etc.

With this panorama in mind, a group of researchers from the Chemistry Institute of the University of São Paulo in Brazil, decided to organize an Intensive Electrochemistry School. Since 2006 School of Electrochemistry is annually organized at IQUSP. The target audience is graduate students and young doctors from all over the world. The number of participants is limited to 25-30 to ensure access to equipment for developing the experiments in small groups. The main goal of the school is to provide the initial theoretical and experimental bases to improve knowledge related to different electrochemical techniques allowing a better understanding of the phenomena of charge transfer. The completion of theoretical and experimental moduli of the course aims at deepening the knowledge of electrochemical techniques to maximize the use of computer programs that accompany the equipments.

The first participants of the School were researchers (graduate students, pos docs and young professors) coming from the whole country. In the second year, many participant from different latinoamerican countries, i.e. Argentina, Colombia, Chile, Uruguay and Peru, applied for the School and very soon became traditional in the region. In 2013, a joint version together with the Southampton Summer School was held in São Paulo, with the participation of approx. 80 participants from all over the world. This was a breakthrough and, from this year onwards, the international character remains with the change of the language from Portuguese to English for all the activities and the continuous affluence of participant from very different counties.

The whole experience will be presented with statistics, and successful networking established as results of this very enriching experience.

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Fabrication of Paper-based Electrochemical Devices in Flat Cardboard Using Laser Scribing Technique

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Laser scribed technique has recently been reported in the literature as a simple and large-scale tool to fabricate carbon nanostructures in polymeric materials to manufacture energy storage devices [1,2]. In this work, we demonstrate a new approach to pattern carbon porous materials in flat cardboard platform using CO_2 laser printer. The described process is a cost-effective and reagentless method which allows the fabrication of electrochemical devices in different geometries for remote applications. The developed sensors were characterized by Raman Spectroscopy, Voltammetry, Electrochemical Impedance Spectroscopy, Scanning Electron Microscopy, Thermogravimetry and X-ray Photoelectron Spectroscopy analysis. Based on the characterization analysis it was observed the formation of different carbon materials, as graphene structures, modulating the experimental parameters, i.e. laser power and type of paper used. Fig. 1 shows the electrochemical characterization using potassium ferricyanide/ferrocyanide as a redox probe. The developed sensors were evaluated for several analytical applications indicating a great potential of the proposed fabrication method for the development of paper-based portable sensors.

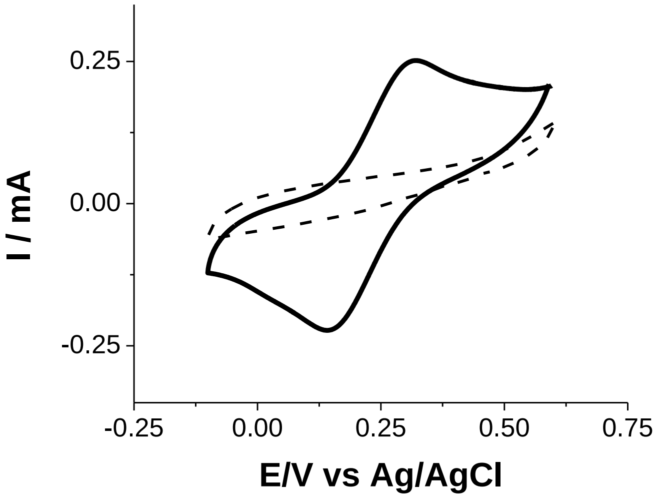

Fig 1. Cyclic voltammetry of laser scribed carbon electrode recorded before (--) and after (-) addition of 5 mmol L^{-1} ferricyanide/ferrocyanide. Scan rate of 10 mV s^{-1}. Supporting electrolyte: 0.1 mol L^{-1} KCl.

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Anodic Dissolution of Tungsten Carbide at High Current Densities

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Tungsten carbide is the main component of cemented carbide materials. Cemented carbides are widespread used as cutting tools in wood processing, metal working or as punching tools. Unfortunately, cemented carbides are difficult to machine due to their high hardness. Therefore, electrochemical machining (ECM) can be a promising alternative machining technology. However, ECM of cemented carbide is not yet really established in the industry and the dissolution mechanism of tungsten carbide under ECM conditions are scarcely investigated. ECM usually works at high current densities (up to 100A/cm^2) and voltages (up to 30V). The present work focuses on fundamental electrochemical investigation of the anodic dissolution behavior of pure tungsten carbide in aqueous sodium hydroxide solution (1 mol/l) by galvanostatic pulse measurements at different applied current densities. Additionally, selected experiments were carried out in a special designed through flow cell which offers the possibility to observe the anode surface *in-operando*. The experimental method is detailed described elsewhere [1]. At low current densities and voltages (e.g. 5A/cm^2 and 6.5V) no gas evolution on the anode was detectable. Again, the dissolution of tungsten carbide is strictly influenced by the microstructure (crystal defects and crystallographic orientation of the grains) as supplementary SEM and EBSD investigations shown (Fig.1).

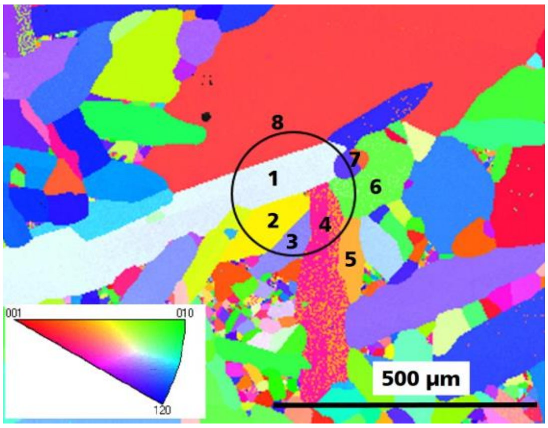

Fig.1a: EBSD image of WC-surface before electrochemical experiments. The circle marks the in-operando observed area)

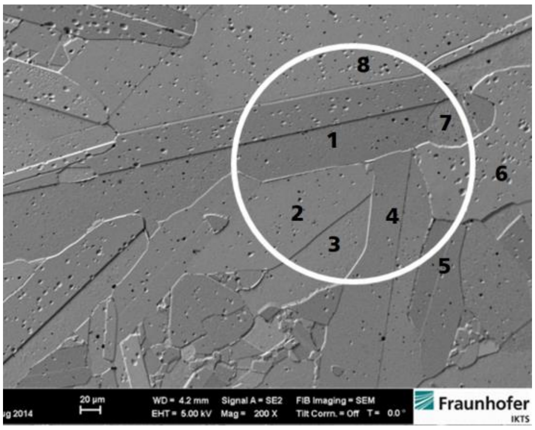

Fig.1b: SEM-image of the WC-surface after the experiment (5A/cm^2). The circle marks the in-operando observed area)

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Real-time Electrochemical Monitoring of Controlled Cargo Release for *in vitro* Delivery

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Osteoarthritis is a debilitating condition of synovial joints, leading to pain and severe limitations in mobility. The condition proceeds via initial mechanical stress combined with low grade inflammatory processes, and over time cartilage is lost. Unfortunately, natural cartilage has limited regenerative capabilities, in part due to avascularity. For this reason, a proposed treatment is delivery particles able to locally release specific cargo to promote cartilage regeneration.

Nano-sized particles are highly suited as delivery vehicles due to their many advantages including tunability, adaptable surface chemistry providing sensing ability, high cargo loading and prolonged circulation time (1). They can be tailored to release cargo under selected environmental stimuli including response to chemicals mimicking intracellular environments (2), temperature, and the presence of biological compounds. We have developed nanoparticles able to release cargo in response to the presence of selected enzymes. Monitoring the release from particles is generally performed via fluorescently labelled cargo (2), however, here we demonstrate that it can also be performed using electrochemistry. Known electroactive compounds will be used as mimics of cargo for preliminary experiments (3, 4).

The aim of these particles is to deliver cargo *in vivo* in order to promote cartilage cell growth. Measuring cargo release using electrochemistry in an *in vitro* setting is used as a model. Microdialysis will be introduced as a sampling technique for the non-destructive monitoring (5) of *in vitro* samples. In this work an electrochemical protocol for the real-time monitoring of cargo release will be discussed and preliminary findings shown. This study will provide novel insights and can be translated to compare cargo release from different particles and under different environments.

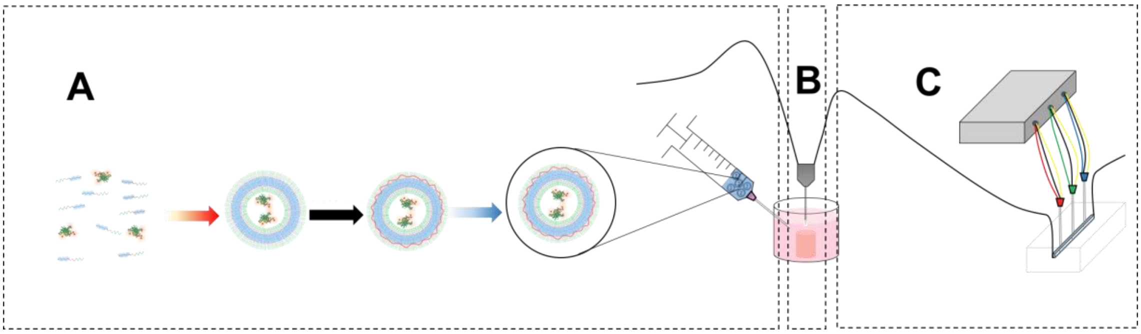

Figure 1. Schematic showing the overall system. A) Formation of the particles containing cargo. B) Sample collection *in vitro* with microdialysis. C) Analyte measurement using electrochemistry.

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Application of New Conjugate of Cyclodextrin and Folic Acid in pH-Sensitive, Targeted Therapy with Anthracycline Drugs

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Anthracycline drugs have been used for nearly forty years for the treatment of several malignancies. Hundreds of analogs of the first anthracycline antibiotics: doxorubicin and daunorubicin have been synthesized and evaluated. Multiple molecular mechanisms were proposed to explain the cytostatic and cytotoxic effects induced by these drugs. The specific toxicity is due to reactive forms of oxygen, which are produced in redox reactions of anthracyclines such as Fenton reaction. This specific toxicity can be reduced by creating a complex between anthracycline molecule and cyclodextrin.

The main drawback in the clinical use of anthracyclines is the easily developed resistance of pathogenic cells to these anticancer agents. The drug resistance can be a congenital feature or some cells can develop the ability to resist drug action during treatment. The linking of anthracyclines with drug carriers armed with targeted ligands for cell specific targeting can be proposed [1]. The drug carriers are not able to cross the cell membrane directly, but can penetrate into intracellular space by the receptor mediated endocytosis.

One of the most frequently used targeting ligands is folic acid. It is believed that folic acid allows targeting, as it specifically binds to folate receptors (FR) overexpressed in the cancer cells and it may cross through cell membranes by receptor mediated endocytosis.

Furthermore, studies of the tumor cells show that the pH of pathologically changed cells is lower than that of the normal cells. This difference of pH has been taken into consideration in designing new pH-dependent drug carriers.

In the present study, we synthesized an innovative cyclodextrin derivative for anthracycline (doxorubicin and daunorubicin) targeted drug therapy, characterized by ~~a~~ low cardiotoxicity. The cyclodextrin was functionalized with targeting substituent (folic acid) through the pH sensitive triazole linker. Cyclic and square wave voltammetry as well as calculations by molecular modeling prove that the modified cyclodextrin is able to form a strong complex with anthracycline due to proton-acceptor π-π interactions between the aromatic rings in the drug molecule and aromatic residues in the side chains of the cyclodextrin. In addition, appropriately modified cyclodextrin is able to protect not only against cardiotoxic effects of the drugs, but also allows selective delivery of the drug to the pathological cells. Electrochemical studies were confirmed by MTT cytotoxicity tests and visualized by confocal microscope.

This work was supported by grant 2014/13/B/ST5/04117 from NSC

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A General Theoretical Approach to the Voltammetry of Multi-electron Transfers at Microelectrodes

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Multi-electron transfers are found in a number of scientific and technological fields, including systems associated with energy storage and conversion (as in molecular electrocatalysis, redox flow batteries), organic materials, biomolecules, metallic nanoclusters, functionalized nanoparticles, etc.

For the characterization of this kind of processes by means of voltammetric techniques, a general analytical solution is presented in this communication, very easy and fast to implement and applicable to any number of reversible electron transfers *per* molecule, any technique and any electrode geometry. The theory also considers those situations where the redox species take part in one or multiple chemical equilibria in solution such as (de)protonations, ion associations, complexations and isomerizations.

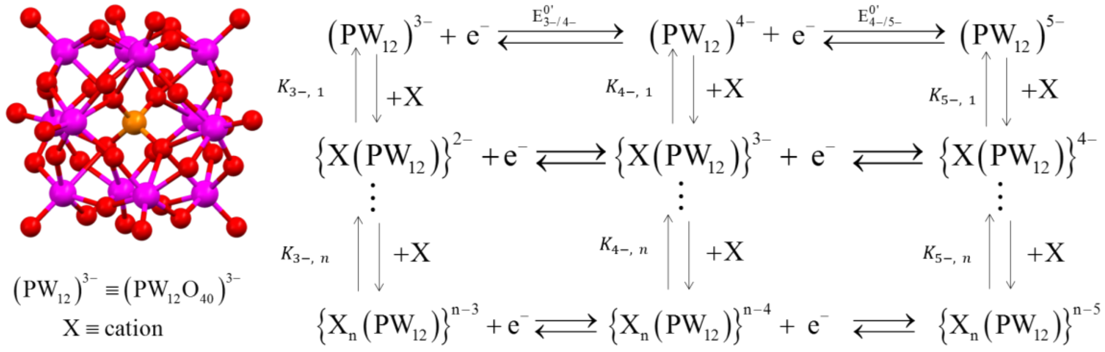

Figure 1. Two-electron reduction of the Keggin-type polyoxometalate $[PW_{12}O_{40}]^{3-}$, with the different redox species undergoing ion association with cation X present in the electrolyte medium [1].

The general expression obtained for the current-potential-time response of multi-electron transfers will be particularized for a variety of experimental systems and for the most widely-used voltammetric techniques, namely: cyclic voltammetry, square wave voltammetry and differential pulse voltammetry.

First, the influence of the geometry of the working electrode will be discussed under transient and steady state conditions, including common microelectrode geometries (discs, bands, rings, hemispheres) as well as of their arrays. Next, the thermodynamic 'interdependence' between successive electron transfers (*eg*., the degree of electronic communication between different redox centres in a macromolecule) and its effect on the voltammetric signal will be considered. For its quantification, suitable criteria and techniques will be established for both simple electron transfers and for transfers complicated by coupled chemical equilibria [2]. In the second case, the determination of the corresponding equilibrium constants will also be addressed. The theoretical results will be applied to the investigation of ion pairing effects on the electrochemistry of Keggin-type polyoxometalates (Figure 1), which are frequently employed as electrocatalysts.

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TiO_2 nanotubes modified with ZIF-8 (Zeolites Imidazole Frameworks) used for capturing and photoelectroreduction of CO_2

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Abstract

In the contemporary world, the dilemma of meeting the growing demand for energy without increasing environmental damage through the exploitation of fossil fuels is a matter of extreme interest [1-2]. The reduction of carbon dioxide to products with high added value such as formic acid (FA), methanol (MeOH) and ethanol (EtOH) for example represents a reaction of great interest, in view of two main problems today: Global warming and the decline in fossil fuel reserves [2]. The present work investigates the use of TiO_2 nanotubes (NT) modified with ZIF-8 nanoparticles (Zeolites Imidazole Frameworks) to promote the reduction of CO_2 in products with high added value. In order to do so, it evaluates the incorporation of ZIF-8 in the nanostructured material, the entrapment of CO_2 in the complex and the influence of electron donors (ascorbic acid-AA) on the formation catalysis of FA, MeOH and EtOH using photoelectrocatalysis (PEC) , photocatalysis (PC), photolysis (PT) and electrocatalysis (EC). The assays were performed under optimized conditions of support electrolyte 0.1 mol L^{-1} pH 6.8 and 0.2 mol L^{-1} ascorbic acid subjected to UV / Vis irradiation for 3 hours. PEC measurements were performed under potential control of -0.70V and + 0.10V versus Ag / AgCl reference electrode and a DSA counter electrode. The same potentials were also used for the EC experiments, however, in the absence of light. For the PC tests only the working electrode was inserted into the system and for the PT only the light composed the reaction medium. The carrier electrolyte was saturated with bubbling CO_2 gas at T = 5.0 ° C for 1h. The products obtained were analyzed by gas chromatography coupled to flame ionization detector and ion chromatography. The results showed that under TiO_2 NT electrodes modified with ZIF-8 and AA promoted maximum conversion (0.28 mmol of FA, 1.4 mmol of MeOH and 0.20 mmol of EtOH). The results obtained showed that the use of ZIF-8 incorporated to the NT of TiO_2 facilitates the adsorption of CO_2 on the surface and formation of carbamates increasing the amount of CO_2 adsorbed, reduced primarily by the electrons generated during the oxidation stages of the AA used as mediator in the process.

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Measuring dynamic impedance spectra: a comparison between different filtering strategies

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Dynamic electrochemical impedance spectroscopy allows collecting information in a large range of frequencies (up to 5 decades or even more) while the system undergoes a forced or natural change. In this way, electrochemical impedance spectroscopy can be properly defined and measured for studying unstable and / or non-stationary systems [1]. Recently we have demonstrated that such impedance spectra can be fitted with classic equivalent circuits [1]. The measurement is performed by using a multi-sinusoidal perturbation, however the data extraction is not trivial and it can give origin to artifacts, as well as high noise-to-signal ratio, in the impedance spectra. Instead of employing the typical short time Fourier transform (STFT) algorithm, already proposed by Bond et al. in 1980 [2], we have proposed the use of dynamic multi-frequency analysis (DMFA), which is based on the reformulation dynamic impedance through the formula:

$$Z(\omega_0,t)=\frac{\mathrm{iFT}[\Delta U\cdot f(\omega_0,bw)](t)}{\mathrm{iFT}[I\cdot f(\omega_0,bw)](t)} \qquad (1)$$

where ΔU and I are the Fourier transform of voltage and current, respectively, f a filter function with bandwidth equal to bw and centered at angular frequency ω_0. This definition takes advantage of digital filters, which can be designed very flexibly. We used a family of quasi-rectangular filters based on the formula (see figure):

$$f(\omega_0,bw)=\frac{[1+\exp(-n)]^2}{\left[1+\exp\left(-n\cdot\frac{\omega-\omega_0+bw}{bw}\right)\right]\cdot\left[1+\exp\left(n\cdot\frac{\omega-\omega_0-bw}{bw}\right)\right]} \qquad (2)$$

where n is a parameter defining the shape of the filter, ω the integration variable. In this work, we show a comparison between the classic STFT, with modifications also proposed by Sacci et al. [3], and our approach, which is based on the use of formula (1) and the filter in eq. (2). In particular, it will be shown how the filtering strategy affects the noise-to-signal ratio of the impedance at low frequencies. Using simulated and experimental data on redox couple in solution, we have observed that the STFT algorithm, even with the Blackman-Harris window introduced by Bond [2] and the background subtraction proposed by Sacci et al. [3], gives origin to a relevant level of noise, whereas the DMFA can still recover impedance data with good quality. Moreover, we have developed a new strategy for investigating aperiodic transients, which, coupled with the DMFA approach, can recover both dynamic impedance and *dc* component. Finally, results for two different systems, namely intercalation of ions in Prussian Blue derivatives host structures and silicon electro-dissolution, will be shown.

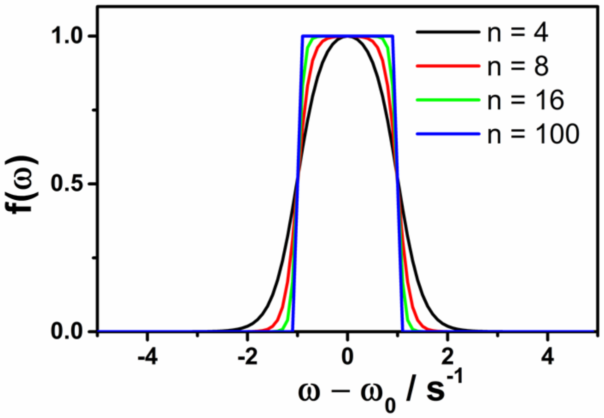

Figure: Quasi-rectangular filters used in the dynamic multi-frequency analysis, shown in the time domain. The sharpness of the filter depends on the parameter n.

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Heat-Treatment of Pt Nanoparticles Sputter Deposited on Multi-Walled Carbon Nanotubes for Oxygen Reduction Reaction

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Recently platinum nanoparticles (PtNPs) supported on multi-walled carbon nanotubes (MWCNT) have been successfully used to catalyse oxygen reduction reaction (ORR) in proton exchange membrane (PEM) fuel cells. It has been found that the shape and size of the PtNPs play an important role in ORR activity. In the present study heat-treatment has been applied to modify the surface morphology of the electrocatalysts [1]. The aim of the study is to observe heat-treatment effects on the ORR activity of Pt/MWCNT electrocatalyst and to optimize the conditions for heat-treatment.

PtNPs were deposited on acid-treated MWCNTs modified GC electrodes. In order to observe effects of the morphological change on the ORR activity, the prepared Pt/MWCNT electrodes were subjected into tube furnace for heat-treatment at different temperatures ranged from 300 to 700 ºC, in inert atmosphere. Surface morphology of the heat-treated Pt/MWCNT electrocatalysts were then studied by high-resolution scanning electron microscopy (HR-SEM). Further characterization of the surface was performed by electrochemical techniques like CO stripping and cyclic voltammetry in Ar-saturated 0.1 M KOH and 0.05 M H_2SO_4 solutions. After decontamination and characterization of the electrodes surface, the ORR was carried out in O_2-saturated acidic and alkaline media. It was revealed that the annealed Pt/MWCNT electrodes show higher specific activity values than commercial Pt/C. Moreover, the electrodes annealed at 300 ºC showed maximum specific activity value. Tafel slope values were calculated from RDE results which confirmed that charge transfer is the rate determining step for O_2 reduction. The number of electrons transferred per O_2 molecule as calculated by the Kouteckey-Levich equation was close to 4 indicating a typical 4-electron O_2 reduction pathway.

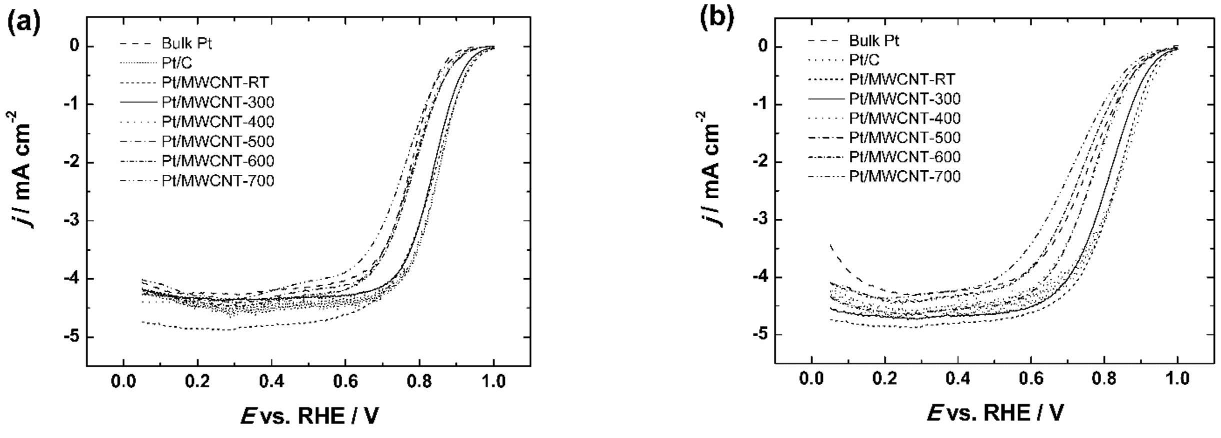

Figure. Comparison of RDE polarization curves for oxygen reduction reaction at 960 rpm in oxygen-saturated (a) 0.1 M KOH and (b) 0.05 M H_2SO_4 solutions. $v = 10$ mV s^{-1}.

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Electrodeposition of Cu-Ge Alloys from an Alkaline Electrolyte

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Various examples of induced codeposition have been reported in the literature and their mechanisms have been partly understood. The induced deposition of Germanium with transition metals has been reported by Brenner, but it is still unexplained. In this work, by using cyclic voltammetry and quartz crystal microbalance, we propose a co-deposition mechanism from an alkaline electrolyte. Induced codeposition is rationalized in terms of the limited Ge growth by H-termination, and by the activation of the Ge-H bond by Cu, resulting in the formation of adsorbed species leading to alloy growth, in parallel with formation of H_2 gas.

The morphology, composition and microstructure of Cu-Ge thin films are characterized; the Ge content in the deposits increases with decreasing applied potential, showing at first a series of FCC solid solutions, and around 25 at% Ge the formation of an ordered orthorhombic Cu3Ge intermetallic compound (ε-phase). The dependence of the resistivity of as-deposited Cu-Ge on Ge content exhibits a non-monotonic behavior. A minimum value was found around stoichiometric Cu3Ge. The ε-Cu3Ge thin film displays a resistivity of 7.5 μΩ cm-1 (~50 nm) and 25 μΩ cm-1 (~1 μm), increasing with the deposition duration, probably due to the progressive incorporation of oxygen.

Electrodeposition of Functional Nanomaterials

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The integration of electrodeposition steps into the fabrication process of electronic devices is well established in the case of microchip manufacturing *via* the double Damascene process(1) and has a lot to offer in the preparation of materials for a range of applications, such as solid state memory, thermoelectrics or infrared detection. In addition to providing a relatively green and scalable method for the preparation of thin film materials, electrodeposition brings significant advantages in the filling of high aspect ratio nanostructures compared to more conventional preparation processes, such as PVD or CVD.

We have developed an electrolyte system based on compatible tetrabutylammonium chlorometallate metal sources in non-aqueous electrolytes (3, 4) that allows the one-pot preparation of a wide range of functional materials, such as GeSbTe(2), CdHgTe, and BiTe. An example of a nanostructured phase change memory device prepared from this electrolyte system is shown in Figure 1 (2).

We will present the electrodeposition and subsequent electrical behavior of GeSbTe solid state memory materials and CdHgTe infrared detector materials and contrast their properties to the properties of conventionally prepared materials.

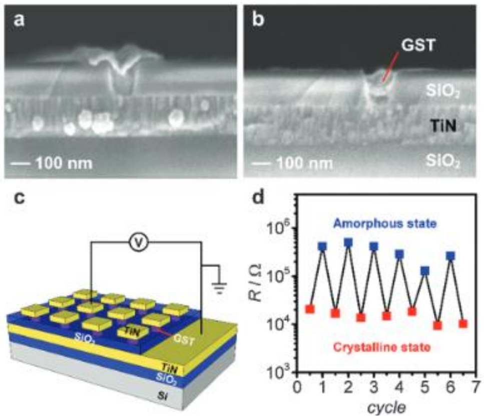

Figure 1 Cross-sections of GeSbTe solid state memory materials electrodeposited into nanostructured substrate (a and b) and the electrical switching behavior (d) of a device fabricated from these materials (c). Figure reproduced from (2) – Published by the Royal Society of Chemistry.

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Super-Efficient Powder Pulse Electrodeposition for Possible Additive Manufacturing Applications

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Electrodeposition is commonly used for the deposition of metallic and composite coatings. It is useful as it can coat complex 3D structures and can be used for the deposition of alloys. There are a few disadvantages; it is relatively slow to build up thick coatings and in some cases the current efficiency can be low.

In this study a fundamentally different method for carrying out electrodeposition is demonstrated. Here instead of dissolving metal from the anode and depositing it on the cathode a powder of the coating metal is put in contact with the cathode and pulse plating sequentially dissolves metal from the powder and then deposits it between the powder grains. A single metal grain used for initial experiments as presented in **Erreur ! Source du renvoi introuvable.**. By this method super-efficient deposition (efficiency >100%) can be achieved, and thick layers can quickly be deposited.

This can in principle be carried out in any media but in this study ionic liquids were used to increase the current efficiency of the process. The method is demonstrated using both zinc and copper. It is shown that using these media certain crystal planes can be promoted and ordered deposits are obtained. The morphology of the surfaces was characterized using SEM, X-ray diffraction, and 3D optical microscopy techniques.

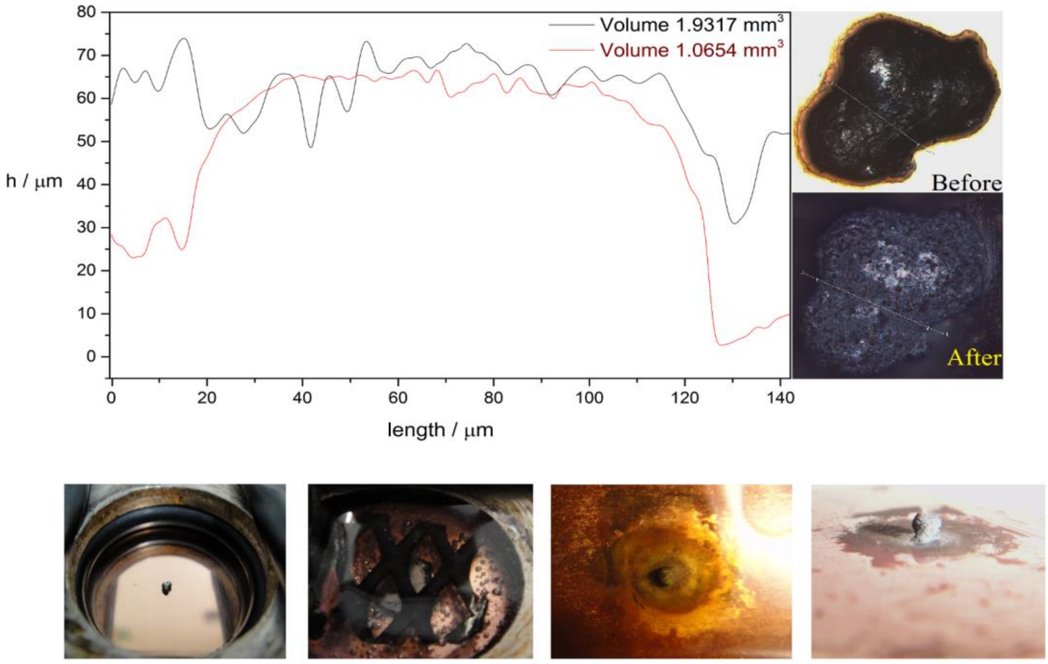

Figure 1 Single zinc metal powder placed onto copper substrate. Current density is 7 mAcm^{-2}. Pulse periods are 1 second dissolution and 3 second deposition. Volume of the first dry particle was 1.93 mm^3 represented as black line. Volume of fused particle was measured 1.06 mm^3 represented as red line.

Photoelectrochemical Visible Light Zero Bias Hydrogen Generation with Membrane-Based Cells Designed for Decreasing Overall Water Electrolysis Voltage and Water Dissociation (16)

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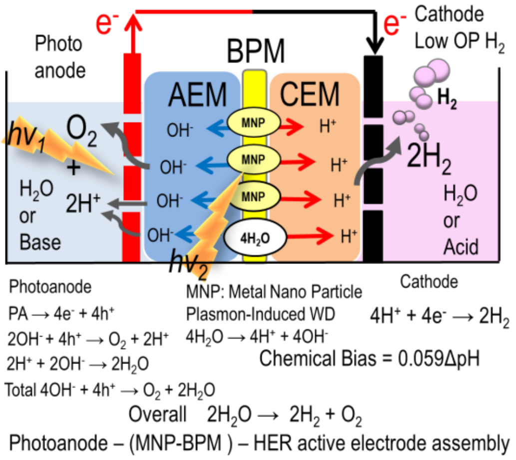
The light-induced water splitting using titanium dioxide (Honda-Fujishima effect) is a milestone in the history of advanced hydrogen generation and artificial photosynthesis under sunlight [1,2]. Reduction of electrochemical water electrolysis voltage is the crucial prerequisite for achieving an efficient PEC visible light hydrogen generation.

Thus we have developed the renewable acid base three-compartment cell (3CC) with a combination of cation (basic) and anion (acidic) exchange membranes (electrolytes) bridging a neutral electrolyte [3]. The onset potential of 0.7 V for hydrogen evolution has been accomplished and succeeded in measuring visible light zero bias photocurrent using a tandem-cell designed to combine n-Fe_2O_3 with chemical bias. The 3CC system is renewable by reversing the applied bias owing to the presence of neutral electrolyte in the middle compartment.

Extending our concept, we should make water fuel. How to supply H^+ and OH^- from H_2O as the fuel is the problem encountered. We notice the presence of BPM [4] in the course of 3CC experiment and carried out hydrogen generation derived from water dissociation using BPM. We have created a two compartment cell (2CC) separated by BPM sandwich electrodes as shown in Fig. Grid type DSA (Pt mesh cathode) was in contact with AEM (CEM) side of BPM, [DSA | (AEM) BPM (CEM) | Pt configuration, BPM sandwich electrodes] [3].



First only distilled water was used for both anolyte and catholyte. Current versus bias scanned at 0.1-20 mV/s exhibits a steep initial rise around 0.65-0.9 V due to H_2O dissociation. We wish to suggest a possibility of electrochemical water splitting into hydrogen and oxygen with less than theoretical 1.23 V at room temperature using OER active electrode | BPM | HER active electrode assembly thin layer cell.

Many electrolyte combinations are possible. A winning combination is base for anolyte and acid for catholyte. All electrolytes used are sustainable in this system. Current enhancement is achieved in acid electrolyte for both compartments.

BPM modification for plasmon-induced WD and grid type photoelectrode formation are now underway.

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Uniform Zn-layer Deposition during Double Zincating on Al: Role of Nitric Acid Dissolution Post Single Zincating

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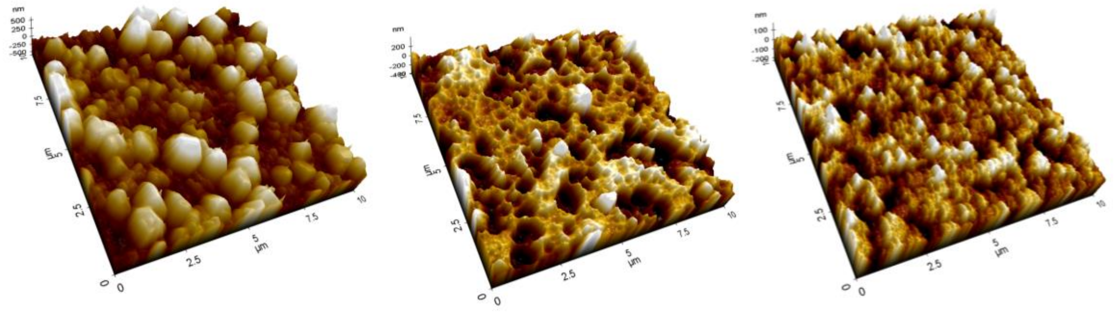
Deposition of various coatings on Al surface is required for variety of functional applications such as for better corrosion resistance, improvement in conductivity, wear resistance etc. These coatings are normally applied on Al surface followed by well-known zincating process (galvanic displacement) in order to obtain adherent overlayers. Adhesion of these overlayers depends on uniformity of Zn films on Al surface and researchers follow either single zincating or double zincating process to eliminate oxide layer interference. However, it was established over the years that double zincating is a better technique in comparison to single zincating to produce a uniform Zn-films on Al surface. It is to mention here that Al substrate undergoes nitric acid dip followed by single zincating prior to double zincating and is a very important step. A quiet good amount of research have been devoted to obtain various adherent coatings on Al and Al-alloys and to find out nucleation mechanism during single and double zincating processes. However, the underline mechanism of nitric acid dipping and its role on subsequent Zn-nucleation is yet to understand fully. In view of this, in the present study, a systematic effort has been made to elucidate the role of nitric acid on Zn-nucleation mechanism followed by single zincating. For this, we have studied the time dependent zinc nucleation on 99.95% pure Al during single as well as double zincating. The Zn-nucleation behavior on Al surface was monitored using AFM and FESEM in detail. Apart from these, the porous surface obtained after nitric acid dissolution was investigated in depth under AFM and FESEM along with EDS. The deposition rate of Zn was estimated using Rutherford Back Scattering (RBS) technique and found quiet high Zn-deposition rate during single zincating compared to double zincating. Both AFM and FESEM results indicated scattered Zn-nucleation along with large grain growth during single zincating unlike uniform nucleation along with fine grain deposit during double zincating. The Zn grain size was further verified by detail XRD analysis. Open circuit potential (OCP) was monitored during single as well double galvanic displacement processes to understand Zn-nucleation behavior. The role of nitric acid dip on nucleation as well as growth of Zn film on Al substrate will be presented in terms of electrochemical as well as Al surface modifications such as porous layer formation, change in chemical nature of top surface, pitting attack followed by Zn root growth underneath Al, etc.



(a) (b) (c)

Fig. 1. AFM surface topography of Al surface after (a) single zincating; (b) nitric acid dipping; (c) double zincating.

Influence of Adsorption of Hydrogen on Its Incorporation during Electrodeposition of Platinum

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Platinum is common material of electrodes for electrolysis and fuel cells due to such properties as corrosion resistance and catalytic performance. The catalytic performance of platinum for hydrogen evolution is especially excellent. Electrodeposition is a common method to produce thin films or nanoparticles of metal. Various studies of the electrochemical deposition of platinum have been reported [1-4]. We recently reported the difference in the platinum electrodeposition behavior of hexachloroplatinate(IV) and tetrachloroplatinate(II) solutions measured by an electrochemical quartz crystal microbalance (EQCM) method [5]. The electrodeposition of metal from an aqueous solution usually accompanies the reduction of protons or water causing hydrogen adsorption and evolution on the deposits. A part of the adsorbed hydrogen is incorporated in the deposited metal films. We have been investigating hydrogen incorporation in electrodeposited metal films using thermal desorption spectroscopy (TDS) [6-8] and reported that a large amount of hydrogen (content in atomic ratio: x = H/Pt = 0.1) is incorporated in platinum films electrodeposited from a solution including dinitrosulfatoplatinate(II) as a metal source [6]. In this study, we investigated the influence of hydrogen adsorption on the electrodeposition of platinum and hydrogen incorporation into the deposited films from a chloro-complex (tetrachloroplatinate(II)) solution by the EQCM method and TDS [9].

0.024 mol dm^{-3} potassium tetrachloroplatinate(II) solution, adjusted to pH 0.8 with hydrochloric acid, was used for the electrodeposition of platinum. A quartz electrode coated with a gold thin film (resonant frequency: 10 MHz, mass change resolution: 4.4 ng cm^{-2}, Hokuto Denko, HX-Q1, HQ-601DK) or pure gold foil (Nilaco, 0.02 mm thick) was used as a working electrode. The thermal desorption of hydrogen from the samples was measured by TDS using a simple vacuum system equipped with a turbo-molecular pump and a mass spectrometer at a heating rate of 5 K min^{-1} from room temperature to 1100 K.

Three types of hydrogen adsorption were observed by the EQCM method: UPD-H1 and UPD-H2, which potential was more positive than the reversible hydrogen electrode (RHE, -0.25 V vs. Ag/AgCl), corresponding to the underpotential deposition of hydrogen on the platinum surface [5, 10], and OPD-H, which was at more negative than RHE, corresponding to the overpotential deposition. UPD-H2 and/or OPD-H inhibited platinum deposition and significantly decreased the current efficiency. Three types of hydrogen incorporation into deposited Pt films were observed by the TDS. 1) At a potential of UPD-H1 (0 V vs. Ag/AgCl), a certain amount of hydrogen was contained in the initial deposits of Pt and no hydrogen was incorporated in the bulk of the Pt films. 2) At a potential of UPD-H2 (-0.1 and -0.2 V), a certain amount of hydrogen was contained in the initial deposits and the hydrogen was uniformly incorporated in the Pt films at content of x = ca. 0.02 in atomic ratio. 3) At a potential of OPD-H (-0.3 V), a large amount of hydrogen (x = 0.1) was incorporated in the Pt films uniformly accompanied by hydrogen evolution. OPD-H increased the hydrogen content.

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Electrochemical Properties of Praseodymium and the Formation of Ni-Pr Intermetallics in LiCl-KCl Eutectic Melts

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Rare earth-transition metal alloy is one of the important application fields, and it is receiving ever-increasing interest in the recent years due to their excellent magnetic properties, hydrogen absorbing or permeable properties, and catalytic properties [1,2]. This work presented the electrochemical behavior of Pr(III) on Mo/Ni electrodes and electrochemical implantation on a Ni electrode in LiCl-KCl eutectic melts. The influence of potential and current density on the formation of alloy was studied at different times. Only $PrNi_2$ phase was identified by XRD. The SEM was employed to further investigate the relationship of time with potential and current density. Fig. 1 illustrated the SEM (a)-(f) images and column diagram (g) about $PrNi_2$ alloy. As shown in Fig. 1 (a)-(f), $PrNi_2$ alloys obtained by potentiostatic electrolysis at -1.75 V and -1.9 V (vs Ag/Ag^+) for 2 h, 4 h and 6 h, respectively. Coherent and dense $PrNi_2$ films with thickness of about (a) 0.4 mm, (b) 0.77 mm, (c) 1.73 mm, (d) 0.62 mm, (e) 0.92mm and (f) 3.2mm were observed. According to the comparison of data above in Fig. 1 (g), it confirmed that the growth rate is higher at more negative potential and at the same potential with a longer time. It is worth noting that the growth rate is faster than the linear rate and Ni matrix completely becomes $PrNi_2$ alloy in (c) and (f) images.

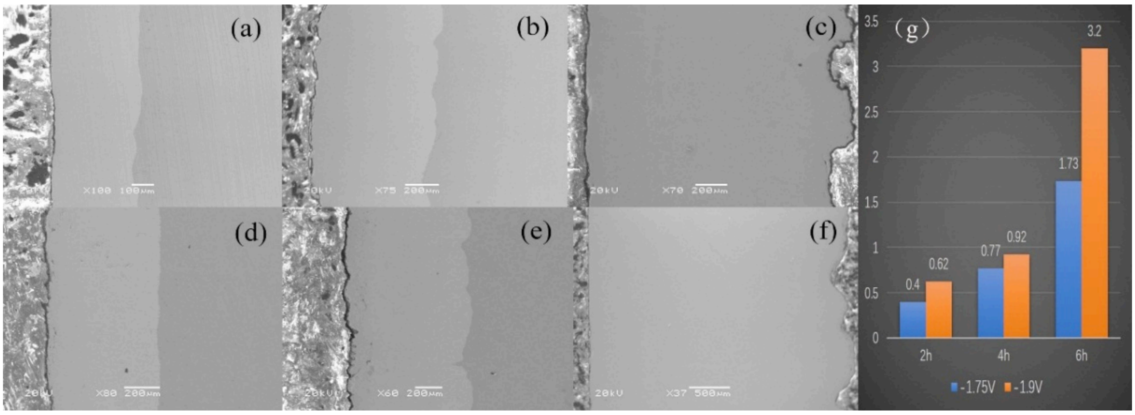

Fig. 1 SEM (a)-(f), images and column diagram (g) about $PrNi_2$ alloy

Acknowledgments

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Application of Dual Dynamic Voltammetry for the Interpretation of Certain Features of the Interface Stress vs. Electrode Potential Curves of Gold

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The method of dual dynamic voltammetry, i.e. applying dynamic potential programs to the generator and the collector electrodes of a generator-collector system simultaneously, is a promising new method for studying the mechanisms of electrochemical processes [1-3]. By applying this method to a gold/gold rotating ring-disk electrode (RRDE) it could be shown that the sharp change in the slope of the interfacial tension vs. potential curve recorded in the oxide reduction region of gold in sulfuric acid solutions [4] is accompanied by the formation of soluble, electrochemically reducible gold species which can be detected at the ring electrode. The 3D representation of the data could be effectively used to reveal the formation of electroactive species at the disk.

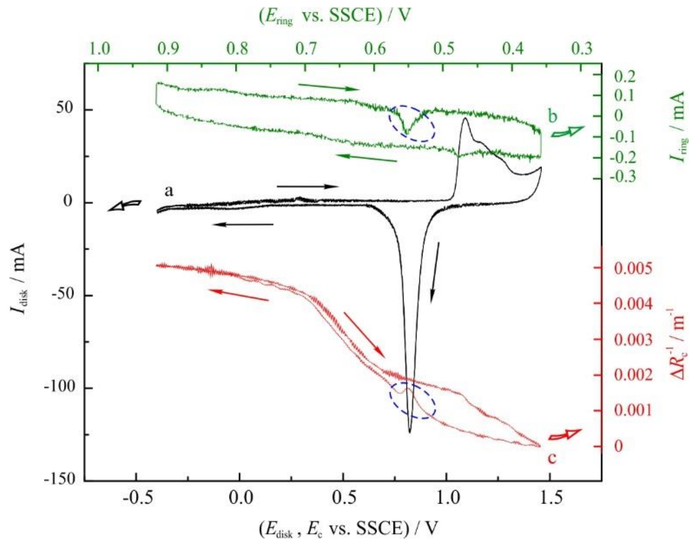

Fig. 1. Cyclic voltammograms simultaneously recorded at the gold disk (a) and the gold ring (b) of the RRDE in 0.05 mol·dm^{-3} H_2SO_4 solution. Sweep rates: 100 mV·s^{-1}, rotation rate: 500 rpm. Changes of the curvature ΔR_c^{-1} of a gold coated cantilever with the electrode potential (E_c) in the same solution (the change of the interfacial tension is proportional to the change of the curvature).

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Electrochemistry at Liquid Metals: Sensing and Actuation

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Recently there has been a significant research effort in the area of liquid metals. In particular eutectics that are liquid at room temperature based on gallium and indium (GaIn) as well as gallium, indium and tin (Galinstan) have been investigated for a variety of applications including soft electronics, repairable circuits, MEMS devices and plasmonics [1-4]. The advantage of these materials is that they have high electrical conductivity, high density and extremely low vapour pressure. To broaden the applicability of liquid metals their surface chemistry can be manipulated via growth of an oxide layer or modification with semiconducting nanomaterials to generate photocatalytically active materials [5]. Another area of interest is the controlled actuation of soft objects which has promise for many future environmental, biological or industrial processes. This has been achieved at microscale objects with a variety of stimuli including light, chemical fuels and magnetism [6].

In this work we describe how the liquid metal galinstan (70 % Ga, 20 % Sn and 10 % In) can be electrochemically actuated in electrolytes of a wide pH range by application of an electric field. To improve performance we show that coating droplets of liquid galinstan with semiconducting nanomaterials significantly affects the velocity of liquid metal droplets [7]. This concept is further developed by utilising galinstan as a liquid metal enabled pump in a closed-loop open-top channel whereby electrowetting/deelectrowetting at the surface of the liquid metal in a dynamic electric field induces a pumping action to give flow velocities of up to 5400 µL/min [8]. Finally we show that the surface chemistry of liquid galinstan can be physically or chemically modified via immobilisation of nanomaterials, gallium leaching or galvanic replacement of the liquid metal to create materials that can be used as electrochemical sensors for heavy metal ion detection or as heterogeneous catalysts [9].

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Single-Molecule Electronics: Chemical Reactions at the Single-Molecule Level

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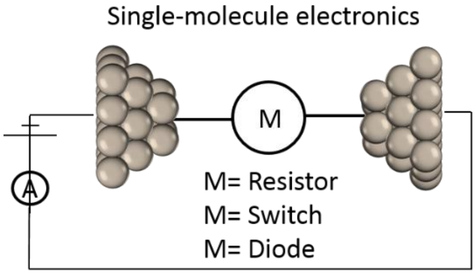
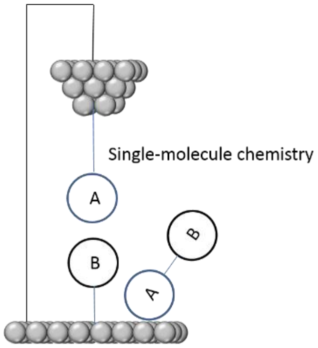


The field of single-molecule electronics has gone through a tremendous renaissance in the last few years. It has transformed from a fundamental characterisation tool [1-2] to a new approach to study chemical reactivity and to fabricate single-molecule devices. Using a concoction of chemistry and electronics, the idea of using single molecules as the key components in nanoscale electronic devices is now closer to reality. Unique properties inherent in single molecules may also allow the production of novel nano-devices whose behaviour falls outside the performance observed in conventional electronics. The main unsolved issues are currently the stability of the contact between a single molecule and an electrode and the limitation with regards to the untunable electronic properties of conventional metal electrodes which narrows the applications of molecular junctions. Mechanically-stable single-molecule contacts to electronically tunable electrode materials will contribute to the realisation of single-molecule electronics.

The focus of this presentation will be on our efforts in creating single-molecule wires, diodes and switches,[3-6] and to build strategies for studying chemical reactions at the single-molecule level.[7-8] Emphasis will be given to the implementation of scanning tunneling break junction approaches in studying chemical reactions. Target reactions include isomerization, bond breaking and forming.



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Structural and Transport Properties of $Na_{0.44}MnO_2$ Cathode Material for Rechargeable Na-ion Batteries

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Improvements in rechargeable batteries performances attract a great deal of attention, both in the portable and stationary applications market. Nowadays, lithium-ion batteries are considered the best technology for rechargeable energy storage because of their high energy density, high efficiency and long cycle life. However, research efforts are devoted to find alternative chemistries, based on abundant, cheap and environmentally friendly materials. In this context, sodium-ion rechargeable batteries are acquiring increasing importance.

In general, layered transition metal oxides and polyanionic compounds are employed as active materials for the positive electrode in Na-ion batteries. Na_xMnO_2–based compounds, being eco-friendly, cheap and easy to synthesize, are also of particular interest. $Na_{0.44}MnO_2$ presents a peculiar crystalline structure, in which Mn (III) ions, in pyramidal coordination, and Mn (IV) ions, in octahedral coordination, are connected to form tunnels running along the *c* crystallographic axis. Within the tunnels, the Na ions are placed on partially occupied crystallographic sites, either within small tunnels (Na1) or larger S-shaped tunnels (Na2 and Na3). This characteristic structure ensures high ion conductivity for the material, especially along the direction of the tunnels, which offers an advantageous path for the intercalation and migration of sodium ions.

In this study we investigate the structural and transport properties of $Na_{0.44}MnO_2$ by means of high temperature neutron diffraction and classic molecular dynamics simulations, in order to shed light on the intercalation properties of this interesting material. The evolution of structural parameters along with temperature shows that no phase change is expected in the whole temperature range considered (30-800°C) and that the three sodium ion positions are all partially filled, even at room temperature. Na-ion migration within the tunnels is clearly visualized through analysis of the Na-ion trajectory plots from molecular dynamics and both intra and inter channel diffusion are investigated. Attention is paid to the potential formation of Na-Mn antisite defects in the structure and their effect on the intercalation mechanism.

Electrochemical Extraction of La on Al and Cu Electrodes in LiCl-KCl Melts

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The electrochemical behavior of La(III) on Cu and Al electrodes were studied in LiCl-KCl eutectic by a series of electrochemical techniques, such as cyclic voltammetry, square wave voltammetry and open circuit chronopotentiometry. Compared with cyclic voltammogram and square wave voltammogram of La(III) obtained on an inert W electrode, a series of reduction peaks were observed on a reactive Cu and Al electrodes, because of the formation of La-Cu and La-Al alloy compounds(shown in Fig. 1).

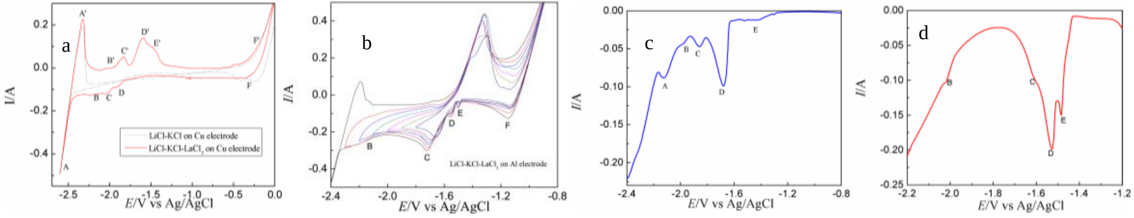

Fig. 1 CVs obtained in LiCl-KCl-$LaCl_3$ melts on (a) Cu electrode and (b) Al electrodes; SWVs obtained in in LiCl-KCl-$LaCl_3$ melts on (c) Cu electrode and (d) Al electrodes. S=0.659 cm^2; Frequency：10Hz.

According to the results of cyclic voltammetry and square wave voltammetry, potentiostatic electrolysis was carried out at different applied potentials on Cu electrode and Al electrode, respectively. Fig. 2 presented the SEM(scanning electron microscopy) image and EDS (energy dispersive spectrometry) analysis of deposits obtained by potentiostatic extraction at -2.0 V for 7 h on Cu electrode (a and b) and Al electrode (c and d) in LiCl-KCl-YCl_3 melts at 823 K.

The calibration curve was obtained on linear relationship of peak currents and concentration of La (III) in LiCl-KCl melts. Meanwhile, the extraction efficiencies were calculated by I inductive coupled plasma atomic emission spectrometer and calibration curve, respectively, the highest extraction efficiency could reach 96.4% on Cu electrode and 98.9% on Al elelctrode by potenostatic electrolysis at -2.0 V for 7 h, respectively.

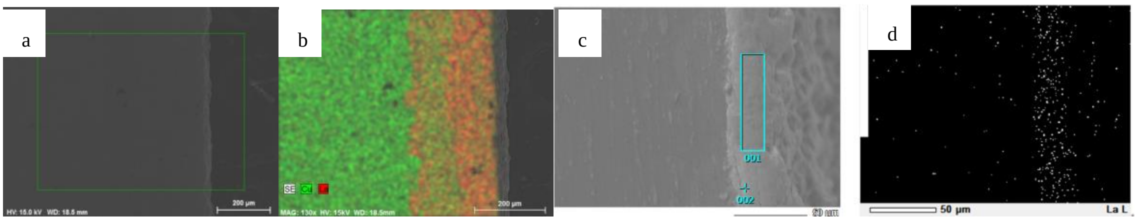

Fig. 2 SEM image and EDS analysis of deposits obtained by potentiostatic extraction at -2.0 V for 7 h on Cu electrode (a and b) and Al electrode (c and d) in LiCl-KCl-YCl_3 melts at 823 K.

Acknowledgement
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The law of change of equilibrium potentials of Lanthanide alloys and Alkaline-earth metal on Zn-coated electrode

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To achieve sustainable development of nuclear energy and Zn based intermetallic compounds because of their perfect electrochemical properties, efficient studies of spent fuel get a unprecedented concern in Generation nuclear energy [1,2]. Molten salt based electrolysis will must be an effective method in future technology. Therefore, the model equation of the law of change of equilibrium potentials can be used to get the accurate equilibrium potentials of corresponding intermetallic compounds.

The electrodeposition of lanthanide iron(□)and Alkaline-earth iron (□) on Zn-coated electrodes in chloride melts were studied by cyclic voltammetry, Square wave voltammetry and Open circuit chronopotentiometry. The process of deposition is accompanied with iron dendrite formation [3]. Interestingly, after achieving a steady state for intermetallic compound alloys deposition on Zn-coated electrode in the LiCl-KCl based melt. Infect, the intermetallic compound formation mechanism of Rare Earth (□) and Zn(□) was that Zn(□) got electrons firstly, result in the working electrons was zinc-coated liquid membrane electrode. Afterwards the Rare Earth (□) got electrons into elementary. The zinc and other mental elements combined with the formation of intermetallic compounds.

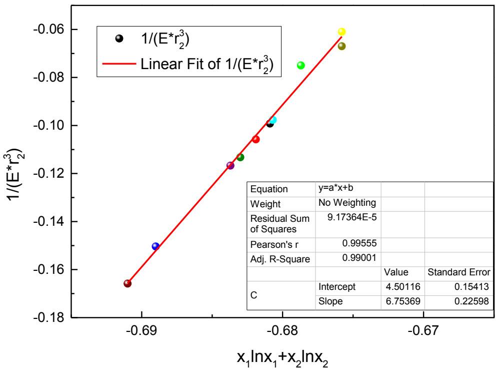

Fig. 1 The linear fit of the law of change of equilibrium potentials of Lanthanide alloys and Alkaline-earth metal on Zn-coated electrode

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A new grading rule of equilibrium potentials of lanthanide alloys: implications for electrolysis based spent nuclear fuel pyroprocessing

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To achieve closed nuclear fuel cycle and sustainable development of nuclear energy, efficient pyroprocessing of spent fuel becomes a core concern in Generation IV nuclear energy [1]. Molten salt based electrolysis will be an essential method in future pyroprocessing technology. On the other hand, as neutron poison, lanthanides belong to the most detrimental elements for the realization of the so-called partitioning & transmutation (P&T) strategy, and must be separated from actinides as much as possible [2]. Therefore, investigating the electrochemical properties of actinides and lanthanides is of pivotal importance. Nevertheless, in light of the chemical similarity of trivalent actinides and lanthanides, the chemistry of actinides can be simulated and predicted somewhat through exploring lanthanide elements which are more readily accessible [3, 4].

This work reports the electrochemical behaviors of lanthanides on several cathodes in LiCl−KCl molten salt. We discovered that the equilibrium potentials of lanthanide alloys present a significant "Bimodal Effect". In comparison with the periodic rule of equilibrium potentials and atomic radii of lanthanides, an important mathematical model can be derived out. Based on this model, we can extrapolate the electrochemistry of other elements on different electrodes. At the meantime, it was found that the slopes of curves fitted by the mathematical model are different on various cathodes. Moreover, the relationship between the atomic radius and the model slope displays a linear nature. According to this linear relationship, we can conveniently predict the value of slope and calculate the equilibrium potentials of lanthanide alloys on Cu, Ni, Fe and other cathodes from the atomic radius of the cathode material. As shown in Fig. 1, the straight lines between the atomic radii of lanthanides and the calculated values of equilibrium potentials on all cathodes (Al, Zn, Co, Cu, Ni and Fe cathodes) were gathered.

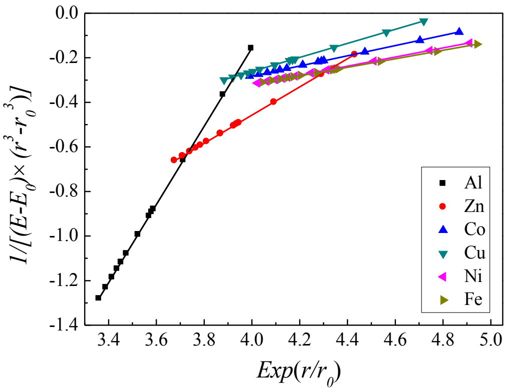

Fig.1 The linear relationship between the atomic radii of lanthanides and the calculated values of potentials on Al, Zn, Co, Cu, Ni and Fe cathodes.

Acknowledgments

This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.

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The Role of Internal Cathodic Reactions during the Crevice Corrosion of Ni-Cr-Mo Alloys

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Ni-based alloys, containing measureable amounts of Cr and Mo, represent examples of *superalloys* used to avoid costs associated with material failure. Although these alloys exhibit low corrosion rates in a range of media, they are susceptible to localized breakdown of the native oxide film that gives them their corrosion resistance. This makes them susceptible to processes such as crevice corrosion. Understanding how alloying elements control the damage due to such corrosion processes will enable the design of alloys with an optimized composition. During crevice corrosion, metal dissolution within the occluded region is generally thought to be supported by O_2 reduction on surfaces exterior to the crevice. However, following initiation, metal dissolution in the acidified environment within the crevice can couple to the reduction of protons on surfaces inside the creviced region. The occurrence of this process has been demonstrated through a series of galvanostatically controlled experiments in which the extent of damage was found to be greater than could be accounted for by O_2 reduction alone. This was demonstrated by showing that the applied charge consumed by O_2 reduction could not account for the total amount of crevice damage determined by weight loss measurements. We are studying the effect of alloy composition, particularly Cr and Mo contents, on the extent of proton-driven crevice propagation. Repeat experiments show that up to an additional 50% of propagation damage can be caused by this internal H^+ reduction reaction. Consequently corrosion damage predictions based on the availability of oxygen and other oxidants in the service environment may significantly underestimate the actual extent of corrosion on Ni-Cr-Mo superalloys. Also, we have demonstrated that the deposition of Mo-rich corrosion products can stifle active metal dissolution and suppress the internal H^+ reduction reaction.

EIS monitoring of *Acidithiobacillus thiooxidans* biofilm formation on graphite surface

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One of the technologies associated with the production of bioenergy are Microbial Fuel Cells (MFC) which use microorganisms that oxidize diverse compounds, transferring charge due to microbial metabolism (redox reactions) to the anode. However, most of the studies on bioelectrogenesis using MFC have been limited to the use of organic wastewaters from different effluents [1]. Inorganic wastewaters from mining industry and mineral bioleaching process have a prospective that has not been fully explored. Moreover, it has been found bioelectrogenic activity during the biooxidation of reduced sulfur species (RSS), e.g. S^{2-} S^0, and $S_4O_6^{-2}$ [2,3] by sulfooxidizer bacteria as the acidophile *Acidithiobacillus thiooxidans*. The use of RSS in the anodic chamber of a MFC is promising since the low activation overpotentials. In this work, cells of *A. thiooxidans* colonized a graphite surface, resulting in a bioelectrode. The obtained bioelectrodes were electrochemically characterized by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry in a electrochemical cell, during 7 days. The EIS showed an increase of the capacitance (detected at 0.03-10 Hz) that correlates with the cells attachment and biofilm formation on the bioelectrode, and with the presence of ions in the biofilm/graphite interface, as scanning electron microscopy images indicated. Additionally, the charge-transfer resistance decreased from 55 to 1 kΩ after seven days of immersion. The results indicated a possible charge transference due to microbial activity. M. Méndez-Tovar acknowledges to CONACYT for PhD grant 212534.

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Analysis of the Synergic Effects in $LiFePO_4/Li_2CuO_2$ Cathode Blends for Li Ion Batteries Via Electrochemical and EPR Experiments.

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Much of the focus in improving the specific energy in Li-ion batteries is centered on the cathode, specifically designing new active materials; moreover, a promising alternative is the use of 'blended' electrodes, which are comprised of at least two different active materials working synergically. Although the principle behind these collaborative properties is not yet fully understood, the reasoning behind this proposal is based on the correlation of property-function of each component. Blending two or more cathode materials can result in a cathode with fewer of the drawbacks than the parent materials, allowing for an optimized performance compared to what would be possible with the individual materials. $LiFePO_4$ and $LiCoO_2$ are two of the most commercial cathode materials because of their high stability and adequate specific capacities, but are unable to meet the higher capacity demands of newer technologies. Li_2CuO_2 is a promising cathode material with a specific capacity of 490 mAh/g, notwithstanding it undergoes irreversible phase changes during cycling, resulting in poor cyclability and a specific capacity far lower than its theoretical capacity[1]. The objective of this study is to take advantage of the stability of commercial active materials, such as $LiFePO_4$ and $LiCoO_2$ to stabilize the high capacity Li_2CuO_2 phase for practical use. Preliminary results of the $Li_2CuO_2/LiFePO_4$ blends have shown an improved capacity, albeit still below the theoretical capacity of Li_2CuO_2, and a slight improvement with respect to the cyclability. The method used to blend these materials as well as the inclusion of the conductive and binding additives and the order of addition during the blending have all shown to affect the battery's performance. Electron Paramagnetic Resonance (EPR) experiments have shown that electrodes blended with a ball mill presumably lead to the formation of stable oxygen vacancies which have an effect on the synergy which is not observable in pure Li_2CuO_2 blended cathodes or physical mixtures. Additionally, the presence of the conductive and binding additives during the blending process appear to result in a more homogenous mixture, preventing the reversion of Li_2CuO_2 into its precursors during the blending process, thus promoting higher specific capacities. The authors thank CONACyT-SENER- 416 Sustentabilidad No. 245754 for the financial support.

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Characterization of Anodes during Extended Reversal Test

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Anode degradation during fuel starvation is an important failure mechanism in automotive PEMFC. The strategy used at AFCC to mitigate this failure mode is to impart water splitting functionality (OER) to the anode layer. The addition of this functionality helps capping the anode potential, effectively reducing the rate of carbon corrosion of the main anode catalyst (Pt/C), which provides hydrogen oxidation functionality (HOR) during normal operation. The mechanism of anode degradation during cell reversal is not yet clear; in particular it is not clear at what relative rate the HOR and OER functionalities are lost and it is also not clear how the anode structure changes during reversal. The purpose of this study was to combine electrochemical (anode EPSA) and structural (STEM-EDX and STXM) analysis to characterize anode during the extended reversal test.

Investigation of the Influence of Electrolyte Thickness and Geometric Parameters on the Galvanic Corrosion between Zinc Plate and Stainless Steel Rods

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Engineering alloys susceptible to localized corrosion (e.g., aluminum alloy) in connection with relatively electrochemically noble fasteners (e.g., stainless steel) are frequently encountered in aircraft. When these two types of materials are electrically connected and exposed to a moist atmospheric condition which results in either droplet or thin film electrolyte formed or materials surface, there is a high possibility that a corrosion cell can be established due to galvanic coupling when breakdown of corrosion protection coating occurs. There are numerous experimental studies in the literature concerned with galvanic corrosion in atmospheric conditions, nevertheless pertinent modeling work is very limited that focuses on quantitative characterization of corrosion damage as a function of external variables in atmospheric condition.

There have been many literature studies that demonstrate the effect of electrolyte layer thickness on cathodic kinetics of several metals and engineering alloys, indicating that across the mesoscale length (1um~1mm), the cathodic limiting current density is inversely proportional to electrolyte layer thickness. Nevertheless, how electrolyte layer thickness impacts the degree of galvanic corrosion quantitatively is not well documented in literature. Furthermore, the physical location of cathodic materials inserted in the anodic materials will introduce different corrosion damage distributions. How to quantitatively predict the distributions as a function of location of cathodic materials is of interest in this study.

The overarching goals of this work are to use modeling to the predict electrochemical and corrosion distributions that develop during galvanic corrosion between a SS316 rod and a Zn plate under thin film electrolyte condition, and to investigate the impact of electrolyte layer thickness and location of SS rod on the corrosion damage along the Zn plate by comparing modeling results with experimental ones. For the modeling work, a finite-element based method using the Laplace Equation as the governing equation has been implemented to compare calculated potential and current density distributions along a rectangular Zn plate when a SS rod is introduced at the center and edge of the Zn plate, respectively. Interactions between two SS rods is also simulated. The current density distributions are converted to corrosion damage distributions via Faraday's Law based on the assumption that pure Zn experiences uniform corrosion under these conditions. For the experimental work, the rotating disk electrode technique is utilized to measure the cathodic kinetics of SS316 with different rotating speeds to simulate a variety of thin film electrolyte conditions, and a flat cell is applied to evaluate the anodic kinetics of Zn. These experimentally determined kinetics serve as boundary conditions in modeling work. Secondly, a series of exposure tests with pertinent geometry setup between SS rod and Zn plate in modeling work are conducted in a RH=98% chamber with controlled uniform electrolyte layer thicknesses pertinent to modeling. Post corrosion damage from exposure testing is characterized by optical profilometry.

Determination of the stability limits for carbon-based electrochemical capacitors

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Electrochemical capacitors are devices that accumulate the charge in the electric double-layer formed at electrolyte/electrode interface. An involvement of such processes results in fast and efficient charging/discharging properties and makes electrochemical capacitors a very reliable and attractive power source.

This work presents a new approach to observation of activated carbon electrodes interaction with neutral aqueous electrolytes and its effect on the stability performance of electrochemical capacitor.
It has been demonstrated that the charging parameters influence the lifetime of electrochemical capacitors significantly. Especially for water-based systems, the overcharging can cause irreversible damages that lead to device failure.

On the other hand, microporous carbons applied as negative electrodes in water-based electrolytes demonstrate the possibility for hydrogen electrosorption and storage. Maintaining the electrode potential slightly below the hydrogen evolution potential remarkably increases the lifespan and improves the power/energy balance of the device.

In this work, the implementation of various electrochemical techniques and *in-situ* Raman spectroscopy allowed to establish the optimal working conditions for microporous carbons in water-based electrochemical capacitors. Insightful analysis of hydrogen storage and evolution process in neutral, aqueous electrolytes allowed a better understanding of aqueous capacitors degradation process.
The combination of the data obtained from electrochemical analysis and *in-situ* Raman spectroscopy of carbon electrodes allowed to predict the safe operational voltage limits of Li_2SO_4-based systems. Finally, a new, quick method for estimating the working voltage limits for carbon-based electrochemical capacitors was proposed. The method has been validated by comparison with results from actually accepted testing methods such as galvanostatic cycling and voltage floating.

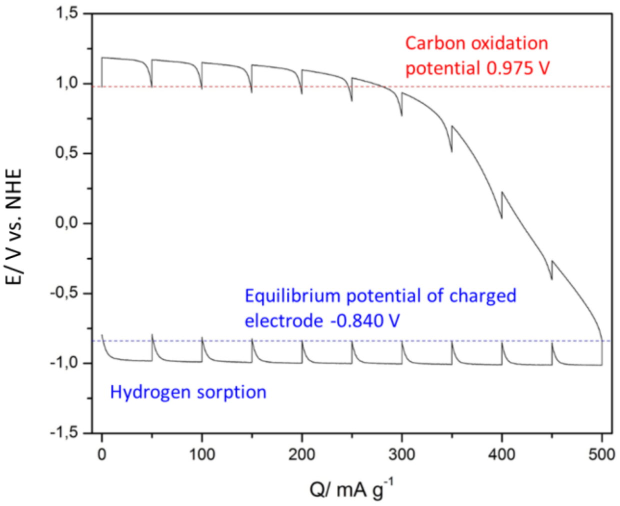

Figure 1 Galvanostatic Intermittent Titration Technique curve for carbon cloth ACC 507-20 in 1M Li_2SO_4, current density 0.5 mA g^{-1}

Pulsed electrodeposition of Cu-W alloys

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Research on amorphous tungsten alloys remains popular due to the attractive properties of these alloys and still a good chance of improving their key parameters. Tungsten cannot be electrodeposited from aqueous solutions alone, while it is possible to obtain its alloys with one or more elements from the iron triad [1, 2]. Recently it has been found that in addition to iron group metals copper and silver make good partners for electrochemical alloying of tungsten [3, 4].

We have shown that it was possible to electrodeposit a good-quality, compact and adhesive layer of copper–tungsten alloys from citrate baths in direct current regime [5]. The maximal content of tungsten was not satisfactory, it oscillated around 10 $\%_{at}$. In addition the alloys had a complex internal structure that was built of two major phases. These obtained deposits were composed of pure copper nanocrystals immersed in a tungsten-rich nanocrystalline/amorphous phase. The presence of two distinctly different phases could be caused by the fact that no thermodynamically stable binary form of tungsten and copper could be found. Anyway, limited miscibility of Cu and W was observed during electrodeposition of Cu-W alloys.

A disadvantage of the alloy mentioned previously was the presence of copper excretions. To reduce the number of them, we decided to perform electrodeposition of Cu-W in pulsed-current regime. This approach also allowed us to increase current efficiency (CE) and tungsten content in comparison to the results obtained in the direct current regime. We have found found that an increase in tungsten content was strongly related to CE of the process. The appearance of the alloy was attractive. The alloy exhibited a light orange color and a satin shine. The authors were able to obtain even dozen-micrometer thick deposits. Then a combination of key parameters of the alloys, such as high tungsten content (up to $20\%_{at}$), unique internal structure and good appearance, raised hopes regarding their new industrial usage and further development of this nanostructured coverage.

The obtained results for both Cu-W alloys: one deposited under pulsed conditions, and the other under direct current regime will be presented. The emphasis will be given to material internal structure and its correlation with content of tungsten in the alloys and conditions of the deposition process.

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High performance conducting polymer electrodes for hydroquinone/benzoquinone redox

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Here we report on the redox reaction of hydroquinone/benzoquinone (H_2Q/Q) at conducting polymer electrodes. The study shows that conducting polymer electrodes present higher electrochemical performance than Pt electrodes for this specific reaction even though its conductivity is three orders of magnitude lower. This together with the low temperature solution processibility makes conducting polymer electrodes a promising alternative electrode material in the application of fuel cells based on quinones as a fuel. Cyclic voltammetry and rotating disk electrode measurements are used to study the electron transfer reaction of H_2Q/Q at electrodes. It is a single step two-electron two-proton transfer reaction and the rate is promoted with the thickness of the conducting polymer film. The mechanism is further supported by the evolution of the electrochemical potential versus pH. The large current density obtained for thick layer of conducting polymers suggest that the organic quinones have large diffusion coefficient and penetrate easily into the organic electrodes because of their charge neutrality. Note that the kinetics of that reaction depends on the composition of the conducting polymer electrode. The comparison of the kinetic rate constant of the reaction for various conducting polymers and glassy carbon electrodes demonstrate a true electrocatalytic effect with a significant lowering of the overpotential. Hence, we propose that quinones found in nature could be an interesting source for organic fuels for fuel cell applications based on conducting polymer electrodes.

Electrochemical generation of ozone using Ir-Sn-Sb oxide anodes.

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Ozone has wide applications in various fields because is one of the most powerful oxidants currently available. An attractive method to produce ozone is via water discharge on dimensional stable anodes [1], and also on PbO_2, SnO_2, or glassy carbon electrodes [2]. In this context, this work deals with the electrochemical production of ozone on Ir-Sn-Sb oxide anode; this film was supported onto Ti by the Pechini method [3]. It is important to mention that the use of this type of electrode has not been used to the production of ozone. The electrosynthesis of ozone was made in a divided mode reactor, containing a Ti-Ir-Sn-Sb oxide anode and stainless steel as a cathode, separated by a Nafion membrane to separate both compartments. The electrolyte used was 0.5 M $HClO_4$ at pH 3. Rotating disc electrode tests were performed at different rpm to find the potential interval where the ozone formation occurs, Fig. 1. Bulk electrolysis were performed in the filter press flow cell at different flow rates of 0.6, 0.8 and 1.0 L min^{-1} and current densities of 7, 8 and 9 mA cm^{-2}. The above mentioned conditions were established to find the optimal electrosynthesis of ozone on the Ti-Ir-Sn-Sb oxide anode. The results found at 7 mA cm^{-2} and 0.8 L min^{-1} show that the production of ozone on Ti-Ir-Sn-Sb oxide anodes is possible, Fig. 2.

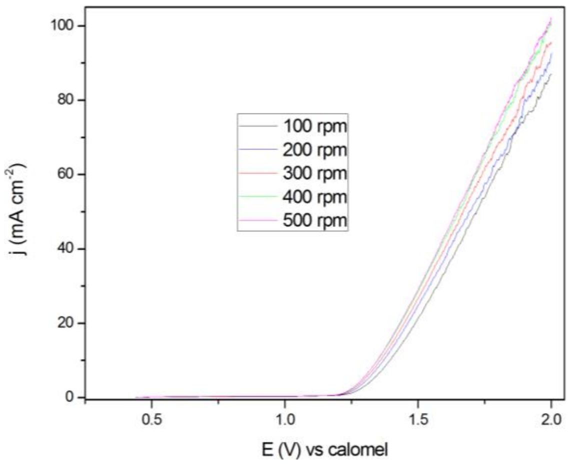

Fig 1. RDE Polarization curves of the Ir-Sn-Sb oxide anode in $HClO_4$ 0.5 M at pH3.

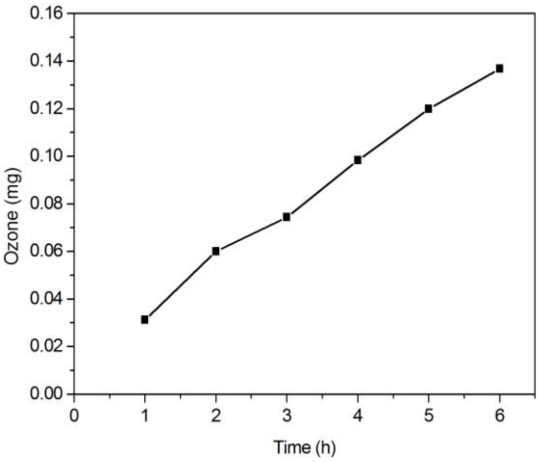

Fig 2. Mass of ozone produced on Ir-Sn-Sb oxide anode during bulk electrolysis.

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Electrocatalytic Oxygen Reduction Activity and Durability of Pt-Ni Alloy Nanostructures Supported on Nitrogen-Doped Carbon

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Carbon-supported platinum group metals (PGMs) are used as oxygen reduction reaction (ORR) electrocatalysts at cathodes in polymer electrolyte fuel cells (PEFCs). Since platinum reserves are limited, Pt-Ni alloy electrocatalysts for the ORR have been intensively studied. One of the highly active Pt-Ni alloy electrocatalysts is a carbon-supported Pt-Ni alloy nanoframe.[1] This electrocatalyst exhibits high catalytic ORR activity and almost no activity loss after 10,000 potential cycles. In the practical point of view, further improvement of the durability is required. The use of nitrogen-doped carbon as the catalyst support might improve the catalytic activity as well as durability because it is expected that nitrogen doping in carbon supports may modulate the electronic structure of the catalyst and/or give strong chemical bonding between the support and the catalyst.[2]

Herein, we report electrocatlytic activity and durability of Pt-Ni alloy nanoframes on nitrogen-doped carbon supports to understand effects of the nitrogen content on the catalytic activity and durability. We used carbon black (Vulcan), *N*-doped carbon and graphitic carbon nitride (g-C_3N_4) were used as catalyst supports. Pt-Ni alloy nanoframes[1] and *N*-doped carbon[3] were prepared according to the literature. For the preparation of g-C_3N_4, melamine was heated at 600 °C under air for 2 hours. Linear sweep voltammetry of Pt-Ni alloy nanoframes on supports was carried out in 0.1 M $HClO_4$ using a three electrode setup under oxygen. The reference electrode of Ag|AgCl (sat. KCl) and the counter electrode of platinum wire were used.

TEM images of Pt-Ni alloy nanoframes on supports suggest that amounts of Pt-Ni nanoframes increase with increasing nitrogen content (**Figure 1**). The ORR of Pt-Ni nanoframes on *N*-doped carbon also depends on the nitrogen content and Pt-Ni nanoframes on the *N*-doped carbon with a nitrogen content of 9% showed the highest ORR activity.

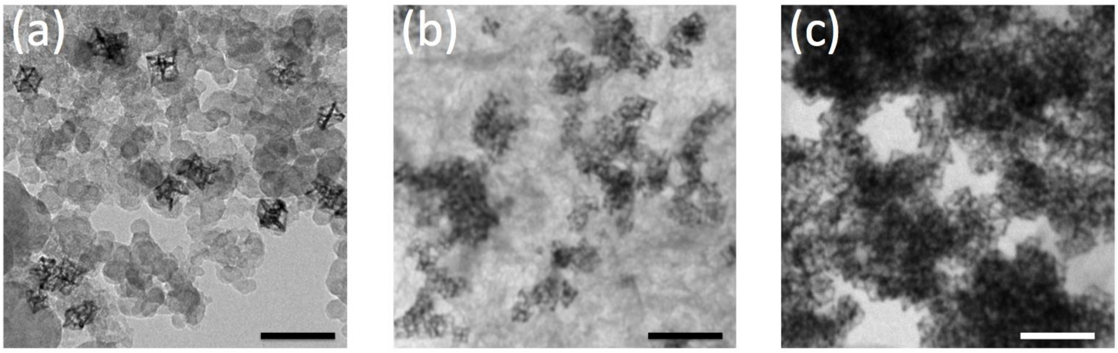

Figure 1. TEM images of Pt-Ni nanoframes supported on
(a) Vulcan, (b) *N*-doped carbon and (c) g-C_3N_4 (scale bar: 100 nm).

Acknowledgments
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P2-Type $Na_x(Li,Ni,Mn,Fe)O_2$ for Advanced Na-Ion Batteries

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Sodium layered oxide materials have been extensively studied as positive electrode materials for Na-ion batteries. Our group has reported that P2-type $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ (FeMn) consisting from abundant elements in the Earth's crust, delivered large reversible capacity of 190 mAh g^{-1} with good cycle stability.[1] Moreover, P2-type $Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$ (LiMn), activated by applying high voltage like Li_2MnO_3, also delivers ca. 200 mAh g^{-1} without significant irreversible capacity at initial cycle.[2] However, operating voltage of these materials is low, which is disadvantageous to achieving higher energy density. Among the layered oxides reported so far, P2-type $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ (NiMn) shows relatively high operating voltage and reversible capacity of 160 mAh g^{-1} at the initial cycle, but the capacity decays during cycles in 2.5 – 4.5 V. In this study, we synthesize new solid-solution of $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$-$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$-$Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$ to improve the electrode performance of endmembers.

The samples were synthesized by solid-state reaction. Na_2CO_3, Li_2CO_3, α-Fe_2O_3, $Ni(OH)_2$, Mn_2O_3 were mixed, pelletized and then heated at 900 °C for 12 h in air. Galvanostatic charge/discharge tests were conducted using coin-type cells. Positive electrodes consisted of the active material, acetylene black and PVdF with a gravimetric ratio of 80:10:10. Metallic sodium was used as a counter electrode. The electrolyte used was 1.0 mol dm^{-3} $NaPF_6$ / PC.

Fig. 1 shows XRD patterns of the obtained samples represented as a molar ratio of NiMn : FeMn : LiMn in the solid solution. Diffraction peaks of the samples can be indexed with *P*6$_3$/*mmc*, and P2-type solid-solution products of $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$-$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$-$Na_{5/6}[Li_{1/4}Mn_{3/4}]O_2$ were successfully synthesized without any impurities. Fig. 2 shows reversible capacity vs. cycle number plots of the samples. In comparison to NiMn, the solid solution samples exhibit better cycle stability. Especially, 22:7:7 sample delivered reversible capacity of ca. 125 mAh g^{-1} and show over 99% of initial discharge capacity at 30th cycle. Relation between the electrode performance and phase transition will be discussed in detail.

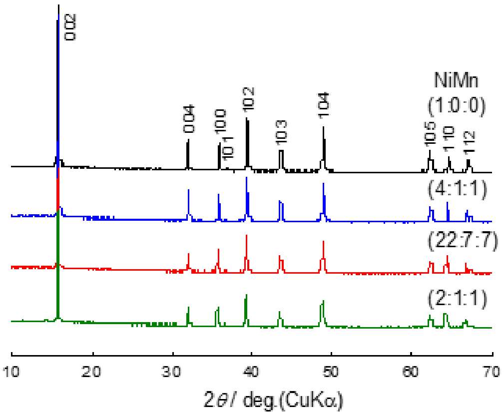

Figure 1 X-ray diffraction patterns of NiMn and the solid solutions of 4:1:1, 22:7:7, and 2:1:1.

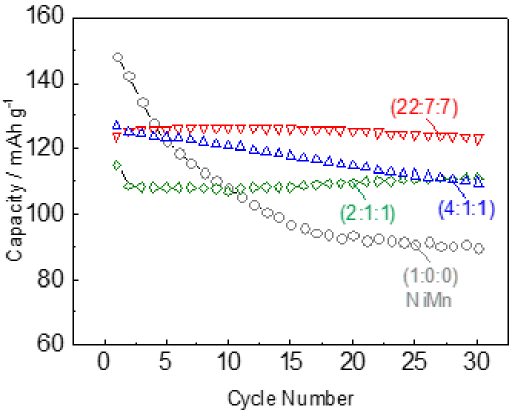

Figure 2 Cycle stability of NiMn and the solid solutions of 4:1:1, 22:7:7, and 2:1:1.

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Electrochemical Study of Rhodium Electrodes Modified by Pt Submonolayer Towards Ethanol Electrooxidation

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The electrooxidation of ethanol has been widely studied because of its possible application in proton exchange membrane cells. Many efforts have been devoted to disentangle its oxidation mechanism and how this mechanism depends on the ethanol concentration and the surface structure and composition of the electrode.[1] The goal is to obtain CO_2 as the final product at the lowest potential and the highest current. Among pure metals, Pt has the highest catalytic activity in acid media, but the final product of the oxidation is a mixture of CO_2 and acetic acid. The ratio of products strongly depends on surface structure of Pt. In order to increase the activity of Pt, other metals, namely, Ru, Os, Sn and Rh have been added to the surface to diminish the overpotentials and to increase the selectivity of the oxidation towards the formation of CO_2.[2] On the other hand, the opposite combination, Pt deposited on Rh electrodes, has not been studied yet. Rh electrodes are not active for the oxidation of ethanol. However, it has been shown that a single layer (or submonolayer) of a metal deposited on a different substrate can have electrocatalytic activities larger than any of the two bulk metals.[3] The aim of this work is to determine the electrochemical behavior of Rh electrodes modified by Pt (sub)monolayers for ethanol oxidation, analyzing the effect of the surface composition on the electroactivity performance and stability of the Rh-Pt surface. The cyclic voltammograms for three different Pt coverages on the Rh(111) electrode are shown. The deposition of trace amounts of Pt on the Rh surface triggered a significant change in the voltammogram of these surfaces. The voltammogram in sulfuric acid solution exhibits a pair of peaks at 0.15 and 0.05 V, which are associated to the competitive adsorption of hydrogen and sulfate on the electrode surface. In the initial deposition stages of Pt, which are carried out in two concentrations (10^{-5} and 10^{-6}M, H_2PtCl_6) cycling the surface at range of 0.03 – 1.0 V (50 mV s^{-1}) in sulfuric acid (0.1 M). In the initial deposition stages of Pt, these peaks become significantly sharper and more reversible. Increasing the Pt coverage led to the increase of the sharp peaks and the increase of a broad signal between 0.06 and 0.35 V characteristic of hydrogen adsorption on Pt. The oxide region of Rh diminishes progressively as Pt is added, then the Pt amount was determined using this fact, once Pt oxide occurs at potential above Rh oxide, the Pt recovery degree obtained were 0.28 and 0.55 ML. After Rh-Pt characterization, the surface was submitted to ethanol oxidation. Rh is not active for this molecule, then the real contribution comes from of Pt deposited. The CV showed a relevant current when compared to Rh non-modified. The Rh electrode was modified with small amounts of Pt, the activity of the electrode increased significantly taking into account the current. It should be highlighted that the coverage in this case was only 0.28 ML of Pt and the current densities (calculated according to the Pt amount) were higher than those measured for the Pt(111) electrode, which is a surface much active for ethanol reaction, the onset potential was practically the same when compared to Pt(111). Another peculiar feature of this electrode was played by its performance, a comparison of current density cycle by cycle with Pt(111) surface, showed an interesting result, the mean oxidation peak at 0.72 V increases as the electrode is swept in ethanol solution (0.5 m), even after 40th the current did not diminish, it keep stable. While for Pt(111) the behavior is completely different, the density current diminishes due to poisoning of species strongly adsorbed. The chronoamperometric curves obtained at different potentials (0.40 – 1.0 V) also confirms the results of CV curves. After the oxidation experiments, the Rh-Pt was submitted in electrolyte in order to check the surface, the voltammetric profile is so close of that initially obtained during the Pt deposition process, then the Rh-Pt electrode is very stable, because no Pt was lost during all experiments.

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Modeling the solvent effects at the water/Pt interfaces

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For aqueous electrocatalysis, in comparison with heterogeneous catalysis at gas-solid interfaces, the effects of solvent makes modeling more complicated. Thus, for many trends based modeling, the solvent effects have been largely neglected in the DFT calculations but been corrected based on the energetics obtained from water-bilayer models. Such a scheme provides a practical framework for understanding the basic thermodynamics and kinetics of complex electrocatalytic reaction networks and for identifying useful candidates for new electrocatalysts. But the solvent (i.e. liquid water) may have distinct effect for reaction intermediates with same radical (e.g. OH). Actually, even for same reaction intermediates, the effects may depend on the chemical nature and the geometrical structure of the electrodes. The effects may modify the thermodynamics and kinetic of reactions, but still largely unknown.

In the present talk, we will combine standard DFT calculations with ab initio molecular dynamics simulation to probe the solvation effect of various reaction intermediates at liquid water/Pt interfaces. We will start from the solvent effect of OH by comparing with those obtained from various water-bilayer models. We will show the coverage dependent solvent effect so to understand the hydration state of OH under oxygen reduction conditions, which is still under debate in the community, i.e. whether hydrated OH or non-hydrated OH is the plausible ORR intermediate. We will use the established methodology to understand the solvent effect of the other reaction intermediates, such as those involved in oxygen, NOx and COx electrochemical reduction reactions. We will further study the geometry dependence of the solvent effect and show the limitation of the transitional scheme of the post-correction. We will close by establishing the thermodynamics of various reaction intermediates on Pt(111) and Pt step surfaces with explicit solvent effects.

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Electrocatalysis of Direct Methane Oxidation on Transition Metal Catalysts

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Methane (CH_4) has long been a major feedstock for producing methanol or higher hydrocarbons. The current industrial processes for large-scale methane conversion is based on the inefficient, highly energy-consuming and technically demanding multi-step process including steam reforming to syngas ($CO + H_2$) and following CO hydrogenation to methanol. Achieving economical direct and selective methane conversion under mild conditions is a long outstanding research and development challenge in both industry and academia [1, 2].

Here, we will discuss the results of our initial investigation of the electrochemical oxidation of methane in aqueous solution on copper (Cu) based materials, starting from CuRu alloy to zeolite-encaged tri-copper clusters. Particularly, we have observed that the CuRu alloy film showed a clear activity in methane-saturated 0.1 M NaOH electrolyte with an onset potential at ~ 0.9 V (vs. RHE). Interestingly, this onset potential coincided with that of Cu(I) to Cu(II) oxidation, which may imply how redox chemistry of Cu with more than one oxidation state can be utilized to generate active oxygen species (e.g. O_2^-, O^-, O_2^{2-}) on the surface. When 10-minute chronoamperometric (CA) measurements were carried out at 0.95 V the CH_4 oxidation showed a quite high activity over the first 3 min and then the reaction current became smaller and smaller over the next 7 min. The current shoulder over the first 3 min gives a reaction rate of ~1.1 μmol/hr/cm^2 assuming the final product was methanol. Decaying current after the first 3 min could be attributed to the oxidation of the majority of Cu(I) to Cu(II) while the presence of both Cu(I) and Cu(II) is needed for electro-oxidation of methane. Nonetheless, the high activity over the first 3 min is indeed very encouraging. Moreover, the time-dependent *in situ* SEIRAS (surface enhanced IR reflection absorption spectroscopy) spectra recorded during the CA measurement of CH_4 oxidation showed the presence of CO adsorbed on Cu (the 2070 cm^{-1} band) and an still unidentified species at 1405 cm^{-1}which we speculate to be intermediate species of the methane oxidation. That the decreasing water band at 1610 cm^{-1} is also consistent with the CH_4 oxidation, in which water react with methane to form methanol. We will compare the above results with those obtained on zeolite-encaged tri-copper clusters.

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Electrochemically Driven Deformation and Fracture in Solid State Batteries

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Solid electrolytes in Li ion batteries are attractive for many applications because of their thermal and electrochemical stability. In particular these materials can enable the development of high energy density, lithium metal based batteries. Much of the prior work on solid electrolytes has focused on increasing ionic conductivities, whereas the chemo-mechanical aspects of integrating solid state electrolytes into electrode and battery structures are not well understood. The work presented here addresses mechanical responses at interfaces between active materials and a solid electrolyte that results from electrochemically driven volume changes in the active electrode materials. To enable widespread use of solid electrolytes in practical batteries, a fundamental understanding of the chemo-mechanical behavior of these types of interfaces is needed. This investigation employed vanadium oxide based cathodes in polyethylene oxide (PEO). The active material undergoes relatively large volume expansions during Li insertion (up to 30% at full capacity), which leads to large strains compared to other common cathode materials. Synchrotron imaging was used to directly observe these changes inside of *full* electrode stacks. Detailed mechanics-based models were then developed to interpret the experimental observations.

Evidence of Alteration to DNA Monolayers via Ruthenium Hexaammine Measurements

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Ruthenium (III) hexaammine chloride (RuHex), a redox active molecule, is capable of binding electrostatically and stoichiometrically to the phosphate backbone of DNA. Electrochemical methods using RuHex, which include cyclic voltammetry, chronocoulometry and AC Voltammetry, are used to characterize DNA self-assembled monolayers either by measuring DNA coverage [1, 2, 3] or monitoring changes in DNA configuration within these self assembled monolayers [4, 5]. While these methods are widely used, changes to the DNA monolayer are observed and reported here. These changes can undermine the DNA coverage measurements made and negatively impact further use or examination of the DNA monolayers. DNA monolayers were assembled using fluorescently labelled thiolated DNA on monocrystalline gold and characterized with in-situ electrochemical fluorescence microscopy imaging (iSEFMI) before and after using RuHex based electrochemical methods. The technique iSEFMI is used to measure the coverage and packing environment of the DNA monolayer in select regions. [6] Comparisons between the two fluorescence images taken before and after RuHex measurements revealed an uncontrolled decrease in DNA coverage for specific regions on the surface. We herein examine and report evidence of damage in the DNA monolayer as a result of RuHex measurements.

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Surface-Enhanced Infrared Absorption Spectroscopy of Nitric Oxide Reductase Immobilized on Au Electrodes

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Nitric oxide reductase (NOR) catalyzes the reduction of nitric oxide (NO) to nitrous oxide (N_2O). N_2O is not only a greenhouse gas 310 times as poweful as carbon dioxide but also a main contributor to the depletion of the ozone layer.[1] About 70 % of N_2O emission on earth is derived from NOR. However, NO reduction mechanism on NOR is still unclear[1]. Protein film voltammetry (PFV) of NOR immobilized on carbon electrodes has been studied to determine the redox potentials of the Fe co-factors (**Figure 1[2]**) and to understand the electrocatalytic activity of NOR.[3,4] However, PFV of NOR is insufficient to fully understand the reaction mechanism.

In this study, we have investigated cyclic voltammetry and surface-enhanced infrared absorption (SEIRA) spectroscopy of NOR immobilized on Au electrodes to elucidate the NO reduction mechanism. SEIRA spectroscopy can be performed with electrochemical measurements and can provide structural information of molecules/proteins on the electrode surface selectively.[5]

Au-coated Si prisms were prepared by using an electroless deposition method.[6] NOR was immobilized directly on bare Au/Si prisms or via a self-assembled monolayer of carboxyl group-terminated molecules. SEIRA spectroscopy of NOR-modified electrodes was performed at an incident angle of 70°. The counter and reference electrodes were Pt flag and Ag|AgCl (sat. KCl), respectively. SEIRAS and linear sweep voltammetry of NOR-modified electrodes was performed in aqueous solution containing 50 mM 2-morpholinoethansulfonic acid at pH 6.5 under Ar or NO.

Linear sweep voltammograms of NOR-modified electrodes showed reduction current under NO but did not under Ar, indicating that the catalytic activity of NOR was maintained even on a noble metal of gold. SEIRA spectra of the NOR-immobilized electrodes showed characteristic amide I and II bands, indicating the presence of NOR on the electrode surface. The SEIRA spectra recorded under NO also showed two bands in the range from 1600 to 1800 cm^{-1}, assigned to NO molecules bonded to non-heme Fe_B and to the heme b_3. This result suggests NOR immobilized on the Au electrodes catalyzes the NO reduction in the *trans* mechanism.[1]

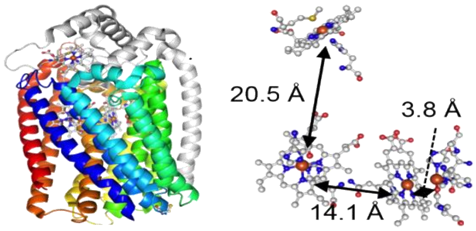

Figure 1. Structure of NOR and Iron co-factors in NOR.

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Liter-volume Supercapacitive Microbial Fuel Cell

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Anode and cathode electrodes of a microbial fuel cell (MFC) were recently investigated as the negative and positive electrodes of an internal supercapacitor (SC-MFC). The electrodes were self-polarized due to the red-ox reactions taking place at the electrodes interfaces without the utilization of any external power supply. The anode was colonized by electro-active bacteria that negatively polarized the electrode. The air-breathing configuration allow the cathode to be in aerobic conditions and therefore, the cathode was positively polarized. High current/power discharges were shown in previous studies concerning a glass bottle SC-MFC with volume of 0.125 L [1,2].

In this work, MFC with an empty volume of 1 L was tested in standard and supercapacitive mode. The system was a box of 24 MFCs with all the anodes connected in parallel and with also the cathodes connected in parallel. Cylindrical terracotta caves was used as separator and membrane between anode and cathode. Folded carbon veil was used as anode and it was wrapped around the cylinder in contact with the terracotta. Activated carbon (AC), carbon black (CB) and PTFE were mixed and pressed on a stainless-steel mesh as current collector. AC-CB-PTFE was the cathode used in these experiments and it was inserted inside the cylinder in contact with the terracotta. Five different electrolytes with solution conductivity of 2.0 $mScm^{-1}$, 5.1 $mScm^{-1}$, 7.1 $mScm^{-1}$, 10.0 $mScm^{-1}$ and 13.2 $mScm^{-1}$ were investigated simulating wastewater with different ionic strength. Power generated increased with the solution conductivity. Particularly, the peak of power curve was 3.22 mW, 4.22 mW, 5.24 mW, 6.26 mW and 7.2 mW respectively. The MFC was also used as SC-MFC. Also in this case, P_{max} enhanced with the increase in solution conductivity. The peak of power curve was 7.2 mW, 10.4 mW, 13.9 mW, 14.1 mW and 18.0 mW electrolytes with solution conductivity of 2.0 $mScm^{-1}$, 5.1 $mScm^{-1}$, 7.1 $mScm^{-1}$, 10.0 $mScm^{-1}$ and 13.2 $mScm^{-1}$ respectively.

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Fenton and Electrochemical reactions in the treatment of effluent from the orange soft drinks industry.

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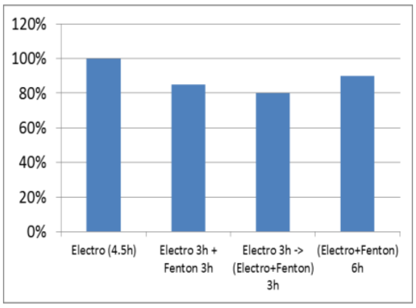
The soft drink industry generates a high amount of effluents, mainly from the washing of machinery, containers, pipes and the installation itself. The water consumption can vary from 1.7 to 2.2 liters per liter of produced refrigerant. The generated effluent has a very complex composition, ingredients of soft drinks can vary widely, due to different consumer tastes and preferences. Major components include primarily water, followed by carbon dioxide, caffeine, sweeteners, acids, aromatic substances, and many other substances present in much smaller amounts.[1] In the present work we have tried to propose an effluent treatment methodology using electrolysis with DSA as anode, Fenton reactions and the associated processes. The studied effluent was a solution with 2.5% orange soda in a total of 0.25 L of distilled water in pH 3. The efficiency of process was evaluated by Chemical Demand of Oxygen (COD) reduction, and toxicity was evaluated by germination of *Lactuca sativa*. Firstly was carried out the treatment with Fenton reaction (0.5 mM Fe^{2+} and 100 mM H_2O_2), where no COD reduction was observed, possibly due to the presence of sugars which react with iron (Fehling reaction), abstracting the catalyst from the Fenton reaction. In the electrochemical reaction, carried out applying current density of 90 mA cm^{-2} for 6 hours, using sodium sulfate and sodium chloride (0,05 M) as support electrolytes, the effluent reached 80% COD reduction after 3 hours of reaction and 100% in 4.5 hours. The purpose of using the associated processes was to oxidize the sugar present in the effluent by electrochemistry reducing the inhibitor of the Fenton reaction. In the associated processes, at first we carried out the electrochemical reaction for 3 hours, followed by the addition of Fenton reagents (0.5 mM Fe^{2+} and 100 mM H_2O_2) and the reaction was conducted for more 3 hours. Under these conditions (Electro 3h + Fenton 3h), the COD reduction reached 85.27%, which was less efficient than the electrochemical process alone. In the second associated experiment, we performed electrolysis for 3 hours, and after, we added the Fenton reagents, and the reactions (electrolysis and Fenton) were conducted for more 3 hours. The reaction (Electro 3h) plus (Electro+Fenton 3h) lead to the maximum reduction, 80%, of COD. The last associated process, electrochemical and Fenton reaction together, was conducted for 6h (Electro+Fenton 6h) resulting in a maximum reduction of COD of 90%. Figure 1 shows a comparison of these results. It was evidenced that the electrochemical process alone shows better efficiency in treatment of the orange soft drinks. After 24 hours of the end of the reactions, we collected the samples for the toxicity bioassays. The time (24h) was necessary to eliminate residual hydrogen peroxide, which is harmful to *L. sativa* germination. In the toxicity bioassays, it is considered as germination inhibition the test with germination index (GI) <80; do not present significant toxicity the values of $80 \leq GI \leq 120$, and germination stimuli values of GI > 120. The effluent generated by all the tested processes showed high toxicity (GI < 80). Even in the chronic test (with dilution) a very low GI, less than 35% was observed (Table 1).

Table 1. Germination Index (GI) of *Lactuca sativa* in effluent after a 24h treatment.

(%) treated effluent	Electro (4.5h)	Electro 3h + Fenton 3h	Electro 3h -> (Electro+Fenton) 3h	(Electro+Fenton) 6h
25	22.1	36.4	27.0	32.5
50	23.5	16.1	12.0	17.2
75	11.1	4.9	2,3	5.5
100	0.3	3.2	0	0

Figure 1. COD Reduction



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Copper- and Nitrogen-Incorporated Carbon Electrocatalyst with Bio-Inspired Multinuclear Active Sites for Oxygen Reduction Reaction

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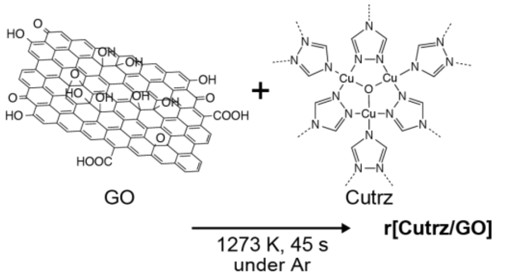
Platinum group metals (PGMs) are widely used as cathode materials in polymer electrolyte fuel cells (PEFCs) to electrochemically catalyze the oxygen reduction reaction (ORR) to water. Since PGMs are rare and expensive, they should be replaced by electrocatalysts based on earth abundant elements for the widespread commercialization of PEFCs. Intensive efforts have been devoted to developing non-PGM ORR electrocatalysts such as Fe- and Co-based electrocatalysts. Fe- and Co-based electrocatalysts have been prepared in pyrolysis and have shown high ORR activity and durability.[1] Compared with these electrocatalysts, much less Cu-based electrocatalysts have been reported, although a metalloenzyme of Laccase is known to efficiently catalyze the ORR at the multinuclear copper active center.[2] One of the successful copper-based ORR catalysts is a multinuclear copper complex of 3,5-diamino-1,2,4-triazole.[3] This catalyst has a dinuclear core, which serves as the catalytic active site for the efficient ORR,[4] and shows high ORR activity in alkaline solution.[3,5] Furthermore, the heat treatment of this complex for a short period of time[6] gives a *Cu*,*N*-doped carbon electrocatalyst, which shows higher catalytic activity than the precursor.[7]

Herein we report a *Cu,N*-doped carbon electrocatalyst (r[Cutrz/GO]) with multinuclear copper active sites for the ORR. The catalyst was prepared in pyrolysis at 1273 K for 45 s from the mixture of a multinuclear copper complex of a nitrogen-rich ligand of 1,2,4-triazole (Cutrz)[8] and graphene oxide (Scheme 1). Cutrz has a trinuclear copper core, the structure of which is similar to that of the catalytic active site of Laccase.

Linear sweep voltammograms (LSVs) of r[Cutrz/GO] were recorded over a wide pH range (pH 1–pH 13) under oxygen. The ORR activity increased with increasing pH. The activity at pH 13 was higher than that of Pt/C. Control samples prepared from the mixtures of graphene oxide with $CuCl_2$ or the 1,2,4-triazole ligand showed lower catalytic activity than r[Cutrz/GO] did, indicating that the trinucler complex of Cutrz works as the template for the formation of catalytic active sites with high activity. Physicochemical measurements including *in situ* X-ray absorption spectroscopy using an electrochemical flow cell[5] demonstrated that multinuclear copper active sites were incorporated in *N*-doped carbon and might play an important role in high catalytic activity for the ORR.



Scheme 1. Preparation of r[Cutrz/GO]

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Evaluation of electrochemical impedance spectroscopy as a method for monitoring corrosion of stainless steel in molten nitrate salt

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Solar energy has been gaining popularity for generation of electricity, especially at locations characterized by high direct normal irradiance (DNI), which in case of Atacama Desert in Chile is one of the highest in the world. However, the daily intermittence of the solar resource presents a challenge for providing electricity that would suit the round the clock demand. One of the technologies for equalizing solar-based electricity generation is that of concentrated solar power (CSP) relying on capturing thermal energy of sun and storing for generation of electricity via thermomechanical system. The critical element of the entire process is heat transfer fluid (HTF) used for storing and conveying heat. Molten salts are the HTF of choice, operating at temperatures between melting point and the upper limit of their thermal stability. The ionic nature of molten salt poses a risk of corrosion to the storage materials, which undetected might compromise integrity of the entire system. Localized corrosion is the most dangerous because of the involved mechanical stresses that might produce cracking. In this context, we explore the applicability of electrochemical impedance spectroscopy (EIS) for evaluation of the localized corrosion at the conditions specific to thermal storage of solar energy.

In this work, we study the long term progress of corrosion of stainless steel grades AISI 304, 316 and 430 exposed to commercial mixtures of nitrate molten salts at the low and high temperatures specific to solar tower technology of CSP, employing both gravimetric and electrochemical characterization. In particular, EIS is used to monitor evolution and stability of the surface films. The results are complemented with characterization of the exposed surfaces by spectrometric and microscopic techniques.

Keywords
Concentrated Solar Power (CSP), Thermal Energy Storage (TES), Corrosion, Molten Salts

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Synthesis and Characterization of Metal Complexes Containing Thiophene Units Toward Metallopolymers to Modify Electrodes

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Over the last decade, conducting metallopolymers (CMP) have attracted growing interest and considerable efforts have been directed toward their molecular engineering, because they offer potential applications in the field of emerging technologies [1,2]. This kind of materials offer important opportunities to combine the features of organic polymers, with their abilities to become electric conductors via chemical or electrochemical doping, with magnetic, optical, redox or catalytic properties arising from the presence of transition metals [3].

In this respect, we present here the synthesis, spectroscopic and structural characterization of a new Schiff base ligand and of the corresponding square-planar complexes containing appended thiophene moieties (Figure 1).

The modified electrodes were prepared through the electro-oxidation of solutions containing the monomers (10^{-2} mol L^{-1}) and 0.1 mol L^{-1} of tetrabutylammonium hexafluorophosphate in anhydrous CH_2Cl_2, by 50 successive potentiodynamic cycles in the optimal potential window (in both cases it resulted -1.5 to 2.5 V *vs* Fc/Fc$^+$ cuple).

The thin film modified electrode response was studied in a 0.1 mol L^{-1} of tetrabutylammonium hexafluorophosphate solution in CH_2Cl_2 in order to establish, on the one hand, the effect of the central metal and, on the other, the possible use that can be given to these electrodes modified with new materials of this type, in utilities such as cathodes for batteries or especially analytical sensors as redox polymers.

Figure 1 shows the voltamperometric profiles corresponding to the response of these complexes during it electro-oxidation, which gives rise of the formation of the polymeric deposits.

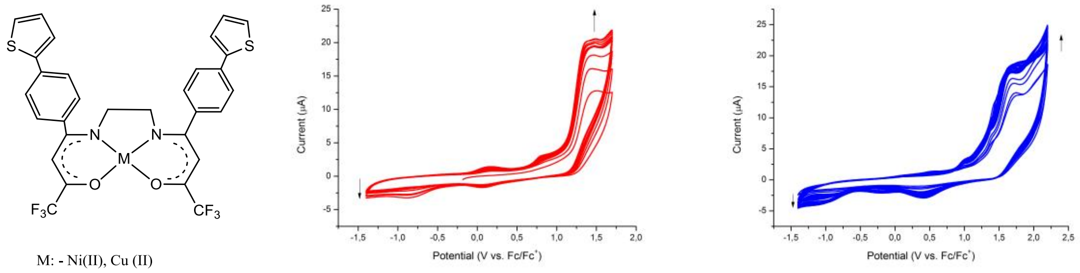

Figure 1. Synthesized complexes (left); voltamperometric responses on Pt disc electrode of: 10^{-2} mol L^{-1} copper (center) and nickel (right) complexes in 0.1 mol L^{-1} of tetrabutylammonium hexafluorophosphate, CH_2Cl_2.

Acknowledgments

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EIS Analysis of Commercial Lithium-ion Battery for Long-term Charge-discharge Cycling under Various Temperature Conditions

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A lifetime of batteries is one of the most important issues for energy storage systems. Non-destructive measurement methods are demanded on accelerated testing in the development of a lithium-ion battery (LIB) for longer lifetime, to provide shortening development period and reducing development cost. Electrochemical impedance spectroscopy (EIS) is the effective method of non-destructive investigation for batteries. We already proposed an equivalent circuit for a broad range of impedance spectra. [1,2] The electrochemical impedance of the electrodes in a commercial LIB at various states was analyzed to evaluate by this circuit. In this study, we focused on an analysis of a degradation of the LIB for the long term charge-discharge cycling under various temperature conditions.

A commercial pouched LIB with a nominal capacity of 5 Ah for an electric assist bicycle was used in this work. The batteries were charged and discharged with a constant current (CC) protocol between 3.0 and 4.2 V with a rate of 2 C at 5, 25 and 45 °C. The discharge capacities of LIBs were measured with a rate of 1/3 C at 25 °C. The impedance of the batteries was measured by Biologic VMP3 with AC signal amplitude of 0.4 A in the frequency range from 100 kHz to 10 mHz at 25 °C. Before the impedance measurement, the batteries were charged at a rate of 1/3 C to 4.2 V, and were maintained for 3 h.

During continuous charge-discharge cycling of LIB under 5, 25 and 45 °C, the discharge capacities gradually decrease to less than 80% until 13,100, 2,500 and 600 cycles, respectively (Fig. 1). Commercial LIB under the conditions of 45 °C was degraded rather than four times faster than 25 °C. The frequency responses at 10 mHz increased with charge-discharge cycles on each condition. The variety of frequency responses accompanying the cycling at 25 °C is shown in Fig. 2. EIS analysis using the equivalent circuit imply that the degradation is attributed to the resistance increase of the both electrode. We will present the EIS analysis using equivalent circuit on the testing with charge-discharge cycles in detail.

This work was partly supported by “Research & Development Initiative for Scientific Innovation of New Generation Batteries” from NEDO, Japan.

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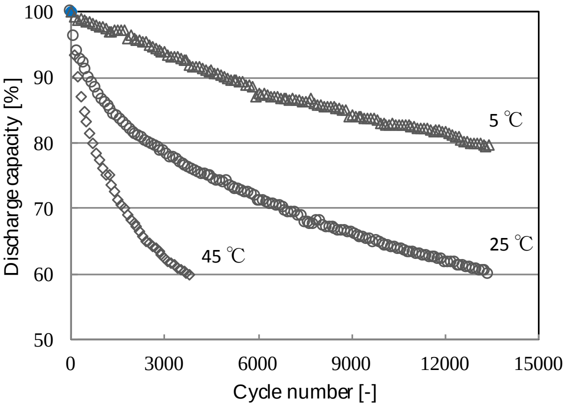

Fig. 1. Discharge capacity with charge/discharge cycling.
△: 5℃, ◇: 25℃, ○: 45℃.

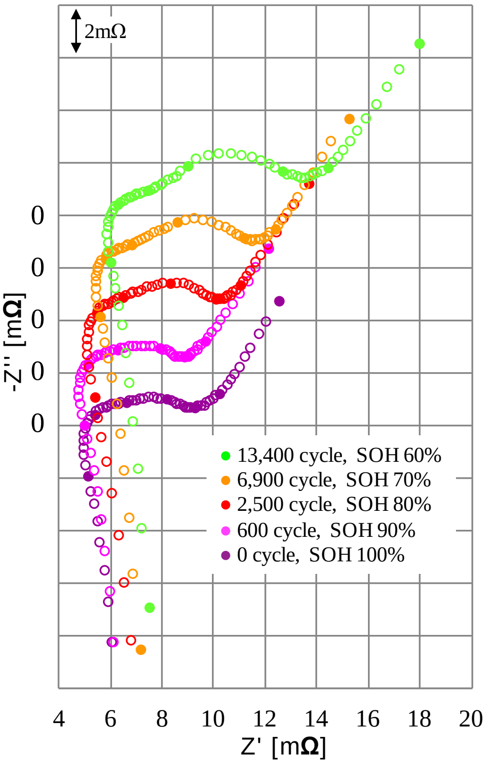

Fig. 2. Experimental impedance spectra of LIB at SOC 100% with charge/discharge cycling (2C, 25 °C).

Fiber-Optic Laser Absorption Spectroscopy Techniques for Measuring Water and Oxygen Transports in PEM Fuel Cells

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Water and oxygen concentrations in proton exchange membrane (PEM) fuel cell are key factors in determining its power generation performance. Therefore, it is essential to establish diagnostic tools for understanding their transport phenomena inside operating fuel cells. Previously, several researchers have demonstrated the ability to measure species distributions in gas channels of working PEMFCs using micro gas chromatograph (μGC) [1-2]. Although GC method achieves high-accurate gas analysis, it takes a long time (at least two minutes) to collect a gas sample and identify a species. On the other hand, tunable diode laser absorption spectroscopy (TDLAS) technique has been also applied to gas concentration measurement in PEMFCs [3]. TDLAS is one of the high-speed and high-sensitive absorption spectroscopy techniques which measure the absorbance of a species and identify its concentration using infrared diode laser. Since laser beam is directly injected into gas channels, in-situ monitoring of water and oxygen concentrations can be performed on operational fuel cells with a high time resolution of millisecond.

The authors now develop a fiber-optic gas sensor based on TDLAS, and apply it to the measurement of water vapor and oxygen concentration in flow channels of PEMFCs. The introduction of small-scale fiber optics enables the in-situ laser diagnostics within narrow channels of 1mm x 1mm. In this study, a transmission/reception integrated fiber-optic probe was first developed to detect absorption spectra of water in millimeter-scale channels of PEMFCs. This probe is compactly composed of one light-projecting fiber and six receiving fibers, which are coaxially arranged. Since multiple optical signals detected using six receiving fibers are synthesized, the fringe noise in them can be effectively canceled. Furthermore, the TDLAS system with the fiber-optic probe was constructed as shown in Fig. 1, and the concentration measurement of water vapor was tentatively attempted using a simulated flow cell. It was noted that the water concentration can be accurately estimated from the peak-valley ratio of the second-harmonic (2f) and the fourth-harmonic (4f) absorption spectra. The measurement accuracy of water mole fraction is less than 0.3% in the range of 3 to 26% at 70 deg. C. Secondly, to detect oxygen absorption spectra in a simulated flow cell based on TDLAS, the long-path optical system was established along the channels. It was confirmed that the peak-valley height of 2f absorption spectrum rises progressively with an increase in oxygen concentration. The measurement accuracy of oxygen mole fraction is less than 2% in the range of 15 to 21%. These results suggest that the fiber-optic TDLAS has the ability to accurately monitor in-situ water and oxygen transports within actual PEM fuel cells.

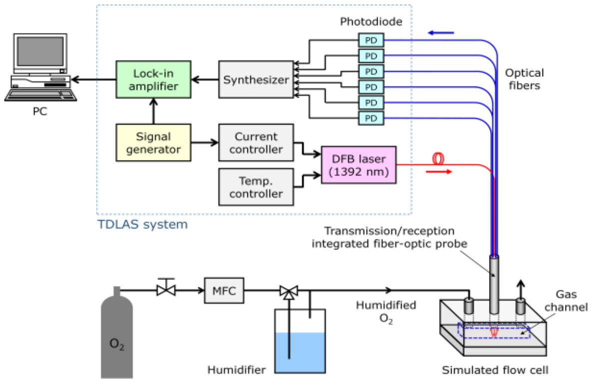

Fig. 1 TDLAS system with fiber-optic probe for measuring water vapor concentration in a simulated flow cell.

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Synthesis of Manganese Dioxides as Redox Mediator and Support for Sulfur Cathode in Lithium Secondary Battery

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Sulfur-based cathodes are one of the promising cathodes for lithium secondary batteries with high energy density, safety, and low cost, because of its high capacity (1675 mAh/g-sulfur), low toxicity, and abundance in nature. However, sulfur cathodes have intrinsic problems such as low ionic and electronic conductivities and dissolution of intermediate polysulfides (Li_2S_x: $4\leq x\leq 8$). To solve the problem, we have investigated a sulfur/ Ketjenblack (S/KB) composite cathode covered with polypyrrole film, which is a permselective film toward lithium ion. [1,2] Although the polysulfide dissolution from S/KB cathode into electrolyte solution was suppressed by the polypyrrole coating, there is a room for S/KB cathode itself to be improved. There is a report that a monoclinic birnessite manganese dioxide (δ-MnO_2) support can improve charge-discharge property, which functions as a redox mediator to enhance the reaction rate capability of polysulfide redox. [3] In the present paper, for the purpose to improve a utilization ratio and charge-discharge rate capability of sulfur as the active material, we investigated synthesis process of manganese dioxides and evaluated their charge-discharge properties.

The manganese dioxides were synthesized by mixing KB and $KMnO_4$ under heating. During the synthesis, KB is oxidized and MnO_4^- is reduced into MnO_2. [4] Controlling amount of $KMnO_4$ and heating time, hollandite manganese dioxide (α-MnO_2) and δ-MnO_2 were obtained, which were confirmed by X-ray diffractometry. S/α-MnO_2 or S/δ-MnO_2 composites were prepared with the S/MnO_2 weight ratio of 1:1, then the cathodes were prepared by mixing S/MnO_2, acetylene black, and polyvinylidene difluoride with the weight ratio of 75:15:10. A 2032 coin-type cells were assembled using Li foil anode and 1M lithium bis (trifluoro methanesulfonyl) imide (LiTFSI) /1,2-dimethoxyethane (DME) - 1,3-dioxolane (DOL) (1:1, vol.%) electrolyte.

Figure 1 shows the discharge capacity and charge-discharge efficiency with charge-discharge cycles of S/α-MnO_2, S/δ-MnO_2, and S/KB cathodes. Although at low C-rate, the discharge capacities of S/α-MnO_2 and S/KB cathodes were almost same, at high C-rate, the discharge capacities of S/α-MnO_2 was lower than that of S/KB cathode, this would be because of reaction interruption and/or low electric conductivity by α-MnO_2. On the other hand, S/δ-MnO_2 cathode demonstrated higher discharge capacity and better C-rate capability than S/α-MnO_2 and S/KB cathodes. This result implies that δ-MnO_2 act as a mediator to enhanced the reactivity of polysulfides. In the poster, the charge-discharge properties and physical properties of synthesized MnO_2 will be discussed in detail.

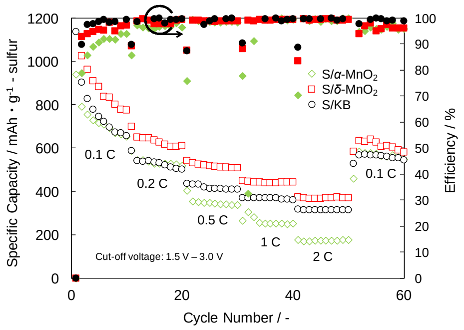

Fig. 1 Discharge capacity and charge-discharge efficiency with charge-discharge cycles of S/α-MnO_2, S/δ-MnO_2, and S/KB cathodes. Cut off voltage is 1.5 V – 3.0 V.

Acknowledgement

This work was partly supported by the “Advanced Low Carbon Technology Research and Development Program, Specially Promoted Research for Innovative Next Generation Batteries (ALCA Spring)” from the Japan Science and Technology Agency (JST), Japan.

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Evaluation of Carbon Felt for High Potential Redox Couples

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Redox flow batteries (RFBs) are flexible in design due to de-coupling of power and energy, thus making them attractive for large scale energy storage applications. This technology is capable of interfacing with renewable energy sources and provides an alternative solution to balancing power consumption and generation.

Carbon-based electrodes are typically used in RFBs due to their high performance, low cost and suitable porosity and high surface area [1]. Vanadium redox flow batteries [2], one of the more commonly studied redox couples, typically uses carbon felt or carbon paper as the electrode material. Recent studies in all iron batteries also use carbon as the electrode material for similar reasons [3]. Investigations have also improved performances of these electrodes by modifying them with electrocatalysts [4], however few studies have investigated the basic carbon felt electrodes, especially their long term performance and durability.

This study investigates the performance of carbon felt electrodes in four high potential redox couples: vanadium, bromine, manganese and iron. Four separate cells were simultaneously monitored over a time period of about 200 hours, while continuously operating at fixed current densities. Initial cyclic voltammagrams were used to determine appropriate current densities for each electrode/redox couple. AC impedance was also measured prior to charging each of the four batteries. Intermittent polarization and ac impedance data were measured during the 200 hours of charging, showing degradation of the carbon electrodes in some cases. A difference in electrode mass between the initial and final masses degradation of the felt for the bromine and manganese couples.

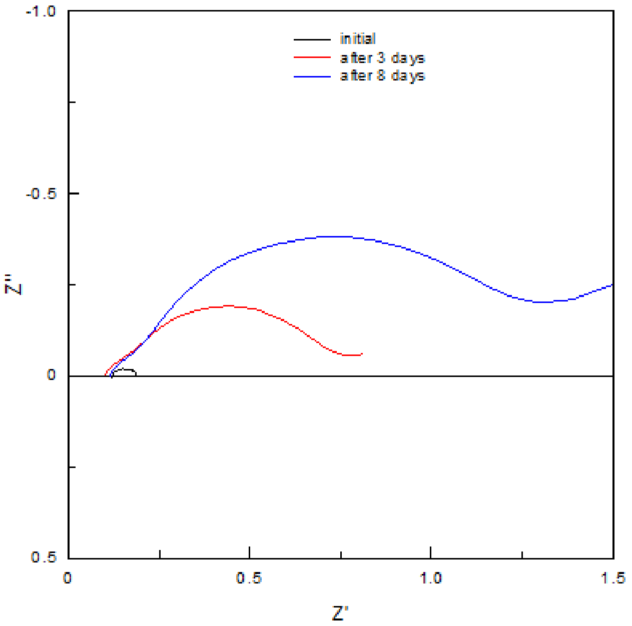

Figure 1: AC Impedance of Br^-/Br_2 (1.07 V vs NHE) reaction in Bromine battery (1M HBr + 0.1M Br_2) showing charge transfer loops for initial state, after 3 days and 8 days respectively.

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Dynamic Multi-Frequency Analysis of the Oscillatory Electro-dissolution of p-type Silicon

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The anodic electro-dissolution of p-type silicon in fluoride containing media has gained lots of interest in recent years, however the reaction mechanism of the oscillatory dynamics that govern this process is still not fully understood [1, 2]. The electro-dissolution reaction can be roughly described by the formation of silicon oxide through the electrochemical oxidation of silicon, which can occur via a tetravalent or a divalent reaction mechanism (formula 1), and the subsequent purely chemical etching of the oxide layer by the fluoride species in the solution [3].

$$Si + 4H_2O + \nu_{VB}h^+ \rightarrow Si(OH)4 + 4H^+ + (4 - \nu_{VB})e^- \qquad (1)$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \qquad \text{(tetravalent)}$$

$$Si + 2H_2O + \nu_{VB}h^+\ Si(OH)_2 + 2H^+ + (2 - \nu_{VB})e^-$$

$$Si(OH)_2 \rightarrow SiO_2 + H_2 \qquad \text{(divalent)}$$

By applying a constant voltage to the silicon sample, stable oscillations with frequency of 0.025 Hz were observed in presence of 60 mM NH_4F solution and a series external resistance. In order to measure the impedance spectra of this highly complex system and extract the dynamic behavior of the reaction kinetic steps, dynamic multi-frequency analysis (DMFA) [4] was used, with which 2000 impedance spectra per oscillation were recovered. Each impedance spectrum was composed by 25 frequencies, covering the range from 1.8 kHz down to 1.44 Hz. Due to the series external resistance, impedance at frequencies higher than 1.8 kHz would not give any further information about the system. Each impedance spectrum acquired during the cycling was fitted with a parametric electrical equivalent circuit (EEC), presented in the inset of the figure, that considered both, the tetravalent and the divalent oxidation mechanism. As anodic silicon oxide films exhibit a non-ideal capacitive behaviour, probably due to disk current density distribution, constant phase elements were introduced in the EEC to evaluate the experimental results. In doing so, it was possible to observe the temporal development of the kinetic parameters R_s, Q_h, n_h, R_{ad}, Q_{ad}, n_{ad} and R_{ct} and their dependence on the effective potential.

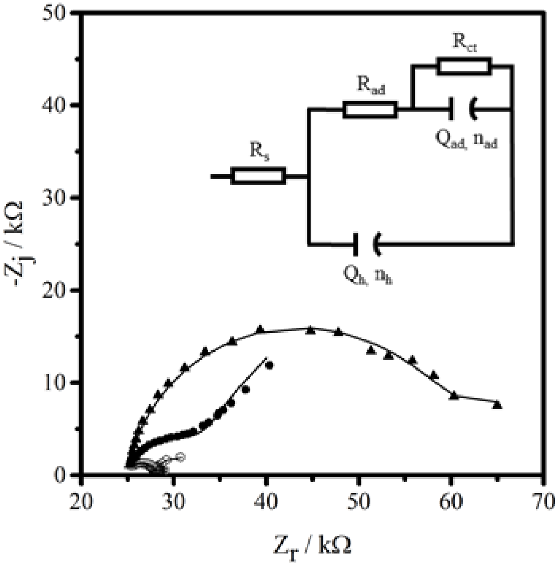

Figure: Nyquist plots of the impedance recorded during the silicon electro-dissolution reaction and fitted spectra.

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Enhanced Electrochemical Properties of Nb-TiO_2/Sulfur Dual Layered Structure Applied to Lithium-Sulfur Batteries

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Lithium sulfur batteries represent a promising energy storage system because of high energy density and low cost. However, polysulfide shuttle effect which leads to rapid capacity decay and lowers Coulombic efficiency during cycling is the major adverse. This study presents a facile way to ameliorate the migration of polysulfide by introducing dual layer structure design. Nb-TiO_2 coated Sulfur was prepared by two-step Blade coating on Al alloy at ambient temperature. The melted sulfur mixed MCMB as electrode was covered with Nb-TiO_2 graphite composite passivation layer. Nb doped TiO_2 provides additional conductivity and delivers extra capacity. To trap the sulfur during the charge and discharge processes, water-soluble polymer Poly (ethylene oxide) and Poly (vinylpyrrolidone) mixture was incorporated to better bind with LiS and Li_2S due to its oxygen and nitrogen-containing groups. The electrochemical potential window from 2.6V to 1.7 V, high rate, charge-discharge and long cycle test has shown improved electrochemical properties with the aid of dual layered design. The enhanced electrochemical performance of Nb-TiO_2/Sulfur dual layer Structure was attributed to the Nb-doped TiO_2 passivation layer that effectively facilitates Li^+ ion diffusion which inhibited shuttle effect.

Keywords: multilayer, functional groups binder, lithium sulfur battery

Shape Transformation of Pt Nanocrystals With High-index Facets and Low-index Facets

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The shape of metal nanocrystals (NCs) has a huge impact on the physical and chemical properties, such as spectroscopy, catalysis, biology, and energy[1]. Until now, almost all shapes of metal nanocrystals have been synthetized through wet chemical method and electrochemical method. Electrochemical method show unique advantage in shape-controlled synthesis of Pt NCs with high-index facets[2]. In this study, by using square-wave potential, we achieved the shape transformation of NCs with low-index facets, such as from cube to octahedron, and shape transformation of NCs with high-index facets and low-index facets, such as transformation from cube to tetrahexahedron. We observed the gradual shape transformation of the NCs. The effects of the size and the distribution density of Pt NCs, the concentration of Pt precursor, as well as potential of the square-wave, on the shape transformation were discussed. It is found that the etching and the regrowth of Pt NCs which can be tuned by changing the experimental parameters play the key role for the shape transformation. This study provides new insights into the nanocrystal growth habit and shape transformation.

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New insights into the structure changes and interface properties of Li_3VO_4 anode during the initial cycle by in-situ XRD and EIS

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ABSTRACT: Li_3VO_4 has been regarded as a new-type anode of lithium-ion batteries in recent years, which has a high theoretical specific capacity of 394 $mAhg^{-1}$, a proper potential for Li^+ insertion/de-insertion (~1V) and a good rate capacity. However, its low initial coulombic efficiency, poor conductivity and poor cycle performance restricts its development. In order to figure out the cause of the low initial coulombic efficiency of Li_3VO_4 material, the nano-sized Li_3VO_4 material was synthesized by citric acid-assisted sol-gel method. The lithium storage behaviors of the prepared Li_3VO_4 material were studied by *in-situ* XRD and *in-situ* EIS techniques. *In-situ* XRD results indicated that there was irreversible phase transformation of Li_3VO_4 during the initial charging/discharging process. *In-situ* EIS experiment was performed during potentiostatic intermittent titration technique (PITT) process to discuss the formation of the solid electrolyte interface (SEI) on the Li_3VO_4 and the kinetics of lithium ion diffusion. It is worth to point out that this is the first time to prove the existence of SEI on Li_3VO_4during initial charging/discharging process by *in-situ* EIS experiment. It turned out that their reversible phase transformation and the formation of SEI on Li_3VO_4were the two important reasons causing the low initial coulombic efficiency of Li_3VO_4 material.

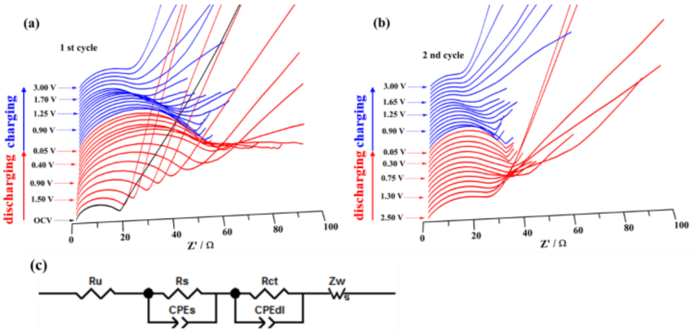

Figure 1. *In-situ* EIS profiles of Li_3VO_4 at (a) initial cycle and (b) second cycle, and the equivalent circuit (c).

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Electrochemical Na-insertion/extraction property of Ni-coated phosphorus prepared by an electroless deposition method

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One of the next-generation energy storage device that use Na-ion as the charge carrier, Na-ion battery (NIB), has attracted more and more attention because of its low cost and natural abundance of sodium. Development of host materials which can absorb much Na per its formula weight has been needed to realize NIB with a higher energy density. Black phosphorus has attracted much attention as an anode material because of its high theoretical capacity of 2596 mA h g^{-1}. The theoretical capacity is about ten times larger than that of carbon-based materials, and is the highest value in previously-reported active materials such as Sn (847 mA h g^{-1}), Sb (660 mA h g^{-1}), and Pb (485 mA h g^{-1}). Si electrode, however, shows poor cycling performance due to low electronic conductivity and significant volume changes during sodiation and de-sodiation reactions. In the case of using a composite electrode consisted of an active material, a conductive additive, and a binder, when electrons move from a current collector to an active material on the side close to a counter electrode, there are electron transfers (*i*) between a current collector and an active material, (*ii*) between active materials, and (*iii*) between a conductive additive and an active material. Each the transfer paths inevitably include the active materials, that is, an electrical conductivity strongly affects an electrode performance. On the other hand, nickel plating has been widely used for surface coating to enhance the durability of the base material. In the present study, we tried to improve cycling performance of phosphorus-based electrode by metalization using an electroless desposition of Ni.

Black-phosphorus was prepared by a mechanical milling (MM) method using a high-energy planetary ball mill (Classic Line P-6, FRITSCH) in an argon atmosphere. Ni-coated phosphorus was synthesized by electroless desposition. 4.8×10^{-3} M hydrazine monohydrate (N_2H_4-H_2O) as the reducing agent was dripped into aqueous solution including 5.6 ×10^{-4} M Ni(COOH)$_2$-4H$_2$O as the Ni source, 1.6 ×10^{-4} M ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (EDTA-2Na), 4.8×10^{-3} M lactic acid [CH$_3$CH(OH)COOH] as the complexing agents, and Pd-activated phosphorus powder (1.0 g L^{-1}) under agitation using magnetic stirrer. After stirring at 80 ºC for 60 min, the suspension was filtered and washed with deionized water. The washed precipitation was dried in vacuum at 80 ºC for 1 h to obtain Ni-coated black-phosphorus as the final product. Since the conditions mentioned above corresponds to 5 wt.% Ni-deposition, the concentration of the respective reagents is needed to be increased depending on Ni amount.

30 wt.% Ni-coated phosphorus electrode exhibited the best cycling performance with a reversible capacity of 600 mA h g^{-1} at the 60th cycle, whereas pristine black-phosphorus electrode showed a capacity of only 140 mA h g^{-1}.

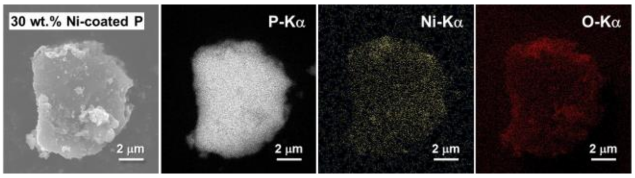

Fig. 1FE-SEM images and EDS mapping of Ni-coated phosphorus particles. In the case of treatment so as to make Ni amount be 30 wt.%, the actual weight ratio of Ni determined by WDS measurements was 32 wt.%.

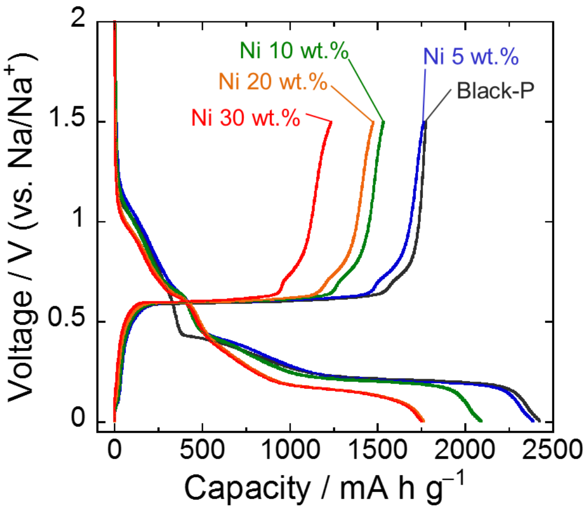

Fig. 1 Initial charge−discharge profiles of Ni-coated phosphorus electrodes at a rate of 256 mA g^{-1} (0.1*C*) in the voltage range of 0.005−1.500 V (vs. Na/Na^{+}).

Electrochemical Visualization of Intracellular Hydrogen Peroxide at Single Cells

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In this Letter, the electrochemical visualization of hydrogen peroxide inside one cell was achieved first using a comprehensive Au-luminol-microelectrode and electrochemiluminescence. The capillary with a tip opening of 1− 2 μm was filled with the mixture of chitosan and luminol, which was coated with the thin layers of polyvinyl chloride/nitrophenyloctyl ether (PVC/NPOE) and gold as the microelectrode. Upon contact with the aqueous hydrogen peroxide, hydrogen peroxide and luminol in contact with the gold layer were oxidized under the positive potential resulting in luminescence for the imaging. Due to the small diameter of the electrode, the microelectrode tip was inserted into one cell and the bright luminescence observed at the tip confirmed the visualization of intracellular hydrogen peroxide. The further coupling of oxidase on the electrode surface could open the field in the electrochemical imaging of intracellular biomolecules at single cells, which benefited the single cell electrochemical detection.

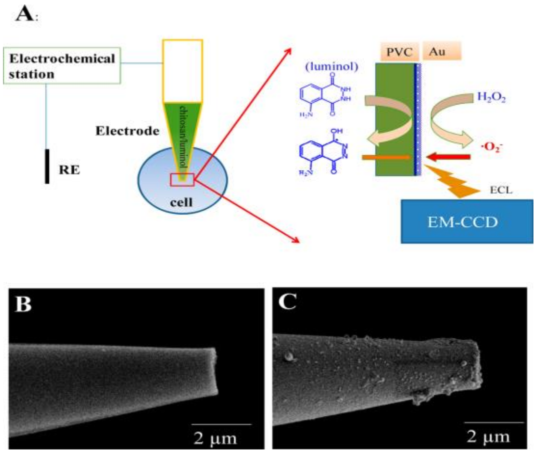

Figure 1. (A) Schematic system used for the electrochemical Imaging of intracellular hydrogen peroxide. (B) SEM image of capillary. (C) SEM image of luminol/chitosan capillary coated with PVC/NPOE.

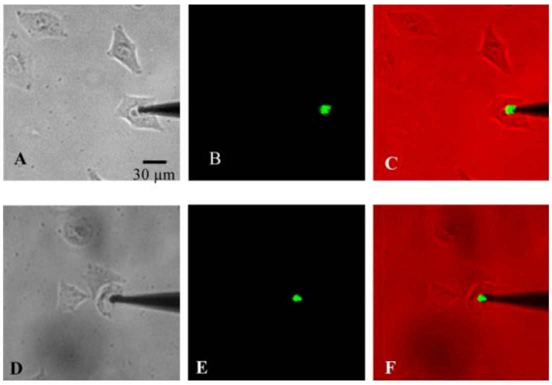

Figure 2. (A) The bright-field image of the microelectrode in the cell loaded with H_2O_2; (B) the luminescence image; (C) the overlapping image; (D) the bright-field image of the microelectrode in the cell stimulated with PMA; (E) the luminescence image; (F) the overlapping image.

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Electrochemiluminescence Imaging for Parallel Single-Cell Analysis of Active Membrane Cholesterol

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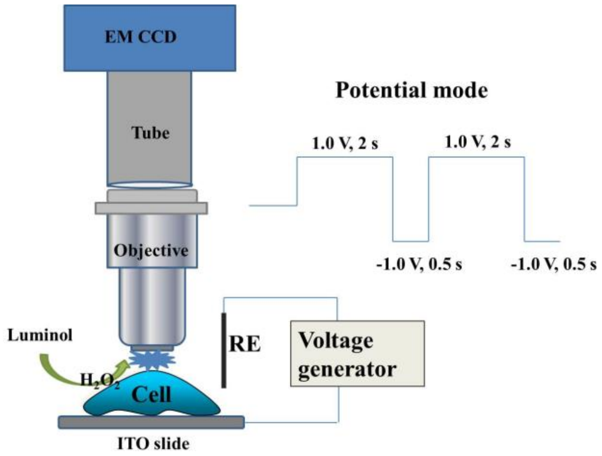
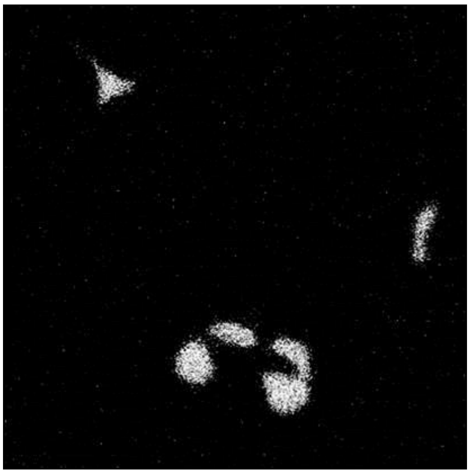
Luminol electrochemiluminescence (ECL) imaging was developed for the parallel measurement of active membrane cholesterol at single living cells, thus establishing a novel electrochemical detection technique for single cells with high analysis throughput and low detection limit. In our strategy, the luminescence generated from luminol and hydrogen peroxide upon the potential was recorded in one image so that hydrogen peroxide at the surface of multiple cells could be simultaneously analyzed. Compared with the classic microelectrode array for the parallel single-cell analysis, the plat electrode only was needed in our ECL imaging, avoiding the complexity of electrode fabrication. The optimized ECL imaging system showed that hydrogen peroxide as low as 10 μM was visible and the efflux of hydrogen peroxide from cells could be determined. Coupled with the reaction between active membrane cholesterol and cholesterol oxidase to generate hydrogen peroxide, active membrane cholesterol at cells on the electrode was analyzed at single-cell level. The luminescence intensity was correlated with the amount of active membrane cholesterol, validating our system for single-cell cholesterol analysis. The relative high standard deviation on the luminescence suggested high cellular heterogeneities on hydrogen peroxide efflux and active membrane cholesterol, which exhibited the significance of single-cell analysis. This success in ECL imaging for single-cell analysis opens a new field in the parallel measurement of surface molecules at single cells.





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Investigation of persulfate production on BDD anode by understanding the impact of water concentration

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The persulfate ($S_2O_8^{2-}$), also known as peroxydisulfate ion, is a strong oxidant and has been used for the degradation of organic pollutants in wastewater sewage treatment plants, water with high content of synthetic dyes (textile industry and food), and soil contaminated by oil, among others. So this work uses the electrochemical oxidation with boron doped diamond anode (BDD) for further study of persulfate generation of reactions that occurs in situ and streaming. For such studies have been developed a micro and macro BDD electrode as an anode to conduct the electrolysis experiments, and oxidation with sulfuric acid (H_2SO_4), sodium dodecyl sulfate (SDS) and sodium sulfate (Na_2SO_4) in different concentrations. The results showed that hydroxyl radicals can be generated electrochemically at the anode at high concentrations of BDD favor secondary reactions such as the formation of oxygen. However from the results obtained, the favored reaction is the production of persulfates, then identified by spectrophotometry, minimizing oxygen production and enables the opening of persulfate formation. Therefore it can be concluded that the persulfate production is feasible from the reaction between the radical $^{\bullet}OH$ and SO_4^{-2} in solution. No formation of oxygen in certain concentrations was the key to the completion of the persulfate being formed by two different mechanisms. Another important result was the production of the persulfate oxidant from the electrochemical oxidation of sodium sulfate (Na_2SO_4) in the presence and absence of the surfactant Sodium Dodecyl Sulfate (SDS) at different concentrations. Different current densities were used for oxidations by using a continuous flow system, containing with boron doped diamond (BDD) electrode. The results confirm that a good oxidant production was obtained in the solution containing 0.05M sodium sulfate and 0.0017M SDS when subjected to a current density of 60 mA cm^{-2}. Also, the current density 30 mA cm^{-2} showed good results for this same solution.

PGM-free catalysts for improved performances in microbial fuel cell

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Biological Fuel Cell (BFC) is an interesting technology that exploits microbial/enzymatic catalytic capabilities to harvest energy from organic and inorganic matter. Among BFCs, microbial fuel cell (MFC) is a bioelectrochemical system that utilizes both electrochemical and microbiological aspects to convert organics and pollutants while generating the electricity at room temperature and in neutral media.

One of the main factors limiting the power output of MFC is the oxygen reduction reaction (ORR) at the cathode. Due to its high reduction potential, sustainability, and natural abundance, oxygen is the most used and practical oxidant at the cathode. Major issues concerning ORR are i) high overpotentials; ii) low kinetics and iii) high ohmic resistances of the existing cathodes. To decrease the overpotentials and increase the reaction kinetics, catalysts mainly based on i) carbonaceous materials, ii) platinum-based materials and platinum group metal-free (PGM-free) materials on a carbon support have been used in the cathode fabrication.

High surface area carbonaceous materials like Activated Carbon (AC), graphene-based materials, carbon nanotubes (CNTs), carbon nanofibers etc., can be used in cathode formulation due to their low cost, high durability, conductivity and mechanical strength, they are suitable for ORR in MFCs. But their higher activation overpotential is hindering its large utilization in MFC systems. To enhance the MFC performance by overcoming these losses, metal-based catalysts represents another avenue for exploration. Pt and Pt–based materials are also used in air-breathing cathode catalysts in MFCs. Since Pt is expensive, rare and sensitive towards catalyst poisoning, this diminishes the practical application of it in MFCs. PGM-free catalysts are based on carbon/Nitrogen matrix with atomically dispersed transition metal: Fe, Co, Ni, and Mn (M-N-Cs) are the most used earth-abundant metals in PGM-free cathode catalysts in MFC. Despite slightly higher cost in cathode manufacturing, the utilization of PGM-free catalysts guarantees superior performance compared to AC, and it assures high durability in long-term operations.

In this current work, we are showing a comparison among various PGM-free M-N-C catalysts for ORR synthesized using the same preparation method with identical initial ingredients and organic precursors but with different metals. The transition metals used in the experiments are Fe, Co, Mn, and Ni. All the catalysts have been prepared by utilizing Sacrificial Support Method (SSM). The catalysts were studied using rotating ring disk electrode (RRDE) technique and then integrated in air-breathing cathode and tested in repeatable and equal operating conditions. Fe-AAPyr (where AAPyr = Aminoantipyrine) catalysts showed the highest performance compared to Co-AAPyr, Ni-AAPyr, and Mn-AAPyr. In RRDE, Fe-AAPyr showed the highest onset potential and the highest half-wave potential and the lowest H_2O_2 production. Fe-AAPyr seems to have a 4e- transfer mechanism. In parallel, Co-AAPyr, Ni-AAPyr, and Mn-AAPyr showed a probable 2x2e- transfer mechanism with higher H_2O_2 produced [1].

Once the PGM-free catalysts were incorporated into the air-breathing cathode, they outperformed AC-based (metal-free) cathode by 31-102%. Durability tests results indicated a relatively good stability of Metal-AAPyr with losses in 32 days quantified to 21-30%. With increasing electrolyte solution conductivity, the performance output reached a maximum of 482±5 $\mu W cm^{-2}$ at the highest solution conductivity of 63 mS cm^{-1} investigated [2].

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Refractory Metal Doped TiO_2 as Corrosion-Resistant Electrocatalyst Supports for Proton Exchange Membrane Fuel Cells

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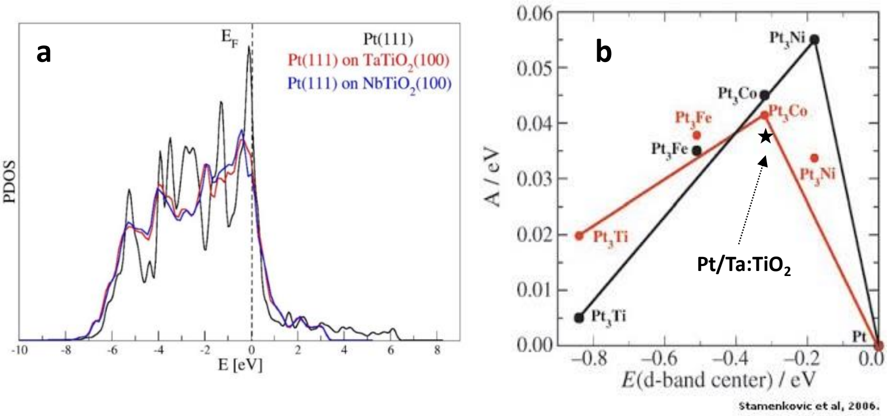
Catalyst active site and support corrosion, particularly at the cathode, of PEMFC's is a technological challenge in fuel cell design. Carbon based supports are particularly susceptible to electrochemical corrosion, and for this reason more stable support materials are needed [1]. Pt supported on TiO2 is reported to have improved corrosion resistance for ORR compared to carbon supported catalysts [2]. However, the low intrinsic conductivity of TiO_2, as well as the high cost of Pt, require further materials optimization before these technologies become market viable.

Here, we will present on efforts to alter the electronic environment of TiO_2 by doping with Ta, Nb, W, and Mo to improve the conductivity of the support, as well as stabilize Pt on the support surface. DFT was used to calculate the band structures of doped M:TiO_2 (4 at% , M=Ta, Nb, W, Mo) which shows that these materials will be n-type semiconductors, where the Fermi level is pushed to the top of the conduction band. The density of *d*-states for the Pt supported on M:TiO_2 was then calculated and compared to that of unsupported Pt. A shift in the *d*-band center was found for all doped materials, with the lowest shift being that of Ta:TiO_2 (-2.34 eV), Figure-1a. Alloying Pt with Co and Ni has been shown to reduce overpotential for ORR where a similar *d*-band center position was observed for Pt_3CO and Pt_3Ni [3]. Shifts in the *d*-band center to lower values reduce the strength by which these alloys bind oxygen, which is responsible for the reduced ORR over potential as compared to Pt, Figure-1b. Based on these results, we predict Ta:TiO_2 will not only possess improved conductivity, but also facilitate a reduction in ORR overpotential.



Stamenkovic et al, 2006.

Figure-1: **a)** Projected Density of States (PDOS) of Pt(111) and Pt(111) on Ta:TiO_2 and Nb:TiO_2 **b)** Volcano plot of ORR activity for Pt_3Co and Pt_3Ni as a function of *d*-band center position.

To maximize the electrochemically active surface area, the M:TiO_2 support must have high specific surface area, 70-100 m^2/g. To achieve this, the Sacrificial Support Method (SSM) has been applied where water soluble Ti precursors are impregnated onto high surface area fumed silica, CAB-O-Sil-EH5. The dried material is then pyrolyzed in a H_2 atmosphere at 950°C, after which the silica is leached in KOH. The high surface area Rutile phase TiO_2 is then impregnated with a Ta precursor and again pyrolyzed. The resulting material possesses a BET surface area of ~60 m^2/g and a conductivity of 0.9S/cm, which is several orders of magnitude more conductive than *neat* rutile phase TiO_2. Electrochemical performance studied by RDE experiments (CV and AST) will be presented, along with further improvements synthetic techniques.

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Electrocatalytic Oxidation of Acid Yellow 36 Azo Dye via Fenton-Like Reaction with Active Chlorine and Iron Ion

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Around 70% of the world dye manufacture corresponds to azo compounds [1], which have a complex chemical structure containing one or various azo groups (-N=N-) as chromophore, linked to aromatic systems. Azo dyes are broadly employed in textile industries, highly polluting in terms of the color and chemical oxygen demand of their discharged effluents, with dye contents up to 250 mg L^{-1}, along with other toxic constituents. This impedes light penetration and leads to health problems due to their carcinogenic, toxic and mutagenic properties. Their resistance to biodegradation by conventional treatments in wastewater treatment plants justifies their large persistence in the aquatic environment. Investigation is then needed to develop powerful treatments to eliminate azo dyes from wastewater.

This communication presents the results obtained for the degradation of a 0.46 mM Acid Yellow 36 solution (100 mg L^{-1} of total organic carbon) in a 35 mM NaCl + 25 mM Na_2SO_4 mixture at pH 3.0 by electro-oxidation (EO), electro-Fenton-like and photoelectro-Fenton-like. The trials were carried out in a 2.5 L flow plant with a filter-press cell equipped with a purpose-made Ir-Sn-Sb oxide anode and a stainless steel cathode. Comparative tests using pure $NaClO_4$ or Na_2SO_4 as electrolyte were made to better assess the role of active chlorine in the mixed electrolyte. The influence of Fe^{2+} addition to the latter medium, either in the dark or under UVA irradiation, was studied to give strong evidence of the occurrence of a Fenton-like reaction, described by the equations (1)–(5), being the homogeneous $^{\bullet}OH$ the main oxidant for Acid Yellow 36 removal.

At the anode: $$2\,Cl^- \rightarrow Cl_{2(aq)} + 2\,e^- \qquad (1)$$
In the solution bulk: $$Cl_{2(aq)} + H_2O \leftrightarrows HClO + Cl^- + H^+ \qquad (2)$$
$$HClO + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + Cl^- \qquad (3)$$
At the cathode: $$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (4)$$
In the bulk under UVA iradiation: $$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (5)$$

Figs. 1a and b demonstrate a clear enhancement of the color removal and the degradation of the dye in the electro-Fenton-like and photoelectro-Fenton-like treatments as compared to the EO (without Fe^{2+}).

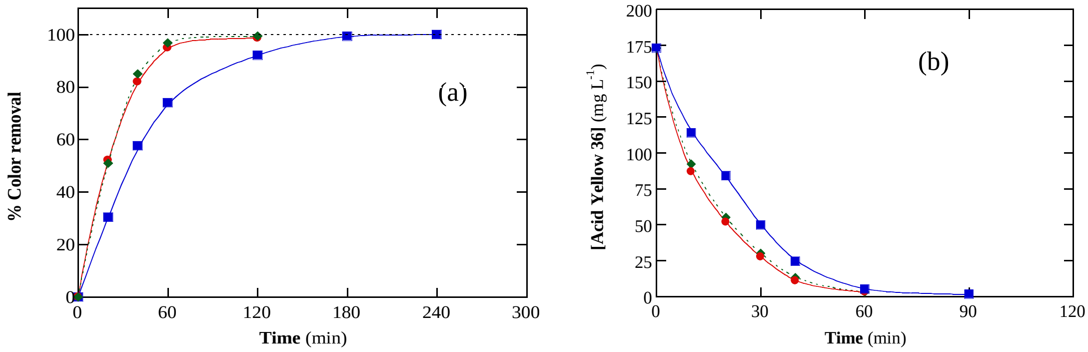

Fig. 1. (a) Variation of the percentage of color removal with electrolysis time for the electro-oxidation of 2.5 L of 0.46 mM Acid Yellow 36 solutions in 35 mM NaCl + 25 mM Na_2SO_4 (■) without Fe^{2+} addition and with (●) 1.0 mM Fe^{2+} (electro-Fenton-like process) or (◆) 1.0 mM Fe^{2+} + UVA irradiation (photoelectro-Fenton-like process) at pH 3.0 and 30 ºC in the flow plant at j = 150 mA cm^{-2} and liquid flow rate of 200 L h^{-1}. (b) Dye concentration decay for the same trials [1].

Acknowledgements

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Visualization of water formation in polymer electrolyte fuel cells using *in-operando* X-ray computed tomography

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Polymer electrolyte fuel cells (PEFCs) are a promising alternative to conventional combustion engines for automotive applications due to high efficiency and zero tail-pipe emissions. The current state of the art PEFCs use Platinum (Pt) as a cathode catalyst, however there have been recent significant advancements in Platinum group metal (PGM)-free catalyst layers. The Department of Energy has published a target Pt content for PEFCs of 0.125 mg/cm2 by 2020 since the high cost of Pt can currently account for up to 35% of the total PEFC stack cost [1]. PGM-free catalysts offer a distinct cost advantage over traditional Pt catalysts due to their material abundance, therefore they have the potential to ~~exceed~~ meet this DOE target. For both Pt and PGM-free catalysts, understanding the morphology of the catalyst layer can aid in the development of new ~~catalysts~~ electrodes with better transport properties. One of the most effective ways to do this is to image ~~these catalysts~~ *in-operando* PEFCs, so water distribution and any morphological changes ~~that the dynamic effects of the running fuel cell~~ can be included in the analysis. Our work focuses on water transport through the catalyst layer, which we imaged using synchrotron X-ray computed tomography (CT).

In order to image these processes *in-operando*, we developed two X-ray low attenuation hardware for PEFCs~~transparent fuel cells~~, one for ~~Micro~~micro-CT (~~which images with a~~ resolution of 1.3 µm) and one for ~~Nano~~nano-CT (resolution of 60 nm). The ~~Micro~~micro-CT cell is in a later stage of development than its ~~Nano~~nano-CT counterpart and has already produced promising results. We visualized water formation in a PGM-free PEFCs and found that most of the liquid water forms at the catalyst layer/membrane interface when run at constant current density and two different constant temperatures, 30ºC (Fig 1) and 60ºC. ~~(Fig 1).~~ One of the main challenges in the ~~Micro~~micro-CT cell design was maintaining a constant temperature distribution along the length of the channel. We used graphite plates for their high electrical conductivity and their high in-plane and low through-plane thermal conductivity. This allowed them to maintain a relatively constant temperature distribution along the length of the channel (Fig 2).

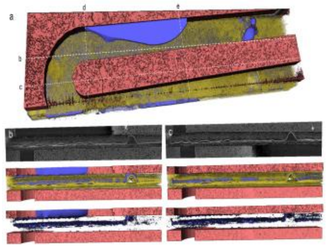

Fig 1. Volume rendering of operating PGM-free PEFC at 30°C

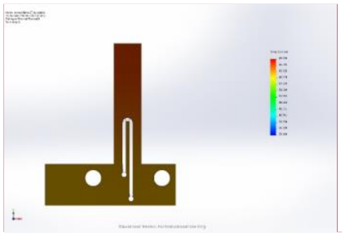

Fig 2. Temperature distribution in graphite plate of ~~Micro~~micro-CT cell with heater on top for use in 60°C operation

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Electrochemically Tunable Affinity Separation with High Energetic Efficiencies for the Removal of Organic Pollutants from Water

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The global prevalence of contaminated water resources by organic pollutants, such as pesticides, dyes, pharmaceuticals, and endocrine disrupting compounds, has raised concerns about potential deleterious effects on the environment (particularly aquatic ecosystems) as well as human health. High separation efficiencies for the removal of organics from water have been achieved using conventional processes such as adsorption, distillation, and solvent extraction, as well as more recent technologies such as advanced oxidation treatment and membrane separation. However, the overall separation processes inherently associated with these methods usually involve energy-intensive steps (e.g. requirement for high temperature or pressure) and/or environmentally unfriendly processes (e.g., use of organic solvent and additives, generation of secondary pollutants).

Here we introduce a conceptually new approach to water treatment using electrochemically tunable affinity separation (ETAS), which exploited electricity as the external stimulus for control over organics-water separation. The key to implementing ETAS is the design of a stimulus-responsive adsorbent system with its surface hydrophobicity programmable by an electrical potential. Such an adsorbent displays an electrically-controlled affinity toward neutral organic molecules, enabling the use of exquisite electrical swing to release and capture organics in a cyclic fashion. The ETAS concept is fundamentally different from previously-reported electrochemically controlled separation strategies which rely mainly on controlling electrostatic interactions between an electrode surface and a charged target molecule, such as capacitive deionization, ion concentration polarization, and electrochemically switched ion-exchange.

ETAS is expected to show higher energy efficiencies and incur lower environmental costs than established methods for separation of neutral organics from water, since ETAS operates at room temperature and pressure, requires almost no need for organic solvents and additional chemicals for extraction and/or adsorbent regeneration, and produces no secondary pollutants during operation. ETAS also exhibits a number of unique advantages. First, ETAS can achieve multiple levels of hydrophobicity and thus affinity towards organics since the external electrical signal (e.g., potential) can be tuned with high precision, permitting a systematic adjustment of the ratio between the hydrophobic and hydrophilic moieties. Second, because the potential of an ETAS adsorbent can be changed locally in real-time, the hydrophobicity of such an adsorbent can be modulated with a high spatiotemporal resolution, unlike traditional responsive systems based on chemical (e.g., CO_2, pH, reductant, oxidant) and thermal stimuli due to the presence of mass diffusion and/or heat dissipation processes that hampers the precise delivery of this stimulus over location and time. Moreover, ETAS-integrated devices enjoy common advantages of electrochemical systems, such as modularity, portability and low-cost. These features would make ETAS an economically viable platform technology for developing countries where water scarcity and environmental pollution are even more serious and imminent issues to be addressed.

As a proof of concept, we construct a model ETAS system composed of a nanostructured polyvinylferrocene/polypyrrole (PVF/PPY) hybrid conformally coated on a carbon cloth composed of bendable carbon fibers. Using this ETAS system, we demonstrate that the PVF/PPY polymeric surface can undergo an electrically-induced hydrophilic-hydrophobic transition and thereby enabling highly flexible control of capturing and releasing of a model neutral organic pollutant Sudan Orange G. Next we present a quantitative energetic analysis of ETAS, providing useful guidelines on how to balance the tradeoff between energy cost and separation extent by manipulation of electrical swing conditions. Furthermore, we introduce a generalizable material design approach to simultaneous improvement of separation degrees and energetic efficiencies, and identified the critical factors responsible for such enhancement via redox thin film simulations and theoretical calculations of electron transfer kinetics.

Niobium and Palladium as Electrocatalysts for Ethanol Electrooxidation Reaction.

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Abstract: Direct ethanol fuel cells have been evaluated as a possible alternative source of clean energy, because it has a high current density and minimal pollutant production[1]. The important challenges of the ethanol oxidation reaction (EOR) are the breaking of the C-C bond and the intermediates formation that block the active sites of the electrocatalyst[2]. PdxNby/C binary electrocatalysts supported on Vulcan XC-72 carbon were prepared by the sol-gel method[3]. The materials were characterized by TEM, EDS, XRD, ICP-MS, Zeta Potential and XPS. The concentration of Pd and Nb in the electrocatalysts was close to the expected, as shown in table 1.

Table 1. The comparisons of Pd and Nb concentrations (mass ratio) obtained by using ICP-MS and EDS.

Electrocatalyst	**Pd expected (%)**	**Pd ICP-MS (%)**	**Pd EDS (%)**
Pd/C	20.00	26.50 ± 1.20	26.62 ± 3.02
Pd_1Nb_1/C	10.00	8.81 ± .1.65	10.74 ± 1.80
Pd_3Nb_1/C	15.00	13.72 ± 0.58	14.08 ± 6.40
Pd_1Nb_3/C	5.00	4.29 ± 0.32	4.35 ± 0.48

The electrochemical activity for EOR of the prepared nanoelectrocatalysts was studied by Cyclic Voltammetry (CV) and Chronoamperometry (CA) versus SCE reference electrode and Pt wire as counter electrode. The current density peak for EOR using Pd_1Nb_1/C is 2.86 times higher than the commercial Pd/C, 45.5 and 15.9 $mAmg^{-1}{}_{Pd}$ respectively, and Pd_1Nb_1/C also has the less positive onset potential for EOR, as shown in figure 1a. Pd_1Nb_1/C had 2.35 times higher current density than Pd/C for EOR as shown in Figure 1b.

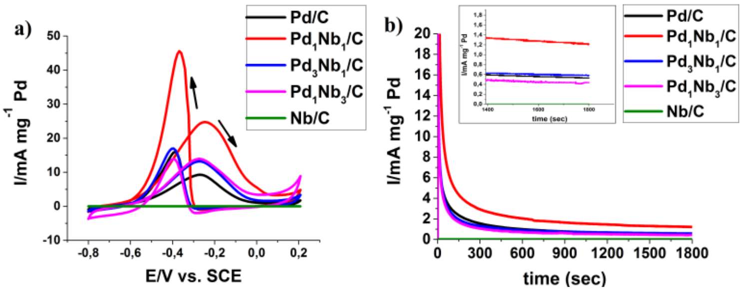

Figure 1. Electrochemical study of Pd_xNb_y/C electrocatalysts in 1.0 mol L^{-1} KOH solution at room temperature. (a) Cyclic voltammograms using 1.0 mol L^{-1} ethanol and 1.0 mol L^{-1} KOH, measured over potential range from −0.80 to +0.20 V vs. SCE, at sweep rate of 10 mV s^{-1}. (b) Chronoamperometry 1.0 mol L^{-1} CH_3CH_2OH with applied potential of -0.4V for 1800 seconds.

Potential zeta analysis showed that Pd_1Nb_1/C has 2.88 times higher conductivity than Pd/C, 0.00502 and 0.00174 mS/cm , respectively, improving the transport of charge in the electrocatalyst. We propose that Nb decreases the poisoning on Pd surface by CO due to the bifunctional mechanism, where Nb supplies oxygenated species to the active sites of the Pd with adsorbed CO for CO oxidation[4]. Therefore, Niobium is a promising co-catalyst for electrocatalysis of ethanol in alkaline medium for Pd-based electrocatalysts.

Acknowledgments: Fapesp (2015/10314-8), CNPq (150532/2016-4, 406612/2013-7) and Capes.

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Effect of imidazole and their derivatives on corrosion inhibition

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Mild steel is widely used as a construction material for pipe work in the oil and gas down hole tubular, flow lines and gas production, such as down hole tubular, flow lines and transmission pipelines in petroleum industry. Corrosion of oil field result in causing significant environmental pollution by the oil spill situation at the time of pipeline damage due to their corrosion. Several methods of the most effective corrosion control consider using the corrosion inhibitor (CI) such as imidazole, benzodimidazole, and their derivatives

In our research we investigate that some imidazole CI candidate such as and imidazole and imidazole derivatives are adopted as corrosion inhibitor. We will measure their corrosion speed, degree of corrosion and then suggest the optimum formulation of CI candidates to reduce corrosion in pipeline

Effect of imidazole and amine mixture on corrosion inhibition

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In our research we investigate that some imidazole and amine mixture are adopted as corrosion inhibitor. We will measure their corrosion speed, degree of corrosion and then suggest the optimum formulation of CI candidates to reduce corrosion in pipeline

Polymeric Metal Phthalocyanines as Versatile Active Materials in Supercapacitors

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While numerous p-doped conductive polymers have been investigated for applications in supercapacitors, relatively few studies have explored the use of n-doped materials, probably due to the small number of stable examples. Previous work in our laboratory demonstrated that various tetraaminophthalocyanines (TAPcs) could be electropoymerized and subsequently subjected to an electrochemical annealing process to yield moderately conductive and very durable n-doped thin films. Moreover, by using Ni or Cu as the central metal, extremely broad conductivity windows were observed. In this study, a series of polymeric metallophthalocyanines (MTAPcs) was prepared and studied with respect to morphology, specific capacitance, and other electrochemical properties. In addition, the cycling stability of these systems was examined in several different electrolytes, and a ligand scaffolding approach employing nitrogen donor bridges such as pyrazine or 4,4'-bipyridine resulted in significant durability improvement. Preliminary data from mixed-metal poly-MTAPc copolymers was particularly interesting, with multiple faradaic peaks superimposed on an extremely broad, largely non-faradaic background spanning nearly 3 Volts.

Utilization strategy of iron based layered oxides as cathode materials for Sodium ion batteries

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O3-type $NaFeO_2$ is a promising candidate as positive electrode materials for rechargeable Na batteries. However, its reversible range of sodium extraction is relatively narrow (x = ca. 0.4 in $Na_{1-x}FeO_2$) because of the irreversible structural change. However, substitution with other transition metal (Co, Ni, & Mn) on $NaFeO_2$ has been proved to be good strategy to suppress the irreversible phase transition due to iron migration.

One of them are O3-$NaFe_{0.5}Co_{0.5}O_2$ which showed around 160mAh/g with relatively good capacity retention when cycling in a voltage range 2.5-4V at 0.05C rate. Surprisingly, this cathode material showed irreversible phase transition when charge to 4.5V. The result shows that half substitution of iron was not enough to suppress the migration of iron at high voltage region. Herein, we report that additional nickel substitution on iron site of $NaCo_{0.5}Fe_{0.5}O_2$ demonstrates full suppression of iron migration even at high voltage.

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Degradation mechanism of $NaFeO_2$ as cathode materials for Na-ion Batteries at high Voltage region

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The iron based layered oxides cathode materials are promising candidate as rechargeable batteries for large scale electrical energy storage system due to low cost and abundant element on earth. Many type of iron based layered oxides such as secondary, tertiary, quaternary layered cathode compound for Na ion batteries have been studied. Most of these studied showed severe loss of cycle performance at high Voltage. To improve performance of Iron based layered oxides, especially at high voltage region we need better understanding the redox reaction of Fe^{3+}/Fe^{4+} during sodium extraction. In this study, the oxidation state of Fe and phase transition of layered $NaFeO_2$ cathodes for sodium-ion batteries during charge were investigated. In situ X-ray Absorption revealed the Fe^{3+}/Fe^{4+}redox reaction doesn't shift the Fe K-edge to higher energy during Na intercalation. These result were reinforced with ex situ Near X-ray Edge Absorption result. Instead of Fe, the emerging of new peak on the pre-edge of the oxygen K-edge, indicating charge compensation of Oxygen during the whole Na extraction process.

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Boost Energy Storage Efficiency by using Ionic Liquids Mixtures – Experimental And Theoretical Insight

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Energy storage topic becomes a critical element for Smart Grids that are currently being implemented. One of the highest priorities in the European policy funding is focused on scientific and technological research accomplishments in the field of inventive energy storage solutions such as Electric Double-Layer capacitors (EDLCs). The capacitive performance of electrochemical devices is greatly affected by the ion concentration profile at the electrode/electrolyte interface. The application of ionic liquids (ILs) as electrolytes in order to achieve higher capacitive performance systems is crucial dependent on a deep understanding about IL structure−property relationships [1,2].

The formulation of ionic liquids mixtures become an important and alternative route to enhance the energy storage performance and simultaneous allow a deeper understanding about the microscopic mechanism that is governing the electrode-IL interfacial structure [3].

The differential capacitance enhancement using IL-IL mixtures was found to be tuned by a judicious choice of highly asymmetric anion $[B]_x$-anion $[C]_{1-x}$ mixture composition ($[A][B]_x[C]_{1-x}$, [A] represents the cation, [B], [C] each anion and x and (1 − x) represents the mole fraction of each IL). The results points to the existence of an optimal IL mixture composition and an electrode potential at which the differential capacitance of the mixture approximately 3 times boosted comparatively with their pure stating materials. The correlation between differential capacitance, potential of zero charge (pzc) and charge density curves vs. the mixture composition is presented and discussed.

In parallel, molecular dynamics (MD) simulations were performed in order to understand the interactions between different anions in the IL mixture.

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η-Metallopolymer (Poly[Ni(*Salpn*)] for Electrocatalytic Detection of the Dissolved Oxygen by Electroanalytical Method

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Currently, the oxygen reduction have been studied in the theoretical and practical in many biological processes and chemical synthesis. In this work has developed a novel electrochemical sensor based on nickel-salpn polymeric film modified electrode was constructed for determination of dissolved oxygen.

All voltammetric measurements were carried out in a 20 mL thermostatic glass cell containing three-electrodes: platinum electrode coated with a thin film of nickel–salen polymer as working electrode (surface area of 0.071 cm^2), a saturated calomel electrode (SCE) as the reference, and a platinum auxiliary electrode.

The film was prepared and electropolymerized at a platinum electrode in CH$_2$Cl$_2$/0.1 mol L^{-1} TBAP (deoxygenated solution) by cyclic voltammetry between 0.0 to 1.4 V vs. SCE.

The determination of dissolved oxygen was studied by cyclic voltammetry on a satured solution of oxygen, via bubbling 0.5 mol L^{-1} KCl solution with pure O$_2$ at room temperature for 30 min and dissolved oxygen in the aqueous solution was 9.7 mg L^{-1} calculated from its saturated solubility in this medium of the atmosferic air in the solution, observing the increase of current of peak cathodic, we can observe the peak potential of -0.234 V vs. SCE to the electrode unmodified, and -0.147 V for the modified electrode, this difference in reduction potential (0.087 V), shows the electrocatalytic performance metallopolymer (Figure 1A).

Figure 1B shows the cyclic voltammograms concerning the addition of sulphite in a potential range of -0.3 to 0.8 V vs. SCE, with successive additions gave the O$_2$ concentration between 3.95 to 9.7 mg L^{-1} KCl solution 0.5 mol L^{-1} (pH 4). According to the analytical curve it was possible to obtain a linear relationship between the cathode current value and the dissolved oxygen concentration, showing a linear range of 4.92 to 9.2 mg L^{-1} and a limit detection of 2.37 mg L^{-1} (r = 0.995, n = 9).

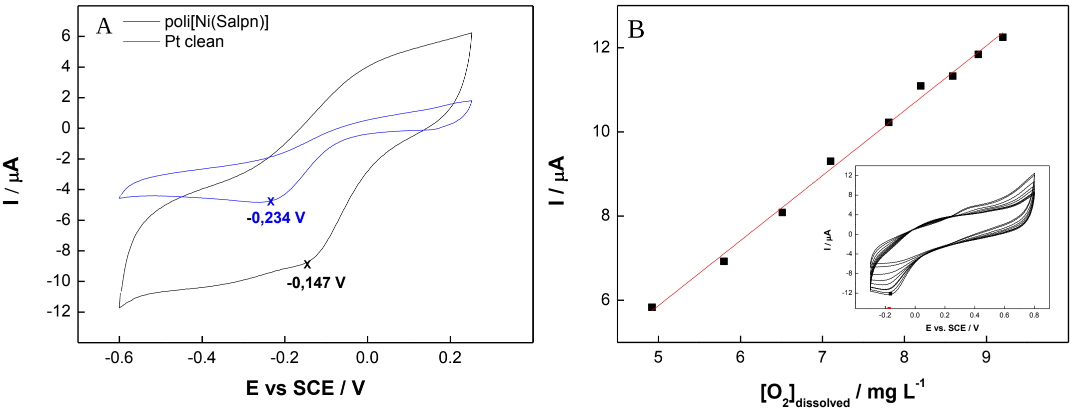

Figure 1- A) Cyclic voltammogram obtained for (blue line) unmodified platinum electrode (black line) electrode modified with poly [Ni (Salpn)] in the presence of 9.2 mg L^{-1} of dissolved oxygen in KCl 0.5 mol L^{-1} (v = 25 mV s^{-1}). B) Response sensor front different concentrations of dissolved oxygen (4.92 to 9.2 mg L^{-1}) (v=25 mV s^{-1}) in KCl 0.5 mol L^{-1}. Insert: voltammetric response of the sensor to different concentrations of dissolved.

Spectro-electrochemical Platform for *in situ* Dynamic Chemical Analysis of Catalytic Cascade Systems

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A 3D microfluidic device with a nano-plasmonic surface is established for the detection and quantification of a complex catalytic cascade reaction. This platform uses porous media to induce capillary flow to distribute microliter volumes of analytes to reaction and detection zones. This device can be used to study individual reactions, or as presented here, be used to fully characterize a multimodal catalytic cascade system. By using Surface Enhanced Raman Spectroscopy (SERS), *in situ* spectral imaging under dynamic flow conditions is possible. A multi-layered device that consists of separate zones for catalytic oxidation allows for optimization of channel design, flow properties, timing between reactions for increased product formation, and the encompassment of electrodes. Microfluidic technology is an ideal platform for cascade systems because control of the reaction variables, reaction rates, and isolation of reaction environments is integrated directly into the device.

A proof-of-concept reaction that will be studied is the electrochemical oxidation of glycerol ($C_3H_8O_3$) to carbon dioxide (CO_2). The oxidation reaction scheme is shown in Figure 1.

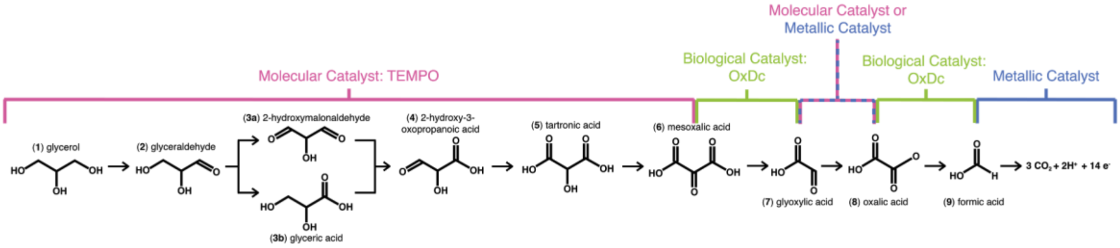

Figure 1: Multimodal catalytic cascade reaction scheme

As shown in Figure 1, the cascade reaction utilizes three catalyst modalities (molecular, biological, and metallic). The electro-oxidation of a large molecule, glycerol, to mesoxalic acid can be efficiently catalyzed by the small, organic oxidation catalyst TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl. TEMPO can oxidize oxygen-containing functional groups, but cannot break carbon-carbon bonds.[1] The enzyme oxalate decarboxylase (OxDC) will be used to break the C-C bonds of mesoxalic acid and oxalic acid.[2] The incorporation of a metallic-based catalyst will oxidize formic acid to CO_2 to gain the final electrons and complete the reaction.

This reaction scheme lends itself well to the engineering of a proof-of-concept design of a 3D porous media platform because it has the following challenges: (i) the complex electro-oxidation of glycerol to mesoxalic acid by a single catalyst, (ii) the immobilization of an enzyme onto a non-aqueous platform, (iii) the electrochemical control of specific portions of the cascade (reactions not catalyzed by OxDC), and (iv) the success of a complete cascade reaction that needs to completely oxidize a large, energetic molecule to CO_2. Due to the sensitivity of the SERS substrate, rapid data acquisition with strong spectral signal enhancement of analytes at low concentration will be shown.

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Electrolytic Regeneration of Granular Activated Carbon Saturated with Diclofenac

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Emerging pollutants in wastewater like diclofenac, represent a risk to the water bodies in which they are been spilled since conventional wastewater treatment plants are not able to degrade this compound. In addition to not being completely degraded, diclofenac can react with other compounds generating pollutants with higher toxicities, such as polycyclic aromatic hydrocarbons and heterocyclic compounds. Due to the large consumption of anti-inflamatories like diclofenac and its condition of recalcitrant organic compound, a progressive accumulation is being generated, causing its presence even in drinking water.

When diclofenac is adsorbed in to the activated carbon, it can be successfully removed from the water, however the problem get transferred from the liquid to the solid phase; additionally, the activated carbon regeneration involves a high cost thermal regeneration process, which implies high energy consumption, material losses and the release of contaminating gases. In this context, a promising technique that involves the coupling of the adsorption process and the subsequent electro-oxidation of the adsorbed diclofenac, was assessed at laboratory scale.

Samples of synthetic diclofenac solutions were passed through an electrolytic cell loaded with activated carbon in the cathodic compartment, the process was performed in a batch recirculation process to ensure saturation of the activated carbon with the pollutant; the determination of the optimal contact time by adsorption isotherms was performed. For the regeneration process, the electrolytic cell was polarized, producing the desorption of the contaminants and the subsequent oxidation in the BDD anode. Regeneration efficiencies up to 80% were achieved during the essays.

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The Barrier and Electrochemical Properties of CVD Graphene on Copper Substrate

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Growth of graphene using CVD method (so-called CVD graphene) on polycrystalline copper surface gives a possibility to obtain large-area, mainly one or two layers graphene coatings [1]. The results of many investigations indicate that graphene can provide a barrier substantially reduce the corrosion rate (e.g.[2,3]), however the tightness of real graphene coating is a fundamental feature of a barrier protection [4]. The experimental investigations of barrier properties of graphene layers included the development of methodical bases for characterization of obtained layers in the following working conditions: (i) as a barrier protection against corrosion and protection against processes leading to the loss of solderability (mainly the oxidation processes of copper substrate); (ii) as a barrier to the formation of intermetallic phases; (iii) as a part of the coupling which allows to bond graphene materials with other components.

The μ-Raman Spectroscopy (μ-RS) is very sensitive on the properties of graphene layers and this method enable the possibility to characterise the following properties: (i) number of layers of graphene coating; (ii) type and density of defects, (iii) deformation/stresses in graphene coating and (iv) doping charge [5]. Simultaneously, this method permits the determination of corrosion products and their changes during corrosion process [3], as also increase of intermetallic phases in some conditions during formation processes in soldered joint. The relatively large areas of sample can be analysed on the base of set of spectra from the small areas (about 1 μm in used experimental conditions). This allows the formulation of a statistical description, and a graphical representation of the distribution of a heterogeneity of graphene layers in micro-areas simultaneously with description of corrosion products during corrosion process. The surface topography and roughness of the different substrate were examined using atomic force microscopy (AFM, tapping mode). The examinations of the barrier properties in soldering processes were done using tin and tin-zinc alloys on the copper substrate covered by CVD graphene. The processes of the electrodeposition of Sn and Sn-Zn layers from citrate solutions on graphene/copper substrate were investigated and optimal parameters were determined. The barrier properties of selected layers in the formation processes of intermetallic phases were characterized in different conditions (in ambient, ageing (160ºC) and spreading (250ºC) temperatures) by Raman spectroscopy, X-ray diffractometry and cross-section microscopy analysis (SEM/EDS).

The obtained results indicate a strong influence of defects in CVD graphene materials (types, density), an important role of copper substrate preparation (topography, roughness) and corrosion products as well as an influence of electrodeposition conditions on the barrier properties of graphene layers (damages of graphene coatings by improper electrodeposition conditions). The multilayered graphene coatings (or multilayered areas of coating) have better anti-corrosion performance than a single layer.

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Effect of nanoparticle incorporation in silane-polymer composite coating on corrosion protection of Mg-Zn-Al alloy in aggressive media

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The electrochemical behavior of magnesium-aluminum-zinc alloy with composition Mg(93)Zn(1)Al(6) alloy is studied in acidic sulfuric acid and acidic sulfuric acid containing 3.5% NaCl aqueous electrolytes. Electrochemical techniques including D.C polarization and electrochemical impedance (EIS) measurements are used to characterize the behavior of the alloy in these electrolytes. The data indicated the direct dissolution of the alloy as evidenced from ICP measurements and surface examination after exposure to the corrosive media.

The alloy was treated with a silane-polymer coating that proved effective in protecting the surface against corrosion. The silane-polymer coating is further treated with metallic nanoparticles to improve its corrosion protection ability and film quality. The protecting film is composed of 1,2-bis(triethoxysilyl)ethanepoly(vinyl alcohol) hybrid (TESEPVA).

The hybrid film was applied to the alloy surface either by sequential spin-coating or layer-by-layer spin-coating. Surface examination of the alloy or film-coated alloy was performed before and after exposure to the corroding electrolyte. The techniques used are: field-emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray analysis, X-ray photoelectron spectroscopy (XPS) and surface enhanced Raman spectroscopy (SERS).

The film thickness and surface wettability were also determined with the film displaying relative increase in the hydrophobic character.

Phospholipid Surface Films for Doxorubicin Delivery: A Combined Electrochemical, Thermodynamic and Pharmaceutical Study

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New strategies in drug delivery involve the use of complex platforms, formed by functionalized liposomes, like drug carriers towards the target tissues. The stability of these lipidic vesicles is strongly dependent on the bilayer components and the interactions among them [1]. Moreover, the liposomes often include nanoparticles anchored to their surface, so the interactions with the metal can also affect the global stability of the drug carrier. These factors can also affect the drug-lipid interactions [2]. Doxorubicine (DOX) is an anti-cancer drug which has a high toxicity and a very low remaining time in blood. To prevent both problems new drug-delivery methods are being investigated, including the use of bioconjugated gold nanoparticles (AuNPs) as DOX carriers. The capability of AuNPs to induce local heating by the absorption of NIR radiation permits the release of DOX in the tumoral area.

In the present work, the thermodynamic analysis of the Langmuir's isotherms of mixed lipidic films has been performed, and the most energetically favorable formulation was then used to study the "in vitro" release process of DOX-loaded liposomal formulations . Simultaneusly to the pharmaceutical study, the electrochemical methodology is applied to analyze the stability of the lipidic films and their interactions with gold, by transferring the films on the Au(111) electrode and studying the coated electrode/electrolyte interface in the presence and in the absence of DOX.

The Langmuir's isotherms of films formed with variable proportions of di-myristoil phosphatidylcholine (DMPC), cholesterol and dodecyl ammonium bromide (DDAB) have been recorded. The thermodynamic analysis of the isotherms provides the optimal formulation that could be used in the liposomes. The interactions with the drug are considered by comparing the isotherms in the presence and in the absence of DOX in the subphase.

The Langmuir films have been transferred by the Langmuir-Shaeffer method to the surface of a gold Au(111) electrode, in an electrochemical cell. The stability of the film in the electrified interface is analyzed by the impedance method as a function of the potential.

The most stable lipidic composition inferred from the thermodynamic analysis has been used to formulate liposomes loading DOX . The in vitro" release kinetics of the drug from the carriers is studied. The different profiles of DOX released evidenced the presence of liposome surfaces functionalized with AuNP and the influence of local temperature on the drug release behavior.

On the other hand, the electrochemical study of DOX reduction on gold, either on bare Au (111) electrodes as on Au (111) electrode modified with the mixed Langmuir-Shaeffer film [3] has been performed. Under the experimental conditions used, the results suggest the absence of mass transport phenomena in both cases, especially when the Au (111) surface is modified with the lipidic layer. The results are compared and correlated with the results of the pharmaceutical study.

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Redox Activity of Sulphur-based Electrolytes in Supercapacitor Application

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Several forms of activated carbons have already been implemented and widely investigated as electrodes for electrochemical capacitors. Aqueous solutions based on inorganic salts demonstrated effective operating voltages around 1.6 V, and several interesting strategies have been furthermore implemented to improve these systems, including redox activity of the electrolyte.

This work is focused on the electrochemical performance of the activated carbon electrodes operating in various electrolytes containing sulphur-based species. Since sulphate (SO_4^{2-})-based aqueous solutions have already been widely investigated, this study will discuss the electrolytes with containing $S_2O_3^{\ 2-}$, SO_3^{2-} and S^{2-} anions and their interaction with a carbon electrode. The results obtained clearly indicated that sulphur plays an important role in the charge accumulation process and has an excellent redox chemistry. Dependently on the electrolyte pH, the ionic specimen might be easily reduced or oxidized and perfectly preserves the activated carbon surface against oxidation. Moreover, the affinity of sulphur to the carbon surface promotes a sulphur-carbon bonding and creates additional redox active site on the electrode surface.

A variety of electrochemical methods used in the study confirmed that a specific formulation of the electrolyte with sulphur-based redox shuttle might remarkably enhance the electrode capacitance (up to 300 F g^{-1}) and the operating voltage (up to 2.0 V). Moreover, *operando* Raman spectroscopy proved that sulphur-carbon bond is reversibly created while the charge transfer occurs. Furthermore, high energy density (ca. 26 Wh kg^{-1}) maintained at excellent power rates (1 kW kg^{-1}) has been preserved during 10 000 charge/discharge cycles with reversibility of 97%.

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The Nucleation and Insertion Dynamics in Lithium Intercalation Materials in 2D

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Phase separating materials such as lithium iron phosphate and lithiated graphite are widely used as electrode materials in batteries. Using phase-field modeling, the present work employs the general Cahn-Hilliard-Reaction (CHR) models based on nonequilibrium thermodynamics to study in 2D the nucleation in solid materials [1], nuclei stability and interactions during the process of lithium insertion. In the various geometries studied, the symmetry of nucleation is broken at low insertion rates, suggesting that previous models that assume certain symmetry conditions should be revisited. The merging of nuclei on the intra-particle and inter-particle level is due to both diffusion and surface reaction. Nuclei coarsening due to reaction is analytically understood by relating its growth rate with its equilibrium chemical potential and the applied overpotential via the regular perturbation method. It is also extended to anisotropic cases, which can be important in many solid materials. At higher currents, the system transitions to symmetric lithium insertion and phase separation. Eventually, high enough currents may lead to the suppression of phase separation in 2D depending on the size of the system. Such analysis extends further beyond the known reduction of the spinodal gap for the CHR model in 1D [2] and the 1D Allen-Cahn reaction (ACR) model [3] at high currents. The effects of elastic strain and surface wetting are also considered. The results reveal pathways of lithium redistribution within an ensemble of particles. The theoretical framework and simulation results of the models presented in this work have been verified in experiments [4]. Therefore, the present work serves as a basis to understand and extract useful electrochemical information from the 2D lithium concentration profiles obtained from experiments.

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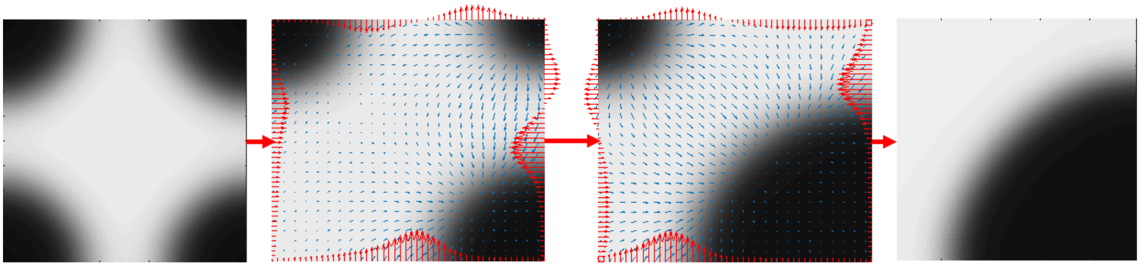

Degradation Mechanisms and Kinetics of Electrochemical Oxidation of Chlorinated Pollutant *p*-Chlorobenzoic Acid

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Water pollution from chlorinated aromatic compounds is of great concern due to their carcinogenic and toxic characteristics. Conventional physical-chemical and biological treatments demonstrate low removal efficiencies of these compounds. In this context, electrochemical advanced oxidation processes have emerged as a feasible alternative to mitigate aromatic pollutant fate. Electrochemical oxidation using anodes with high overpotential of oxygen evolution, such boron-doped diamond (BDD), allows *in situ* electrogeneration of hydroxyl radicals ($^{\bullet}$OH) by reaction (1).

$$H_2O + e^- \rightarrow {}^{\bullet}OH + H^+ \qquad (1)$$

The hydroxyl radical is a highly oxidant species that mineralizes the organic pollutants by non-selective attack. This study focuses on the oxidation of *p*-chlorobenzoic acid (PCBA), which is considered one of the most representative chlorinated aromatic compounds. The understanding of the degradation mechanisms are of high relevance in considering the application of electrochemical water treatment technologies as environmentally-friendly alternative.

In this research, the influence of the applied current density (j) and initial pollutant concentration on the overall performance of the electrochemical treatment was considered. Solutions of 1.9 mM of PCBA (corresponding to 100 ppm of total organic carbon (TOC)) at pH 6.5 and 0.5 M of Na_2SO_4 were treated from 16.6 mA cm^{-2} to 100 mA cm^{-2}. It was observed that the treatment time required to attain complete mineralization and PCB degradation decreases with the increase of j. However, the respective current efficiency decreases from 20 % to 8% which supposes an unnecessary increase of the energy consumption per order. Therefore, 66.6 mA cm^{-2} was defined as the optimum parameters that allows attaining complete mineralization after 360 min of treatment with maximum efficiency per cost.

The treatment of solutions containing PCBA from 20 ppm of TOC to 200 ppm of TOC illustrates the influence of the initial pollutant concentration on the electrochemical treatment performance. Higher mineralization current efficiencies were observed when the initial concentration was increased, because the superior organic load increases the number of organic events with $^{\bullet}$OH, therefore decreasing the relevance of parasitic reactions. Nevertheless, a decrease in the pseudo-first order rate constants was observed because as the initial PCBA concentration is increased, the greater amounts of by-products produced competes with PCBA for the $^{\bullet}$OH.

The degradation pathway of PCBA was defined from the identification of organic by-products (aromatic compounds and low molecular weight carboxylic acids) by HPLC. Four different aromatic intermediates have been identified along with several carboxylic acid by-products. The mass balance suggests that the remaining TOC at the end of the electrolysis corresponds mainly to carboxylic acids such oxalic acid. This results are of high relevance because they demonstrates not only the complete abatement of PCBA but also the removal of all aromatic by-products.

Acknowledgements: M. Lanzarini-Lopes acknowledges the Interdisciplinary Graduate Educational Research Traineeship – Solar Utilization Network fellowship form National Science Foundation (USA). This work was partially funded through the Nano-Enabled Water Treatment Technologies Nanosystems Engineering Research Center by the National Science Foundation (EEC-1449500).

Effects of Rinse Water pH on the Anti-Corrosion Properties of Trivalent Chromium Process (TCP) Conversion Coatings on AA2024-T3 Alloy

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Trivalent chromium process (TCP) conversion coatings are replacements for the historically-used chromate conversion coatings (CCC). These coatings are part of a multi-layer coating system that is typically used to protect aerospace aluminum alloys from corrosion when in service. Unfortunately, the anti-corrosion performance of TCP on Cu-rich Al alloys, like AA2024-T3, is inferior to that provided by CCC. Work is ongoing in our laboratory to better understand the coating chemistry and physical structure on this alloy as well as the early stage failure mechanisms. We are also studying how different post-treatments of the TCP coatings affect their anti-corrosion performance. In this presentation, we will report on how the final rinse water pH affects the coating structure and anti-corrosion performance. Two commercial TCP coatings were studied: Bonderite T5900 (Henkel) and 650 ChromitAL (SurTec). Both coatings were formed by immersion on degreased and deoxidized alloys. The final coating rinse (2 min immersion) was with 0.1 M phosphate buffer at pH values of 5, 6, 7 and 8. Aging effects (7-days in lab air) were also investigated. Electrochemical methods were used to evaluate the corrosion resistance of the coatings in naturally-aerated 0.5 M Na_2SO_4 + 0.05 M NaCl at room temperature. SEM/EDS and contact angle measurements were used to characterize the coatings. Preliminary results indicate that the maximum corrosion protection might be achieved at pH 6 (greater suppressed anodic polarization currents and more positive E_{pit}). Additionally, preliminary results indicate that the two conversion coatings perform differently after the pH rinse.

Electro-elution of Aurodicyanide Adsorbed on Granular Activated Carbon

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In the gold extraction industry, facilities using the activated carbon technology accounts for the majority of the gold production in the world. In this technology, the adsorption and desorption processes are the essential unit operations to concentrate the diluted gold solutions.

In the desorption stage, the aurodicyanide is eluted from the activated carbon typically by the Zadra and AARL processes, or its variations. In these processes, temperatures higher than 100 ºC and pressures up to 500 kPa are used, during 8 to 72 hours per batch. Also, a high concentration of NaCN (up to 5%) and NaOH (up to 2.5%) are added to the elution solution.

To improve the elution process, an electro-elution procedure has been developed in this investigation. In the proposed process the desorption is enhanced by the electric current passing through the system, operating at atmospheric pressure and room temperature. This alternative avoids the addition of cyanide and have the possibility of the simultaneous activated carbon regeneration during the elution process, making it an environmentally friendly and less risky process. Also, the electro-deposition of the metallic gold is achieved at the cathode of the electrolytic cell where the elution occurs, favoring the intensification of the process, making it possible to integrate the two processes into a single equipment.

The studies in the present investigation confirm the elution of the gold loaded in the activated carbon up to 70% with the simultaneous electrodeposition at the cathode of 98% of the eluted gold using a current density of 24 mA cm^{-2} for 4 hours.

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The authors would like to thank Colciencias and the Universidad del Valle for funding the doctoral studies of Christian E. Alvarez-Pugliese, the scholarship of Jovannis Commas-Cabrales and the project: "Recuperación de oro y tratamiento de aguas residuales en la industria aurífera de la región pacífico Colombiana 1106-669-45250". Finally, the authors would like to thank Angela Victoria Elvira Marulanda and Estefannya Carvajal Cruz for their support on the preliminary laboratory studies of this investigation.

Carbon nanotubes as conductive additives in aqueous processing of NMC532 electrode

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Abstract

The Li-ion battery (LIB) market has been expanding in recent years due to the growing market of electronics and development of electric vehicles (EVs) [1]. Further improvement of energy density and reduction of cost is required for EVs to compete with internal combustion engines. Manufacturing cost reduction is of particular critical importance to meet the U.S. DOE Vehicle Technologies Office (VTO) ultimate cost target of $125/kWh. Lithium transition metal oxides are the state-of-the-art cathode active materials providing capacity. Inactive materials such as carbon black are used for electronic conductivity and polymers are used for particle cohesion and current-collector adhesion purposes. Polyvinylidene difluoride (PVDF) is the most widely used binder for positive composite electrodes, which is dissolved in the volatile, expensive, and toxic NMP solvent during electrode manufacturing. Therefore, efforts have been made to study alternative binder/solvent systems, preferably for aqueous electrode formulations. It has been shown that processing cost can be decreased significantly when water-based manufacturing is used in conjunction with thick electrode designs [2].

This study investigates the processing and performance associated with aqueous processing of NMC cathodes using different conductive additives. It was found that carbon nanotubes (CNTs) can be uniformly distributed on the surface of NMC particles (see Fig 1b), which forms a good electronic conducting network. In contrast, carbon black does not cover the NMC surface well as shown in Fig 1a. A detailed discussion on electrochemical performance, as well as correlation of performance to processing parameters and electrode structure, will be given.

Acknowledgement

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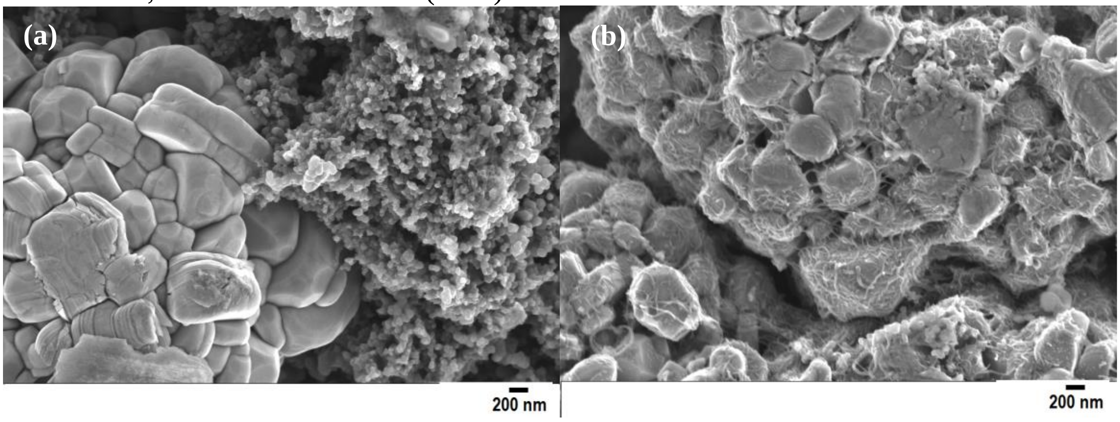

Figure 1. SEM images of NMC composite electrodes using (a) carbon black and (b) carbon nanotubes as conductive additives.

Remediation of petroleum from contaminated soil by electrokinetic, Fenton and phytoremediation technology

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During the recent years, an increasing interest in the remediation of soil and water with petroleum has been attained. The search for novel sources of water has become a topic of the major interest, in particular in countries which serious problems of permanent or stationary lack of water. The objective of this study was to evaluate the capacity to decontaminate polluted soils with PAH and TPH using a combination of three: Electrokinetic (EK) Remediation, Fenton and phytoremediation after that, the soil toxicity was evaluated respects its capacity for plating sunflower seeds (helianthus annuus). To do this, long tests in laboratory scale were performed in order to comprehend the effect and mechanisms in the soil in more realistic conditions. In this work, experiments were performed by using 4 kg of real soil, as samples, and these were collected at a gas station in the city of Natal (Northwest of Brazil). The soil was spiked with petroleum and metals until attaining an initial pollutant concentration of 10000 mg per kg of soil. Through the experiments, the electrical current, the electroosmotic volume removed from the cathodic collector, pH, conductivity, PAHs concentration and TPHs amounts were monitored to determine the efficacy of the combined treatments. The experiments were performed of 1.0 V cm^{-1} by galvanostatic conditions using MINIPA-33055M power supply during 20 days. Graphite electrodes were used as anode and cathode. Water, Dodecyl sulfate sodium or H_2O_2(10%) was added in catholyte reservoir daily to maintain the moisture level. Five experiments were performed of EK, Fenton, phytoremediation, Electroremediation-Fenton and electro-phytoremediation. Therefore, it is evident that a combined technology of electrokinetic remediation and Fenton reaction is capable of simultaneously removing and degrading of PAHs and TPH in polluted soil. Moreover, this work the percentage of germination to seed was considered as the appearance of a green shoot of foliage above the soil. The germination percentage of the sunflower for Fenton less when comparing, but better results were obtained to EK and phytoremediation because the toxicity level of the soil.

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Low-Cost Paper-Based Electrochemical Device for Metal Analysis in Urine

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Analytical methods for monitoring the concentration of metallic cations in human fluids are very important due to the toxicity of these species for humans, like cadmium and lead. However, other cations, such as zinc and copper, are important micronutrients and their lack may cause metabolic issues. [1, 2]. Urine is an interesting matrix to evaluate the levels of these species in the body since it is a non-invasive fluid that can be used for diagnostic purposes [2]. In this work, a paper-based electrochemical cell was used to analyse zinc in human urine. The device was built using filter paper patterned with printed wax in order to generate hydrophobic barriers to confine the analysed solutions in the unprinted area. The pseudo reference electrode was painted on the paper surface using a conductive silver ink and two leads of pencil graphite (Pentel 2B, 0.7mm) were attached on paper to be used as counter and working electrodes. The standard addition method was carried out to quantify zinc in urine using 0.1 mol L^{-1} acetate buffer solution (pH 4.5) as electrolyte. One ppm of Bi^{3+} was spiked to all solutions to plate in-situ a bismuth film on the working electrode surface to achieve better sensibility and peak resolution. The urine samples were centrifuged before the analysis to remove proteins and solid materials dispersed. The stripping analysis of zinc was performed adding 200 µL of the buffer solution to the electrochemical cell followed by the addition of 50 µL of urine and successive additions of Zn^{2+} standard solution. During the deposition step, sound waves generated by a speaker were used to improve the mass transport of the analyte using a frequency of 1000 Hz. The quantification of zinc in urine at normal levels (ca. 2 µmol L^{-1} [3]) was possible using the proposed device. The Fig. 1 shows the typical behaviour of the standard addition curve obtained where a Zn^{2+} concentration of 6.49 µmol L^{-1} was obtained. As well as for zinc analysis, the proposed method shows a great potential for cadmium and lead analysis in urine.

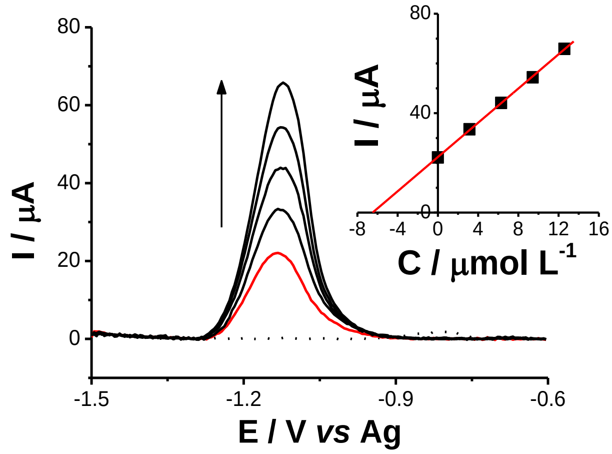

Fig 1. Anodic stripping square wave voltammograms recorded with the paper-based device in 0.1 mol L^{-1} acetate buffer solution (pH 4.5) containing 1 ppm of Bi^{3+} (- -) and after addition of the urine sample (—) and successive additions of the Zn^{2+} standard solution (—). Square wave voltammetry parameters: Amp. = 30 mV, Freq. = 60Hz, step = 5 mV. Accumulation parameters: E = -1.6 V vs Ag during 450s. Inset shows the standard addition curve obtained.

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Functionalised Ionic Liquids as Novel Electroactive Materials

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Ionic liquids can be made intrinsically electroactive by modifying the structure of its ionic constituents with various redox moieties. These phases, which can be liquid around room temperature, provide new opportunities to study and exploit electron transfer reactions as they can behave differently from conventional solute-in-solvent systems. Our research aims at studying the structure-properties relationships of electroactive ionic liquids and orient their design to develop novel redox systems in energy storage devices.

In this contribution, we will demonstrate several design and synthetic strategies to the modification of imidazolium cations and bis(trifluoromethane)sulfonimide anions with ferrocenyl moieties. The electron transfer kinetics and transport properties of the modified ions were studied in diluted solutions of the ionic liquids. Lower heterogeneous rate constants were attributed to factors such as size, ion asymmetry and a higher internal reorganization energy imparted by the addition of a large charged substituent on the ferrocenyl unit. This latter effect is more important in the case of the ferrocenylsulfonyl-(trifluoromethylsulfonyl)-imide (FcNTf) due to the permanent substituent negative charge which provides a zwitterion upon oxidation of the ferrocenyl. A dramatic change in electrochemical behaviour of FcNTf-based ionic liquids is observed for highly concentrated solutions and for the pure liquid phase. Under such conditions, the oxidized zwitterion deposits on the electrode surface as a film which can be removed by reduction. We will reveal that this property, combined with other properties inherent to the nature of ionic liquids, make electroactive ionic liquids relevant for a use as electrolytes in several redox devices. Examples will be provided on energy storage devices like lithium-ion batteries and supercapacitors as well as for self-bleaching electrochromic devices.

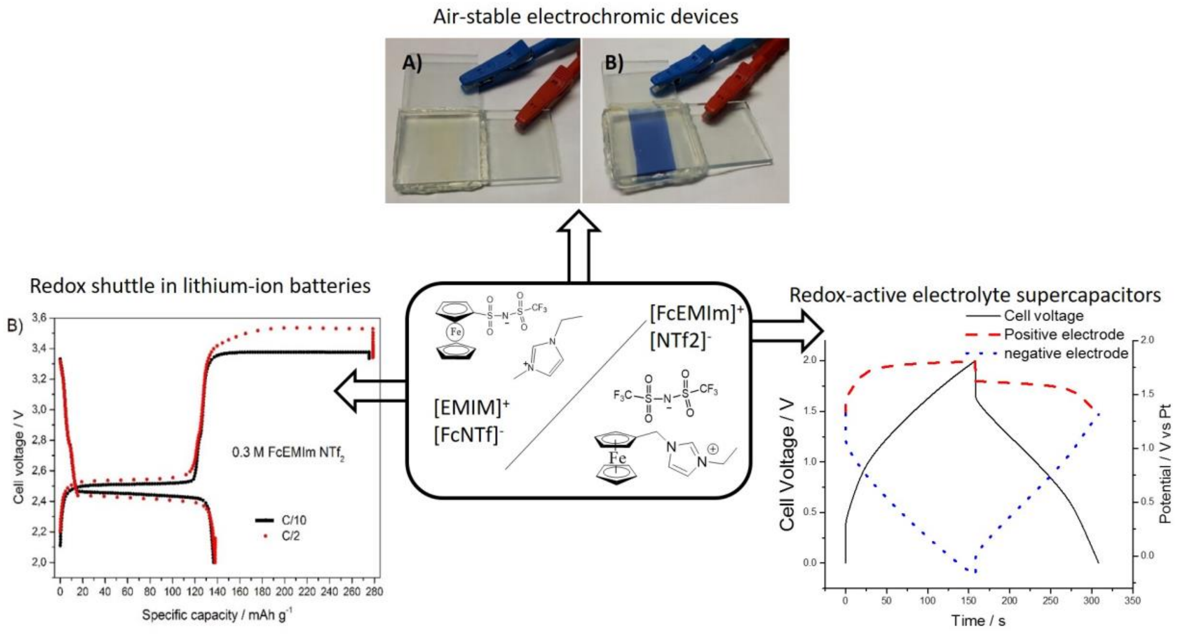

Figure 1 – Ferrocenyl-based electroactive ionic liquids and application examples

Lipidic Cubic Phase Nanoparticles – Cubosomes for Improved Efficiency of Drug Delivery to Cancer Cells

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Bicontinuous lipidic cubic phases (LCP) exhibit a combination of material properties that makes them highly interesting for various biomaterial applications: they are non-toxic, biodegradable, optically transparent, thermodynamically stable in excess water, and can incorporate active molecules of virtually any polarity. An interesting property of cubic phases is also their ability to disperse into nanoparticles - cubosomes. Cubosomes are discrete, sub micron, nanostructured particles of bicontinuous cubic liquid crystalline phase that possess the same microstructure as the parent cubic phase but have much larger specific surface area and their dispersions have much lower viscosity than the bulk cubic phase**.** The structure and dynamics of lipidic mesophases, and their interactions with guest molecules can be tailored by applying additives, thereby achieving novel materials with improved functions for drug delivery. [1, 2] By developing of the tailored LCNP incorporating an anti-cancer drug, it may be possible to target the delivery of drugs to the site of disease and reducing unwanted side effects.

Doxorubicin (DOX), a model drug that contains an amine group and a hydrophobic part, was loaded into the cubic phase and cubosomes. The size and morphology of the prepared nanoparticles were characterized using dynamic light scattering and cryo-transmission electron microscopy. The inner cubic structure of the prepared materials was confirmed by SAXS. SAXS and DLS results demonstrate that the introduction of DOX does not significantly modify the inner structure of the cubosome, as well as their size and charge. The pH-dependent drug release profiles, evaluated by voltammetry, demonstrated the ability to trigger the release of the drug from the cubosome carrier to the environment of the cancer cells, where pH is lower. The anticancer effect of DOX loaded cubosome on the KB and glioblastoma T98G cell lines were found to be highly efficient and allowed employing lower concentration of DOX to inhibit the proliferation of cancer cells than those of free DOX. To provide selective targeting, folic acid (FA) having affinity to receptors on cancers cells was attached to the cubosome. KB cells, were used as model cancer cells since they express high levels of folate receptors. Cancer cells treated with DOX-loaded cubosomes imaged by confocal microscopy showed increased membrane affinity. Folate attached to cubosome was found to speed the cubosomes uptake as a result of receptor–ligand interactions.

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Simulation-Based Degradation Assessment of Dynamic Load Cycles for Lithium-Ion Batteries

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The insufficient lifetime of lithium-ion batteries is one of the major cost driver for mobile applications. The battery pack in vehicles is one of the most expensive single components that practically must be excluded from premature replacement (i.e., before the life span of the other components end). Battery degradation is a complex physicochemical process that strongly depends on operating condition and environment.

We present a simulation-based analysis of lithium-ion battery degradation during operation with a standard PHEV test cycle. We use detailed multiphysics (extended Newman-type) cell models that allow the assessment of local electrochemical potential, species and temperature distributions as driving forces for degradation, including solid electrolyte interphase (SEI) formation [1]. Fig. 1 shows an exemplary test cycle and the predicted resulting spatially-averaged SEI formation rate. We apply a time-upscaling approach to extrapolate the degradation analysis over long time scales, keeping physical accuracy while allowing end-of-life assessment [2].

Results are presented for lithium-ion battery cells with graphite/LFP chemistry. The behavior of these cells in terms of degradation propensity, performance, state of charge and other internal states is predicted during long-term cycling. State of health (SOH) is quantified as capacity fade and internal resistance increase as function of operation time.

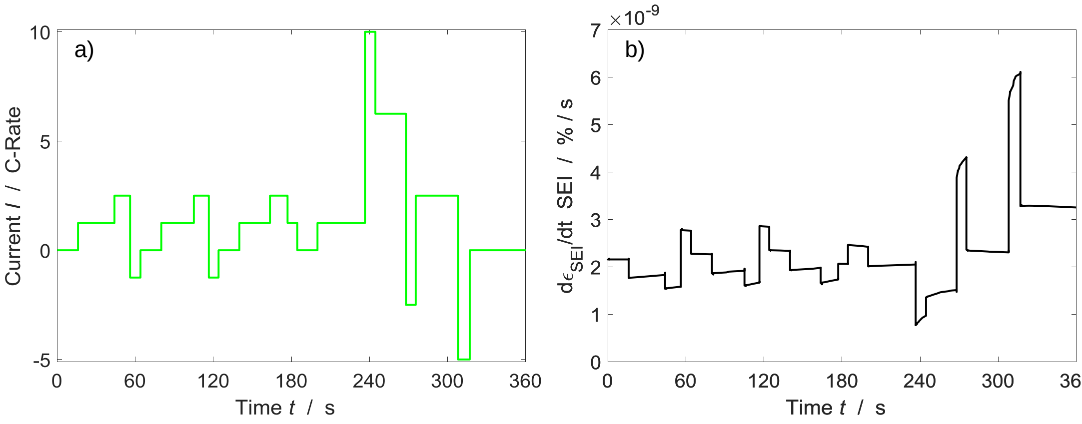

Figure 1: (a) Standard test cycle ISO 12405 (*I* > 0 discharge / *I* < 0 charge) and (b) the related spatially averaged SEI formation rate (in vol.-% SEI per second).

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Tuning Redox Potentials via Steric Crowding: Design of Stable Redox Shuttles to Prevent Overcharging in Lithium Ion Batteries

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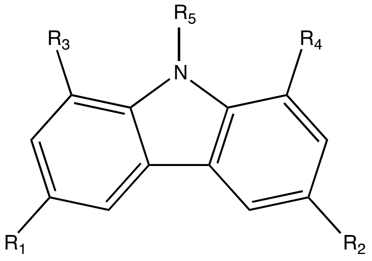
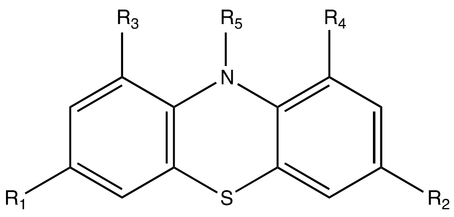
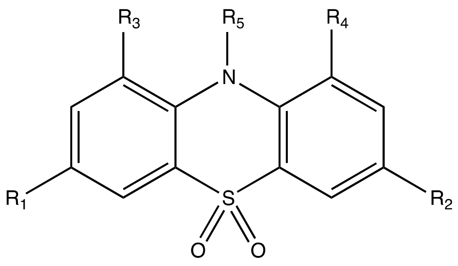
Recent headlines have served to highlight both real and perceived safety issues with lithium ion battery (LIB) technology. One particularly prevalent concern is that of overcharging, which can lead to voltage spikes, gas evolution, and fires in the absence of appropriate safety measures. In general, overcharging can be prevented by employing a battery management system (BMS) that continually monitors the state of charge (SOC) of each individual cell. However, because the cost and complexity of effective BMS hardware and software can be prohibitive, numerous groups have explored the use of “redox shuttles”. These materials are soluble electrolyte additives that display a chemically reversible oxidation at very high potentials (> 4 V vs. Li+/Li). Unfortunately, many promising shuttle candidates possess limited stability (particularly in the oxidized state) and last for only a few charge/discharge cycles.

We have exploited the use of steric factors to prepare a series of carbazoles and phenothiazines that undergo reversible 1-electron oxidation at very positive potentials without creating an electron deficient ring system that would be susceptible to degradation. Examples of these compounds exhibit very well behaved voltammetry, with oxidation potentials ranging from 4.02 to 4.53 V vs. Li+/Li. We have also identified and employed some key substitution patterns that help to achieve the desired results.







Molecular modeling results, synthesis, and electrochemistry will be described. Preliminary data from coin cell testing will also be presented.

Organotypic Culture Models for Predictive Toxicology

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Regulatory agencies face the daunting task of determining whether any of the tens of thousands of commonly used chemicals pose a risk to human health and the environment. The prevailing environmental toxicology paradigm of the past forty years has relied on guideline animal studies that are expensive, pose troubling ethical questions, and are difficult to relate directly to human health hazards due to inter-species discordance. To circumvent theses problems, we use organotypic culture models (OCMs) as experimentally accessible systems of intermediate complexity to advance predictive toxicology. Integrating these OCMs with microphysiometry methods such as electrochemical detection of metabolites creates an amenable and affordable medium- to high-throughput toxicity screening model.

Using multianalyte microphysiometry assays, we can determine both the acute and chronic responses of multiple cell lines to exposures to drugs and other consumer-based chemicals. Our approach has the advantage of providing quantitative information regarding a variety of cellular activities, specifically those centered on cellular bioenergetics based on metabolism, mitochondria function and membrane transport, protein translation, and immune response, and hence can provide a new comprehensive approach to absorption, distribution metabolism, excretion and toxicological profiles.

In our new microfluidic cell-based assays, cells are exposed to low levels of environmental toxicants, ranging from common widespread toxins, like heavy metals and organic pesticides, to more exotic and extreme chemical and biochemical toxins. As these toxins affect the cell's metabolism, the cells respond by changing their consumption of oxygen and glucose and their production of acid and lactate, which can be measured utilizing electrochemical methods and ultramicroelectrodes built into the microwells. After exposing ~100,000 cells to toxin for ~2-4 minutes, we can differentiate changes in cellular bioenergetics between a wide variety of chemicals, drugs, and toxins. By repeating the measurement every 2 minutes for hours to days, we can track the changes in metabolic and signaling activity associated with toxin-induced shifts in cellular homeostasis. By combining all of the information contained in the four-analyte "biosignature" we can observe the metabolic pathway shifting from aerobic to anaerobic metabolism, the depletion of internal energy stores, and the dynamic decoupling of metabolic parameters.

We also focus on the engineering challenges that must be met before OCMs could be used for routine medium throughput screening and are developing self-contained OCM control modules that are reliable, compact and inexpensive. We believe that this approach can be applied to the more general problem of assessing the toxicology of consumer products, industrial chemicals, environmental toxins, and pharmaceuticals.

Growth kinetics and physicochemical characterization of Hf-Nb anodic mixed oxides

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In last decades scientists efforts have been devoted to find new materials to replace SiO_2 as dielectric in micro and nanoelectronics devices. Among transitional metal oxides, HfO_2 is nowadays one of the most suitable materials due to their peculiar features, such as large band gap (5.1-6.1 eV), high dielectric constant (20-25), low leakage current and thermal stability with Si [1]. For electronics applications, uniform, flaw-free and smooth oxides are necessary, joined with a detailed understanding of chemical and physical properties as a function of the fabrication conditions. Anodizing is a low-cost electrochemical technique which allows to grow barrier-type oxides on valve metals (Hf, Nb, Ta, Ti etc.) surface whose structure, morphology, composition and thickness can be easily tailored by controlling the process parameters. Furthermore, by means anodizing it is possible to prepare mixed oxides, starting from metallic alloys substrates. In this frame, recently it was reported that alloying low amounts of Nb to Hf substrate leads to anodic films with higher dielectric constant with respect to that of pure HfO_2 [2]. In order to properly change anodizing conditions to obtain suitable oxides features, a study about growth kinetics of Hf-Nb mixed anodic films is needed, since amorphous-crystalline transition during the oxide growth was reported in literature for similar anodic films, with consequent detrimental effects on oxides properties [3]. In fact, crystalline regions can enable oxygen evolution inside the anodic film during the growth leading to internal cracks or to film breakdown [4].

This work is aimed to study the changes of oxides features during anodic films growth of sputtering-deposited Hf-Nb alloys. Mixed oxides were prepared by anodizing alloys with different Nb content (from 4at.% to 76at.% of Nb) in neutral electrolyte with different growth rates and up to different formation voltages. Morphological and structural features were analyzed by *ex-situ* X-Ray Diffraction, Glow Discharge Optical Emission Spectroscopy, Rutherford Backscattering, Transmission and Scanning Electron Microscopy. An amorphous-crystalline transition was detected during the growth of anodic film on Hf-4at.%Nb with a peculiar double layer structure including a thin amorphous outer layer and a crystalline inner layer. Nb-rich anodic oxides was resulted to be amorphous and no oxygen evolution was detected during the film growth. Photoelectrochemical investigation was carried out in order to study oxides solid state properties such as band gap and flat band potential as a function of oxide composition and oxide thickness. In order to estimate dielectric constant of anodic oxides, differential capacitance and impedance measurements were carried out for all the specimens.

Occurrence of sub-band gap optical transitions was detected, which has been correlated to structural defects in the anodic films (namely oxygen vacancies), whose presence can affect the performances of MOS devices employing anodic oxides as dielectric layers.

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Metal and metal oxide interactions and their catalytic consequences

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Abstract Many industrial catalysts are composed of metal particles supported on metal oxides (MMO). It is known that the catalytic activity of MMO materials is governed by metal and metal oxide interactions (MMOI), but how to optimize MMO systems via manipulation of MMOI remains unclear, due primarily to the ambiguous nature of MMOI. Herein, we develop a Pt/NbO_x/C system with tunable structural and electronic properties via a modified arc plasma deposition method. We unravel the nature of MMOI by characterizing this system under reactive conditions utilizing combined electrochemical, microscopy, and *in situ* spectroscopy. We show that Pt interacts with the Nb in unsaturated NbO_x owing to the oxygen deficiency in the MMO interface; whereas Pt interacts with the O in nearly saturated NbO_x, and further interacts with Nb when the oxygen atoms penetrate into the Pt cluster at elevated potentials (**Figure 1**). While the Pt-Nb interactions do not benefit the inherent activity of Pt toward oxygen reduction reaction (ORR), the Pt-O interactions improve the ORR activity by shortening the Pt-Pt bond distance. Pt donates electrons to NbO_x in both Pt-Nb and Pt-O cases. The resultant electron-deficiency stabilizes low-coordinated Pt sites, hereby stabilizing small Pt particles. This determines the two characteristic features of MMO systems: dispersion of small metal particles and high catalytic durability. These findings contribute to our understandings of MMO catalytic systems.

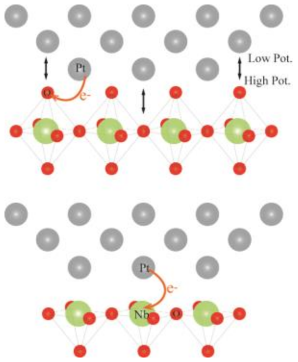

Figure 1. Pt interacts with the Nb in unsaturated NbO_x; whereas it interacts with the O in saturated NbO_x, and further interacts with Nb when the oxygen atoms penetrate into the Pt cluster at elevated potentials.

ACKNOWLEDGEMENT

The authors thank Ford Motor *Co.* for a University Research Program Award. Use of the synchrotron facilities at the National Synchrotron Light Source, beamlines X19A and X3B at Brookhaven National Laboratory, Upton, NY is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, former under Contract No. DE-AC02-98CH10886. This publication was made possible by the Center for Synchrotron Biosciences grant P30-EB-009998, from the National Institute of Biomedical Imaging and Bioengineering. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. Use of Beamline 2-2 at SSRL was partially supported by the National Synchrotron Light Source II, Brookhaven National Laboratory, under U.S. Department of Energy Contract No. DE-SC0012704.

In situ kinetics of the dezincification of Cu-Zn alloys: Uncovering the effect of phase structure and composition

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The precise mechanism of dezincification of Cu-Zn alloys remains an open question with several theories in vogue. These theories may be broadly categorized as either involving the preferential dissolution of Zn [1,2] or the dissolution - redepositon of Cu [3,4]. Each of these theories depict a completely different atom transport mechanism and electrochemical reaction process. Further, the effect of the different metallurgical structures, α and β', on the dezincification behavior have not been clearly identified.

In this work, an *in situ* technique, *atomic emission spectroelectrochemistry* (AESEC), was used to quantitatively measure the kinetics of the elementary reactions during the anodic dissolution of Cu-Zn alloys in naturally aerated soft tap water [5,6]. As a function of time, we measure the dissolution rates of the Zn and Cu, the quantity of excess Cu in the dezincification layer, and the quantity and nature of corrosion product films on the surface. This type of kinetic analysis yields a vision of the entire reaction process. Kinetic profiles obtained during anodic dissolution are compared with elemental polarization curves, where the polarization curve of the material is decomposed into partial Zn and Cu elementary currents, to provide further insight into the electrochemical kinetics of the overall process.

The fate of Cu and Zn in tap water was determined based on a mass / charge balance and X-ray diffraction and Raman study of the scales: Cu^{2+} and Zn^{2+} were the predominant soluble species while the scale was primarily composed of Cu_2O with a trivial quantity of Zn(II). In all cases, Cu_2O is preferentially formed at lower current, and its formation slowed at higher current; Zn^{2+} follows a constant increase with the increase of applied current. The dissolution mechanism of α and β' phase were very different: in an α brass with the Zn content less than 20 wt%, a simultaneous oxidization of Cu and Zn into Cu_2O, Cu^{2+} and Zn^{2+} dominates; with the Zn content increases to 33 wt%, the formation of Cu^{2+} is slowed, resulting in a two stage dissolution: a first stage where only Cu_2O and Zn^{2+} was formed, and a second stage where Cu^{2+} release initiates. In β' brass, however, only the formation of Cu_2O and Zn^{2+} was observed, with no significant Cu^{2+} release observed. The coexistence of α and β' in the dual phase alloy, prolonged the first stage mainly due to its preferential oxidation, and suppressed the subsequent stage of Cu^{2+} release as well.

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New Families of Single-Ion Block Copolymer Electrolytes based on Poly(Ethylene Oxide) and Methacrylic Sulfonamide for Lithium Batteries

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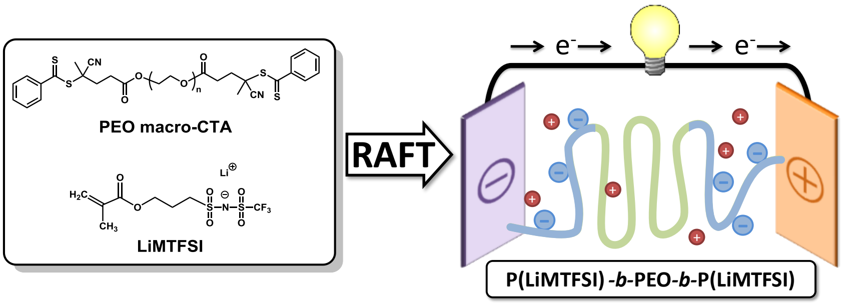
Polymer electrolytes have been proposed as a replacement for conventional liquid electrolytes in next-generation lithium-based batteries, mainly because of their intrinsic enhanced safety and peculiar chemical structure that can be tailored as desired to display unique properties such as lithium-ion transference number (t^+) approaching unity. This new class of materials, namely Single-Ion Conductors, has attracted increasing interest in recent years. Nevertheless, practical application of polymer electrolytes is still limited mainly by low ionic conductivity (σ), which is far below 10^{-5} S cm^{-1} at 25 °C.



Herein, the preparation and characterization of new families of single-ion conducting copolymers based on the specifically designed lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide (LiMTFSI) anionic monomer is described.[1,2] RAFT polymerization was employed to prepare well-defined anionic di- and tri-block copolymers comprising poly(LiMTFSI) and poly(ethylene oxide) blocks.[1] The effect of the macromolecular architecture and molecular weight on thermal and ionic conduction properties is thoroughly discussed. Block copolymers were semi crystalline, with a single glass transition temperature (T_g) due to the miscibility of the amorphous regions of both the blocks. T_g, ranging from –55 to 7 °C, as well as degree of crystallinity (X_c, ranging from 51 to 0%) were both composition dependent. Block copolymers showed very high σ as compared to previous examples (up to ≈ 10^{-4} S cm^{-1} at 70 °C) combined with and impressive $t^+ \approx 0.91$, and wide 4.5 V electrochemical stability. In addition to these promising features, solid polymer electrolytes were successfully tested in $LiFePO_4$/Li cell prototypes at different temperatures providing long lifetime up to 300 cycles, and outstanding rate performance up to C/2 (≈100 mAh g^{-1}).

Acknowledgements

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Electrodeposition of Multi-segment Metallic Nanowires and their Self-Assembling Applications

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Metals are known to have unique thermal, electrical, mechanical, and catalytic properties. Thus, metallic nanowires are promising materials for a variety of applications such as conductive materials for electronics and photonics, electrodes for sensors/biosensors or supercapacitors, as well as connecting and conductive materials for energy conversion and storage devices.[1] Whereas many different methods have been utilized to synthesize metallic nanowires with different characteristics, including chemical reduction, lithography, electrophoresis, VLS growth and self-assembly, electrodeposition has been shown to be an excellent nanowire fabrication method to grow single composition or multi-composition nanowires. Even though electrodeposition is a well-established method, there are still several challenges that need to be overcome to use this technique for the fabrication of more complex structures, such as multi-segment nanowires, to satisfy complex device applications. These challenges are mainly related to the control of electrochemical process and its relation to the structure evolution of the nanowires. In this study, pure tin (Sn) nanowires and multi-segment nanowires such as tin-nickel-tin (Sn-Ni-Sn) and tin-nickel-gold-tin (Sn-Ni-Au-Sn) nanowires were successfully synthesized through a template assisted electroplating method [2], as shown in Figure 1. The porous polycarbonate membrane with nanosized pores was used as a template. One side of the membrane was coated with a layer of silver (Ag) by thermal evaporation in order to seal the bottom of the membrane and form an electrical conductive layer. The nanopores were filled by Sn electrolyte and nanowires grew along the pores in template. For multi-segment nanowires, the electrolyte was changed in sequence to obtain Sn-Ni-Sn or Sn-Ni-Au-Sn nanowires. During the electroplating process, the electrodeposition density was controlled depending on the type of metals electroplated. The length of each segment was controlled by different electrodeposition time. After synthesizing the nanowires, the PC template was dissolved in dichloromethane and the nanowires were released into the solution. Followed by dichloromethane and ethanol cleaning, respectively, the nanowires were stored in the ethanol at room temperature. These multi-segment nanowires with two solder ends can be connected into 2D or 3D structure by using self-assembly method, such as magnetic field assisted assembly.[3] 2D ordered patterns on Si/SiO_2 substrate were fabricated by lithography, and then the nanowires were assembled and soldered onto the ordered electrodes to form effective electrical and thermal connection. These ordered 2D or 3D structures can find various applications such as sensors/biosensors or phase change materials (PCMs).

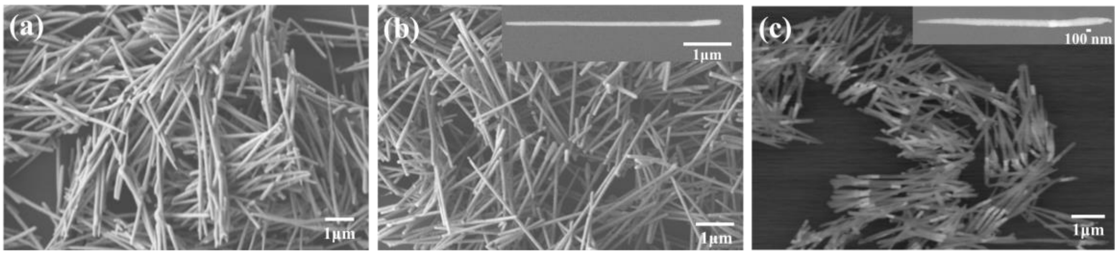

Figure 1. SEM images of Sn based nanowires: (a) pure Sn nanowires; (b) Sn-Ni-Sn nanowires; and (c) Sn-Ni-Au-Sn nanowires.

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Investigation of Cyanoacrylate Adhesive Bond Curing and Durability using Electrochemical Impedance Spectroscopy and Chronoamperometry

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Cyanoacrylate (CA) polymerisation is normally triggered by traces of basic substances at the adhesive/substrate interface resulting in rapid formation of large molecular weight polymers. However there are some disadvantages, for instance, increasing the bond gap from 10 microns ("zero gap bond") to 100 microns can increase bond fixture time from a few seconds up to several minutes, sometimes limiting their service capabilities. The aim of this work is to use Electrochemical Impedance Spectroscopy (EIS) and other surface analytical and chemical laboratory techniques to gain improved understanding of the processes responsible for performance limitations of such adhesives.

EIS will be employed to provide insights into the rates and mechanisms of the interfacial CA polymerisation process, which are known to be independent of bulk polymerisation processes. In addition examination of the time-dependent and spatial behaviour of EIS data, in conjunction with a mathematical model based on the diffusion of monomeric and/or polymeric species through the adhesive volume, will aid our understanding of the polymerisation processes occurring in various regions of the adhesive bond, including the edge and the bulk material. By studying the effects of chemical and physical variations, fundamental questions regarding the degradation of adhesive joints by environmental stress will be addressed, thereby enhancing our knowledge of the hydrolytic stability of the CA adhesive bond.

Further research involved the use of Chronoamperometry to investigate the adsorption effect of various additives in CA formulations. By using Ferrocene as probe the electrochemical behaviour of CA adhesives was characterised and compared to model solvents such as Ethylcyanoacetate,

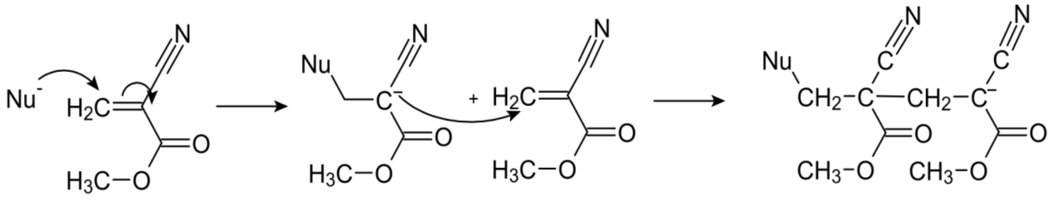

Fig.1. Reaction *Mechanism for the polymerisation of Ethyl Cyanoacrylate*

Boron Doped Diamond screen printed electrodes: morphological and electrochemical characterization

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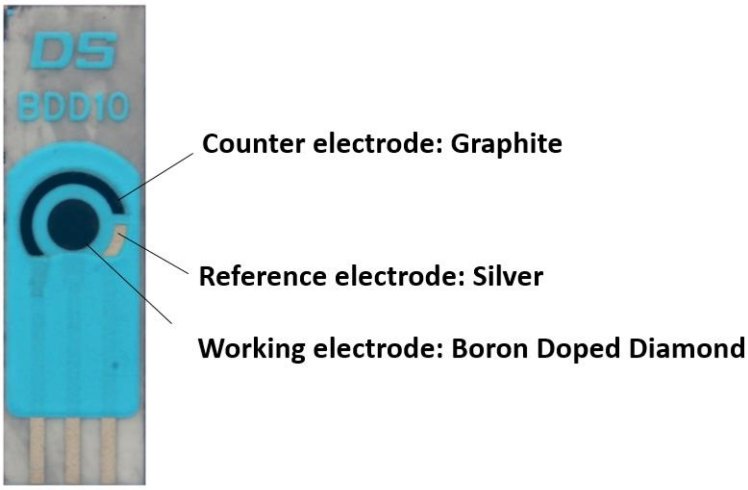
Boron doped diamond (BDD) electrodes are of particular interest as diamond displays the widest known electrochemical potential window in aqueous solution, allowing the electrochemical monitoring of a variety of electroactive species that cannot be detected when using other transducers. Other favorable properties include low background currents resulting in higher sensitivity and improved detection limits, reduced fouling, high chemical stability and biocompatibility.

Screen printing technology allows mass production of low cost thick film electrodes with good electrochemical properties. A wide range of inks and materials can thus be used to mass produce low cost sensor strips.

In this work, we present for the very first time BDD screen printed electrodes. The boron doped diamond has been growth in alumina substrates using chemical vapour deposition technique. Once the BDD has been deposited, carbon and silver inks are screen printed in the substrate to produce these devices.



The morphological characterization was performed using techniques as SEM and Raman spectroscopy resulting a homogeneous diamond layer of 2-3 µm thickness. The characteristic diamond peak is present at 1329 cm^{-1} in the Raman spectrum showing that polycrystalline diamond has been successfully deposited in the alumina substrate.

Electrochemical characterization has shown the widest electrochemical window of the BDD electrodes when compared with graphite and gold screen printed electrodes. The BDD were used to determine Cd(II) and Zn(II) in aqueous samples, allowing their detection by anodic stripping voltammetry in the low parts-per-billion (ppb) concentration range with an adequate analytical performance.

Study of the glycerol electrooxidation over Au surfaces modified by Cu

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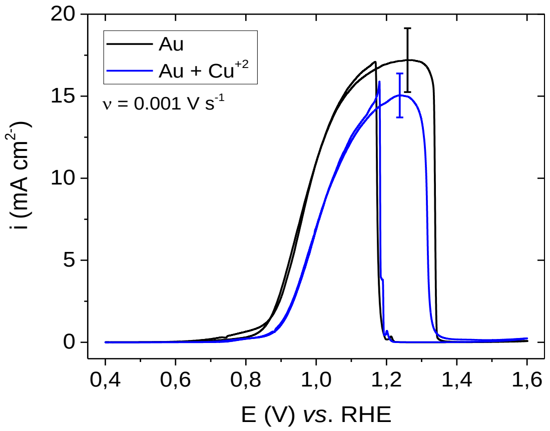
Abstract: The increasing global demand for energy has been rising the claim for alternative energy sources, such as biodiesel, which is employed as an alternative for fossil fuel. The biodiesel production generates glycerol (GlOH) as main co-product, a polyol used chiefly by the pharmaceuticals and cosmetics industries, in amounts that surpasses its demand. This low cost co-product might be used, in principle, for energy generation and the production of value-added products. The effective utilization of GlOH represents a major contribution to the viability of biodiesel, thus a fundamental understanding of its oxidation mechanisms is essential. The GlOH electrooxidation (GEO) has been studied by combining voltammetry with techniques such as in situ Fourier transform infrared spectroscopy (FTIR) [1] and on-line high performance liquid chromatography (HPLC) [2]. In the present work, GEO is studied by using cyclic voltammetry (CV) on a polycrystalline gold electrode (Au_{pc}) in presence and absence of Cu^{+2} ions. Figure 1 shows that the presence of Cu^{+2} does not generate significant changes in the CV response in presence of GlOH, however no conclusions can be drawn concerning the reaction selectivity. Interestingly, Figure 2 shows that the Au_{pc} is strongly affected by the presence of Cu^{+2}, even in the potential domain where the GEO occurs. With the aim of understanding the dependence of the selectivity with the experimental conditions and to understand the interfacial phenomena observed here we will perform in situ RAMAN spectroscopy and on-line HPLC experiments.



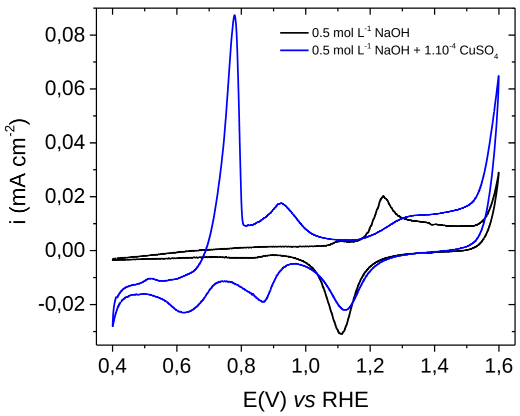


Fig. 1 GEO in 0.5 mol L^{-1} NaOH + 1 mmol L^{-1} GlOH in absence (*black*) and presence (*blue*) of 1.10^{-4} mol L^{-1} $CuSO_4$. Scan rate is 0.001 V s^{-1}. **Fig. 2** CV response of Au_{pc} in 0.5 mol L^{-1} NaOH (*black*) and 0.5 mol L^{-1} NaOH + 1.10^{-4} mol L^{-1} $CuSO_4$ (*blue*), magnified by 10x. Scan rates are 0.01 V s^{-1} and 0.001 V s^{-1}, respectively.

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"*Inherently Chiral*" Ionic Liquid Media: Enantioselective Voltammetry on Achiral Electrodes

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To achieve chiral voltammetry, an alternative strategy to using chiral electrodes is to work on achiral electrodes in a chiral medium. In this frame, chiral ionic liquids (CILs) should perform much better than chiral organic solvents, on account of their higher intrinsic order; and, by analogy with the recently introduced "*inherently chiral*" electrode surfaces of unprecedented enantiorecognition ability [1-4], "inherently chiral" ionic liquids (ICILs) should perform better than CILs.

To obtain ICILs we started from 3,3'-bicollidine, an inherently chiral atropoisomeric bipyridine scaffold of easy synthesis from cheap reagents, converting by dialkylation its antipodes into enantiopure bicollidinium double salts. With appropriate choice of the alkyl chain length and of the counter anion the melting points were lowered below room temperature, yielding enantiopure ICILs. Of these we highlighted the huge enantioselectivity in chiral voltammetry tests, employing them as low-concentration additives in a commercial achiral ionic liquid. The tests were performed on commercial achiral screen printed electrodes (SPEs), using the same chiral probes previously used for testing inherently chiral surfaces. The enantiomer peak separation is huge, comparable to that obtained working with inherently chiral electrodes, and of course specular employing the (*R*) or (*S*) additive.

Importantly, similar and even better performances as low-concentration additives can also be obtained with smaller terms in the bicollidinium double salt series, solid at room temperature but of much easier synthesis. The enantiomer peak separation is modulated by the additive concentration (even reaching ~0.35 V) and by the achiral ionic liquid in which it is employed. The medium enantioselectivity holds with chemically different probes, even of applicative interest, like DOPA. Such results point to the possibility to obtain outstanding enantiodiscrimination on achiral electrodes even employing the new compounds as minority components in a commercial achiral medium [5].

The work is currently under further development, aiming to consolidate, widen and rationalize the first results; a selection of the most recent achievements will be presented and discussed.

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Influence of Photoanodes Structural Characteristics on the Solar Photoelectrocatalytic Properties of TiO_2 Coatings

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Titanium dioxide (TiO_2) is one of the materials of the next future due to their mechanic characteristics, biocompatibility and high stability and photocatalytic properties. Taking advantage of such photocatalytic properties, TiO_2 can be employed in a wide spectrum of different advanced functional material applications such as auto-cleanable surfaces or decontamination devices to improve environmental quality. The photocatalytic properties of TiO_2 are related to its semiconductor condition. When TiO_2 is irradiated with UV light, the transition of an electron from the filled valence band to the empty conduction band is promoted by Reaction (1), with an energy band gap of 3.2 eV, generating highly oxidative holes (h_{vb}^+) and reductive electrons (e_{cb}^-). The holes thus formed can react with water either from air humidity or from an aqueous media generating hydroxyl radical ($^\bullet OH$) from Reaction (2), the second strongest oxidizing species known after fluorine.

$$TiO_2 + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \qquad (1)$$

$$h_{vb}^+ + H_2O \rightarrow {}^\bullet OH + H^+ \qquad (2)$$

However, the photocatalytic activity is strongly lost due to the fast recombination of electrons promoted to the valence band either with unreacted holes by Reaction (3), returning to the ground state.

$$e_{cb}^- + h_{vb}^+ \rightarrow TiO_2 + \text{heat} \qquad (3)$$

The application of either a constant bias anodic potential or a low constant anodic current density to the TiO_2 subjected to UV illumination in photoelectrocatalysis allows extracting the photo-induced electrons by an external electrical circuit, thus inhibiting the recombination Reaction (3) and consequently, improving the photocatalytic performance. However, different intrinsic parameters of the photoanodes could influence the photoelectrochemical performance.

In this work, several photoanodes were synthesized by means of atmospheric plasma spray technology obtaining highly stable TiO_2 coatings with a wide range of structural characteristics. The influence of different parameters were assessed from the performance of the different TiO_2 coatings on the decolorization efficiency of a solution of Acid Orange 7 (AO7) using natural solar light as free and renewable UV source in the so-called solar photoelectrocatalysis (SPEC) process.

It was found that the crystalline phases of TiO_2 (anatase and rutile) were more photocatalytic than non-stoichiometric TiO_2 sub-oxides. The coatings with higher proportion of crystalline phases then presented better photoelectrocatalytic performances. However, the generated TiO_2 sub-oxides enhanced the coatings conductivity favoring their application as photoanodes, being the presence of these phases also relevant for SPEC application. The structural characterization of the coatings revealed a slight influence of the TiO_2 thickness with an optimum value of about 200–230 μm. The property with higher influence resulted to be the 3D superficial roughness because the photocatalytic processes took place on the coating surface. When a larger specific area was available to be irradiated, a major photogeneration of oxidants occurred, with a considerable enhancement of the SPEC degradation of AO7. The best SPEC photoactivity was obtained for the coating with major content of crystalline phases (rutile and anatase), greater 3D superficial roughness and appropriate thickness.

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Flow synthesis of methanol-tolerant Pt nanoparticles within carbon microspheres as durable oxygen reduction reaction electrocatalysts

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Direct methanol fuel cells (DMFCs) are attractive for their possible implementation in portable applications, due to the high energy density of methanol, and their relatively high energy-conversion efficiency. Like in the proton exchange membrane fuel cells (PEMFCs) fed by hydrogen, the sluggish kinetics of the oxygen reduction reaction (ORR) that occurs at the cathode presents a challenge for their further commercial development [1]. In general, Pt-based materials represent the current state-of-the-art catalysts for ORR because of their activity [2,3], however, further improvements in durability are necessary for large scale commercialization of fuel cells. Additionally, DMFCs present a problem of methanol crossover, whereby the non-reacted methanol permeates the cathode compartment through the polymer membrane causing a decrease in the performance of the cathode catalyst. Therefore, durability and tolerance to methanol crossover of Pt-based electrocatalysts for ORR are the main challenges to the widespread commercial applicability of DMFCs.

Herein, we report a combination of ultrasonic spray pyrolysis (USP) and heat-treatments for the synthesis of active and highly durable platinum nanoparticles embedded within carbon microspheres (PtNP@CMs) as electrocatalysts for ORR, showing high durability and excellent tolerance to methanol crossover in acid environments. The catalytic activity for the ORR was found to be strongly influenced by the Pt content of the sample. Results indicate that low Pt loadings and higher treatment temperatures yield the highest ORR mass activity, as expected based on microscopy analysis of PtNP@CMs. The durability of the catalysts was evaluated in acid solutions via accelerated stability tests, which showed that losses in mass activity are minimized for low Pt loadings and high treatment temperatures. Notably, the most durable PtNP@CM catalyst synthesized display no statistical difference in mass activity after 3500 cycles. Furthermore, the most active catalysts showed an excellent tolerance to the addition of 3 M of methanol measured via a current-time (i-t) chronoamperometric method at 0.55V. We discuss the structural and chemical properties that might be at the origin of the excellent durability. The intrinsic scalability of the proposed synthetic method holds promise for commercial applications of these materials.

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Refining Precious Metals in Molten Sulfide Electrolytes

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Previous metals recycling and electrorefining processes today require numerous steps, costly in labor and capital. In particular, the solvents used today require careful management in order to minimize their environmental impact[1]. Molten sulfide electrolytes show promise as an alternative electrolyte for recycling metals from electronic waste, in particular precious metals such as gold, silver and platinum.

Experimental data show that an electrolyte composed of molten Na_2S-ZnS at the eutectic composition can dissolve Au and Ag at levels comparable to industrial solvents, making it a possible alternative to aqua regia and nitric acid, respectively. The molten sulfide electrolyte superheated to 800°C is shown to contain up to 135 g/L of silver. In similar conditions, gold can reach 261 g/L. These concentrations are of the same order as used in industrial aqueous electrorefining of those two metals[1,2]. Electrochemical measurements have shown that Na_2S-ZnS is a stable supporting electrolyte that can allow for the oxidation of Ag at the anode and the reduction of Ag ions into Ag metal at the cathode.

While the chemistry of Ag and Au in molten Na_2S-ZnS, including the underlying thermodynamics and transport properties, remains under study, the proposed poster will explore the viability of molten sulfide electrolytes as a medium for refining electronic wastes containing Au and Ag. Results of electrorefining in lab-scale cells with various anode and cathode materials will be presented. It is put forth that developing a common solvent for various several precious metals is necessary to alleviate the current multistep nature of precious metals electrorefining.

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FeCoSiB Alloy as an Efficient Electrocatalyst for Hydrogen Evolution Reaction in Alkaline Environment

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Hydrogen is expected to play in the relatively near future a role of an efficient and clean energy carrier. In order to fulfil the concept of the hydrogen economy, hydrogen shall be preferably produced from water by its electrolytic decomposition using electricity originating from the renewable sources. Alkaline water electrolysis represents a promising way to fulfil this task. When the alkaline water electrolysis is compared with alternative proton exchange membrane (PEM) process, it is clearly visible that it lags behind mainly in terms of intensity and flexibility. This is due to the fact that PEM water electrolysis utilizes: (i) thin polymer cation selective material as separator of the anode and cathode compartment and (ii) efficient electrocatalysts for hydrogen and oxygen evolution. On the other hand, these electrocatalysts are platinum metals based (Pt for hydrogen and IrO_2 for oxygen evolution). Industrial alkaline water electrolysis utilizes composite inorganic diaphragm of significantly higher thickness as separator and electrodes made from steel (hydrogen evolution) and nickel (oxygen evolution). As the diaphragm is replaced by anion selective polymer membrane separator, flexibility and partially efficiency of the alkaline water electrolysis will raise rapidly. In order to further increase process efficiency and intensity, it is necessary to develop efficient, stable and cheap (non-platinum based) electrocatalysts. When focused on non-platinum hydrogen evolution electrocatalysts, high surface Raney Nickel represents a clear choice. However, overpotential of hydrogen evolution reaction on nickel increases in time at higher current densities due to the formation of the hydride on the electrode surface [1]. Another interesting approach represents application of amorphous alloys which can show behaviour and properties different from the crystalline metals [2].

In this study $Fe_{60}Co_{20}Si_{10}B_{10}$ is used as a promising representative of this type of materials. Its activity towards electrochemical hydrogen evolution in alkaline environment is followed. $Fe_{60}Co_{20}Si_{10}B_{10}$ is prepared via rapid solidification by melt spinning. Catalysts prepared as ribbon were milled for 8 hours obtaining thus particles with average diameter of 17.8 µm. Prepared powder of $Fe_{60}Co_{20}Si_{10}B_{10}$ is consequently used as catalyst on the Nickel foam as substrate. Three different ways of the catalyst activation were compared in order to achieve maximum performance of the alkaline water electrolysis. SEM, XRD, XPS, cyclic voltammetry, linear polarization and testing in laboratory scale single cell alkaline water electrolyser coupled with electrochemical impedance spectroscopy are used to characterize $Fe_{60}Co_{20}Si_{10}B_{10}$ catalyst thoroughly. Results obtained show that properly activated $Fe_{60}Co_{20}Si_{10}B_{10}$ catalyst represents promising material with very good electrocatalytic activity and long term stability.

Acknowledgement

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Connecting Anodic Gas Evolution in Aqueous and High Temperature Molten Electrolyte Systems Via the Current Interrupt Technique

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Direct electrowinning of chalcophilic metals (Cu, Mo, Re, Pb, Zn, Ag, Cd, Ni) from their native ore concentrates is an energy-efficient method of extraction that avoids production and subsequent need to capture SO_2, a feature of traditional pyrometallurgical routes of extraction. Instead, the electrolytic approach produces easily-condensable and environmentally-benign elemental sulfur. Figure 1 shows a schematic of an electrolysis cell that accomplishes such electrowinning using a molten metal sulfide supporting electrolyte. This approach, termed Molten Sulfide Electrolysis (MSE), has the following advantages: high solubility of feedstock due to the similar chemical nature of the supporting electrolyte, high current density (>10kA·m^{-2}), liquid metal production, semi-continuous operation, and a benign, condensable anodic product. It has been postulated that gas evolution at the anode may control the efficiency of the electrolysis [1]. To properly engineer the anodic interface requires detailed knowledge of the hydrodynamic behavior during the evolution of gas. Unfortunately, thermodynamic and physicochemical properties of liquid phase sulfides are poorly known, if at all. The current interrupt technique (CI) has been utilized to measure the effect of gas evolution on sources of overpotential including solution resistance and supersaturation of vapor species [2,3]. The present work aims to interpret electrochemical measurements made in molten sulfide electrolytes by utilizing dimensionless correlations established for gas evolution in systems with well-quantified physical and thermodynamic properties such as aqueous hydroxide solutions and molten chlorides. CI measurements were made in conjunction with optical observations during the evolution of oxygen at a gold anode in aqueous potassium hydroxide solution and during chlorine evolution at a glassy carbon electrode in a molten chloride electrolyte. Thus, steady state potentials and the transient behavior of the potential decay curve can be directly mapped to the hydrodynamic conditions observed in operando. Upon establishing a similarity between oxygen evolution and chlorine evolution, these results will be applied to describe mass transfer conditions during anodic evolution of sulfur in molten sulfides.

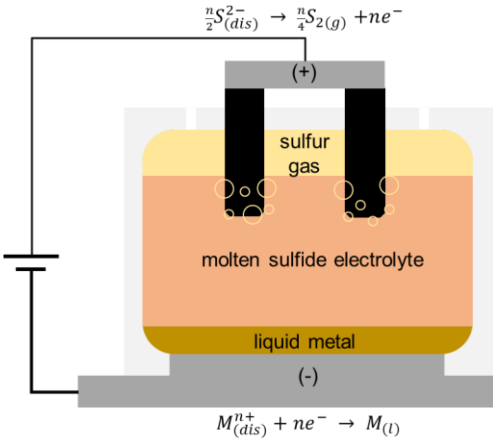

Figure 1. Schematic Diagram of an MSE reactor accomplishing the reaction:
$MS_x \rightarrow M + S_2$

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Integrating Inorganic Catalysts into Biotic Synthetic Catalytic Cascades

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Nature has evolved complex enzymatic mechanisms to facilitate multi-catalytic cascades for the full and complete metabolization of organic substrates. These mechanisms are contained within enzyme complexes known as metabolons, which promote the directed transfer of intermediates from one catalytic site to another known as substrate channeling. One of the most promising areas for improving the performance of advanced catalytic systems is the integration of new catalytic modalities such as inorganic catalysts into the framework of synthetic multi-catalytic cascades. We have demonstrated that an inorganic catalyst can be successfully integrated with an enzymatic catalyst in a way that leads to enhanced two-reaction throughput.

To produce a multi-catalytic cascade, the full and complete oxidation of fructose is used as our model system as the metabolism of this organic molecule is multifaceted and allows for several cascade pathways. For this research, we are concentrating on the last two steps: oxalic acid → formic acid → CO_2. 3D-graphene nanosheets (3D-GNS) have been synthetized and explored as a novel platform that enables incorporation of inorganic catalysts with other catalytic modalities[1] for utilization within this cascade. 3D-GNS has been characterized as having a high surface area, excellent electrical conductivity, increased porosity, and improved transport kinetics. Pd nanoparticles decorated on the 3D-GNS (Pd/3D-GNS) have high activity and low onset potential towards the electro-oxidation of formate, have high stability under applied potential and are less susceptible to poisoning and deactivation. Oxalate Decarboxylase (OxDC) has also been immobilized on 3D-GNS (OxDC/3D-GNS) using 1-pyrenebuthanoic acid succinimidyl ester to ensure that the formate production remains localized within the scaffold.

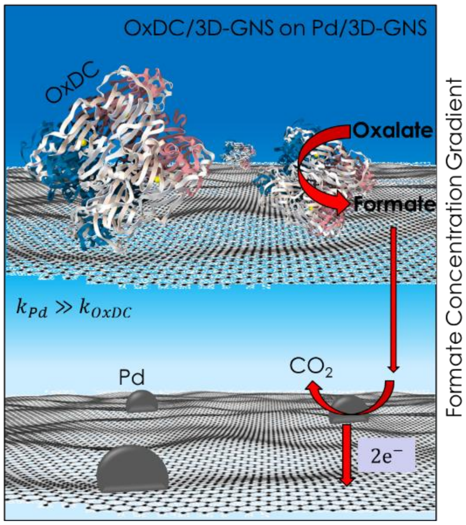

Figure 1. Top: Schematic representation of OxDC/3D-GNS on Pd/3D-GNS.

By integrating these two catalysts together to create a hybrid system, we have introduced a layered deposition, which has shown increased two-step reaction throughput (Figure 1). As OxDC is not electrochemically active, electrochemical experiments, which measure the current due to formate oxidation on Pd, were utilized to characterize the efficiency of oxalate oxidation. Two different depositions of OxDC/3D-GNS and Pd/3D-GNS were tested. One deposition was comprised of a mixture of OxDC/3D-GNS with Pd/3D-GNS as a control in comparison to a layered deposition in which OxDC/3D-GNS layer was applied on top of Pd/3D-GNS layer. Formate Dehydrogenase Assay was utilized to determine the amount of formic acid in the bulk solution. Scanning electron microcopy and confocal Raman spectroscopy were employed for the characterization of the synthetized systems. Decreased amount of the intermediate is detected in the bulk solution with the layered deposition of OxDC/3D-GNS on Pd/3D-GNS corresponding to the increase in electrochemical activity. We can, therefore, conclude that the deposition of OxDC/3D-GNS on Pd/3D-GNS creates a nanoporous architecture for the two-system hybrid catalyst that allows for rapid delivery of the substrates/intermediates.

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Electrochemical Detection of Nitric Oxide in Zebrafish Embryos

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The reactive oxygen/nitrogen species (ROS/RNS) interplay is known to have both beneficial and destructive action in living organisms. However, the detection of oxidative/nitrosative stress markers is still a great challenge due to their low concentration, high reactivity, and short life-time in biological settings. Electrochemical approaches were shown to have several advantages over conventional ROS/RNS detection methods, with potential for application in the biomedical field. This presentation will cover our latest results in the development and use of electrochemical microelectrodes for *in vivo* detection of nitric oxide (NO) as a representative marker of nitrosative stress. Zebrafish (*Danio rerio*) embryos are used as a powerful biological model to demonstrate the applicability of the microsensors in an *in vivo* model. This presentation will show the use of microelectrodes for measuring the NO concentration profile along the intestine of zebrafish embryos. The electrochemical measurements are cross-validated by the use of fluorescence imaging and NO-specific pharmacological manipulation. Our results demonstrate the potential of electrochemical techniques to generate information about oxidative/nitrosative stress markers in biological settings.

Invited Talk in Symposium 3:
Electrochemical Diabetes Immunosensors: Looking at Non-glucose Markers

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Simplicity, sensitivity, selectivity, low-cost, and miniaturization are unique features that can be obtained from electrochemical immunosensors. Diabetes is a complex chronic immune disorder that requires extensive medical care with multifactorial risk-reduction strategies beyond the glycemic control. Diabetes is characterized by abnormally high blood-glucose levels that can result from either insulin deficiency (type 1 diabetes, T1D) or insulin resistance (type 2 diabetes, T2D). In contrast to T1D, T2D is typically associated with unusually high levels of insulin secretion by the beta cells within the pancreas. Recent statistics by the American Diabetes Association reported that 29.1 million Americans (i.e., 9.3% of the population) had diabetes and 86 million Americans (age 20 or older) had prediabetes, which was an increase from 79 million in 2010. Although glucose biosensors have been successful in diabetes management, considerable attention is now focused on developing diagnostic assays for measuring ultra-low levels of non-glucose biomarkers with the goal to identify the type of diabetes, to establish methods for early prediction, and additionally assess risk factors related to cardiovascular, kidney, and vision complications.

While absorbance, chemiluminescence, and radio-label based immunoassays for serum insulin detection are currently available, these methods require chemical/enzymatic labels and their tedious conjugation to antibodies along with the needs for substrate, reagents, and specific instruments (e.g., a fluorometer for fluorescent label detection). In contrast, we believe that nanomaterial based biomarker isolation and detection strategies are robust and allow versatile applicability to various detection techniques (e.g., both optical and electrochemical). Thus, increasing the simplicity of the diabetes biomarkers assay with high sensitivity is very advantageous.

We present here an electrochemical mass sensor coupled to a surface plasmon microarray for measuring pM insulin in serum and whole blood clinical samples. We extended this measurement by designing pyrenyl carbon nanostructure based voltammetric immunosensor. Recently, we have understood the combination of covalent and non-covalent carboxylation carbon nanotubes for sensitivity enhancement of serum insulin immunosensors. We additionally applied the pyrenyl carbon nanostructure strategy for a small-molecule urine marker with 6 ppb detection limit. We are currently extending the measurements to diabetes serum autoantibodies by utilizing aqueous dispersions of graphene carboxylic acid modified electrodes. In summary, our immunosensors for crucial non-glucose diabetes biomarkers are novel, timely, and possess considerable significance for diagnostic applications.

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Microstructure and Electrochemical Properties of Ni-Ti-O Nanosheets Supported on Ni Foam

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Direct methanol fuel cell (DMFC) is a promising green resource because of its high theoretical energy density and environmental friendliness. Current research is focused on the development of catalyst materials with low cost, high performance, high stability, and durability. DMFC's performance is essentially governed by the electrocatalyst and the support materials.

Ni-Ti-O nanosheets arrays were fabricated on 3D porous nickel substrate as as following：(1) $Ni(OH)_2$ with nanosheets synthesized by hydrothermal method; (2) $Ni(OH)_2$/Ni foam were treated by thermal diffusion of Ti for obtaining Ni-Ti-O nanosheets. Scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron (TEM), high resolution transmission electron microscopy (HRTEM) were used to the micro morphology and phase of $Ni(OH)_2$ and Ni-Ti-O nanostructure. The methanol catalytsis performance and capacitance properties of these electrodes were investigated by cyclic voltammetry and charge-discharge tests. The results show that the phase of Ni-Ti-O nanosheets fabricated on 3D porous nickel substrate are NiO and TiO with polycrystalline form; The permeation of Ti result in oxygen vacancies in NiO nanosheets and produce synergistic effect with Ni, which makes that the electrocatalytic property of methanol oxidation of Ni-Ti-O nanosheet electrode is much larger than that of Ni(OH)2 and NiO electrode; When the the mass ratio of Ni foam and Ti powder (R) is 1:24, at a current density of 5 mA•cm^{-2}, the area specific capacitance of Ni-Ti-O electrode is 2.15 F•cm^{-2}, which is 3 times more than that of $Ni(OH)_2$/Ni foam electrode (0.67 F•cm^{-2}).

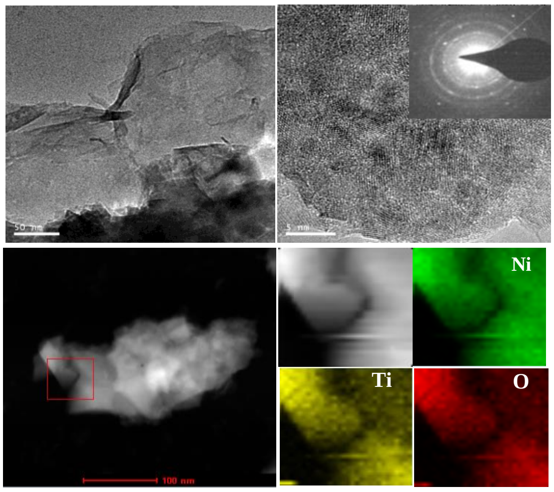

Fig.1 TEM images of Ni-Ti-O nanosheet and EDX mapping

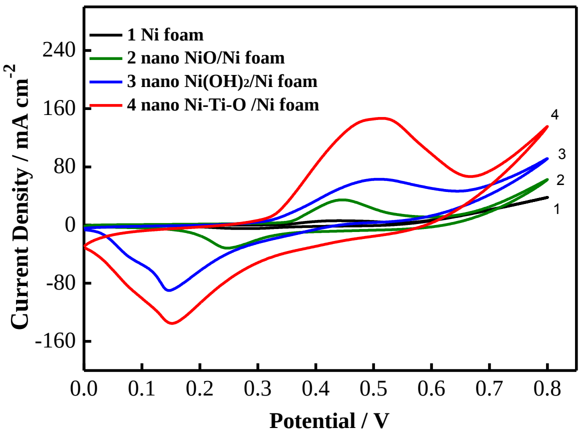

Fig.2 CV curves of the as as-prepared electrodes (test in 6 M KOH, scan rate: 50 mV•s-1)

Self-rearrangement of Silicon Embedded Micro Carbon Sphere as anode materials for high-energy and long-life lithium-ion batteries

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In recent years, electric vehicles (EVs) mostly rely on high energy density for driving long distance. Therefore, silicon with high capacity of 4200 mAh/g which is advantageous for by handheld electronic devices and required to increase driving distance of EVs is the best candidate of anode materials for LIBs. However, a big challenge for silicon is facing with dramatic volume expansion problem during few lithium alloy/dealloy processes. Nevertheless, the repeated large volume change of silicon can cause unstable solid electrolyte interphase (SEI) with exponential growth of particle pulverization. To deal with those aforementioned problems, in this work, silicon embedded carbon sphere (Si/CS) was introduced by using facile way which is hydrothermal synthesis method. Different from conventional carbon coating method, this approach not only can sustain high intensity of vulnerable contacts between Si and carbon layer but also can stabilize SEI after several operating cycles of lithium-ion battery. For the point of view in volumetric capacity, micro spherical Si/CS which is 470.58 mAh cm^{-3} shows four times higher than commercial carbon anode which is mesocarbon microbeads (MCMB). The material characterizations were exhibited by outstanding performance with a gravimetric capacity as high as 1200 mA h g^{-2} at a 0.2A g^{-1} rate based on the mass of both Si and C, as well as a discharge rate capability of 1 min 30sec while retaining a capacity of 780 mA h g^{-2}. This facial novel design of silicon suggests a beyond development for anode material technologies in LIBs.

ORR Activity Of Mesoporous N-Modified Carbon Doped With Non-Noble Metals. Effects of metal and nitrogen precursors.

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Fuel cells for low temperature applications are the subject of intensive research because they offer promise of reducing consumption of primary fossil fuels and greenhouse gas emissions. A difficulty comes from the kinetic behaviour of cathodic oxygen reduction that requires some form of effective catalytic promotion to proceed fast enough to meet fuel cell power requirements as for instance in the case of automotive transportation. Platinum and Pt-alloys are at present the best catalysts for oxygen reduction in PEM fuel cells. Nevertheless, due to the natural scarcity and cost of platinum, a very interesting challenge is to find an alternative non-precious, though less catalytically performing, material. Among others, nitrogen-modified carbons doped with non-precious transition centres (Fe, Co, etc.) are of interest because of the flexibility by which composition and morphology can be tailored by preparation.

In this work we present some results on oxygen reduction by various Pt-free catalysts obtained by carbonization and calcination of nitrogen compounds/sugar mixtures in the presence of a metal salt (Fe, Co, Cu, Ag and alloys of these metals) and a silica gel as mesopore templating agent.

Catalysts were characterized by physical, chemical and electrochemical methods. Results are given in terms of the influence that nitrogen compounds and metal centres exert on oxygen reduction potential, on the presence of a limiting current and on reaction mechanism.

Characterization of Electrolyte Transport Properties and Techno-Economic Analysis of Redox-Active Polymer Flow Batteries

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Traditionally, redox-active small molecules have been used in redox flow batteries (RFBs). Such materials are susceptible to the parasitic crossover of electroactive species through a porous separator, and require the development of expensive ion exchange membranes (IEMs) to achieve reasonable capacity. Viologen redox-active polymer (RAP) solutions have shown great promise as candidate electrolytes to mitigate crossover in non-aqueous RFBs through size-exclusion, enabling the use of relatively inexpensive porous separators in lieu of IEMs.

This study investigates the ionic conductivity and viscosity of RAP solutions in acetonitrile as a function of solution composition, followed by prediction of system-level performance and reactor cost for a RAP-based RFB. Ionic conductivity is found to be of the same order of magnitude as typical Li-ion battery electrolytes, indicating that RAP macromolecular design does not limit the mobility of conducting ions in solution. They also show Newtonian rheology across the entire range of solution composition studied. The electrochemical performance of a RAP-based RFB is predicted by accounting for capacity losses due to electrolyte mixing, and polarization within the RFB reactor. Techno-economic analysis is used to evaluate the impact of active species concentration and operating conditions on RFB reactor cost. Reactor cost and pumping pressure are found to vary significantly with respect to both electrolyte composition and operating conditions. Factors governing the nature of these variations have been elucidated, and conditions corresponding to the achievement of minimum reactor cost have been identified.

Minimum reactor cost is found to lie between 11-16 $\$$ kWh^{-1} across the entire range of active species concentrations studied, which is very close to the estimated target mean reactor cost of $\$13.8$ kWh^{-1} for RFBs. Deviation in the transport properties of RAP solutions from the behavior based on the Nernst-Einstein equation has enabled the achievement of low cost RFB reactors even at high active species concentration. Both ionic conductivity and dynamic viscosity have been found to vary significantly upon reduction of viologen to the +1 oxidation state, suggesting a dependence of electrolyte transport behavior on state-of-charge. This study holistically evaluates RAPs as potential active species for RFBs based on trends in electrolyte transport properties, electrochemical performance, and reactor cost. The methodology used here could potentially serve as an approach for examining other candidate active species for RFBs.

Simulation of electrochemical adsorption system for water treatment

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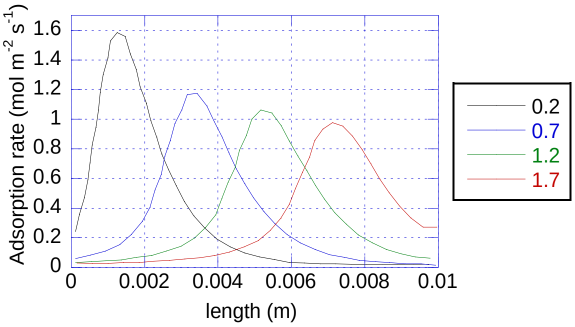
The global water crisis has been a major problem in the modern world. Emerging water pollutants such as organic pharmaceuticals, heavy metal cations and metal oxoanions has drawn great attention from regulatory agencies in the US and Europe. Electrochemical method for deionization is an emerging technique for removing dissolved, charged species from aqueous solutions and has been previously applied to brackish water desalination, waste water remediation and water softening [1].

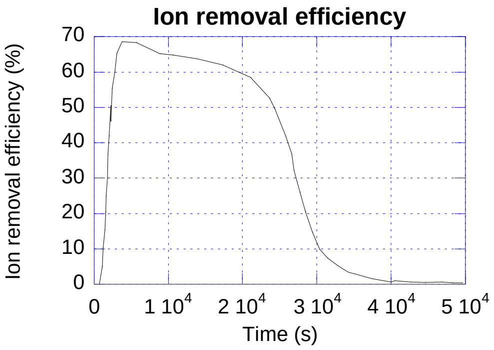
It has been shown by Su et al. that electrochemically responsive (pseudo-capacitive) electrodes consisting of a polyvinyl ferrocene/CNT composite material can enhance the pseudo-capacitance of the electrodes beyond electrostatic adsorption capacity.[2] The facile solution-based preparation method of the electrodes is able to enhance the deionization capacity of the electrode and can selectively remove ions from low concentration brackish or ground water, which provides an alternative way for water treatment.

The selectivity of the electroactive species has been studied and verified using DFT simulation, which is due to the specific binding of the charged species to the electroactive species at the electrode. The electrochemical adsorption system is also studied using numerical simulation by finite volume method via solving the transient Nernst-Plank equations in a two-dimensional channel. The concentration profiles of both the target ions and the electroactive species at the surface of the electrode are simulated to select the proper operation time for optimum separation performance, as shown in Figure (a) and (b). This gives us quantitative insights into the application of electrochemical adsorption methods for future water treatment options.

(a)



(b)



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Synthesis of mixed metal oxides nanomaterials with enhanced photocatalytical activity by combination of direct laser fabricated-alloys and cathodic corrosion

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Hydrogen production via photoelectrochemical water splitting is a promising approach for energy storage. However, this technology is not fully deployed due to the limitations of current photocatalysts to harvest solar energy and the limitations of the photocatalyst to carry out the oxygen evolution reaction (OER) at appreciable rates.

One of the routes towards the optimisation of metal oxide photocatalysts for the OER and water splitting involves doping the metal oxide semiconductor resulting in changes of the width and position of the semiconductor band gap. However the preparation of doped metal oxide nanomaterials is not straight forward and quite often the current synthesis methods result in metal segregation.

Here we present a combinatorial approach for the synthesis of new mixed-metal oxide nanoparticles. First, we will report the synthesis of binary and ternary bulk alloys with well-controlled composition by the Direct Laser Fabrication (figure 1A).[1,2] The process is followed by the synthesis of metal oxide nanoparticles with well-defined and homogenous composition using the cathodic corrosion method (Figure 1B).[3,4] The cathodic corrosion allows a fine control over the particle size and surface structure of the nanoparticles. We will present the structural characterization of different mixed metal oxide nanoparticles and their photocatalytic activity towards the Oxygen Evolution Reaction.

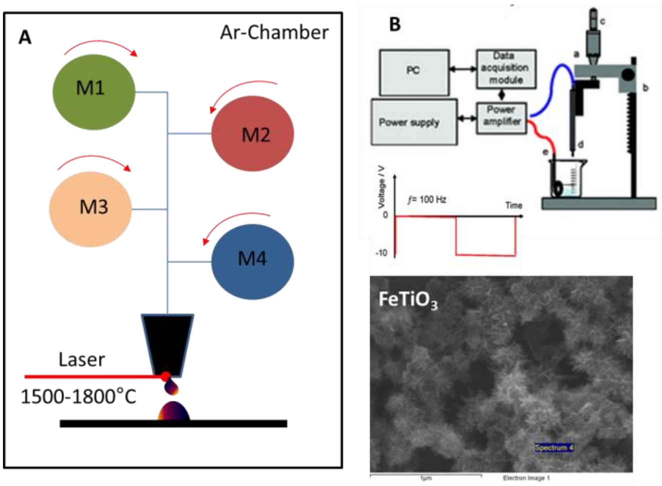

Figure 1. (A) Simplified experimental setup for the synthesis of metal alloys by direct laser fabrication. M1-M4 correspond to feeding motors of different metal wires. **(B) Upper Pannel:** experimental setup for the cathodic corrosion synthesis of the nanoparticles: (a) support, (b) coarse screw, (c) fine micrometric screw, (d) working electrode, and (e) high surface area electrode. Square wave potential program applied. **Bottom panel:** Scanning Electron Microscopy of $FeTiO_3$ nanoparticles. The nanoparticles were synthetized from an Fe:Ti (91:9 % wt.) alloy prepare with the direct laser fabrication method.

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Effect of Heavy Water on the Interactions of Hexammine Ruthenium(III) and Hexammine Cobalt(III) with Self-Assembled Monolayers of DNA

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The interaction of single stranded DNA immobilized on gold electrodes with hexammine ruthenium(III) (RuHex) and hexammine cobalt(III) (CoHex) was investigated in order to find the optimal potential jump with respect to chronocoulometric and electrochemical quartz crystal microbalance (EQCM) experiments. The effect of normal water (H_2O) and heavy water (D_2O) on the interaction of the cationic redox species with 35-base DNA strands was monitored *in-situ* by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at different scan rates. The ssDNA was immobilized on gold surfaces via a thiol linker to form a compact, mixed self-assembled monolayer along with 6-mercapto-1-hexanol (MCH) following a similar protocol proposed by Steel et al.[1] We observed a remarkable shift in reduction peak potential from –400 mV for CoHex in H_2O to –700 mV in D_2O as the solvent (FIG. 1A). In great contrast, RuHex did not show such a potential shift. The effect of D_2O upon the scan rate behavior was also different with Cohex. The effect was also visible in differential-pulse-voltammetric experiments (Fig 1B). Since the viscosity of heavy water is only 20% higher compared with normal water, we believe that these findings indicate a kinetic isotope effect upon the binding of the CoHex complexes with DNA. CoHex is known to influence the secondary and tertiary structure of DNA forming intermolecular bridges between strands.[2] The involved hydrogen bonds can be influenced by kinetic isotope effects. This could be used in the future to study the structure and behavior of DNA layers and regarding hydrogels on electrodes.

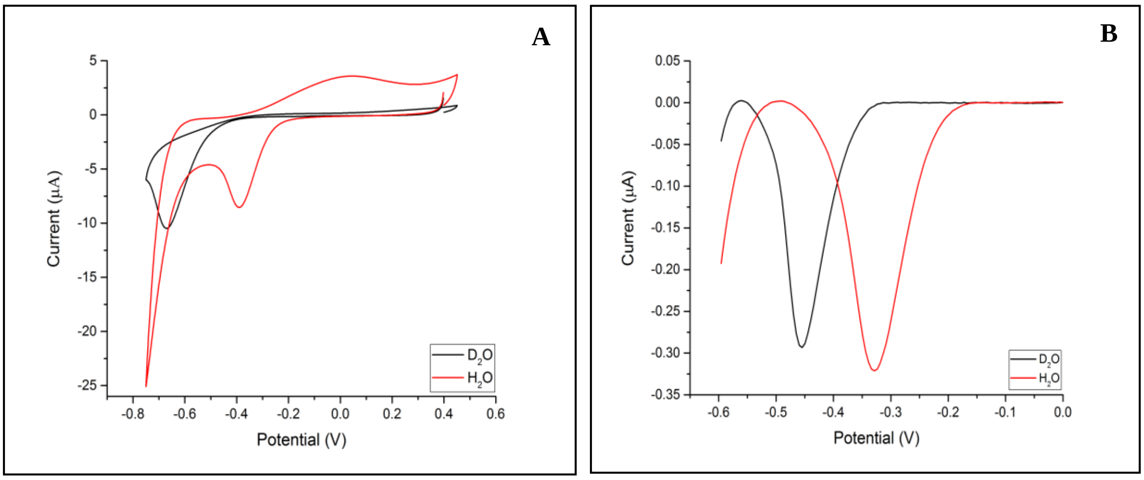

Figure 1. A) Cyclic voltammograms of 50 µM CoHex at DNA modified gold electrode; scan rate 250 mV s^{-1} B) Differential pulse vltammograms of 50 µM CoHex at DNA modified gold electrode; scan rate 25 mV s^{-1}. Electrolyte was 10 mM Tris/H_2SO_4 buffer in H_2O or D_2O at pH 7.2.

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A Novel Multi-Sine Excitation Procedure for Impedance Spectroscopy Supports Automatic Drift Correction and Online Error Determination

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The traditional way to measure impedance using single-sine (monochromatic) excitation is the most transparent and robust way to find reliable EIS data. Compared to the time saving polychromatic (i.e. multi-sine) excitation, the advantage of single-sine excitation is the unequivocal assignment of harmonic content in the response signal to unwanted interference. Systematic analysis of these harmonics allows for the determination of a reliable measurement variance for every single data sample immediately after raw data collection is complete. For decades, such a procedure named “Weighted Harmonics Autocorrelation” has proven its benefit for the EIS instruments of the authors group [1]. Another helpful feature is owed to the periodicity of the monochromatic excitation: unwanted time drift contributions can be calculated from succeeding periods of the response signal for the reconstruction of the drift-free response. This allows for an automatic drift correction [2].

These valuable features are hardly achievable using standard multi sine techniques. Here, even in the absence of interference, the response signals are neither periodic nor free of harmonics. In spite of the fact that monochromatic techniques have the better relationship between information density and time effort [3], it is sometimes preferable to use multi-sine whenever the total measurement time is crucial for practical reasons.

In this poster, a novel multi-sine excitation method will be presented that keeps the advantages of automatic drift correction and online error determination analogous to the monochromatic single-sine procedure.

Keywords: EIS, error determination, drift correction, multi-sine, single-sine

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Accurate Automatic Temperature Calibration of Directly Heated Electrodes

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Heated electrodes are used for the enhancement of electrochemical analysis, by the application of Joule heating. Due to heating a temperature gradient is created near the electrode surface. The temperature pulse potentiometry method is used to perform a temperature calibration for the heated electrode, and apply the desired temperature during analysis. The applied temperatures throughout the electrode have a dependence on resistance and current of the AC (50 kHz) heating pulses. An open-circuit potentiometric measurement was performed on a gold loop screen-printed electrode (Au-SPE) with five automatic heat pulses. The resistance of the Au-SPE was also measured by determining both heating current and voltage during heating pulses (*Figure 1-right*). The resistance and resistivity were also determined for each heat pulse by its temperature dependence by maintaining the calibration solution, (5 mM Ferri/Ferro cyanide in 0.1 M KCl) at 20 °C. The temperature calibrations for three Au-SPEs were shown to be reproducible and precise, with a RSD for temperature <2 ppt, and <22 ppt for resistance. The resistance was then used for the determination of one power step for a specific temperature. The determination of a common conversion factor, will allow us to minimize the time of the temperature calibration considerably by performing 1-point initializations for each single electrode chip.

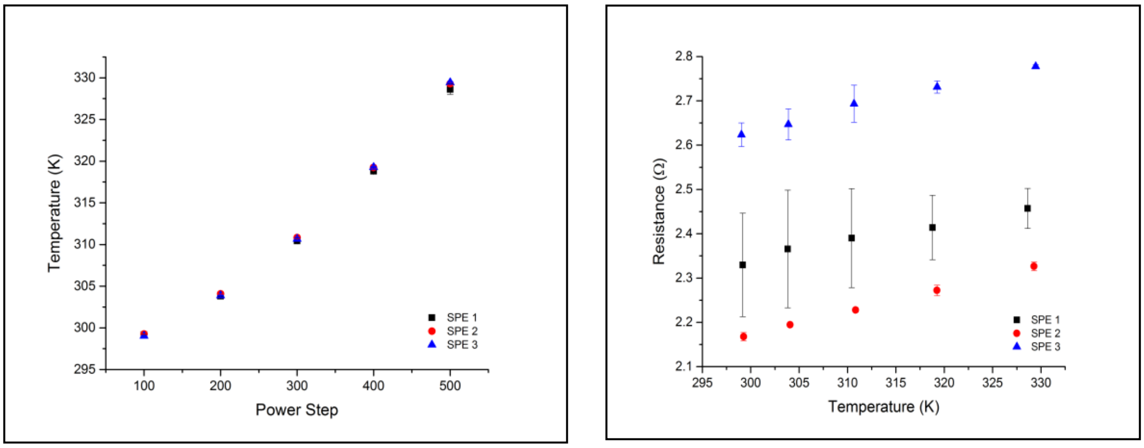

Figure 1: (Left) Automatic potentiometric temperature calibration of three Au-SP in 5 mM ferri/ferrocyanide in 0.1 M KCl. (Right) Resistance measurements at different temperatures, in each heating pulse, of three Au-SPE. Temperatures were calculated from the open-circuit potentiometry measurement using a temperature coefficient (β= -1.6 K/mV).

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Consecutive Reaction Kinetics of Paracetamol – Studied at Directly Heated Electrodes

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Electrochemical analytical techniques are very powerful and versatile tools to study compounds of pharmaceutical interest. Especially, voltammetry is a practical electrochemical technique, which offers high sensitivity, and accuracy. Acetaminophen (paracetamol) is a well-known electro-active compound with an interesting EC-type reaction mechanism. The oxidation product undergoes a consecutive reaction catalyzed by protons leading to an inactive product. Therefore, the reduction signal is visible at pH 7, but not in acidic solution [1,2]. The aim of this project was to study the influence of temperature on the electrochemical behavior of acetaminophen and it's oxidation products using gold electrodes in Britton Robinson buffer (pH 7.4). The Electrochemical study was performed under two different conditions: (1) Heating the entire electrolyte with all electrodes and (2) heating the gold electrode only. Cyclic voltammetry was performed within a potential window of -0.2 V to 0.8 V for both cases. It was found that the reduction peak of acetaminophen-products increased slightly when the bulk was heated at different temperature; however, the reduction peak disappeared when the gold electrode was heated directly using a 50 kHz AC. This is the first example of cyclic voltammetry at heated electrodes, where the forward peak response increases with temperature, while the reverse scan response disappears. Also visible are features that can be caused by electrode passivation as described earlier [3]. This contribution will discuss the various effects of reaction kinetics, as well as mass transport by diffusion and thermal convection.

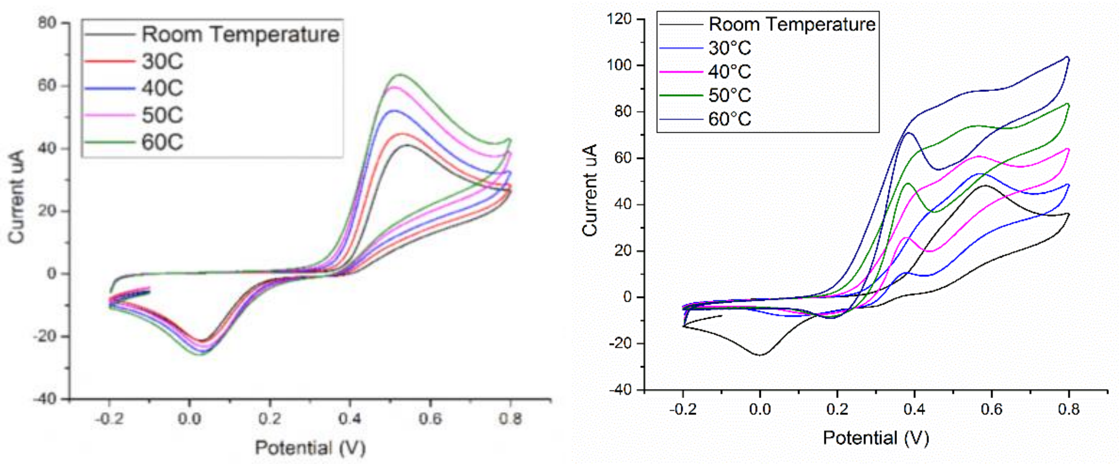

Fig. 1. Cyclic Voltammetry of 200 ppm acetaminophen in Britton Robinson buffer (pH 7.4) at various temperatures **left)** using gold electrode in heated bulk electrolyte, and **right)** using a directly heated gold electrode in cold electrolyte.

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The Electrochemical Engineering Program at Case Western Reserve University

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The Chemical and Biomolecular Engineering Department at Case Western Reserve University is the home to one of the most comprehensive electrochemical engineering programs in the US. This program was established in the 80's as the engineering counterpart to the renowned electrochemistry program that Prof. E. Yeager has established in the chemistry department. Profs. Landau, Liu, Savinell, Wainright, and Martin established research programs focusing on electrodeposition, electrochemical sensors, batteries and fuel-cells, and electrolytic processes. The recent addition of Profs. Akolkar, Renner, and Gurkan, reinvigorated the program and assure its continuation. As a complement to the research program we offer a multi-faceted educational program incorporating the following courses:

- 'Electrochemical Engineering': The base course that most students interested in the program take. The course covers the fundamental principles of electrochemical systems, current and potential distribution, and electrode and cell designs. Acquaintance with common electrochemical processes is gained through examples and case studies.
- 'Corrosion Fundamentals': The course covers the thermodynamics and kinetics of processes leading to corrosion. Electrochemical testing, corrosion monitoring and techniques to stifle corrosion are studied.
- 'Electrochemical Energy Storage': Batteries and supercapacitors related to renewable energy systems are introduced. Related fundamental electrochemistry concepts, materials and techniques are described. Challenges, current literature and future opportunities in energy storage are discussed.
- 'Special Topics in Electrochemical Engineering': A seminar course, addressing advanced topics of interest and based on studying current and classical articles in the literature.
- 'Chemical Engineering Applied to Microfabrication and Devices': This is not strictly an electrochemical course, however, the students fabricate in the lab section an electrochemical sensor.
- 'Workshop on Electrochemical Engineering': This one-week workshop is primarily directed at industry and government researchers who desire a background in electrochemical engineering principles and application of them. Often our graduate students audit this course.

In addition to the above listed courses, students also have the opportunity to take a fundamental electrochemistry course from the chemistry department, and courses related to electrochemical materials in the materials science and engineering department. Details about course/curriculum mechanics and facilitating/encouraging graduate student participation in these courses will be discussed in the presentation.

Undergraduate chemical engineering students often take the classes as part of an 'electrochemical engineering breadth elective sequence'. In addition, our undergraduate students are exposed to electrochemical processes through two experiments in the general senior laboratory: one involving a fuel-cell gas reformer, and the second, remediation by plating of a waste copper stream. We offer research experience opportunities to undergraduate students in our research programs. About ten undergraduates annually, take advantage of this opportunity, with significant portion of those students co-authoring publications and/or enroll in graduate chemical engineering programs.

To introduce electrochemical engineering to a broader undergraduate population and encourage students to pursue graduate studies, we have just established an NSF-funded 'Research Opportunity for Undergraduates (REU)' summer program in electrochemical engineering. This program will place rising juniors and seniors from other universities in our electrochemical research laboratories during the summer. The research program will be accompanied by lectures and seminars on electrochemical topics, communication skills, and professional development.

The presentation further describes the program, focusing on its unique details.

Comparing Electrochemical and Electroless methods for the Selective Surface Modification of the 111 Surface on a SAM modified Gold Bead Electrode

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The removal of a thiolate self-assembled monolayer from a gold surface can be achieved via reduction at negative potentials. The electrochemical removal of the SAM from different surfaces of various crystallographies shows that the {111} surface requires the least negative potential[1]. Careful control of the reduction potential can result in a surface in which only the {111} surface has been disrupted and ready for further modification with another adsorbate. The optimum potential is determined for this electrochemical process through the use of a single crystal gold bead electrode, fluorophore labeled thiols and fluorescence microscopy[2]. Selectively removing and substituting the {111} surface is of interest when working with gold nanorods since the ends are primarily {111} while the sides are either {100} or {110} [3]. A different method for applying a reducing potential is required when working with the gold nanorods. An electroless approach is tested using the gold bead electrode, where the electrode potential is controlled through the use of a reducing agent ($NaBH_4$). Fluorescence image analysis of the modified electrode surface reveals that this electroless approach can achieve similar selectivity in the surface modification of preferentially only the {111} surface. The presence of oxygen complicates this controlled process and needs to be excluded. The electroless approach should be a viable process if the solution potential can be carefully controlled and the selective replacement process not interfered with by the surfactant stabilizing the nanorods. Preliminary results on nanorod modification will be presented.

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In-situ corrosion of Nickel-based catalysts during OER studied via DEMS

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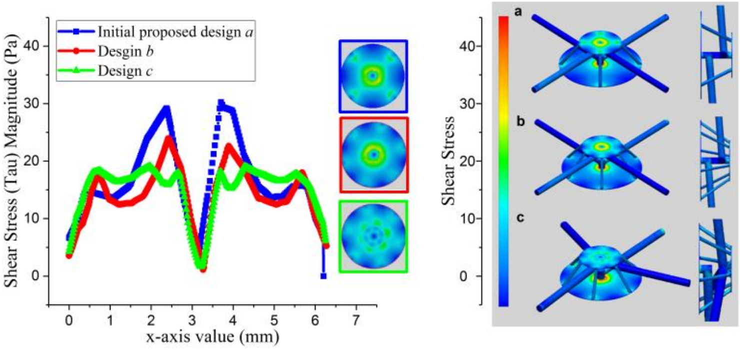
We present here the work on non-noble metal oxide catalysts for oxygen evolution reaction, OER. The use of non-noble metal in OER catalysts integrating Nickel metal such as Nickel-Iron (NiFe) alloys shows great proprieties for alkaline PEM cell[1].

NiFe layered double hydroxide particles and oxyhydroxides films generally show good stability in short term tests in alkaline conditions. However, it has been suggest the existence of correlation between OER activity and the corrosion of metal oxides[2]. Furthermore, there is a limitation on methods available for checking corrosion during OER. The proposed methods are electrochemical quartz crystal microbalance (EQCM) and inductively coupled plasma mass spectroscopy (ICP-MS) applied to the electrolyte[3,4].

We present here the in-situ differential electrochemical mass spectroscopy (DEMS) as a technique capable to demonstrate and evaluate corrosion on oxide catalysts. We investigate OER catalysts in presence of isotope-water to gain information on the context of the direct coupling versus the acid-based mechanism on Ni-based and NiFe catalysts for alkaline media.

Our recent work on DEMS show evaluation of OER catalysts on the estimation of its Faradaic efficiencies in NiFe (oxy)hydroxides and to identify volatile species generated in electrolytes with different pH or containing different ions[5,6]. It has been demonstrated that loss of Faradic efficiency during the cycling at neutral pH can attribute part to the supported carbon-based catalysts corrosion, as confirmed by monitoring the CO_2 signal[6]. Nevertheless, DEMS measurements have shown interesting capabilities on detection of a very small amount of gasses at any point of the reaction due to its high sensitivity and short detection time.

Here we will describe our approaches to study for corrosion of Nickel-based catalysts and provide examples of the significant impact that these studies have had on our understanding of corrosion mechanism. Furthermore, we will discuss the recent development on flow cell with the design of fluid dynamic analysis of the modified dual thin-layer flow cell, especially, focus on electrode compartment.



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Electrochemical Studies of Iodide Adsorption at Au (111) Electrode in Propylene Carbonate

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Organic solvents have an important electrochemical applications: as electrolytes in lithium batteries; as solvents for the electrodeposition of metals, alloys, and semiconductors. Many of these applications involve charge transfer across the electrode/electrolyte interface. Many also involve adsorption steps in a more complicated reaction sequence. In supercapacitors adsorbed ions even play a more direct role. Therefore, the study of the adsorption rate of ionic adsorption in organic electrolytes gives fundamental insights in the factors influencing such single reaction steps. The adsorption rate can be well studied by impedance spectroscopy. [1]

As a model system, we studied the adsorption/ desorption of iodide on the Au(poly) and Au(111) surfaces in aqueous solution and in propylene carbonate containing electrolyte by different electrochemical techniques such as cyclic voltammetry, AC-voltammetry and electrochemical impedance spectroscopy.

In aqueous electrolyte at pH=11, it was found that the adsorption of iodide ion at Au (111) is much stronger than that of hydroxide anion. Iodide adsorption induces lifting of the reconstruction of Au (111) followed by a reversible peak due to iodide adsorption/ desorption process[2].

In non-aqueous electrolyte (propylene carbonate) two broad reversible peaks are present in the cyclic voltammetry due to the adsorption/desorption of iodide at the electrode surface and it is not similar to the case of aqueous electrolyte where the peaks are very sharp. AC voltammetry shows noticeable peaks of the iodide adsorption/desorption process in the same potential range of the CV. These peaks are very separated from the pseudo-capacitive charge. The calculated double layer charge from AC-voltammetry is in the same range of that calculated from the CV. Also the results are confirmed with EIS measurements[3].

A detailed study for the effect of iodide anion concentration, cations and anions of the conductive salt, water content and surface structure on the electrochemical behaviour will be presented. The rate of adsorption of iodide in different electrolytes of the same anion (TBAX, LiX, NaX and KX) increases in the order $TBA^+ < Li^+ < Na^+ < K^+$ depending on solvated cationic size but in case of different anions ($XClO_4$, XPF_6) decreases in the order $PF_6^- > ClO_4^-$ and this is attributed to surface charge density .

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Operation of a microfluidic reactor designed for cogeneration of valuable chemicals and electricity

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Classical chemical production using exothermic reactions is often faced with challenges of energy efficiency and selectivity. Electrochemical production using a fuel cell based reactor could provide a solution for energy saving (by cogeneration of electricity) and for selectivity (by using the optimal electrocatalyst). A novel fuel cell design, the co-laminar flow cell [1], can remove some of the limitations of classical fuel cell reactors as this reactor can operate without the need of an expensive membrane. The electrochemical reactions also benefit from the high surface-to-volume ratio due to the small dimensions of the reactor. The proof-of-concept for cogeneration in this type of fuel cell has been given in [2].

In this work, the reactor operation of the cogeneration microreactor is studied. The electrochemical hydrogenation of nitrobenzene is taken as a case study. This reaction is capable of producing many valuable chemicals, e.g., aniline, p-aminophenol and azoxybenzene. As a counter reaction, the methanol oxidation is used. The performance tested by spontaneous operation of the fuel cell reactor, applying electrical loads of 100Ω and 1000Ω. During operation, the cell, working electrode and counter electrode potentials are continuously monitored. After the experiment, the products that are formed in the reactor are studied in detail by analysing the solution at the outlet. Combining the electrochemical and chemical results, the reactor performance can be interpreted in detail: they provide information on both the efficiency of the process, and on which reactions take place on the electrodes.

Results show that the reactor is capable of conversions up to 64%, and power densities up to 0.299mW cm^{-2}. Higher flow rates have a negative influence on the conversion while having a positive effect on the power density. Both mass transport and crossover phenomena seem to have a substantial influence on the reactor performance. Indeed, it is found that nitrosobenzene is generated in the reactor by cogeneration while aniline is produced at the anode due to oxidant crossover, reducing cogeneration efficiency. The results of this study pave the way for further optimisation of cogeneration microfluidic reactors for the production of fine chemicals.

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Intercalation of Solvated Na-Ions into Graphite

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Graphite anodes are believed to pave the way to commercialization of the Na-ion battery technology.[1] Attempts to electrochemically sodiate graphite from classical carbonate based electrolytes failed in the past, due to energetic instabilities of binary Na-graphite intercalation compounds (GICs) and hampered diffusion of the Na-ions in the graphite lattice.[2, 3, 4, 5] These issues can be overcome by co-intercalating the Na-ions together with a solvation shell, which is not stripped off the ions at the electrode-electrolyte interphase.[6] Here, the reversible formation of ternary Na-GICs upon intercalation of solvated Na-ions into graphite is studied by a variety of *in-operando* techniques, such as electrochemical scanning tunneling microscopy (EC-STM), X-ray-diffraction (XRD) and the electrochemical quartz crystal microbalance technique (EQCM). This study addresses fundamental questions regarding the intercalation mechanism of $Na^+(G_x)_y$-complexes focusing on the concomitant phase transitions and diffusion rates of the solvated Na-ions inside the graphite lattice. The Na-ions are coordinated by y G_x-molecules, where G_x represents linear glyme molecules with x+1 O-atoms. For the four shortest glymes (G_1 to G_4) an intermediate stage 4 Na-GIC (NaC_{48}) is found by XRD upon partial sodiation of the graphite electrode (Figure 1). Full sodiation results in a stage 3 Na-GIC (NaC_{18}, 112 mAh g^{-1}) with the exception of the G_3-system, which forms a stage 2 Na-GIC (NaC_{30}, 70 mAh g^{-1}). STM allows to visualize the phase transitions of monoatomic defects upon ion-intercalation, which is unique so far and which at the same time provides a tool to directly measure diffusion rates of the intercalated $Na^+(G_x)_y$-complexes inside the graphite. The solid electrolyte interphase (SEI) formation is observed by STM and EQCM, while for the latter technique reasonable frequency as well as damping changes are detected allowing to use the EQCM as a novel *in-situ* hydrodynamic spectroscopy,[7] giving further insights into structural properties upon sodiation/de-sodiation of the graphite particles coated in the quartz.

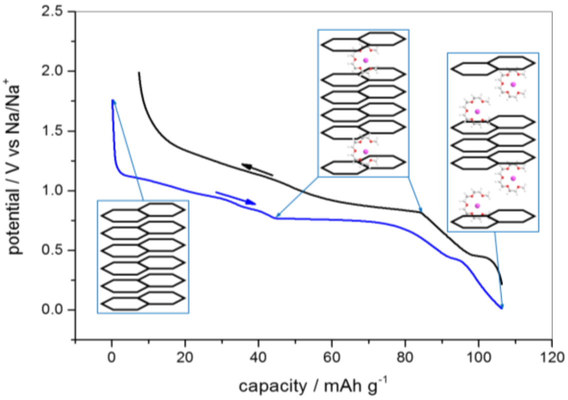

Figure 1: Evolution of the graphite crystal lattice upon intercalation/de-intercalation of $Na^+(G_4)_1$-complexes. (electrolyte: 1 M $NaClO_4$ in G_4, potential sweep rate: 50 µV s^{-1})

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Monitoring Neurometabolic Markers *In Vivo* With Electrochemical Microsensor Arrays

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The process of neurometabolic coupling, encompassing the coordinated interaction of neurons, astrocytes and blood vessels, is poorly understood due to the difficulty of monitoring tonic and phasic changes of metabolic markers in real-time (e.g. glucose, lactate and oxygen) in the brain extracellular space. Microelectrode array (bio)sensors coupled with fast electrochemical techniques (e.g. amperometry) are very attractive for monitoring the concentration dynamics of neuroanalytes *in vivo* with high spatial and temporal resolution and minimal tissue damage. Advances in microfabrication technologies allow for the design of microelectrode arrays (MEAs) platforms comprising multiple platinum sites in a variety of highly reproducible geometrical configurations. Ceramic-based multi-site MEAs have proven to be a versatile and robust microelectrode platform for *in vivo* recordings and are of particular interest for self-referencing recordings and multi-analyte detection in different brain areas.

In this work we have developed oxidase-modified micro(bio)sensors based on MEA platforms for *in vivo* monitoring of glucose and lactate. Furthermore, we have explored such multisite Pt MEAs for high resolution measurements of oxygen in the brain extracellular space. Morphological characteristics and electroanalytical performance of the MEAs were assessed, respectively, by scan electron microscopy and electrochemical techniques. Tonic and phasic changes of glucose, lactate and oxygen in brain extracellular space in both anesthetized and awake rats using the FAST16 electrochemical system (Quanteon, USA) were successfully recorded. Furthermore, local field potential-related information was acquired from the amperometric recordings, simultaneously with neurochemical information, from a single micro(bio)sensor.

Amino-Cyclodextrins Modified Gold Electrodes for Detection of Bentazone

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At present, the construction of transducers modified at a molecular level in a controlled and efficient way remains a great challenge. The immobilization of highly functional macrocyclic receptors is necessary to construct macroscopic artificial assemblies based on molecular recognition. Among the different macrocyclic receptors the family of cyclodextrins is one of the most important. These macrocycles possess a hydrophobic toroidal cavity and therefore are capable to form inclusion complexes with hydrophobic molecules of compatible size. Based on the encapsulating properties of cyclodextrins (CDs), they are an attractive group used as modifier of surfaces.

The most common strategy is the chemisorption of thiolated CDs on gold surfaces with long alkyl as spacers to obtain self-assembled structures. However, the incorporation of the alkyl chains creates an insulating layer that hampers their use in applications based on electron transfer processes. We have previously showed that amino-beta-cyclodextrin can be successfully immobilized on gold by amide bond formation with the carboxylic groups of a self-assembled monolayer of 4-mercapto aminobenzoic acid (MBA) [1]. In this work, mono-amino-β-CD (CD1) and hepta-amino-β-CD (CD7) were immobilized on gold surfaces. Besides, methyl-hepta-amino-β-CD (methyl decorated only on the broader rim, Me-CD7) was also used to modify gold electrodes because the selectivity could be enhanced by the incorporation of specific functional groups on β-CD.

The purpose of the present work was to evaluate the behavior of these modified electrode to detection an organic compound such as bentazone by means of its encapsulation and to compare the effect of methyl group on the encapsulation phenomena. Bentazone is an herbicide widely used in the agricultural industry, as it selectively controls weeds in maize, rice and wheat crops, among others. Their excessive use has a negative impact on the biodiversity of soils and their biological activity.

The immobilization of the CDs on gold was studied by X-ray Photoelectron Spectroscopy (XPS). In the spectra a signal was observed at 162.3 eV corresponding to sulfur forming Au bond and a signal at 399.5 eV assigned to amide nitrogen confirming the immobilization of the CDs. Measurements of the contact angle for theses surfaces were carried out. Naked gold electrode showed a contact angle of 88,7°. This angle is changed to 36,4° when amino-β-CD is on the surface. With methyl-amino-β-CD, the contact angle was 66,9° showing the effect of methyl groups on the broader rim.
The electrochemical oxidation of bentazone on Au-CD1 and Au-CD7 electrodes was evaluated using differential pulse voltammetry (DPV) in phosphate buffer at pH 6, with an accumulation time of 20 min. The peak potential (Ep) of the bentazone oxidation was 0.95 and 0.98 V (vs. Ag/AgCl) on Au-CD1 and Au-CD7 electrode, respectively. This difference of potential is not very significant, however, it could be related to a slightly larger coating of the electrode surface by CD7. Since CD7 possesses more amino groups capable of binding to the carboxyl groups of 4-MBA immobilized on the gold surface generating amide bonds, the electron transfer may be slightly affected. The current intensity increases 30-40% for both Au-CD1 and Au-CD7 versus naked gold electrode. However, when Au-methyl-CD7 is used, the current intensity increases up to 66% versus naked gold electrode. It is clear that the presence of methyl groups give advantage to encapsulation phenomena. The results are analyzed and compared with the association constants reported in solution for inclusion complexes.

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Development of Conductive Oxides as Support of Precious-Metal- and Carbon-Free Oxide-based Cathodes for PEFCs

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Introduction

Development of carbon-free electro-conductive support for precious metal-free oxygen reduction catalyst is required for widespread of polymer electrolyte fuel cells (PEFCs), because carbon materials are unstable at high potential. As the alternative material of carbon, we focused on Magnéli phases titanium sub-oxides (Ti_nO_{2n-1}; $4 \leqq n \leqq 10$), particularly Ti_4O_7, because of its high electron conductivity and high chemical stability in acid electrolyte. Our previous study also demonstrated that Ti_4O_7 is stable in 0.1 M H_2SO_4 at 80°C at high potential.[1] However, the specific surface area of reduced titanium oxide was quite small due to high temperature heat treatment.[2] In this study, we performed hard template method and reduction in 100%H_2 atmosphere to prepare conductive titanium sub-oxides with high specific surface area and electron conductive network structure.

Experimental

Mesoporous silica (SBA-15) was used as a hard template. Titanium oxide was synthesized from titanium nitrate.[3] After titanium source introduced to mesopores of SBA-15, it was calcined 200°C for 5 h in air to produce TiO_2 in the mesopores. The powder was heat-treated in 100% H_2 atmosphere at 800°C for 5 h to prepare Ti_4O_7. Silica template was removed by dissolution with 2 M NaOH aqueous solution at 80°C. Then, oxide powder was washed with distilled water and dried in vacuum at 70°C.

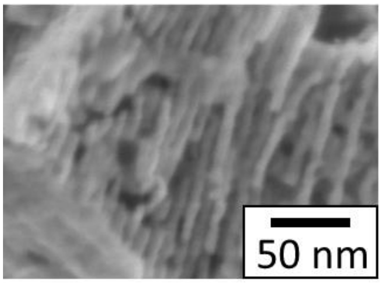

Fig.1 SEM image of oxide support after reduction and removal of template.

Results and Discussion

Fig.1 shows the SEM image of oxide support after reduction and removal of silica template, indicating that rod structure can be observed as a replica of the pores of the silica template. The BET specific surface area was 90 m^2g^{-1}. This value is much larger than that of the reduced oxide (5 m^2g^{-1}) in the same heat treatment condition without template. The crystalline structure was assign to Ti_4O_7 (Fig.2). This support can be one of the promising candidates of alternative carbon support.

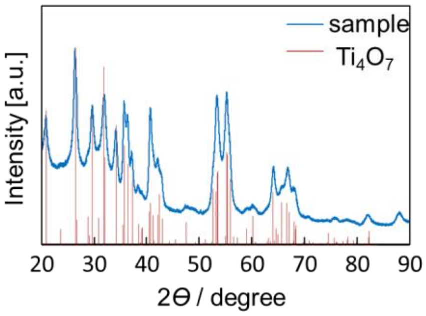

Fig2. XRD pattern of oxide support after reduction and removal of template.

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Role of Organic Solvents in Immobilizing Fungus Laccase on Single-Walled Carbon Nanotubes for Improved Current Response in Direct Bioelectrocatalysis

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Tuning interactions between proteins and solid surfaces is important for rationalizing molecular orientation of redox enzymes immobilized on the electrode to favor an efficient direct bioelectrocatalysis. Supramolecular docking calls for specific "linker" molecules to direct the position of enzyme redox active sites on surfaces of electrodes or conductive nanomaterials, for example, carbon nanotubes (CNTs). In this work we focus on a high-potential fungus laccase, a multi-copper oxidase that catalyzes electroreduction of oxygen, and investigate the regulative effects of organic solvents on laccase immobilization on single-walled CNTs (SWCNTs) and its direct bioelectrocatalytic activity. Herein the maximum reductive current response is dramatically improved by 600% through ethanol-assisted enzyme immobilization, which is a result of ethanol-promoted laccase-SWCNT contact and favorable enzyme orientation on SWCNTs from conformation analysis. Extended investigation on more organic solvents with distinct physiochemical properties show that organic solvents with lower polarity, weaker denaturing capacity and higher vapor pressure are well-suited for assisting DET. This study reveals that organic solvents regulate laccase immobilization for direct bioelectrocatalysis by balancing surface wetting and protein denaturing. It further solidifies our fundamental knowledge of bioelectrochemistry of laccase and may inspire the design of electrode-enzyme interfaces with tunable surface wettabilities.

Keywords: Bioelectrochemistry, Laccase, Direct Electron Transfer

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Photo-electrochemical Water Dissociation using Rh-doped $SrTiO_3$ Surface-modified by Nickel N,N – dimethylamminoethyl amine

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Direct water photo-dissociation using a photo-electrochemical cell instead of the combination of a PV panel and a water electrolysis cell is a topic of great practical interest. Whereas the dual approach, based on individually optimized PV and electrolysis technologies, offers interestingly high conversion efficiency [1], there is an interest to develop integrated devices to perform either direct photon-to-H_2 conversion or photo-assisted water electrolysis. However, the conversion efficiency of photo-electrochemical cells is still insufficient and significant progress is still needed (in particular in material science) before applications can be developed. We report here on the kinetics of water photo-electrochemical dissociation using strontium titanate as photo-active material. Rhodium doping is used to modify the band structure of the perovskite, to extend its light absorption range towards visible light, and to confer a p-type semi-conducting behavior to the material [2]. Figure 1 shows a photograph of the experimental cell used for the experiments. A photo-cathode made of a thin layer of finely powdered $SrTiO_3$-Rh(1%) photo-active phase deposited at the surface of an ITO-coated glass electrode has been used as working electrode. Experiments have been performed in 0.1 M Na_2SO_4 aqueous solutions, using a glassy-carbon counter electrode instead of platinum to avoid cathodic contamination by platinum ions. A calibrated light source (MAX-303, Asahi Spectra) equipped with a UV filter that cuts radiations with wavelength less than 400 nm was used for the experiments. Cyclic voltammograms plotted on Figure 2 show the photo-activity of $SrTiO_3$-Rh(1%) during light on/off experiments. Figure 3 shows the kinetics of H_2 and O_2 evolution during chronoamperometric experiments at E = -1.2 V/SCE, using the $SrTiO_3$-Rh(1%) photo-cathode with and without surface adsorption of Nickel N,N – dimethylamminoethyl amine (a nickel complex used as molecular co-catalyst due to its interesting activity with regard to the hydrogen evolution reaction). A significant co-catalytic effect is put into evidence. The kinetics is approximately doubled, indicating that the kinetics of the surface charge transfer steps might be rate-determining, or at least play a significant role in the overall kinetics of water dissociation. In this communication, we provide a detailed electrochemical analysis of the system and we report on the optimization of the photo-cathode in order to maximize the photon-to-H_2 conversion efficiency.

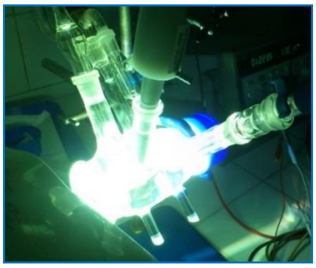

***Fig. 1 :** photo-electrochemical cell used for the experiments.*

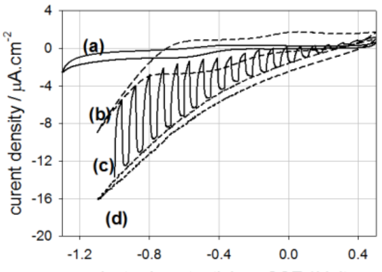

***Fig. 2:** cyclic voltammograms in 0.1 M Na_2SO_4: (a) bare ITO; (b) $SrTiO_3$, dark; (c) $SrTiO_3$, light on/off; (d) $SrTiO_3$, light.*

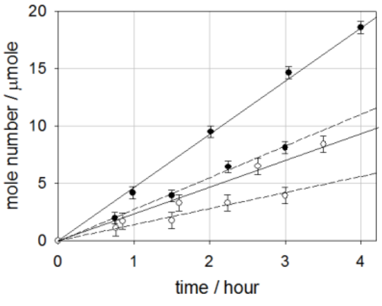

***Fig. 3:** chrono-amperometry at E = -1.2V/SCE; H_2 (●) and O_2 (o) production rates with (−) and without (---) Ni co-catalyst.*

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In-Situ Generation of Metal Nanoparticles from Quasi Reference Electrodes Used in Confined Electrochemical Devices

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Electroanalytical methods can be used to study a great variety of phenomena at micro and nanoscale levels. Many of these methods use electrodes within highly confined fluidic channels, including scanning ion conductance probes to image surfaces, particle delivery experiments to study electrocatalysis, and lab on a chip devices for a variety of biosensing applications. Most of these experiments use a simple two electrode arrangement where the current is measured between a quasi-reference counter electrode (QRCE) and a micro/nano working electrode. In general, a simple two-electrode system is satisfactory when the experimental current is very small. However, as the distance between QRCE and the working electrode decreases in a confined area, individual reactions at the two electrodes can interfere with each other to create undesirable side effects that may lead to erroneous conclusions. We will present evidence for the in-situ generation of nanoparticles by the common non-isolated Ag/AgCl and Cu/$CuCl_2$ QRCEs, including supporting voltammetric and chronoamperometric data. These findings provide useful insights into designing miniaturized electrochemical setups to better probe micro/nano scale phenomena.

Attomole Antigen Detection Using Self-Electrochemiluminous Graphene Oxide-Capped Au@L012 Nanocomposite

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ABSTRACT. In this work, a self-electrochemiluminous graphene oxide-capped Au@L012 nanocomposite was prepared as the label at carcinoembryonic (CEA) antibody to detect attomole CEA antigen. To maximize the luminescence intensity, L012 molecules (luminol analog) were linked with poly(diallyldimethyl ammonium chloride) (PDDA) to form positive charged PDDA&L012 pairs, which were modified on negative charged Au@nafion nanoparticles to construct Au@nafion@PDDA&L012 (Au@L012) complex. Graphene oxide with carboxyl groups was capped at Au@L012 complex through electrostatic interaction to serve as an effective matrix for the covalent attachment of CEA antibody. As compared with the traditional used Au nanoparticles modified with luminol, ~ 740 fold increase of self-luminescence was observed from this new complex so that CEA antigen as low as 0.5 attomole at electrode surface was measurable in absence of any co-reactant. Moreover, the nanocomposite was attached with CEA antigen at MCF-7 cells allowing the detection of CEA antigen from 72 cells. The success in the detection of surface antigen at small population of cells suggested the self-electrochemiluminescence nanocomposite as the new and bio-safe label for the ECL immunoassay, which might push the application of ECL for the cellular immunoanalysis.

INTRODUCTION

Due to high cellular heterogeneity, the analysis at small population of cells or even single cells is critical to elucidate the pathology.[1,2] Since the amount of an antigen at one cell was typically at attomole level or less, the sensitive detection of antigens in this range is needed.

Electrochemiluminescence based (ECL) is an alternative strategy that labels the luminescence probe at antibody or antigen and utilizes the electrochemical generated luminescence from the probe for the analysis.[3,4] Despite the fast development of ECL probe, high concentration of co-reactants, such as millimolar $S_2O_8^{2-}$ or tripropyl amine (TPA), are required to obtain the measurable luminescence. Considering these reagents are harmful to the cells, it is necessary to propose a self-electrochemiluminescence probe with high luminescence intensity as a bio-safe label to facilitate ECL immunoassay in cellular study.

For this aim, the current strategy to form self-electrochemiluminescence probes focus on the covalent linkage of luminophores with the co-reactant groups through the organic syntheses, in which the electron transfer between luminophore and the co-reactive group occurs intramolecularly.[5-7] As the result, these novel probes have been applied for the analysis of proteins and cells without the addition of concentrated co-reactants.[6,7]

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Transmission Surface Diffraction: a New Tool For In-situ and Operando Surface Electrochemistry

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A new surface diffraction method for in situ studies of buried interfaces which employs synchrotron X-ray radiation of high photon energy is presented. In contrast to the standard geometry with grazing incidence angles [1], in this technique a transmission geometry where the X-ray beam passes through the sample is used (Fig. 1). Transmission surface diffraction (TSD) is a powerful and user-friendly method that enables fast simultaneous imaging of the full in-plane structure of solid surfaces in electrochemical environment. Furthermore, it allows surface X-ray diffraction studies with micrometer spatial resolution, opening up the way to map the atomic interface structure of spatially inhomogeneous systems or to study the surface properties of small samples. The feasibility of this approach is demonstrated by TSD measurements of Co and Bi electrodeposition on Au(111) electrodes in microfluidic cell, performed at beamline ID 31 of the ESRF. The formation of the crystal truncation rods (CTRs), changes in the Au CTRs due to epitaxial strain, and the disappearance of the rods corresponding to the $(22 \times \sqrt{3})$ phase of the Au surface reconstruction can be directly observed without lengthy searches in reciprocal space. In addition, in situ microscale mapping of the deposit and substrate properties and studies during Co dissolution are discussed.

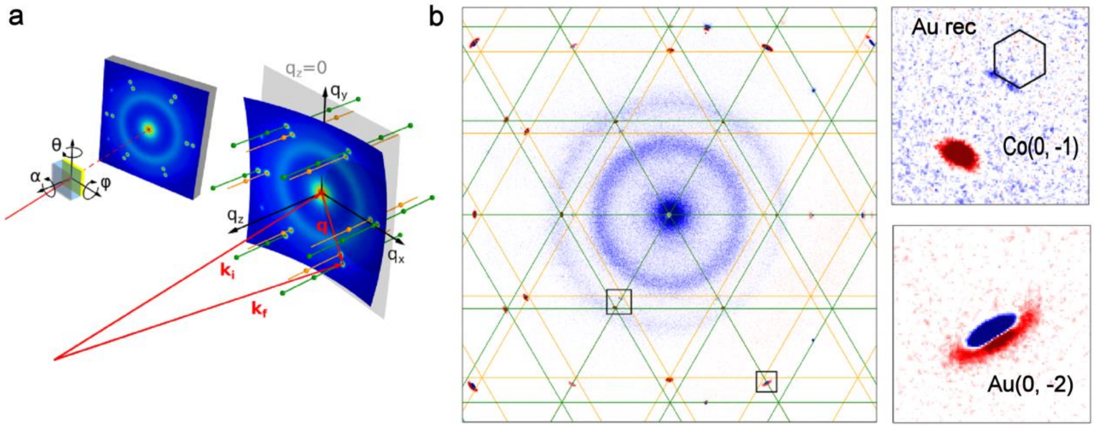

Fig. 1 (a) Real space and reciprocal space geometry of TSD. (b) In situ TSD of Au(111) in 0.1 M NaClO$_4$ + 1.3 mM HCl + 1mM CoCl$_2$, recorded at 40 keV. Shown is the intensity difference between detector images of the Au sample at -0.2 V$_{Ag/AgCl}$ and after electrodeposition of a 20 ML thick epitaxial Co(001) film at -1.05 V$_{Ag/AgCl}$.

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CO_2 and CO Reduction on Mass-Selected Cu Nanoparticles

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Figure 1: Liquid cell for CO_2 and CO reduction.

The conversion of CO_2 to fuels and chemicals, as a means of storing intermittent renewable energy, is of increasing interest for a sustainable society. A broad range of CO_2 reduction products, including methane and ethene, are formed on polycrystalline Cu[1]. The use of nanostructured Cu has resulted in high efficiencies towards CO_2 reduction products at low overpotentials[2,3]. There is particular focus on producing energy dense liquid products.

Here we propose an investigation of the correlation between size and product distribution on mass selected Cu nanoparticles. Both the size and dispersion of the particles will be varied using a cluster source with a time-of-flight mass filter[4]. Tests will be performed in a standard electrochemical cell and the products will be quantified by a combination of gas chromatography, head space-gas chromatography and NMR[5].

The study will give an indication of which sites are most important for the various products, i.e. step-sites, kinks, or terraces. The use of the nanoparticle source allows for well-defined particles with a narrow size distribution, while also avoiding the contaminations inherent in chemical synthesis[4].

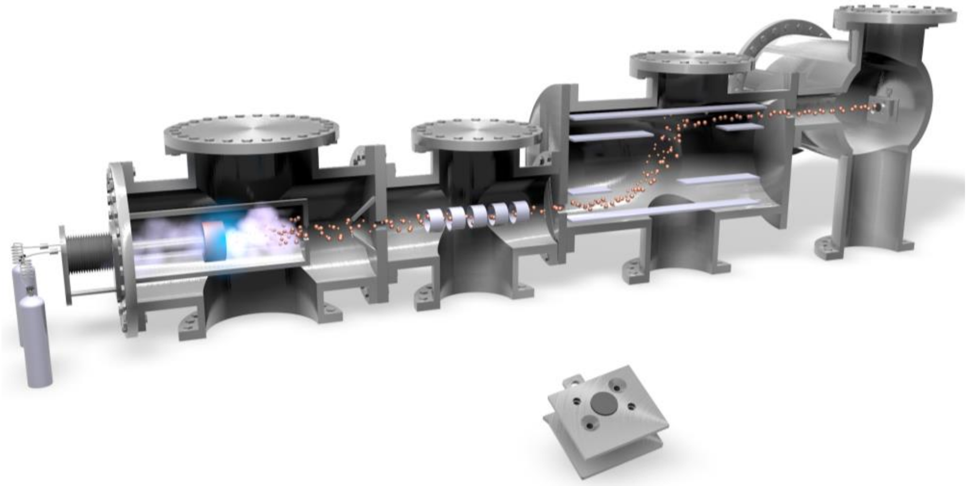
Figure 2: Illustration of nanoparticle source. Curtesy of Jakob Kibsgaard.

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Determination of Oxcarbazepine in Pharmaceutical Formulations and Urine by Pulsed Amperometry in FIA System using Boron-Doped Diamond Electrode

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Abstract: Oxcarbazepine (OX) is a drug with narrow therapeutic index, and thus its determination in formulations is very important for the quality control in pharmaceutical formulations and in biological fluids for pharmacological studies. In this sense, the development of simple, sensitive and selective methods is very important to quantify this drug in pharmaceutical samples. An official method for the determination of OX in pharmaceutical formulations is not described in USP or British Pharmacopoeia yet. However, it can be found in the literature various methods for the determination of OX in formulations and biological fluids using HPLC with UV detectors. Some electroanalytical methods also can be found in the literature and have shown be an attractive alternativeness for the determination of OX in pharmaceutical formulations and in biologic fluids. This is because the electrochemical detection often presents high selectivity and sensitivity for the determination of electroactive compounds, combined with low-cost and fast analyses with less waste generation. Moreover, these electroanalytical methods can be improved in order to obtain a practical and efficient method for routine analysis in pharmaceutical laboratories. Analytical parameters such as reproducibility, simplicity, and analytical frequency can be improved. In this context, this work presents a new method for OX determination by flow injection analysis with multiple-pulse amperometric detection (FIA-MPA), using a boron-doped diamond (BDD) film electrode. Electrochemical detection of OX was optimized in acetate buffer pH 4.0 by cyclic voltammetry, in which OX presented one oxidation process around at +1.5 V versus Ag/AgCl (3.0 mol L^{-1} KCl). OX also showed one reduction process at −1.0 V that is dependent on the oxidation process. Thus, the determination of OX by FIA-MPA detection consisted on the application of a three-potential waveform with sample loop of 200 μL and flow rate of 3.5 mL min^{-1}: (1) at +1.7 V/200 ms, generator potential pulse for oxidation of OX; (2) at −1.1 V/30 ms, collector potential pulse for reduction of the product generated and OX quantification; (3) at -1.3 V/300 ms, potential pulse for cleaning BDD electrode. In the Fig 1, it can be observed that at -1.1 V the OX determination was possible to be performed in urine without the interference of ascorbic acid (AA) and uric acid (UA), which are compounds commonly found in this sample.

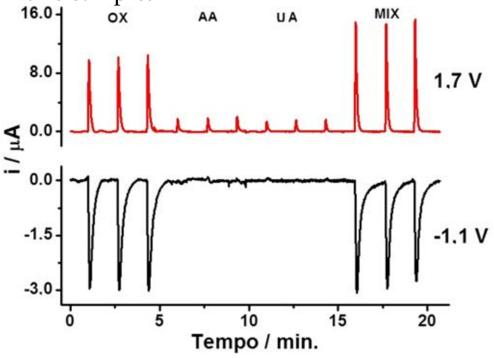

Figure 1. *Amperograms obtained by FIA-MPA detection in supporting electrolyte for triplicate injections of solutions containing 100 μmol L^{-1} of only OXO, only AA, only UA and all together (MIX) in the same concentration. Flow rate 3.5 mL min^{-1}; injection volume 200 μL. Potential pulses on BDD electrode: +1.7 V/200 ms, − 1.1 V/30 ms and -1.3, V/300 ms (not shown).*

The method showed good repeatability (RSD < 1.0 %) for injections of 100 μmol L^{-1} OX and high analytical frequency (65 determinations per hour). The working linear range was obtained from 2.0 to 100.0 μmol L^{-1} with a limit of detection of 0.4 μmol L^{-1}. The recovery tests in all samples were approximately 100 %.

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Durability of Nb-doped TiO_2 Catalyst Support of Polymer Electrolyte Membrane Fuel Cell

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Polymer electrolyte membrane fuel cells (PEMFC) are devices that generate electricity using hydrogen and oxygen as fuel. Electrode reaction take place on catalyst layer and generate electricity when fuels are continuously supplied. Pt/C is used as catalyst for PEMFC, which has advantages of large surface area and high chemical stability. However, when the PEMFC is turned off, the fuel starvation phenomenon occurred in which hydrogen fuel is insufficient inside the cell. As this phenomenon continues, external air is introduced and hydrogen/air boundary can be generated. And the voltage of the cathode electrode can be increased, resulting in the corrosion of carbon support. Electrchemical corrosion of carbon support cause agglomeration of Pt catalyst which result in decrease electrochemical surface area of catalyst[1]. To overcome carbon corrosion problem, the corrosion-resistant catalyst supports, such as carbon nanotubes, carbon nanofibers, tungsten oxide and titanium oxide, nitrogen doped carbon, are being actively studied.

In this work, we tried to overcome the performance deterioration due to carbon oxidation with different titanium oxides as a catalyst support. Titanium oxide is stable at high potential and large surface area, but it has low electroconductivity. In order to resolve this problem, niobium was used as a dopant to increase the electroconductivity of TiO_2 catalyst support. It was known to be promising dopant for TiO_2 because the ionic radii of Nb^{5+} (r=0.70 Å) is similar to the ionic radii of Ti^{4+} (r=0.68 Å) resulting in no lattice distortion[2]. Nb-doped TiO_2 was prepared by the sol-gel method with Ti isopropoxide and Nb ethoxide. Prepared Nb-doped TiO_2 was analyzed with XRD and TEM to determine its structure, particle size and morphology. Pt nanoparticle was supported on Nb-doped TiO_2 with formic acid as a reducing agent. After Pt deposition, the Pt/Nb-TiO_2 obtained was heat treated in a tube furnace at 300℃ for 2 hr under nitrogen atmosphere to remove any trace of by-product from the surface of the catalyst. The electrochemical activity and stability of the Pt/Nb-doped TiO_2 was investigated with cyclic voltammetry and an accelerated fuel starvation conditions.

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Application of IrO_2-Ta_2O_5 | Ti Electrodes to Environment Electrochemistry

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IrO_2-Ta_2O_5|Ti are very appealing for many applications because of their high chemical and electrochemical stability, low cost and exceptional ability to catalyze electrochemical reactions [1]. Also, these electrodes are able to produce hydroxyl radicals ($^\bullet OH$) at the interface level, which may have a large number of applications [2-3]. They usually employ titanium as a support material and can be coated with oxides of transition metals. For this investigation, the electrodes were coated with IrO_2 and Ta_2O_5 due to their excellent performance. There are many investigations focused on the applications of these types of electrodes. Studies focused on coating quality enhancement are important in order to increase their performance, catalytic properties and stability against corrosion.

The main goal of this research is the application in environment electrochemistry of modify titanium electrodes with IrO_2 and Ta_2O_5 by electrochemical deposition and study the changes in the electrode surface during the different stages of pretreatment and modification, in order understand the deposition mechanism and to improve their catalytic activity in the generation of hydroxyl radicals at the interface level [1]: Figure 1. The modified surfaces were characterized by Cyclic Voltammetry (CV), Diffraction X-Ray (DRX), perfilometry, Scanning Emission Microscopy (SEM) and Energy Dispersive X-Ray spectroscopy (EDX). The production of $^\bullet OH$ was monitored by UV-Vis spectrophotometry. Finally, the environment electrochemistry application was to clean polluted water and soil by hydrocarbons.

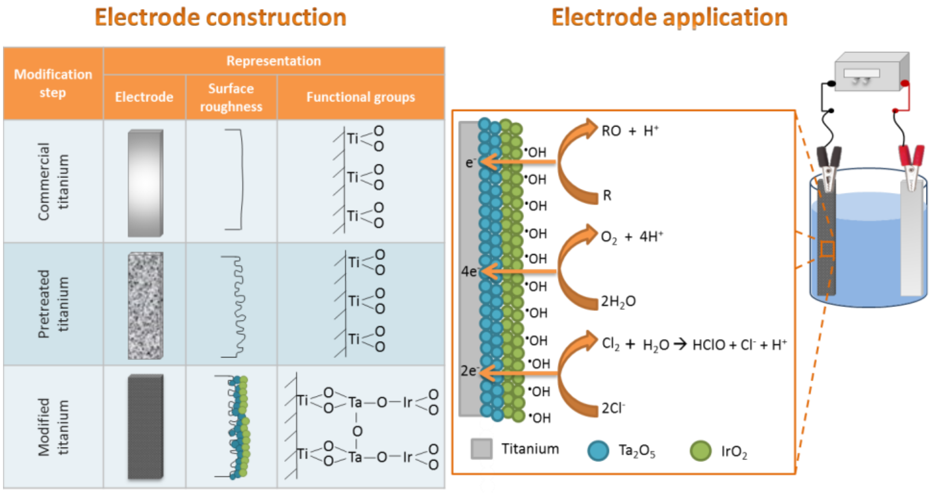

Figure 1. Representation of construction and application in environmental electrochemistry of IrO_2-Ta_2O_5|Ti electrode.

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Detection of Localized Under-Paint Corrosion Using Acid-Base Indicators and H_2 Permeation

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Under-paint corrosion is a problem that has long been known but hard to investigate. Visible signs ~~of corrosion~~ are hidden under the paint, precluding any visual detection of corrosion.

Extensive work has been done on H_2 diffusion inside metals, where a two compartment cell divided by a metal sample attached to two different floating potentiostats is employed. Among the potentiostats, one applies sufficiently negative potential to generate H_2 through hydrogen evolution reaction (HER) on one surface of the metal sample, while on the other surface/the other compartment, the surface is held at a constant potential by the other potentiostat to form H^+ from the diffusing H_2. The current response of this second potentiostat is monitored to give mechanistic information about H_2 diffusion through the metal sample [1,2]. This technique is well established and published by ASTM as a standard [3].

On the other hand, earlier work by the Abruña group employed local pH gradients formed upon methanol oxidation on the electrode surface for visualization of the reaction rate [4]. Local pH changes were used as proxies for the rates of methanol oxidation on different parts of the surface.

We will report on a new technique that combines these two approaches, where the amount of H^+ that is generated on the anodic cell is used as a proxy for the corrosion rate. We utilize a two compartment cell with two floating potentiostats attached to a single metal sample at the same time. Similar to the cell proposed in the standard [3], on one surface H_2 is formed through HER while on the other surface H^+ is formed due to the diffused H_2 and the applied potential. This formed H^+ localizes on the exposed metal surfaces and thus can be used to detect corrosion or cracks under coatings and paints via a simple pH indicator.

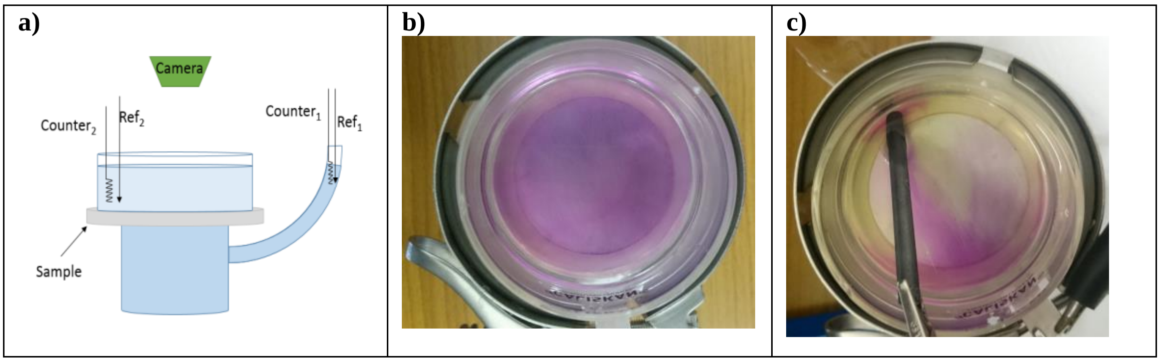

Figure 1- a) Sketch of the two compartment cell. **b)** Initial color of the indicator. **c)** Color change as a result of the applied potential.

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Lyotropic Liquid Crystalline Mesophases of Sulfuric Acid-Non-Ionic Surfactant Stabilizes Lead (II) Oxide in Sulfuric Acid Concentrations Relevant to Lead Acid Batteries

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During the operation of lead-acid batteries (LABs), at the end of a discharge cycle, both the negative and the positive electrodes have Pb^{2+} species, at the end of a charge cycle, the positive electrode is oxidized to Pb^{4+} species while the negative electrode is reduced to Pb^{0} species. Control over the identity of the formed Pb^{2+} species is vital for the battery life [1]. Especially during deep discharge, formation of non-reducible large $PbSO_4$ crystals, termed sulfation, is among the leading causes of LAB failure [2]. Similarly, during the preparation of electrode materials for traditional LABs starts from a mixture of PbO and $PbSO_4$, which is both more readily reducible compared to the $PbSO_4$ and more stable compared to the $Pb_{(s)}$ [1]. The well-known Pourbaix diagram of Pb species clearly show that at the pH range relevant to the operation of LABs, PbO is unstable, in fact only species that is stable is the $PbSO_4$ [1]. Herein, we establish that a sulfuric acid containing, lyotropic liquid crystalline mesophase (LC) with high conductivity (19 mS/cm) has electrochemically active sulfuric acid which enables the formation of PbO at high sulfuric acid concentrations, which is not possible traditionally [3].

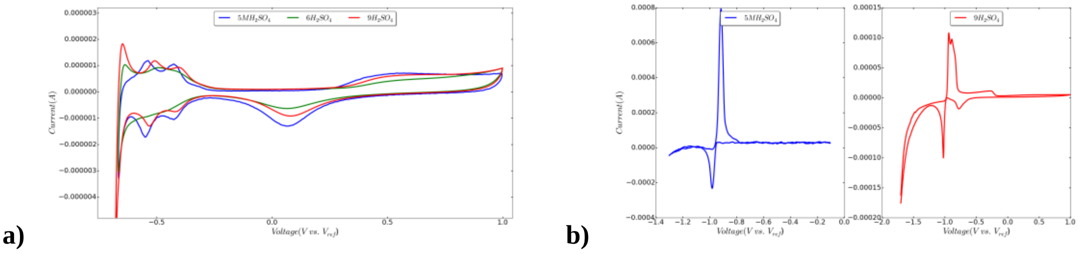

Figure 1-a) Pt in acid CV of LC mesophases and 5M H2SO4. **b)** Pb in 5M H2SO4 and in LC CV.

The electrochemical activity of the sulfuric acid in the LC was established utilizing the well-known cyclic voltammetry (CV) of polycrystalline Pt in sulfuric acid, as shown in Figure 1-a.

Formation of the PbO along with the $PbSO_4$ is confirmed using XRD, CV and by inspection of the color of the formed species which is yellow compared to the white $PbSO_4$. Figure 1-b shows the Pb in sulfuric acid CV in LC and in 5M H_2SO_4 solution. Briefly, the CV in 5M H_2SO_4 solution shows a single oxidation peak attributed to the Pb oxidation to $PbSO_4$, while a single reduction peak of much smaller magnitude, hinting at the extent of reversibility of the process, attributed to the reduction of $PbSO_4$ to Pb. Oxidation region on the CV in LC, however, shows shoulder peaks on the anodic side. Moreover, a new reduction peak, that is not observed in aqueous solution can be seen, showing the formation of a new distinct species. To identify the new species formed, chronoamperometry was performed at various potentials around the oxidation peak. The developed thin films were characterized via XRD and this new species is identified as PbO. The formation of PbO along with $PbSO_4$ is expected to reduce sulfation and improve LABs durability.

The details of the electrochemical activity, along with diffraction will be shown to demonstrate that the LC system is not only electrochemically active, but also stabilizes PbO even in high acidic activity.

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Improvement of Enzyme Immobilization and Porous Structure for Bioanode of Lactate Biofuel Cell

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Enzymatic biofuel cell is a power generation device which decomposes glucose and alcohol using enzymes as biocatalysts and produces electric power, and it is expected to be a promising power source for wearable and implantable medical devices because of its high biocompatibility, small size and simple design. In recent works, lactate has been selected as a fuel for wearable biofuel cell [1-2], since it is abundantly present in human perspiration and can be oxidized by commercially available enzyme. However, there are several technical problems to be solved in order to achieve practicability and popularization. Especially, its power density, durability and safety should be significantly improved beyond a present level. To resolve these issues of biofuel cell and achieve better performance, it is necessary to design the optimum enzyme immobilized electrode. This electrode structure needs to have multiple functions including large reaction interface, good electrical conductivity, sufficient substrate supply, long-term enzyme activity, and prevention of enzyme and mediator detachment. In general, three-dimensional microporous structures composed of carbon nanomaterials such as carbon black and CNT are introduced into enzyme immobilized electrode, in order to enhance effective electrode surface area and increase power density.

In this study, we fabricated several types of enzyme immobilized electrode for bioanode of lactate biofuel cell, and compared their reaction characteristics based on cyclic volutammetry (CV). Firstly, the effect of modification method of enzyme (lactate oxidase, LOD) and mediator (tetrathiafulvalene, TTF) on the bioanode reaction was investigated. Figure 1 shows the cyclic voltammograms for two different LOD/TTF immobilized electrodes. In the electrode (a), the ultrasonicated mixture of LOD and TTF solutions is coated on the GC disc electrode. On the other hand, in the case of (b), LOD and TTF solutions are separately coated on the electrode substrate. It was noted that the oxidation current density of lactate in the electrode (b) is much higher than that of the electrode (a). To maintain high enzyme activity, LOD and TTF solutions should be separately coated on the electrode substrate. Furthermore, the influence of fabrication process of carbon porous electrode on its structure and performance was examined. Figure 2 shows the effect of drying process of carbon slurry on the redox reactions of a mediator at the bioanode. It was found that the heat-dried porous electrode promotes the redox reactions, because carbon particles are strongly sintered during high-temperature heating and the electrical conductivity through the porous layer is improved.

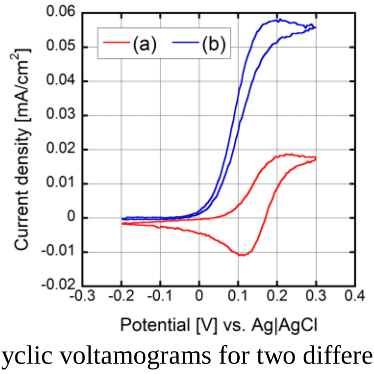

Fig. 1 Cyclic voltamograms for two different LOD/TTF immobilized electrodes: (a) Coated with the mixture of LOD and TTF solutions, (b)Separately coated with the LOD and TTF solutions.

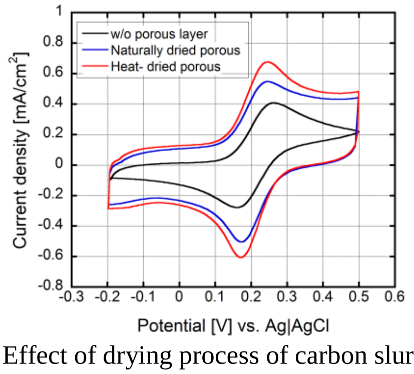

Fig. 2 Effect of drying process of carbon slurry on the redox reactions of a mediator in the porous electrode.

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Impedance-Based, Zero-Free-Parameter Modeling of Energy Storage Systems

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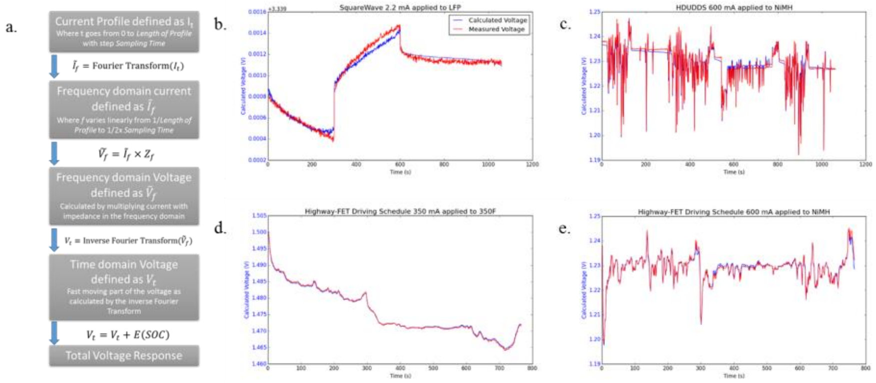
Modeling of energy storage systems are an gaining more importance as batteries and supercapacitors are increasingly finding uses in wildly different fields. In all the applications, being able to accurately model the battery voltage as a function of the applied discharge profile is of great importance. The performance of the selected battery determines the performance of the end-product, in addition to the size and shape.

There are numerous reports in the literature about modeling the voltage response of batteries in response to discharge regimes. Those reports are either compromise accuracy in order to be simple to implement, or at the expense of increased complexity, achieve accuracy. For example, Fan et. al.[1] present a model where the mass transport and kinetics at either electrode is modeled in detail to accurately explain Li ion batteries in high-C rates . In the opposite extreme, Castano et. al.[2] used a simplified Randles cell in order to model a lithium ion system based battery pack. The response captured the battery pack response in broad terms, but missed the fine detail

In addition to the above stated issues, the biggest problem with either modeling approach is obtaining the parameters that explain the battery reactions and materials. These parameters are either obtained from third party experiments or, more commonly, by fitting of electrochemical impedance spectroscopy data of the batteries and the materials they are made of. These fits by design have to make assumptions about the equivalent circuit that is used to fit the data. Moreover, the results of the fit have to be correlated to fundamental properties about diffusion coefficients or kinetic parameters. The existence of free parameters along with ambiguity of the models used call into question the validity of the models and the predictions.



We will report on a new modeling approach that we developed based on impedance spectroscopy data [3]. In order to use the impedance data to the fullest extent without involving any assumptions or fits, we model the response of the battery in the frequency domain. Instead of modeling the response in the time domain, the discharge profile is transformed into the frequency domain. The frequency domain current thus obtained is multiplied by the impedance at every frequency that constitutes the frequency domain signal of the discharge profile. The result of this multiplication leads to the frequency domain voltage, which is then transformed into the time domain. This voltage, is corrected for the DC voltage dependence on the state-of-charge.

Since we make no assumptions about the details, our method is widely applicable across different energy storage systems. We will demonstrate our model on commercial cells with $LiFePO_4$ and NiMH chemistries along with a supercapacitor, all with less than 1% error across different amplitudes and various discharge profiles.

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Electrochemiluminescence Immunosensor Based on Resonance Energy Transfer

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Electrochemiluminescence (ECL) is attracting more and more attention due to its potential advantages over other analytical methods, and a large number of immunosensors have been reported. Recently ECL resonance energy transfer (ECL-RET) has emerged as an effective sensing strategy due to its high sensitivity. However, the difficulty in finding a suitable donor/acceptor pair and the electrochemical instability of the acceptor itself still hinder the development of ECL-RET. Due to the unique photophysical properties and electrocatalytic effect, nanomaterial, especially quantum dots (QDs) and gold nanomaterials, are expected to be promising and ECL donors and acceptors.

We fabricated a sensitive ECL-RET based immunosensor for the detection of tumor markers, using energy tunable CdSeTe/CdS/ZnS double shell QDs and gold nanorods (GNRs) as the donor and acceptor, respectively.[1] Firstly a facile microwave-assisted strategy for the synthesis of green- to near-infrared-emitting CdSeTe/CdS/ZnS QDs with time- and component-tunable photoluminescence was proposed. And, on the basis of the adjustable optical properties of both CdSeTe/CdS/ZnS QDs and GNRs, excellent overlap between donor emission and acceptor absorption could be obtained to ensure effective ECL-ET quenching, thus improving the sensing sensitivity. This approach provided a sensitive response to carcinoembryonic antigen (CEA) in a wide range from 0.001 to 200 pg mL^{-1} with a detection limit of 0.0005 pg mL^{-1}. In another ECL-RET based immunosensor for CEA detection, we explored the ECL-RET properties in graded-gap CdSeTe@ZnS-SiO$_2$ QDs bilayers which were fabricated by layer-by-layer assembly of two differently sized QDs on the glutaraldehyde-activated electrode.[2] The resulting tiny interlayer distance and excellent spectral overlap between these two QDs ensured a high ECL-RET efficiency, and as a result, a greatly enhanced ECLsignal was obtained, which was more than four times higher than that obtained from the bilayer reference samples containing only one type of QDs. The QDs bilayer configuration was applied to fabricate an ECL immunosensor for the determination of CEA with a detection limit of 0.4 pg mL^{-1}.

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Using of binary mixtures of propylene carbonate and 3-methoxypropionitrile for preparing the electrolytes of black dye-sensitized solar cells: Effect of molar fractions on fill factor and global conversion efficiency

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Black dye-sensitized solar cells (DSSCs-BD) were constructed using BD-sensitized nanoparticulate TiO_2 electrodes, PtOx-based cathodes and triiodide-iodide electrolytes containing binary mixtures of propylene carbonate (PC, 2.5cP-viscosity@20°C) and 3-methoxipropionitrile (3MPN, 1.2cP-viscosity@20°C). The solvents were combined to have 3MPN molar fractions (χ_{3MPN}) of 0, 0.25, 0.5, 0.75 and 1. Photovoltaic responses such as conversion efficiencies (η), fill factor (ff) and open-circuit potential (E_{OC}) were obtained as a function of χ_{3MPN} under AM1.5 illumination. Electric parameters associated to the photocells performance were estimated by means of (photo)electrochemical impedance spectroscopy (PEIS) for the same χ_{3MPN} window. The experimental data revealed that the best ff = 0.53 was obtained for χ_{3MPN}=0.25, while the highest η=5.72% was achieved when χ_{3MPN}=0.75. The PEIS spectra demostrated that ff is maximized at χ_{3MPN}=0.25 because this condition conducted to the highest electron recombination resistance (R_{ct}=195.8Ω), but also to the lowest combined ionic transport resistance per viscosity unit of each binary mixture (R_d+R_D=29.67Ω/cP). The last parameter takes place through the TiO_2 pores (R_d) and the electrolyte bulk (R_D), respectively. On the contrast, η was maximized at χ_{3MPN}=0.75 because this new condition allowed achieving the highest value for the ratio R_{ct}/R_{tr} (R_{tr} is the electron trapping resistance along the TiO_2 film), thus promoting the increment of the effective electron diffusion length (L_n) up to 2L (L is the TiO_2 film thickness) [1].

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Metal Nanoparticles Encapsulated Mesoporous Silica Materials: Novel 3D Hybrid Material for Electroanalytical Applications

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Ordered mesoporous silica materials have been on the scientific forefront in the past few years on account of their inherent properties which facilitates them to behave as catalyst support or catalyst themselves. The structural architecture of these materials comprises of an array of ordered pore system having diameters which can be finely tuned between 15-100Å. Along with this, excellent adsorption properties and high surface area made these materials as an excellent candidate to be employed in various fields. Recently metal nanoparticles (M NPs) have also acquired extensive attention of the researchers because of their extraordinary shape, size and morphology dependent catalytic and optoelectronic properties. In electroanalysis, M NPs modified electrodes offer several advantages in comparison to a macroelectrode *viz.* high effective surface area, mass transport, catalysis and control over local microenvironment. However, a major drawback associated with synthesis of M NPs is that they agglomerate in presence of electrolytes. To overcome this problem, chemical reduction of the precursor metal ion is carried out in presence of some stabilizing agents. M NPs supported on various matrices results into nanocomposites which exhibit the advantages of the support matrix as well as the catalytic properties of M NPs. These kinds of nanocomposite have been efficiently utilized in electrochemical sensors, biosensors, electrocatalysis, fuel cells, *etc.* The 3-D mesoporous silicate network provides excellent support for M NPs. In most of the cases the resulting 3-D hybrid material demonstrates the goodness of the intrinsic properties of support matrix as wells as that of the M NPs. Accordingly in this report we present a summarized description of the work carried out by our research group on M NPs incorporated MCM-41 type silica nanocomposites. The use of Au NPs impregnated mesoporous silica spheres for the simultaneous and selective determination of uric acid and ascorbic acid by electrochemical techniques paves way for its clinical and biomedical applications. Further this nanocomposite is successfully employed for the electrochemical determination of environmentally hazardous compounds like hydrazine and nitrobenzene. Furthermore thiol or amine functionalized MCM-41 type silica is used to synthesize Ag NPs and to simultaneously anchor the NPs inside their pores. Such nanocomposites are effective for the oxidative electrochemical determination of nitrite. The electrocatalytic reduction of O_2 and CO_2 using Ag and Au NPs incorporated mercaptopropyl functionalized MCM-41 nanocomposites are also studied. Thus these nanocomposites offer excellent properties which can be judiciously utilized for various electroanalytical applications.

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Electrochemical Study about the Effect of HCl and H_2SO_4 as Surface Modifiers in the Synthesis of Platinum Nanocubes

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The synthesis of Pt nanoparticles with preferential shape/surface structure has received an increasing interest in the last years due to the high number of structure sensitive reactions. Usually, in order to get such shape control, it is required the adsorption of specific adatoms or molecules during the synthesis process, thus, favoring a specific growth pattern of the nanoparticle. In this regard, we have recently developed a method to synthesize Pt nanocubes using high concentrations of HCl [1] and H_2SO_4 [2] in water-in-oil (w/o) microemulsions. In the present work, we show a fundamental study on the effect of the adsorption of increasing concentrations Cl^- and SO_4^{-2} anions using cyclic voltammetry. The concentrations of these solutions were selected mimicking the synthesis conditions of the water phase of the water-in-oil microemulsion in which these shape-controlled nanoparticles are prepared. For this purpose, the three platinum basal planes together with a polyoriented surface have been studied in order to get information about the mechanism in which the highest amounts of Pt nanocubes are obtained for specific acid concentrations.

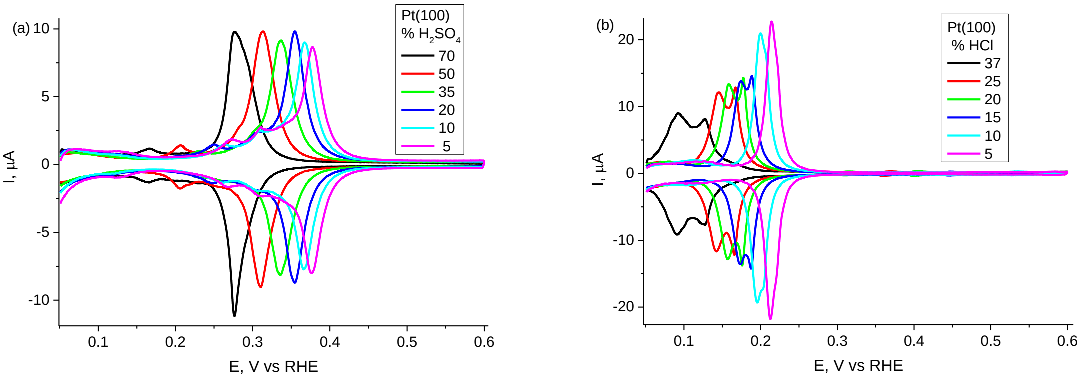

Figure 1. Voltammetric profile of a Pt(100) electrode in different concentrations of (a) H_2SO_4 and (b) HCl at 50 mV s^{-1}.

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Characterization of the Electrode/Electrolyte Interface in the next generation of batteries using Ambient Pressure XPS

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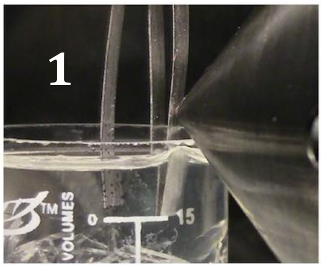
Knowledge of the chemistry occurring at the electrode/electrolyte interface in a battery is considered to be the main key factor in order to understand its general performance (cycling lifetime), and also for preventing the failure. The combination of the *ambient pressure X-ray photoelectron spectroscopy* (AP-XPS) technique (using a "*dip & pull*" approach[1]), with "tender" X-ray synchrotron source (2-8 keV) were used in the *beamline* 9.3.1 at the *Advanced Light Sources* (*LBNL*) to access the solid/liquid interface and to obtain *in situ* chemical specific information on battery systems. Indeed, we have identified an unexpected instability phenomenon at the electrode interface from AP-XPS measurements, which combined with the theoretical simulations allowed us to identify the origins.

In this study, AP-XPS technique was applied for Mg batteries which is considered a major candidate as a beyond lithium battery technology. Electrolyte solution was based on *magnesium (II) bis(trifluoromethane sulfonyl) imide* [$Mg(TFSI)_2$] dissolved in *diethylene glycol dimethyl ether* (diglyme), proposed as a chloride-free alternative candidate for advance Mg batteries[2]. The operating pressure was at 1-2 Torr with diglyme vapor. A three-electrode electrochemistry sample holder was used to facilitate electrochemistry measurements and to create a stable nanometers-thin liquid electrolyte film on the Mg working electrode (WE) surface for investigation (**Figure 1**). Electrochemical measurements were conducted by using a potentiostat controlling potentials referenced to the Mg reference electrode. It is important to highlight that, under those conditions, the photon energy of 4 keV allows to detect photoelectrons ejected from the electrode/electrolyte interface. This technique has general applications to study the solid/liquid interface in both aqueous and non-aqueous systems.

A representative Mg 1s spectra at the electrode/electrolyte interface in presence of 0.8 M $Mg(TFSI)_2$ electrolyte solution is shown in **Figure 2**. Initially, a thin oxide/hydroxide layer with small presence of carbonate covers the Mg metal. After a thin film of electrolyte is created and stabilized on the electrode by the "dip & pull" method, distinct photoemission signal from the $Mg(TFSI)_2$ electrolyte solution is observed at the binding energy of 1303.5 eV. The signal from $Mg(TFSI)_2$ solution could be shifted by varying the electric potentials applied[1]. In this talk, we will provide details about how this spectroscopy technique is used in probing the solid/liquid interface and provides *in situ* chemical information. We will also address the behavior of $Mg(TFSI)_2$ electrolyte at this interface and its response to different electrochemical conditions. This study sheds the light for further characterization of the electrode/electrolyte interface in the next generation of batteries (Mg, Li-S batteries) under *operando* conditions.



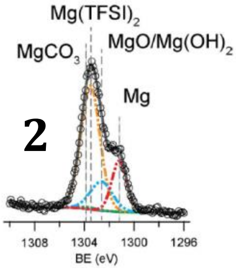


Figure 1. Three electrodes set-up placed into the XPS measurement position after the "dip & pull" method.

Figure 2. Mg 1s spectra at the interface of Mg WE and 0.8 M $Mg(TFSI)_2$ electrolyte solution.

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Probing ultrafast processes at electrode-electrolyte interfaces with photovoltage measurements

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A three electrode system coupled to a conventional potentiostat has a time resolution of, at best, 10 µs (bandwidth above 100 kHz)[1]. However, many charge transfer processes happen on nano- or even picosecond time scales. To measure the kinetics of these processes, all-optical probing techniques using ultrafast lasers are usually adopted. A combination of photocurrent or photovoltage detection with ultrafast laser excitation has been developed very recently.[2] In this contribution, we demonstrate that, using a sequence of two ultrashort laser pulses of different photon energies and detection of the laser induced photovoltage as a function of the delay between the two incident pulses, ultrafast charge transfer kinetics on femtosecond timescales can be resolved.

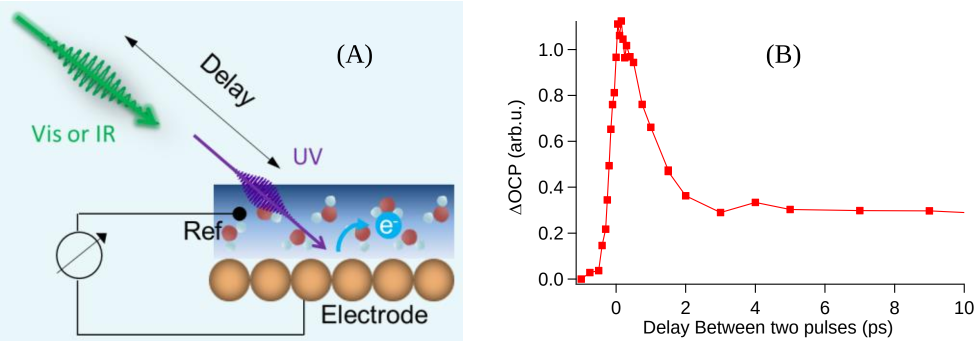

Figure 1. (A) scheme for ultrafast photovoltage detection with two laser pulses; (B) typical time-dependent photovoltage reflecting the reaction kinetics

The system that we studied is as follows: an ultrashort ultraviolet laser pulse is used to trigger some ultrafast reaction at the electrode (*i.e.* electron transfer from the metal electrode to the electrolyte), which creates a large photovoltage. A second energy-tunable ultrafast pulse is used to pump the reaction intermediate or products after a controlled delay. This second pump pulse also causes a photovoltage change. The photovoltage due to the second pump pulse is observed to decay at a rate dependent on the pulse fluence By varying the energy of the second incident pulse, one can resolve the time-dependent spectra of the surface species during the reaction.

We expect this technique to enable the study of ultrafast kinetics of relevant processes directly at the electrode-electrolyte interface, giving valuable mechanistic insight on important electrochemical reactions such as the oxygen reduction reactions (ORR).

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Electrocatalytic reduction of NO_x with polyoxometalate and/or nanoparticles

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Polyoxometalates (POMs) are anionic metal oxide molecular analogues presenting a great diversity of structures and applications. Catalyzed reactions involving small molecules is at the heart of many environmental and energy critical issues to the future. However, the design of the efficient and selective electrocatalysts for these reactions remains a major challenge. One important issue is the nitrate contamination of water which attracts many attention because of the deleterious effect of nitrate on human health and the environment. For these reactions, the development of new efficient and selective catalysts is becoming an urgent mission [1].
In this respect, the association of polyoxometalates (POMs) with metal nanoparticles represents an innovative strategy enabling a combination of multiple catalytic sites in a confined environment. POMs are anionic clusters of highly oxidized early transition metals and oxygen, with remarkable electronic, magnetic and catalytic properties.

In this presentation, the electrocatalytic properties of metallic nanoparticles (Cu, Ag) decorated by polyoxometalates toward the reduction of nitrite and nitrate will be discussed for two types of systems:

- Heteroanionic materials based on polyoxometalate/copper clusters/bisphosphonates [2],
- Nano-hybrid compounds of polyoxometalate / Ag nanoparticles prepared by photocatalytic reduction of silver cation by the POM in the presence of sacrificial donor.

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3.

Defect-engineered N-doped graphene for efficient oxygen reduction

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The platinum has been known as the best catalyst for oxygen reduction reaction in energy conversion technology. However, its high cost and insufficient durability have hindered the large-scale commercialization of the energy devices. Carbon-based metal-free catalysts have been developed to replace Pt-based catalyst, which could reduce the cost and increase the performance efficiency. In particular, heteroatom-doped carbon nanomaterials have been considered as among the potential substitutes for Pt-based electrocatalyst for oxygen reduction reaction (ORR). Recently, research has focused N-doped graphene catalysts.

We present the defect-engineered N-doped graphene for ORR. The porosity and multiple catalytic active sites control electrocatalytic activity. The defect-engineered N-doped graphene show improving catalytic activities due to charge redistribution induced by electronegative N-dopant atoms on their structures. The net positive charge is created on adjacent carbon atoms, which facilitates oxygen adsorption and charge transfer, resulting in enhanced ORR activity. In addition, the enhanced porosity gives rise to more accessible catalytic sites in N-doped graphene.

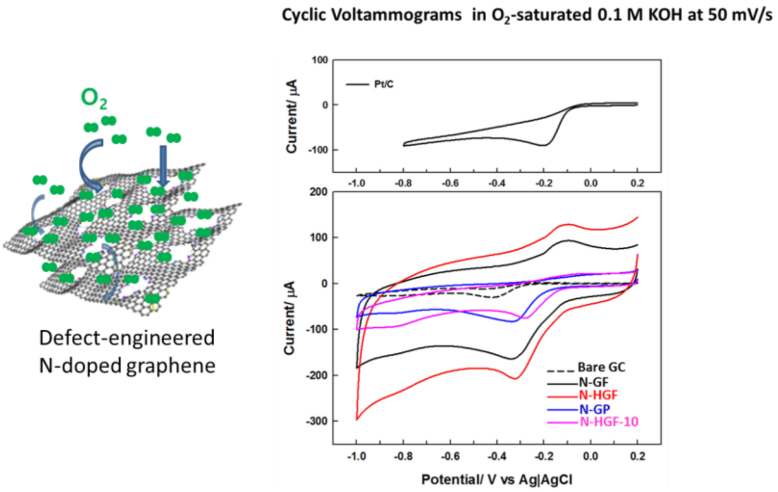

Figure 1. CVs of Defect-engineered N-doped graphene for ORR

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Solid-contact Ion-selective Electrode Array with Anti-fouling Property for Multiplex Ion Sensing in Protein-rich Samples

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Solid-contact ion-selective electrodes (SC-ISEs) have promising niches for clinical diagnostics and homecare applications especially when being fabricated as a test-strip or chip format and having ability for parallel detection of different ions of medical significance. To this end, a cost-effective SC-ISE array fabrication technique with anti-fouling property is desired for the task of multi-ion sensing in a protein-rich sample (e.g., blood, serum, sweat, saliva or urine). In this work, we fabricated a low-cost and small-size SC-ISE array based on a flexible screen-printed carbon electrode (SPCE)/PET substrate. The array was composed of a Na$^+$, K$^+$, Cl$^-$, and Ca$^+$ ISE (electrode area = 2.4 mm^2), which all used electrodeposited polyaniline as the ion-to-electron transducer (IET), and contained a screen-printed Ag/AgCl reference electrode for potentiometric sensing (Fig. 1(a)). Polyaniline IET increased 10% of water contact angle for SPCE and thus showed a reduced water layer effect and potential drift. Polyethylene-polypropylene glycol (F127) was introduced into PVC ion-selective membrane (ISM) for anti-protein adsorption. Fluorescently labeled BSA test (Fig. 2(a)) showed a 93% decrease of protein adsorption for F127-modified PVC ISM as compared with non-modified ISM. Experimental results showed that F127-modified ISE array increased 40% of sensitivity for the ion concentration between 10^{-1}M and 10^{-4}M in human serum as compared with non-modified array. The response time were within 30 seconds. In addition, it was found that F127 modification resulted the pore-structure change of ISM (Fig. 2(b)) which affected ion sensing performance. In summary, polyaniline and F127 are appropriate IET and antifouling materials for construction of a Na$^+$, K$^+$, Cl$^-$, and Ca$^+$ SC-ISE array for multiplex ion sensing in protein-rich samples, and optimization of IET and antifouling modification can maximize sensing performance.

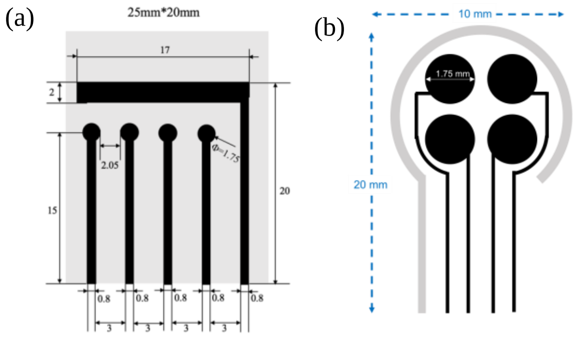

Fig 1. Multiplex ion-sensing array. (a) The pattern used in this experiment. (b) The new pattern which is under development.

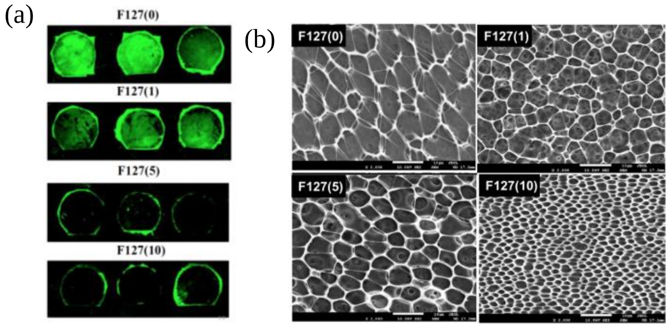

Fig 2. The different proportions of polyethylene-polypropylene glycol are used to identify antifouling and surface morphology for SC-ISE. (a) Fluorescent detection of Cy3-labeled protein adsorption. (b) The compactness of SC-ISE surface shown by SEM.

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Electrochemical Deposition of Niobium from Ionic Liquids

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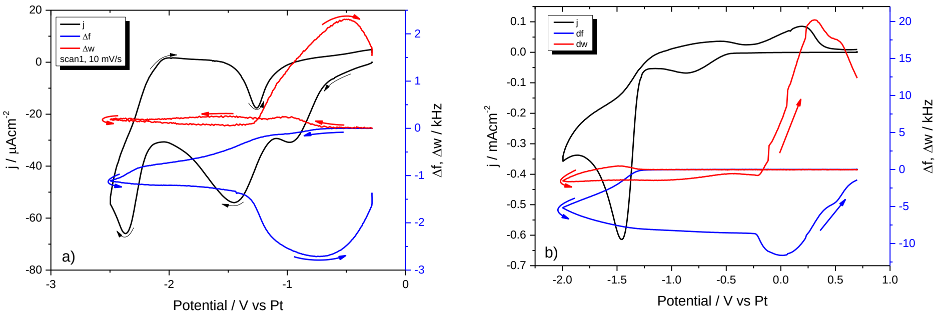
Niobium belongs to the group of refractory metals, and shows advanced properties such as high melting point and good hardness, due to the strong interatomic bonds[1,2]. Furthermore, niobium exhibits excellent chemical and corrosion resistance[3]. This makes niobium coatings very attractive for a broad spectrum of applications, like high temperature applications and equipment for chemical industry[4].

Due to the low standard potential, it is not possible to deposit niobium from aqueous solutions. Ionic liquids (ILs) are a good alternative, and first studies have demonstrated the general feasibility of Nb metal deposition from NbF_5 containing ILs[5,6]. In this work, the electrochemical behavior of different Nb salts in several ionic liquids is studied with the electrochemical quartz crystal microbalance technique (EQCM). A network analyzer is used to measure the admittance between the two Au electrodes (one serving as working electrode) of 10 MHz quartz resonators in parallel to the electrochemical measurements. Figure 1 depicts cyclic voltammograms together with frequency and damping changes obtained by EQCM in 1-N-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imid (BMP TFSI) containing NbF_5. The cyclic voltammogram in 0.25M NbF_5 in BMP TFSI shows three cathodic peaks where the third one is supposed to be coupled with the deposition process. Therefore, a constant potential experiment was carried out at -2.2 V vs Pt, leading to precipitation of a red-brown layer. It is known from literature that the IL/solid interface shows a very complex multilayer structure that can hinder metal cations from approaching the electrode surface, and that additives can disturb these layers[7,8]. Therefore LiTFSI was added to facilitate the electrochemical deposition[5] (Figure 1b). This resulted in much larger current densities and mass changes. The use of $NbCl_5$ as precursor led to very different results. Five distinct peaks were observed both in BMP TFSI and in 1-N-octyl-1-methylpyrrolidinium TFSI (OMP TFSI) that were correlated with changes in the EQCM (not shown here). The origin of this behavior is discussed in detail.



a) b)

Figure 1. Cyclic voltammograms with frequency (Δf) and damping change (Δw) obtained from EQCM for a) 0.25 M NbF_5 in BMP TFSI, b) 0.25 M NbF_5, 0.1 M LiTFSI in BMP TFSI

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Superior Electrochemical Performance in Flake $NiFe_2O_4$ Anode Materials for Lithium-ion Batteries

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Flake $NiFe_2O_4$ anode materials have been successfully developed on a Ni foam substrate using simple, cost-effective hydrothermal growth followed by sintering methods. Firstly, the Ni foam was ultrasonically cleaned with acetone, 1 M HCl solution, deionized water, and ethanol. On the other hand, Fe, Ni salts were dissolved to form a mixed solution followed by adding 2 mmol of NH_4F and stirring for 2 h to obtain the well distributed solution. Then, the solution and the as-prepared Ni foam were transferred into a Teflon-lined stainless steel autoclave and heated at 120 ℃ for 10 h. After the autoclave was naturally cooled down to room temperature, the resultant foam substrate was taken out, washed, and vacuum dried. Finally, the flake $NiFe_2O_4$ materials on the Ni foam substrate were obtained after thermally treated at 350 ℃ in an argon atmosphere for 2 h.

The morphology and microstructure of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrochemical performance was tested by using half-cells (CR2025) assembled in an argon filled glove box. The charge/discharge test was conducted at different current densities for galvanostatic measurement by a battery test system. The cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) were carried out by an electrochemistry system.

The microstructural results show the flake morphology with the desired crystalline structure. Electrochemical results show that the anodes exhibited good cycling performance and rate capability, which delivered a reversible capacity of 1138 mA h g^{-1} after 100 cycles at a current density of 100 mA g^{-1}. Moreover, the materials exhibited the superior rate performance with the highly reversible capacity of 450 mA h g^{-1} even at the current density of 3200 mA g^{-1}. The superior electrochemical performnace could be attributed to the unique flake morphology with large surface area and porosity that are good for facilitating the diffusion of Li^+ and electrolyte into the electrodes and relieving the volume expansion/contraction of the materials during the charge-discharge processes.

Controlled Mesostructures of Solid-Templated Silica: Preparation and Electrochemical Characterization

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In the past decades, mesoporous silica materials characterized by well-ordered microstructure and size- and shape-controlled pores have attracted much attention for the development of functional thin films for advanced applications in catalysis and electrocatalysis, sensors and actuators, separation technologies, micro- and nano-electronic engineering and science [1-3].
In this work, a silica sol in mixture with a polystyrene latex suspension was deposited on ITO conductive glass supports modifying the dimension of the template (30, 60, 100 nm) and the number of successive multi-layered depositions. After the template removal, stable, homogeneous and reproducible transparent thin films were prepared, in which an interconnected porous structure was obtained.

The morphological features and the physicochemical and optical properties of the films were studied by Dynamic Light Scattering (DLS), FE-SEM, AFM, UV-vis transmittance spectroscopy analyses. Moreover, a deep electrochemical characterization was also performed by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements.
In particular, the use of two redox mediator probes [($K_4Fe(CN)_6$) and ($Ru(NH_3)_6Cl_3$)], presenting opposite charge and different diffusional behaviour, allowed the comprehension of the mass and charge transfer phenomena in the silica negatively charged mesochannels (isoelectric point around 2-3), evidencing the effects of spatial confinement and charge selection properties (Figure 1).

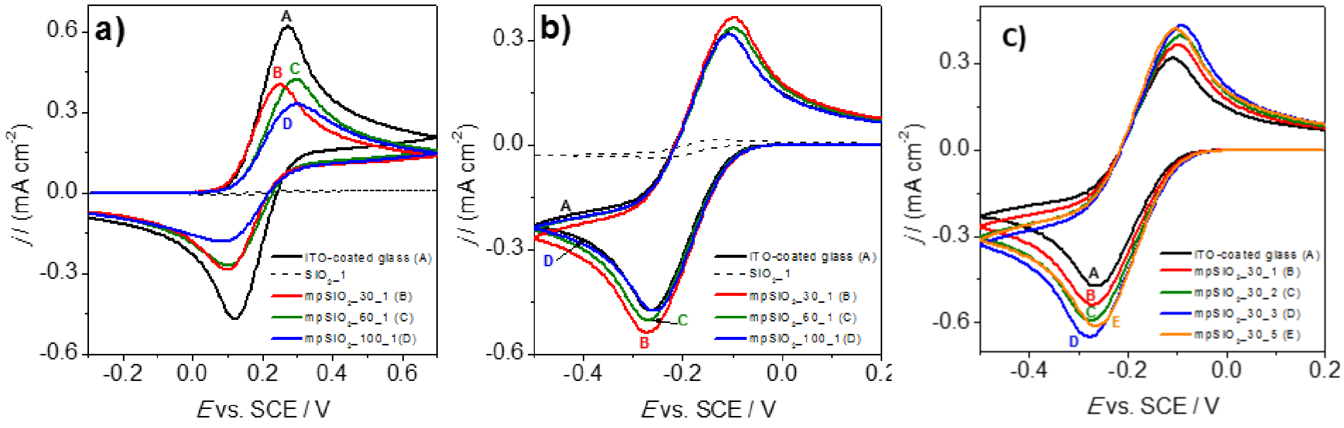

Figure 1. Cyclic voltammograms registered at electrodes modified with a single layer (a,b) or multilayers (c) of silica with different pore sizes (30, 60, 100 nm) in the presence of 3 mM (a) $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ and (b-c) $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{4+}$.

Electrochemical results were also interpreted in the light of water contact angle measurements: samples surface wettability revealed to be a crucial parameter for the sensing properties of the films, in complete agreement with roughness data provided by AFM measurements, according to the Wenzel model.
The easiness of preparation and the interesting properties of these devices pave the way towards their use in trace electroanalysis.

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First-principles calculation of the surface interaction of Li with graphite and oxide

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When the active material is densely packed in *e.g.* lithium ion battery (LIB), the mass transfer of ionic species is not the same as the bulk mass transfer of ionic species in solution. This is because the interaction between the mass transfer species and solid wall of active material becomes significant. This interaction between the wall and the ionic species reduce (or enhance) the mass transfer rate if the surface diffusion rate is very slow (or fast). However, the measurement of surface diffusion in this system is very difficult. In the present study we have used the first-principles calculation for the interaction between lithium and graphite and titanium oxide.

The graphite intercalation compounds(GIC) of lithium is commercially used in lithium ion batterdy (LIB), then a lot of the experimental and theoretical works on GIC have been reported from the invention of LIB. In our previous study[1] we have shown that first-principles calculation based on the local density approximation(LDA) of Ceperley-Alder(CA) type give us some physic-chemical properties, because the LDA-CA calculation accidentally give us the stable interlayer distance between the graphite layers. The interaction between the layers is believed to be van der Waals (vdW) interaction and this interaction comes from the dynamic properties. In 2004 Dion et al. proposed the approximated method that include the vdW interaction in the density functional framework and some people have shown that the their method works! In this study we have used the vdW-DF2 functional[2] in the VASP code[3] for vdW DFT calculation and compare the results without vdW contribution. The energetics and structure of graphite and LiC_6 are in good agreement with the results by Wang et al.[4] The have shown that energetics and structures for Li, K, Na GIC are in good agreement with the experimental results. In our study the energy barriers of the diffusion for lithium ion in LIC6 GIC have been calculated. The energy barrier in the parallel direction of the grapheme plane is 0.3 eV per Li ion without vdW interaction, which is in good agreement with out previous calculation[1]. In the vdW-DF2 calculation the energy barrier is increased up to 0.8 eV, the origin of which may be the attractive character of the vdW interaction between the Li and C. If we expand the C-C interplane distance up to 1 nm which corresponds to the distance between the GIC that contains the solvated intercalants, we have found that the calculated energy barrier in plane direction can be neglected. The dependence of the interlayer distance and the charged state on the diffusion barrier is also calculated and will be presented.

For titanium oxide surface calculation we have considered the anatase (101) surface and the lithium atom on the some site and evaluated the energy barrier. This results will be presented in the meeting.

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Synthesis and Electrochemical Characterization of Lignosulfonate-Stabilized Prussian Blue Nanoparticles

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Nowadays a great interest in the application of biopolymers such as cellulose or lignin derivatives in the development of electrochemical devices can be observed; because they are environmentally friendly, renewable and easy accessible materials [1-3].

Taking into account electrochemical demands, particularly in the field of energy storage, sensor applications and electrocatalytic properties, lignin derivatives seems to be especially profitable. Lignosulfonate is an inexpensive amorphous aromatic biopolymer, which massively arises as a by–product of the sulfite pulping process. From the chemical structure point of view, lignosulfonates have no regular structure, however, they are mainly composed of phenylopropane segments (C_9 units) having hydrophilic sulfonic groups and electroactive methoxyphenol groups. Being polyphenolic compounds lignin derivatives show substantial electroactivity, especially in the range of anodic potentials. This is due to the developing of quinone/hydroquinone redox couple during the oxidation process [4,5].

Lignosulfonates were recently used as electroactive materials and showed remarkable electrocatalytic behavior toward biomolecules such as NADH or ascorbic acid [2]. Moreover, due to possession of negatively charged sulfonic groups, these materials can be considered as polyanions and were used as dopants for conducting polymers [1,5,6]. Thus, they open up new possibilities for the production of cost efficient, environmentally friendly, up–scalable and lightweight energy storage systems as well as electrochemical sensors. We found that lignosulfonates can act as reducting and stabilizing agent in the synthesis of silver and gold nanoparticles [7]. In addition, water soluble lignosulfonates are also able to form complexes with Ni^{2+}, that enable to subsequent preparation of $Ni(OH)_2$ nanoparticles stabilized by lignosulfonate [8].

Prussian blue nanomaterials exhibit excellent performance for H_2O_2 electroreduction, such as high sensitivity, low detection limit and wide linear range. They have been extensively applied as sensor for H_2O_2 and glucose detection [9,10].

The aim of the present work is the synthesis of lignosulfonate-stabilized Prussian Blue (PB) nanoparticles and their electrochemical characterization. The synthesis of nanoprticulate PB was possible because of metal ion complexing properties of lignosulfonate toward iron ions. Probable mechanism of the synthetic route leading to PB-nanoparticles will be presented.

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Differential-Pulse Voltammetric Electrolyte Fingerprinting Using Chemically Modified Electrode Arrays

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Abstract

Ion analysis has been an important and fundamental topic in biomedical, agricultural and environmental fields, and it is generally applied in various domains, such as clinical diagnostics, fermentation and food process control, hydroponics and soil fertility monitoring, water quality check and so on. To date, ion selective electrodes (ISEs) and anodic stripping voltammetry (ASV) are mostly used electroanalytical methods in ion analysis but are confined to single ion sensing and limited applicable electrodes, respectively. In this work, we aimed at combining the advantages of chemically modified electrode (CME) arrays and ultrasensitive differential pulse voltammetry (DPV) technique to develop a new electrolyte fingerprinting approach for multiplex ion sensing and electrolyte composition analysis. In our design, CME arrays composed of different counter ion-dependent redox thin film electrodes (e.g., conducting polymers and Prussian blue (PB) analogues) were deployed to result in a spectrum of selectivity and affinity for different cations and anions,[1,2] while DPV was used for precise and sensitive determination of the ion-dependent redox I-V characteristics for individual CME that interacted with the ions of the electrolyte.[3] To prove the idea, we fabricated a CME array on a PET substrate with screen-printed carbon paste electrode (SPCE) and thin-film electrodeposition techniques, which comprised PB, polypyrrole (PPy), and polyaniline (PANI) electrodes (see Figure 1(a)). Performing DPV electrolyte fingerprinting, we collected the DPV responses for different ions (e.g., K^+, SO_4^{2-}, Cl^-, and NO_3^-) from individual electrode at first and then compared these DPV peak profiles with a mixed fingerprint obtained from an electrolyte mixture and/or a combined electrode signal of the entire CME array (see Figure 1(b)(c)). The DPV curves of the CME array for different K^+-containing electrolytes were reproducible, suggesting the potential for further development as a new ion-analysis platform that might rival ion chromatography, especially when the modern informatics technology allows faster and more precise signal pattern recognition.

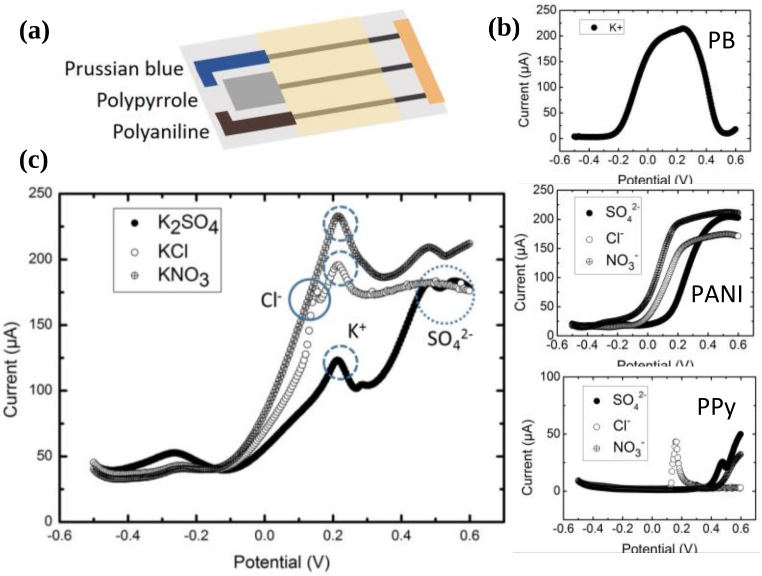

Figure 1.
(a) The CME array composed of PB, PPy and PANI electrodes with different ion-dependent redox properties.
(b) DPV curves of individual PB, PANI and PPy electrodes in response to different electrolytes.
(c) DPV curves of the CME array in response to different K^+-containing electrolytes.

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Electrochemical Detection of Autoantibodies of Multiple Sclerosis in a Microfluidic Device

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Biomarkers are useful tools for performing early diagnosis and prognosis. In this context, synthetic peptides can be used as synthetic antigenic probes to mimic conformational epitopes and for developing label-free diagnostic devices.[1] Glycopeptides CSF114(Glc) were the first family of antigenic probes able to detect autoantibodies with high affinity in sera of Multiple Sclerosis (MS) patients.[1,2] In addition, a previous study showed that their ferrocenyl derivatives Fc-CSF114(Glc) retained their initial biological properties and allowed a bioelectrochemical detection.[2]

In the following, we investigated the detection of human antibodies of MS patients based on the electrochemical oxidation of antigenic probe Fc-CSF114(Glc) in a microfluidic device. This approach was based on a twofold strategy which was (i) to perform electrochemical detections without any preliminary electrode modification and (ii) to improve the detection performances by performing measurements in confined space.[3] Under these conditions, experiments require small amounts of antigenic probes and allow collecting a large number of measurements from biological samples. The specific interaction between Fc-CSF114(Glc) and MS-antibodies was evidenced by comparison with the electrochemical oxidation of ferrocenyl unglycosylated peptide Fc-CSF114 (negative control). Detection of MS-autoantibodies was evidenced by a shift of the oxidation potential of Fc-CSF114(Glc) towards positive values. A mechanism for peptide oxidation was proposed based on a diffusion control of mass transport and formation of adsorbed layers able to mediate electron transfer. This new approach takes part of a strategy aimed at developing innovative and fast diagnostic tools, based on electrochemical synthetic antigenic probes.

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Liquid/Liquid Interfacial Electrode for Programmable Stimulation of Single Living PC12 Cells

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In a classical electrochemical detection system at the single cell level, stimulation to single cells is normally introduced by a micropipette. Owing to their ultrafine orifice size, micropipettes can be used to deliver a small quantity of chemical substances including ions and drugs to the vicinities of single living cells. The modified extracellular microenvironments could subsequently elicit a series of live cell activities such as vesicle exocytosis. Since 1990's, the catecholamine exocytosis from single living cells has been investigated well by electrochemical techniques. However, to our knowledge, a clear quantitative stimulation-response relationship has been barely established for the system due to the uncertain release of the chemicals by the "micropipettes blowing" techniques, including the amount as well as the concentration distribution.

Liquid/liquid (L/L) interface is referred to the interface between two immiscible electrolyte solutions where Faradaic current can be measured as a result of the interfacial transfer of the non-redox ions. In this work, micropipette was employed to support an L/L interface and to act as the electrode for the release of the chemical substances to extracellular microenvironments of PC12 cells. Thus, the delivery of ionic stimulators can be controlled flexibly by the electrochemical parameters applied on the micropipette electrode. Furthermore, programmable stimulation by the L/L interfacial electrodes were explored and their exocytosis responses were evaluated by amperometry. Both the advantages and disadvantages of the L/L interface electrode delivery method will be addressed.

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Bipolar Electrode based Multi-Color Electrochemiluminescence

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Electrochemiluminescence (ECL) is an electrochemically initiated chemiluminescence process, in which molecules or quantum dots are oxidized or reduced at the surface of electrode, to form photon emitting state, leading to luminescence upon return to the ground state. As excitation processes of ECL fundamentally depends on energy of the excited state, multiple electrochemiluminophores can be distinguished by not only their wavelengths of the emission, but also the voltages required for excitation.[1] Multi-color ECL systems, accordingly, have emerged as a powerful tool for the simultaneous detection of spectrally distinct electrochemiluminophores, and study of electron transfer pathways via manipulating the applied potentials. The ruthenium (II) and iridium (III) complexes with tripropylamine (TPA) as a co-reactant show emission maxima spanning the whole visible region, thereby incorporating these two types of complexes, impressive works have been reported towards color-tunable ECL devices. [2,3]

Despite the important development is this area, application of visualized multi-color ECL devices in biological analysis is limited. It is not surprising since most Ru and Ir complexes are insoluble in aqueous solution, which limits its biological application. Recently, we built a closed BPE as a multi-color ECL sensor. The closed BPEs separate ECL reporting pole from the analytes, therefore, such BPE systems hold promise for the fabrication of colorimetric ECL sensor. Since interfacial potential difference between the BPE and the solution drives electrochemical reactions at the extremities of BPEs, through altering the resistance of BPE, a three-color change (green-yellow-red) originated from the mixture of $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_3]$ was observed at the anode, indicating that BPE could indeed be exploited for the development of color selected ECL devices. On the basis of such multi-color BPE-ECL device, an application of screening and semi-quantification of clinical biomarkers, prostate-specific antigen (PSA), by PSA guided deposition of silver bridge which regulated the electronic conductivity of BPE was proposed. Via tuning the emission ratio of multiple electrochemiluminophores, PSA concentrations at cut-off values could be recognized directly by naked eye. As the first multi-color ECL device in biological analysis, BPE may raise the application of potential-resolved ECL to a new level.

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Cheap and Easily Processable Polymer Electrolytes for Sodium Batteries

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The life style of modern civilization is strongly dependent on the use of portable devices, which necessarily require safe and very efficient storage and conversion energy systems. Nowadays, lithium-ion batteries (LiBs) represent the most widely used technology in this respect. One of the arduous challenges in this field is the substitution of conventional liquid electrolytes based on organic solvents, which are volatile and hazardous. Solid polymer electrolytes (SPEs) exhibit appealing properties to replace liquid electrolytes. Moreover, research efforts are directed towards alternative systems to LIBs, because lithium is expensive and its resources are geographically constrained. Sodium exhibits suitable electrochemical properties, close to those of lithium, and it is very abundant. These features make Na-based batteries proficient candidates to replace LiBs, particularly when large-scale energy storage is envisaged.

Here, we offer an overview of our recent developments on polymer electrolytes for Na-ion batteries. Polymer electrolytes were prepared through different techniques, exploiting both UV-curing [1] and simple casting [2]. All samples were thoroughly characterized in the physico-chemical and electrochemical viewpoint. They exhibited excellent ionic conductivity and wide electrochemical stability window, which ensure safe operation at ambient conditions. Electrochemical performances in lab-scale devices are presented, evaluated by means of cycling voltammetry and galvanostatic charge/discharge cycling exploiting different electrode materials (prepared by water-based procedures with green carboxymethylcellulose as binder).

Work on Na-ion polymer batteries for moderate temperature application is at an early stage, only lab-scale cells were demonstrated so far. Nevertheless, with the appropriate choice and optimization of electrode/electrolyte materials (and successful combination thereof), the intriguing characteristics of the newly developed SPEs here presented postulates the possibility of their effective implementation in safe, durable and high energy density secondary Na-based polymer devices conceived for green-grid storage and operating at ambient and/or sub-ambient temperatures.

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Simultaneous Determination of Synthetic Antioxidants by Flow-Injection Analysis with Multiple-Pulse Amperometric Detection

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This work presents the simultaneous determination of tert-butylhydroquinone (tBHQ), propyl gallate (PG), and butylated hydroxyanisole (BHA) using of flow-injection analysis (FIA) in combination with multiple-pulse amperometry (MPA) on a glassy carbon electrode as a detection method. A sequence of three-potential pulses E_1 (+0.40 V, 100 ms), E_2 (+0.55 V, 100 ms), and E_3 (+0.70 V, 100 ms) versus Ag/AgCl was applied continuously in a Britton–Robinson buffer (pH 2.0) carrier solution. In this way, tBHQ is selectively oxidized at +0.40 V, both compounds (tBHQ and PG) are oxidized at +0.55 V and all three compounds (tBHQ, PG, and BHA) are oxidized at +0.70 V. Current subtraction with a correction factor was employed for determination of PG without the interference of tBHQ, and BHA without the interference of tBHQ and PG. During the development of the method, conditions for the determination of antioxidants such as the injected volume and the flow rate were studied and the analytical features such as the repeatability and the calibration characteristics in standard solutions of analytes were performed. As an application, the determination of the antioxidants contained in commercial chewing gum samples was carried out by applying a simple extraction procedure.

The main advantages of the combination of MPA and FIA are their simplicity, low cost of instrumentation, speed of simultaneous measurement and use of small amount of the sample, whereas the method still enables the application to the detection of micromolar analytes quantities.

Keywords: flow injection analysis, multiple-pulse amperometry, glassy carbon electrode, antioxidants

Acknowledgement

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Molten Lithium-Sulfur Cell with Solid Electrolyte

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The lithium-sulfur (Li-S) battery is one of the most practically promising alternative to the current lithium-based batteries, for its high energy density with inexpensive price. Low melting point of lithium and sulfur, and highly insulating nature of sulfur, however, limits its high-temperature applications [1]. Above its melting point, the volatile sulfur directly reacts with the lithium in anode, which decrease the electrochemical capacity. To avoid these drawbacks, the molten salt batteries with lithium alloy (LiSi) anode and iron disulfide compound (FeS_2) cathode are widely adopted due to their high melting temperature [2]. The desirable elements that participate in the electrochemical reaction are the lithium from LiSi and the sulfur from FeS_2, which impose theoretical limitations on molten salt batteries in improving the energy density. In addition, the molten salt used as an electrolyte can leak seriously when the battery is overheated by a thermal runaway, causing electrolyte depletion or short circuit [3]. To remedy these shortcomings, we have proposed a molten Li-S cell consisting of a lithium anode and a sulfur anode, along with solid electrolytes capable of lithium ion transfer and low chemical reactivity at high temperatures. The discharging performance based on the weight of the active material was greatly improved as compared with the conventional molten salt battery. When compared to molten-salt electrolytes, the solid electrolyte has a wide operating temperature range and it also opens up the possibility of rechargeability as well as effectively preventing leakage of the molten active material. When the molten salt film was added to the electrode and electrolyte interface, the contact resistance was reduced and the output characteristics were improved. Molten Li-S batteries have proven to be promising alternatives to molten salt batteries for energy storage applications. If the stability of the charge and discharge system is secured, the application field is expected to be further expanded. This could be a solutions for future thermal battery as well as renewable energy storage to make up for the instability of wind and solar power.

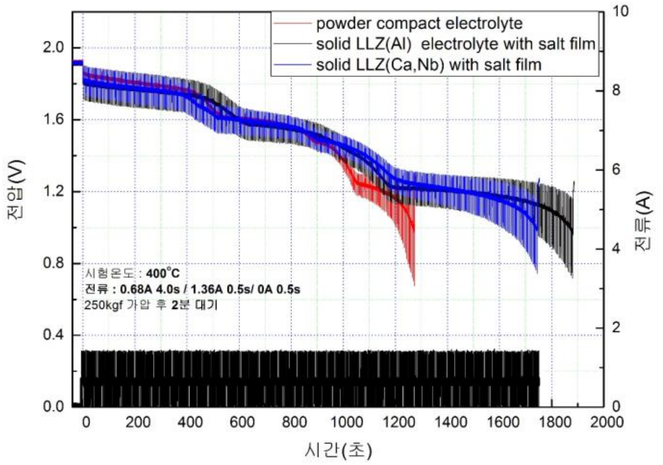

Figure. Discharge characteristics of the lithium-sulfur single cells with the $Li_7La_3Zr_2O_{12}$ (LLZ) solid electrolyte and LiF-LiCl-LiBr molten electrolyte.

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Coupling Anodic Processes with Cathodic H_2O_2 Generation for Environmental Remediation Processes

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Electrochemical processes present potential applicability to remediate a wide variety of environmental issues. Particularly, coupling or pairing the anodic and the cathodic processes in such a way that both reactions contribute to the global objective is an interesting form of optimizing the investment and operating cost of electrochemical reactors [1].

Different anodic processes such as direct or mediated generation of oxidants, photo-assisted TiO_2 oxidation or Fe/Al electro-coagulation are of interest for wastewater treatment. In the opposite electrode, the cathodic reduction of oxygen to *in situ* generate hydrogen peroxide is of great interest thanks to the variety of applications and the environmental compatibility of this compound. In this work, two examples of coupled environmental remediation processes which involve cathodic production of H_2O_2 are under study.

The hydrogen peroxide can be activated by means of Fe salts to yield high-oxidizing species, such as the hydroxyl radical ($OH^{\bullet}$) (Eq. 1) whereas a boron-doped diamond can simultaneously produce $OH^{\bullet}$ radicals by water splitting (Eq. 2):

$H_2O_2 + Fe^{2+} \rightarrow OH\bullet + Fe^{3+} + OH^-$ (Eq. 1)
$M + H_2O - 1e^- \rightarrow M\,(OH\bullet) + H^+$ (Eq. 2)

The peracetic acid (PAA) is increasingly used in the industry, such as disinfectant or for the removal of organic pollutants. In the present work, its synthesis is improved by the in-situ generation hydrogen peroxide (Eq. 3) from acetic acid solution with boron-doped diamond anode. Both processes, the cathodic production of hydrogen peroxide and the anodic oxidation of acetic acid, are combined to increase PAA production [2].

$CH_3COOH + H_2O_2 \leftrightarrows CH_3COOOH + H_2O$ (Eq. 3)

The main innovation under study in the present work is the optimization of two key aspects of the reactor: aeration and cell potential. The air is supplied by means of a Venturi-based jet aerator to eliminate the need for a compressor [3]. Also, the cell potential is minimized by reducing the inter-electrode gap in a novel flow-through microfluidic reactor.

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Acknowledgments

Financial support from the Spanish Ministry of Economy, Industry and Competitiveness and European Union through project CTM2016-76197-R (AEI/FEDER, UE) is gratefully acknowledged.

Anode-Catalyst Contact Resistance as a Limiting Aspect of the PEM Water Electrolysis Performance and Durability

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Proton exchange membrane (PEM) water electrolysis represents a modern version of the electrochemical water decomposition process with numerous advantages over the traditional alkaline route. The most important amongst them are high intensity, flexibility and efficiency of the process. Due to these extraordinary properties, the PEM water electrolysis process is nowadays considered and an inevitable part of vision of a hydrogen economy. This is a strategy allowing change in currently existing centralized energy supply structure based on the conventional and nuclear power sources to the decentralized systems utilizing predominantly renewable ones. In the transition phase then, PEM water electrolysis will serve to convert intermittent excess of the produced electrical energy into the chemical energy of hydrogen to be used as a raw material for suitable chemical or other technologies.

Although the PEM water electrolysis process exhibits extraordinary properties, its wide-spreading suffers from extremely high investment costs related mainly to the anode side of the electrolysis cell. Due to the highly corrosive environment on the anode (highly oxidative potential, acidic environment and occurrence of oxygen in atomic form), only few materials can be applied for its construction. Typical choice represents titanium in suitable form (felt or sintered foil) activated by IrO_2 as an oxygen evolution catalyst. Titanium, however, is a subject of gradual passivation and thus of increasing contact resistance between the electrode and electrocatalyst particles. In order to avoid this undesired phenomenon, titanium surface is prior to IrO_2 deposition modified by platinum. Platinum does not act here primarily as an electrocatalyst, but it fulfils the role of the surface layer protecting base metal against formation of massive passive layer. This approach dramatically increases already high costs of the electrolysis cell production.

In the present study process of titanium anode surface passivation is followed by means of Secondary Ions Mass Spectroscopy (SIMS) in connection with X-ray photoelectron spectroscopy (XPS) and suitable electrochemical techniques. This combination was used to analyze the extent of the surface passivation and composition of the electrode surface in dependence of the electrolysis conditions and duration of the sample exposure to the electrolysis process. In parallel, impact of the anode sample pretreatment (predominantly etching) was followed. It was concluded, that suitable surface etching allows to extend life-time of the anode significantly. Further study is, however, needed to understand this complex problem into the greater detail.

Acknowledgement

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Effect of Electrolyte Acidity on the SPS Decomposition in Cu Electrodeposition

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The Cu superfilling without voids has been demonstrated by curvature enhanced accelerator coverage (CEAC) mechanism with the combinations of organic additives. Detail control in the concentrations and types of the organic additives enables the reliable filling since the bottom-up filling is mainly explained with the increase of accelerator coverage at the bottom of features by the reduction of geometrical area [1].

Decomposition or incorporation of the accelerator occurs during the Cu electrodeposition, which changes the additive concentrations. Especially, SPS, one of the most famous accelerators used in Cu metallization, decomposes through various chemical side reactions on anode, cathode, and electrolyte [2]. During continuous usage of the plating solution, the dissociation of disulfide bonds in SPS on the anode and cathode surface accompanies the production of 3-mercapto-1-propane sulfonate (MPS) and 1,3-propane disulfonic acid (PDS). Several studies revealed that MPS accelerated Cu deposition faster than that of SPS. The addition of MPS deteriorates the filling performance by disturbing the selective Cu deposition on the bottom [3]. It is reasonable to consider that the produced MPS by the decomposition of SPS during the electrodeposition can be rapidly changed to SPS in over pH 2 [4]. The PEG and chloride effects were investigated in high pH solution [5]. However, SPS was not sufficiently checked.

In the present work, we improved the filling performance at higher applied current density by changing the pH of the electrolytes. As shown in Fig. 1, the filling results showed that void was formed at high current density in low pH comparing to high pH condition. It was explained by considering the surface concentrations of SPS and MPS during the Cu electrodeposition based on the pH. As shown in Fig.2, MPS concentration was higher at low pH electrolyte and formation of MPS was increased with increasing of current density, which was related to Fig. 1. Increase of MPS makes void through acceleration effect on the entrance of trench. In addition, the SPS decomposition rate measured by modified CVS method during electrodeposition was increased with low current density under the controlled applied charge. It is possible that SPS coulombic efficiency is not influenced by current density in low value region because the high current density makes the increase of SPS decomposition rate [6]. Furthermore, to check the anode and cathode respective reactions of accelerator in both pH conditions at various current density, MPS and SPS concentration is measured with membrane separator by electrochemical analysis.

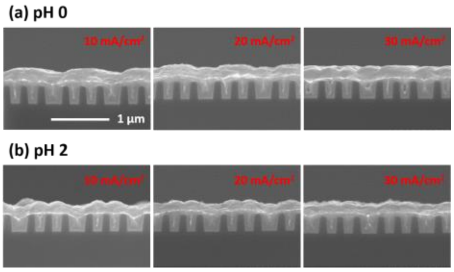

Fig. 1. Filling performance of different pH current density.

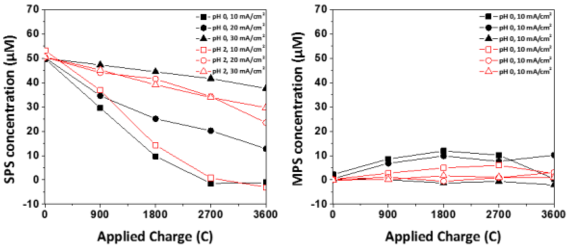

Fig. 2. The decomposition of accelerator concentration in different pH with various current density.

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DFT study on Electrochemical Reductions of CO_2 on Boron-doped Diamond Interfaces

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Boron-doped diamond (BDD) is an attractive candidate for electrochemical reduction of CO_2 due to its unique properties, like wide-potential window, low background current, high stability, and high selectivities,[1] compared to the other electrodes.[2] In this work, we investigated the paths and mechanisms of CO_2 reduction at typical BDD (111) interfaces with H- and OH-terminations, by means of density functional theory (DFT) calculations. The structures of considered products, like CO*, HCOOH*, and HCHO*, as well as several radical species, like COOH*, HCOO*, and CHO*, at the interfaces of water and BDD were investigated using DFT-based molecular dynamics. The pair radial distribution functions show that both possible products and radical species weakly interact with BDD interfaces. To further explore reaction paths, the reaction enthalpies (ΔH) were evaluated using computational hydrogen electrode approach.[3] We found that hydrogenation of CO_2* to HCOO* is energetically favorable than protonation of CO_2* to COOH* on both (111)H and (111)OH surfaces (**Figure 1**). Moreover, ΔH of HCOOH* is lower than that of CO* on both (111)H (ΔH = –0.05 and 0.76 eV for HCOOH* and CO*, respectively) and (111)OH (ΔH = –0.11 and 0.69 eV for HCOOH* and CO*, respectively) surfaces, which indicates formation of HCOOH* is energetically favorable than that of CO*. In addition, further reduction of HCOOH* to HCHO* requires passing the radical special CHO* with high ΔH (1.84 and 1.79 eV on (111)H and (111)OH surfaces, respectively). The mechanism of formation of HCOOH* was further investigated from the electronic states.

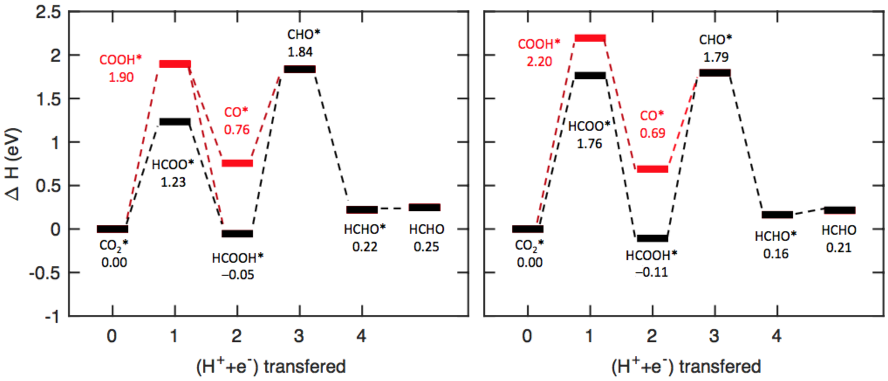

Figure 1. The reaction enthalpies (ΔH) of electrochemical reduction of CO_2 on BDD(111)H (left panel) and BDD(111)OH (right panel) surfaces calculated by means of the computational hydrogen electrode approach.[3]

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Copper Based Ionic Liquids for Heat-to-Power Conversion and Storage

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The energy density of non-aqueous redox flow batteries is limited by the solubility of the redox active species. Recently, copper based ionic liquid (CuIL) $[Cu(ACN)_4][Tf_2N]$ with high charge density of 300 kC L^{-1} and energy density of 75 Wh L^{-1} has been demonstrated [1]. Unfortunately, due to poor electrochemical performance of the redox couples and the unoptimized membrane, the energy efficiencies of 10 to 30 % were reached [1]. We have recently proposed that a similar system can be utilized for conversion of heat into electricity, as the removal of the complexing agent acetonitrile (ACN) by distillation results in the instabilization of the Cu(I), followed by disproportionation to regenerate the starting materials of the charged battery, namely Cu and Cu(II) [2].

The combination of these two approaches, with the addition of a non-aqueous co-solvent improves the electrochemical performance of the half-cell reactions, and results in a system that can be charged also with heat. In this presentation, the electrochemistry and conductivity of different ratios of the CuIL and the co-solvent will be evaluated to obtain the optimum battery performance, and full cell measurements with different membranes will be reported. The battery efficiencies as well as the efficiency of the thermal discharge will be evaluated. Additionally, the option of using Cu slurry electrolytes will be discussed.

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Grain Size-Controlled filling of Through Silicon Via

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Copper is widely used as metallization material because of its superior properties, high electromigration resistance and low electrical resistivity [1]. Thus various Cu electrodeposition methods for metallization have been studied by using organic additives, or controlling current/potential profiles such as pulse/pulse-reverse depositions [2, 3]. However microstructures of Cu interconnection, such as grain size, texture, and grain size distribution, were rarely investigated though they have a strong influence on resistivity and reliability of Cu interconnects [4, 5]. The final microstructure of electrodeposited Cu is determined by accumulated energies within the deposit occur and electrodeposition generates various defect sites originating from impurities in a deposition electrolyte [6]. In particular, a use of organic additives to obtain preferred deposition profiles and/or deposit properties induces defects in the Cu deposit strongly. In Cu interconnection, organic additives are essential because they can control local deposition rate by adsorption on surface being deposited, thereby inducing void-free filling of Cu interconnection. Therefore, revealing the effect of organic additives on grain growth is important for the improvement of line properties in Cu metallization.

Herein, we examined the effects of polyethylene glycol (PEG) and bis-(3-sulfopropyl) disulfide (SPS) on grain growth in electrodeposited films during self-annealing as a basic research (Fig. 1). PEG and SPS are the representative additives, suppressor and accelerator, respectively, for void-free filling of vias and trenches in damascene structure. When they were added together, the drastic grain growth was observed due to their dynamic interaction. However, as the leveler was added, it disturbed their interaction in the approximate condition to top of TSV (Fig. 2). Therefore, we can perform grain size-controlled filling of TSV using these effects of organic additives.

In conclusion, we will investigate grain growth of each condition, caused by residual stress accumulated in the films under the effect of organic additives. And also, we will introduce the method for grain size-controlled filling of TSV using properties of organic additives.

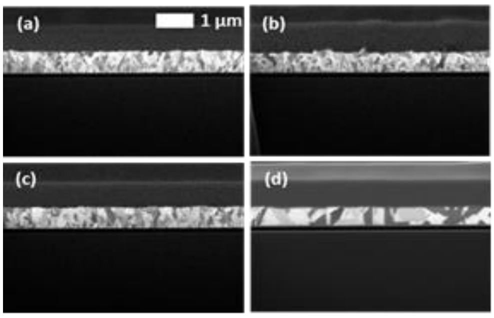

Fig. 1. Focused Ion Beam (FIB) images of films with PEG 3400 and/or SPS; (a): F_{free}, (b): F_{PEG}, (c): F_{SPS}, and (d): $F_{PEG-SPS}$.

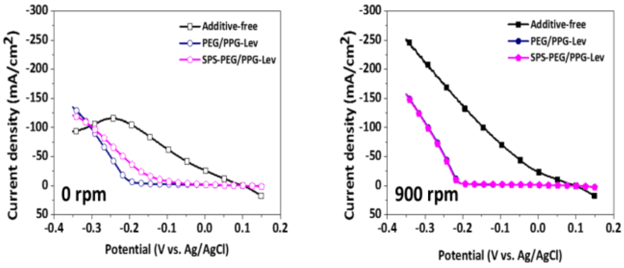

Fig. 2. Linear sweep voltammogram with organic additives at (a) 0 rpm and (b) 900 rpm.

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Electrochemical Investigation of Modified Aluminum Anode Surface for Rechargeable Aluminum-ion Battery

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Problems of environmental pollution and resources limitation have been issued while using fossil fuels, it requires the development of new energy conversion systems such as green energy and lithium-ion batteries. However, the cost of lithium sources such as $LiCoO_2$ and Li_2MnO_4 has been increased. To overcome this drawback of cost and safety issue, the metal-ion battery system, redox flow battery, sodium-ion battery, magnesium-ion battery and aluminum-ion battery[1-2], has been carried out. Aluminum-ion battery, which is one of these alternative battery systems, has been actively studied for decades. Aluminum is abundant in earth's crust and high energy density with 1.06kWh/kg (Li-ion battery: 0.406kWh/kg). Three electron reaction, trivalent Al^{3+} compared to competitive alternative to single electron Li-ion battery, has a possibility to have a high capacity.

Most works for Al-ion battery have been focused on the cathode to increase capacity because the overall capacity is limited by cathode materials in intercalation/de-intercalation system, such as graphite[1], MoS_6[2], V_2O_5 nanowires.[3] However, the aluminum as an anode material modified by either chemical or electrochemical treatment has not been discussed yet. Electrochemically etched aluminum has a large active surface area and has been used as an anode of electrolyte capacitor and its morphology can be easily controllable with applied current density, frequency and chemical etching conditions. Etched aluminum has high density of etch pits that can be active site during charging and discharging reaction.

In this work, we investigated the effects of aluminum as anode on Al-ion battery with graphite and ionic liquid as cathode and electrolyte, respectively. Surface of aluminum anode was enlarged with the applications of AC and DC current in acid solutions. BET analysis shows that both two types of aluminum have large surface area. Surface morphologies with SEM shows high density of pits on etched aluminum: AC and DC etched aluminum have porous and long pits, respectively.

We assembled full cell aluminum-ion batteries with graphite cathode and ionic liquid ($AlCl_3$/[EMIM]Cl=1.3/1) as electrolyte in Swagelok cell. Electrochemical behaviors of aluminum anode were investigated with cyclic voltammetry and cycling test. Additionally, EIS measurement was carried out to analyze the electrochemical interface between aluminum anode and electrolyte. After long cycling test, anodes were disassembled and investigated with XRD and XPS.

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Molten Salt Infiltrated Ceramic Felt Separator for Li/FeS_2 Thermal Batteries

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Thermal batteries which adopt ionically non-conductive solid electrolyte at ambient temperature are primary power sources for military applications that involve elevated levels of shock, spin, vibration, and acceleration [1]. Conventional electrolyte for thermal batteries is composed of eutectic salt, such as LiCl-KCl or LiF-LiCl-LiBr, blended with magnesia (MgO) binder to retain the molten salt by capillary force during operation. Approximately 27 vol.% of MgO is needed to obtain the minimum strength for handling and to retain the molten salts [2]. The high MgO content, however, increases the internal resistance of the thermal batteries because MgO is electrical insulators, which resulting in decrease of energy density. In this study, ceramic fiber separator infiltrated with molten salt were suggested as a substitute for the conventional MgO-containing compacted electrolyte pellet in order to enhance the mechanical strength of electrolyte pellet and electrochemical performances of single cells for highly reliable thermal batteries. The infiltration, robustness and electrochemical performances of Li(Si)/FeS_2 single cells were evaluated. The mean flexural strength of ceramic separators infiltrated with binary molten salt (LiCl-KCl) was ranged from 2.795 to 6.289 $kgf \cdot cm^{-2}$, whereas the mean strength of the MgO-containing electrolyte pellet is 0.01 $kgf \cdot cm^{-2}$, which is exceptionally small compared to that of molten salt infiltrated ceramic separator. The electrochemical performances of Li(Si)/FeS_2 single cells assembled with thin alumina paper separator infiltrated with binary molten salts outperformed in operating time and energy density (Wh/*l*) by 16.5 % and 17.9 %, respectively, compared to the conventional MgO-containing separator. The improved electrochemical performances was attributed to the increased amount of molten salts infiltrated to the ceramic felt compared to the conventional type of separator, about 40 wt.% of MgO binder upon melting, which contributed to the reduced internal resistance and interfacial resistance between separator and electrodes. These results imply that the ceramic felt separator can be a promising alternative to the conventional pellet type separator, enhancing the mechanical strength and electrochemical properties

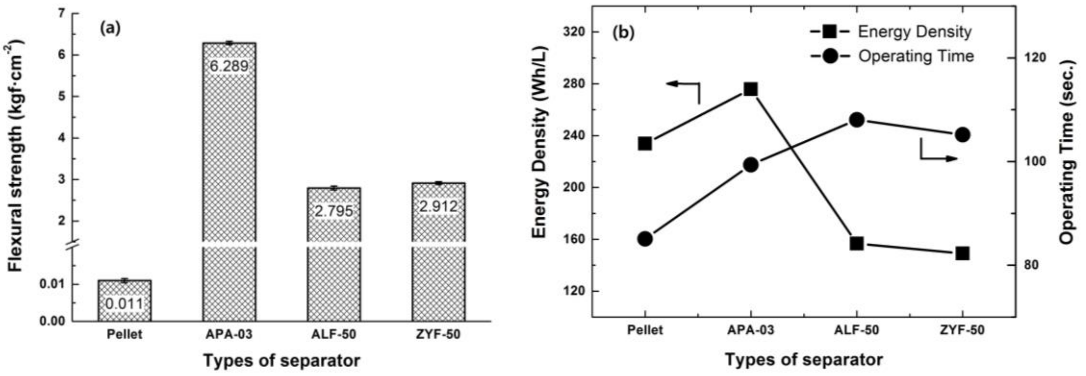

Figure. Flexural strength of ceramic separators infiltrated with binary (LiCl-KCl) molten salt (a) and discharge performances of Li(Si)/FeS_2 single cells (b).

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Self-terminating electrodeposition of atomic scale Platinum film on Titanium Nitride for Selective Electrochemical Reactions

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Platinum (Pt) is one of the most used constituent in a wide range of catalytic material. Although superior intrinsic catalytic activity of Pt, its high costs precludes the development of application, for example, electrode for hydrogen evolution reaction (HER) or low-temperature fuel cells [1]. To this end, various strategies were conducted to reduce the amount of Pt sources and improve the area/volume ratio of the Pt-group metal electrocatalyst, such as synthesis of shape controlled, core-shell/alloy/bimetallic nanoparticle, or foam type of Pt-alloy electrode [2, 3].

The deposition of film Pt layers also has advantage, and especially, electrodeposition of thin film is easy to fabricate and has good reproducibility compared to above nanoparticles or foam type electrode. Thin film contains naturally step-edge barrier to interlayer, which is the reaction site of catalytic material. From this account, nowadays, atomic scale ultrathin film have been performed [4], which is called 'self-terminating electrodeposition'. Self-terminating electrodeposition was conducted by applying small overpotential to form metal nucleation on foreign substrate before terminating by adsorbing hydrogen ion on deposited Pt metal, instantaneously. Adsorbed hydrogen ion terminated deposition. Deposited film by self-terminating electrodeposition may enhance activity for electrochemical oxidation of methanol and formic acid has been reported for ultrathin Pt films [5].

Another major hindrance of large-scale commercialization is carbon monoxide (CO) poisoning of Pt catalyst, which influence durability of catalyst so that support material is also crucial thing when fabricate the catalyst. The ideal catalyst support material should prevent corroding under strong oxidizing condition and have good electrical conductivity. In that sense, titanium nitride (TiN) is the one of the best materials for metallic support material in fuel cells. Moreover, TiN also has a good compatibility with Pt as a HER and OER catalyst by locating N vacancy which dispersed Pt atoms on TiN substrate and increased the ratio of edge/plane of Pt [6].

In conclusion, we will introduce the self-terminating electrodeposition to grow atomic scale ultrathin film and behavior of Pt on TiN substrate. Cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS) were used to analyze the film properties according to the cycle number of film thickness. In addition, catalytic performance was also observed with above information.

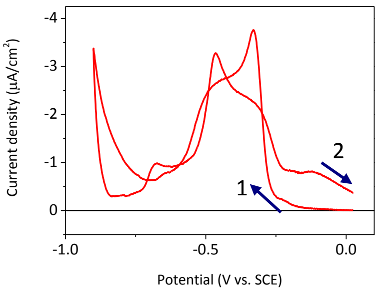

Fig. 1. Voltammetric analysis of Pt deposition.

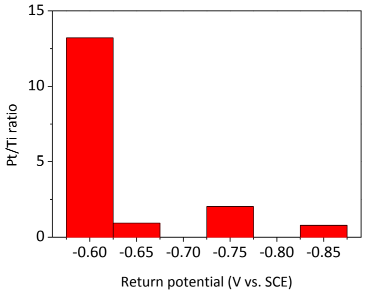

Fig. 2. XPS-derived Pt/Ti ratio as deposition potential.

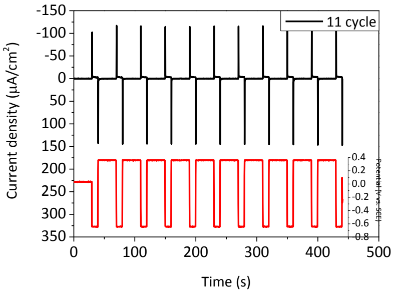

Fig. 3. Current and potential profile for Pt deposited

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Paper-based Biofuel Cell Array
Loading Fuel- and Buffer Salt-containing Paper Sheet

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Enzymatic glucose/O_2 biofuel cells are energy conversion systems in which enzymes oxidize glucose at a bioanode and reduce oxygen at a biocathode. These enzymes are highly safe toward humans, and highly selective for substrates, without leaving toxic residues at room temperature and neutral pH conditions. There are many recent studies on self-powered biosensing systems based on biofuel cells [1].

Paper-based BFCs (PBFCs), that are based on printing technologies, are attracting increasing attention as new energy harvesting systems for sensor tags, wearable biomedical devices, and small electrical devices [2]. Cellulose paper has been used as the substrate for these printed electrodes, which serves as a structural and mechanical support, as well as a proton exchange membrane. Due to its water absorbency, the paper also works as a pump and container by which the fuel solution is transported to the enzyme-immobilized electrodes. The PBFC is light and thin, and has several advantages such as safety during use, disposability, and cost of product. Recently, we demonstrated an array-type PBFCs, which have great potential for improved output power. In the present study, we newly proposed an array-type glucose PBFC loading glucose- and buffer salt-containing paper sheet. The present PBFC is expected to generate output power only by spraying water since the fuel is already loaded on the paper sheet in advance.

We designed a PBFC which was composed of 4-series and 4-parallel cells as shown in Fig. 1. Each area of the anode and cathode was 1 cm^2. The bilirubin oxidase of 10 U and glucose oxidase of 200 U were immobilized onto the cathode and anode surfaces, respectively. Tetrathiafulvalene was used as mediator of anode. The paper electrolyte layer shown in Fig. 1 contained 100 mM glucose and 1 M potassium phosphate. Fig. 2 shows the output power of the present PBFC. When the output power measurement was performed, only a ultrapure water was casted on the paper sheet. The present The open circuit potentials were 2.13 V. The maximum current and power of the 4-series/4-parallel cell was determined to be 0.84 mW,

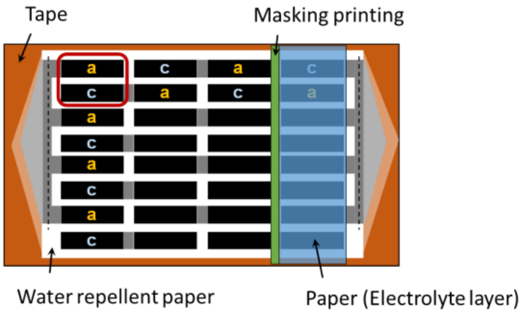

Fig. 1 Schematic illustration of the array-type PBFC

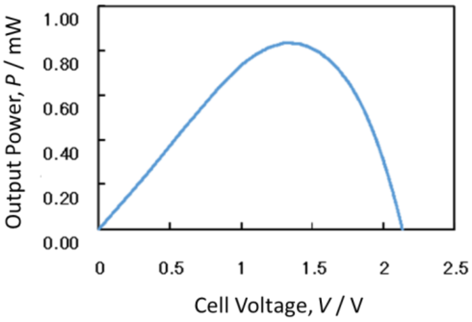

Fig. 2 Output power of the array-type PBFC

Acknowledgement
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Thermodynamic Analysis on the Formation of Anodic Aluminum Oxide Using Averaged Moving Approximate Entropy

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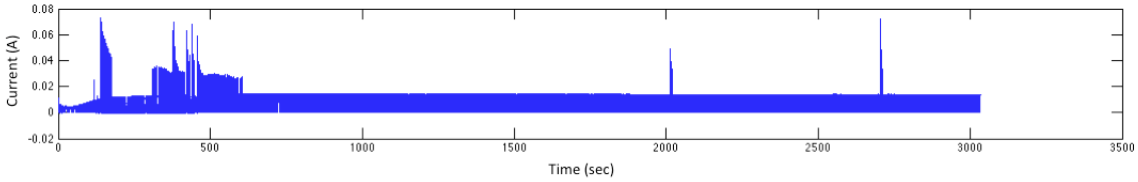
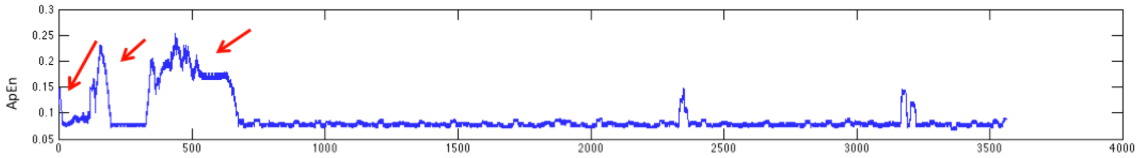
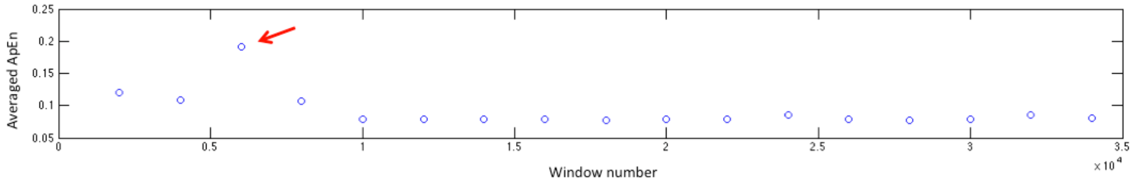
The formation of anodic aluminum oxide (AAO) is a well-researched topic, but seldom do researchers discuss this topic in the view of thermodynamic analysis. This article aims to discuss the formation of AAO grown via hybrid pulse anodization (HPA) under 25 ºC in 0.3 M oxalic acid for 1 hour by using moving approximate entropy (mApEn) algorithm [1]. A hybrid pulse composed of a positive step of 40 V and a negative step of -2 V, each step lasts for 1 second, was given to the low purity (99.5%) aluminum foil to grow AAO pores. The time series for analysis was derived from unfolding the data points of current along time axis (Fig. 1a). We used mApEn algorithm with window width 200 data points to transfer the time series to its thermodynamic profile (Fig. 1b). For revealing the trend of mApEn, the data were further averaged per 2000 data length (Fig. 1c).

The thermodynamic profile of the AAO growing process revealed at least 3 recognizable mechanisms behind the process (arrows in Fig. 1b). The first arrow may indicate the formation of the initial barrier oxide, the second arrow may indicate the non-steady state of pore formation, and the third arrow may indicate the steady-state pore growth [2]. The ApEn profile showed no significant change after the initial of steady-state pore growth (the third arrow in Fig. 1b) which indicated that the number of pores has no significant increase during this stage, and which also may indicated that the rate of pore growth and pore etching due to the electrochemical reaction reached a balance and therefore leads to the steady growth of the AAO pores. The significant increase of ApEn trend variation may refers to a stage of massive pore initiation and formation (arrow in Fig. 1c) during the process. After the pore initiation and formation stage, the ApEn trend tend to decrease and then remains a slight ups and downs, which may refers to the balance between pore growth and pore etching during such electrochemical process. We have demonstrated a method for studying the thermodynamic property of the AAO formation process via HPA method for a single-step AAO growth process.







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Fabrication of Enzyme-immobilized Janus Micromotor based on Amino group-functionalized Polystyrene Particles

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Bubble-propelled nano-/micromotors, converting chemical energy into movement, have enjoyed increased attention owing to a variety of their potential applications, e.g., biomaterial isolation, active drug delivery, and environmental cleaning [1]. Previously reported nano-/micromotors can be broadly divided into two types, i.e., tubular motors, possessing a tubular catalytic layer, and Janus motors, featuring nano-/microparticles covered by a catalytic layer on one side only. Although the design and fabrication of tubular and Janus nano-/micromotors have been extensively studied,1 their practical implementation is still challenging. In the present study, we fabricated enzyme-powered Janus nanomotors based on the amino-group functionalized polystyrene (PS) particles (Fig. 1).

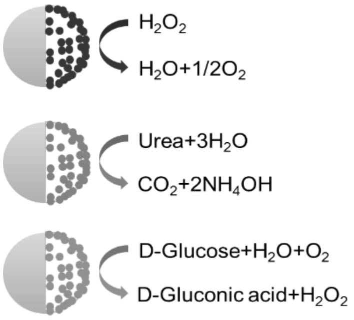

Fig. 1 Schematic of enzyme-immobilized Janus micromotor

PS particles having amino group were prepared by a soap-free emulsion polymerization method [2]. Catalase, urease or glucose oxidase was immobilized by dispersing the PS particles in a phosphate buffer solution containing an enzyme and stirring for 16 hours. The micromotor was analyzed by scanning electron microscope (SEM) and energy dispersion X-ray analysis (EDS). Drive evaluation of the micromotor in solutions of various concentrations was carried out using an optical microscope.

The results of SEM imaging and EDX mapping of Janus nanomotors confirmed that the size of the nanomotor was 850 nm and Au covered only one side of their surface, preventing the affected amino groups from reacting with glutaraldehyde. In this presentation, we investigated the moving speed of the micromotors in detail with movies.

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Stabilization of redox enzymes by kosmotropic anions with ammonium ion for applications to bioelectrochemical devices

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Electro-enzymatic reactions combining oxidoreductase and electrode reactions allow highly selective electrochemical oxidation/reduction of reactants under mild reaction conditions, with a very small overpotential. The technology has already been applied to electrochemical biosensors, enabling selective and quick measurements of specific substances. Moreover, biofuel cells, which convert chemical energy of the oxidation of carbohydrates, such as glucose, in combination with oxygen reduction, under mild condition, have been developed as power sources for wearable devices and self-powering blood glucose sensors.

Glucose dehydrogenase with flavin adenine dinucleotide as a cofactor (FAD-GDH) has received considerable attention as an electrocatalyst for glucose anodes owing to its excellent substrate selectivity toward glucose and lack of O_2 reactivity. The enzyme is already used in single-use blood glucose sensor strips. Bilirubin oxidase (BOD) from *Myrothecium verrucaria* has been used as an electrocatalyst for oxygen reduction catalysts operating under neutral conditions.

Considering the long-term usage of FAD-GDH/BOD based bioelectrochemical devices operating between room temperature and body temperature involving a continuous glucose monitoring system and biofuel cells, output performance is limited by the inactivation of enzymes on electrodes. To extend the lifetime of the enzyme, the use of additives for enzyme stabilization has been studied. In this study, we aimed to prevent FAD-GDH and BOD inactivation using additives in the reaction system.

The thermal stability of FAD-GDH from *Aspergillus terreus* and BOD from *Myrothecium verrucaria* in phosphate buffer solution was substantially improved by kosmotropic anion, like SO_4^{2-}, with ammonium ion. The activity of FAD-GDH with 2 M ammonium sulphate did not change after 30 min heat treatment at 60°C, while no residual activity was observed for FAD-GDH in a solution in the absence of ammonium sulphate. The CD spectral change depending on the temperature revealed that the stabilizing effect of the electrolytes was strongly related to the structural stability of the enzyme, which controls enzyme compaction and irreversible inactivation.

Bilirubin oxidase-catalyzed oxygen reduction cathode using MgO-templated carbons

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1. Introduction

It is important to improve the performance of oxygen reduction biocathode for the development of enzymatic biofuel cells. Porous carbon gathers considerable attentions as electrode materials. We reported high catalytic oxygen reduction current catalyzed by bilirubin oxidase (BOD) using the 40 nm pore size MgO-templated carbon (MgOC).[1] Herein, we investigated the dependence of electrode reaction of BOD on six MgOCs with different pore-size distribution in the ranging from 5 to 150 nm in order to optimize the pore size of MgOC for the BOD-based biocathode. We also further modified 6-amino-2-naphthoic acid (6A2NA)[2] on MgOC surface to induce a favorable orientation of BOD.[3]

2. Experimental

BOD was donated by Amano Enzyme Inc. and used without further purification. Figure1 shows the pore size distribution of MgOCs (Toyo Tanso Co. Ltd., Japan) analyzed by BJH method. MgOC and poly(vinylidene difluoride) were mixed in N-methyl-2-pyrrolidone using an ultrasonicator. The carbon ink was applied on a glassy carbon electrode (GCE, 3mm diameter). The electrode was dried in an oven at 60°C for 12 h to obtain MgOC-modified GCE (MgOC-GCE). The MgOC-GCE was immersed into the BOD solution (1.0 mg/mL) at 4°C for 6 h to adsorb the enzyme. The MgOC-GCE was modified by anodic oxidation of amines in the 6A2NA solution.

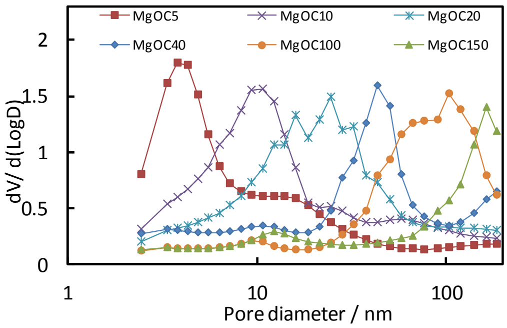

Fig.1 Pore-size distribution of MgOCs analyzed by BJH method. The subscript number indicates the average pore diameter/nm of MgOC.

3. Result and Discussion

Figure 2 shows the dependence of the catalytic current per carbon weight on the pore size of MgOCs. MgOC$_5$-GCE was not able to adsorb a sufficient amount of BOD because the molecular size of BOD (ca. 6 nm) was larger than the pore size. However, the catalytic current was higher than that of MgOC$_{10}$-GCE, because the particle size of MgOC$_5$ was smaller than that of other MgOCs. For MgOC$_{10}$, MgOC$_{20}$, MgOC$_{40}$, and MgOC$_{100}$, as the pore size got larger, the catalytic current increased. It suggests the amount of BOD adsorbed inside the carbon particles increased. For MgOC$_{150}$-GCE, the catalytic current was lower than that of MgOC$_{100}$-GCE. It implies that the multi-layer of BOD limits the substrate supply inside the pore. When 6A2NA was modified on the surface of MgOC$_{100}$, the catalytic voltammogram at low overpotential showed sharp cathodic current increase. The result suggests that the favorable orientation of BOD by 6A2NA modification improved the interfacial electron transfer rate.

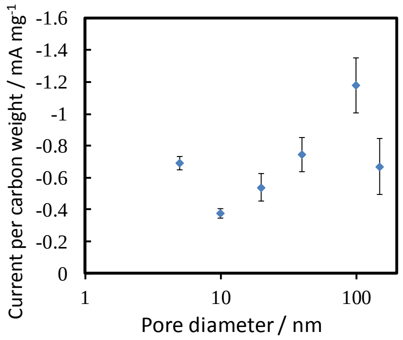

Figure 2. Pore-size dependence of the BOD-catalyzed O_2 reduction current at 0.2 V (vs Ag/AgCl) per carbon weight

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Preparation of Biofuel Cell Anode coated by Poly-(ethylene glycol) Diacrylate Gel

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Recently, electrochemical wearable biofuel cells consisting of a fuel (i.e. sugar and sweat) oxidizing anode and an oxygen reducing cathode have been attracted attention [1,2]. We have reported a flexible paper-based biofuel cell and it's application as a wearable device [3]. To suppress the dissolution of enzymes and mediators during power generation when body fluid is used as a fuel, we focused on a biocompatible hydrogel. In the present study, we newly fabricated a bioanode composed of enyzmes (i. e. glucose oxidase) and poly-(ethylene glycol) diacrylate (PEGDA) hydrogel, immobilized on porous carbon electrode.

The hydrogel was prepared by using PEGDA as a polymer, a ammonium persulfate (APS) as a polymerization initiator, and a N, N, N', N'-tetramethylethylenediamine (TEMED) as a catalyst. These chemicals were dissolved in a phosphate buffer. Each concentration was 0.1 mol L^{-1}. A porous carbon ink using MgO-templated carbon was coated on a glassy carbon disk electrode (MgOC-GCE). The porous carbon ink was prepared by mixing a MgO-templated carbon (MgOC), a poly-(vinylidene difluoride) and a N-methyl-2-pyrrolidone.

A saturated tetrathiafulvalene (TTF) solution and a glucose oxidase (GOD) solution were placed onto MgOC-GCE. The electrode was dried under reduced pressure for 1.5 h. Then, the hydrogel was modified by casting the prepared hydrogel solution onto the GOD-immoblized MgOC-GCE and dried at room temperature under an argon atmosphere. In the prepared electrode, cyclic voltammetry (CV) was carried out at a scan rate of 10 mV s^{-1}. The scan range was changed from -0.2 V to 0.4V.

Figure 1 shows cyclic voltammograms of the bioanode for the hydrogel-coated GOD-modified MgOC-GCE in the presence of 100 mM glucose in 100 mM phosphate buffer (pH = 7.0). A catalytic wave for glucose oxidation was observed compared to the background, indicating the enzymatic reaction was occurred in the hydrogel. In addition, the stability of the bioanode was also evaluated from the cyclic voltammogram (100 cycles), and the corresponding results are shown in Fig. 2. The decrease of the current density was smaller during 100 cycles by coating the hydrogel, compared with the case without hydrogel.

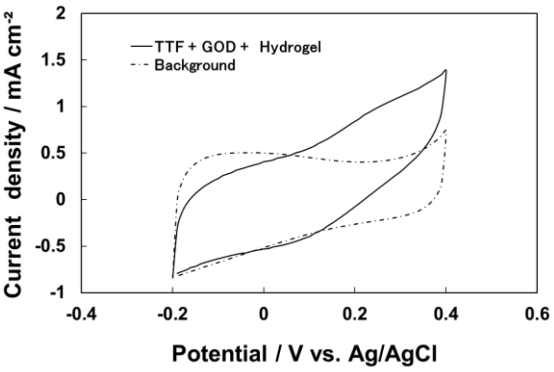

Fig.1 Cyclic voltammogram of Bioanode

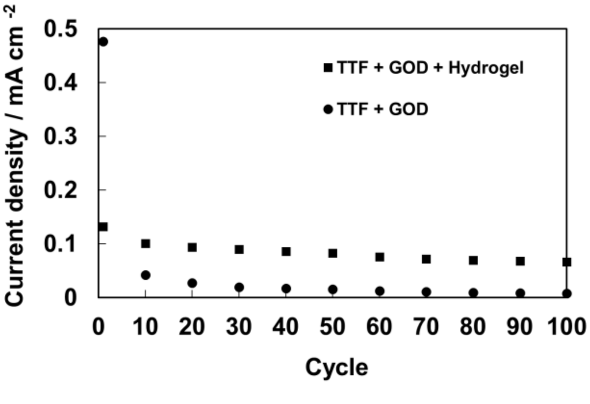

Fig.2 Stability test estimated by Peak Current density of the cylic voltammograms (100 cycles)

Acknowledgement
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Entropy Evaluation of Commercial 18650 Type Lithium Ion Cell

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The entropy evaluation is an important factor for discussing the thermal behavior of lithium ion cells. The heat of the entropy change is related to the used electrode material of the lithium ion cell.[1] The purpose of this study is to investigate the heat generation and endothermic behavior of the cell by measuring the entropy change versus SOC (State of Charge). The used 18650 type lithium ion cell consists of $LiCoO_2$ for the positive electrode and graphite for the negative electrode. The calculation formula for obtaining the entropy change is given by, [1]

$$\mathrm{OCV} = \frac{\Delta H}{\mathrm{nF}} + \frac{T\Delta S}{\mathrm{nF}},$$

where, OCV is open circuit voltage, ΔH is enthalpy change, ΔS is entropy change, F is the Faraday constant, and n is the number of electrons involved in the reaction ($n = 1$).

A commercially available 18650 type lithium ion cell was used in this study.[2] The SOC of the cell was adjusted to 0, 25, 50, 75 and 100%. The SOC adjusted cell was settled in the thermostatic oven (HP-120-25, ISUZU) and the OCV was recorded by changing the temperature inside the oven. The temperature was changed from 20°C to 0°C, then the temperature was raised to 30°C at 10°C step and again fallen to 20°C. The OCV was measured at each temperature for 1 hour using a charge/discharge device (PFX2011, KIKUSUI).

Figure 1(a) demonstrates a time-dependent OCV of the cell, of which the SOC was adjusted to 0%, as a function of temperature. The averaged OCV data were plotted versus temperature as shown in Fig. 1(b). By using the equation, ΔS can be calculated from the slope of the straight line seen in Fig. 1(b). Similarly, OCV measurements were performed for the cell with SOC = 25, 50, 75 and 100% to evaluate the magnitude of ΔS. The results are summarized in Fig. 2. In the figure, at SOC = 50%, an inflection point of ΔS is confirmed. This is the same trend as an SOC-dependent ΔS in lithium ion cells.[1] Since ΔS has a negative value, the result of Fig. 2 indicates that an endothermic reaction occurs during the charging and an exothermic reaction does during the discharge. These results are consistent well with the thermal behavior of the cell during the charge/discharge operation.[3]

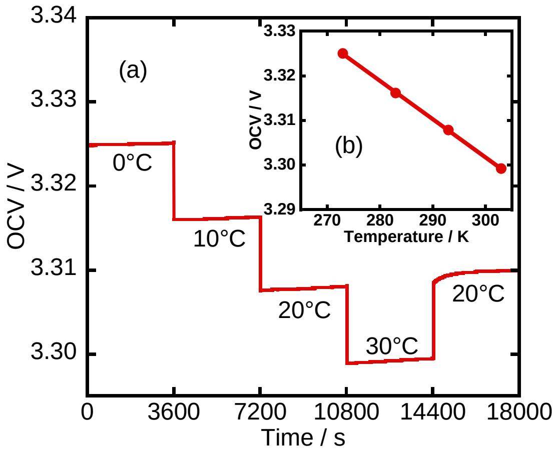

Fig. 1(a) OCV vs. time of the 18650 type lithium ion battery, (b) OCV vs. temperature of the 18650 type lithium ion cell (SOC: 0%).

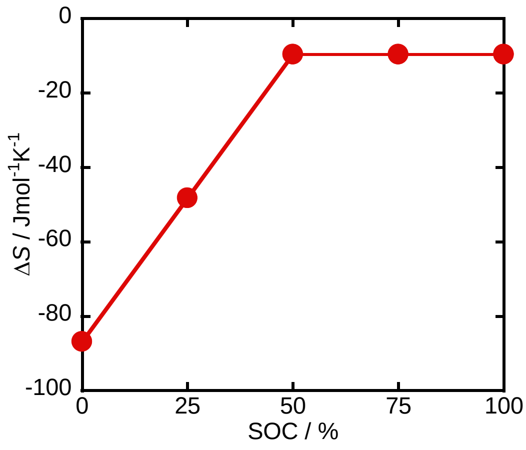

Fig. 2 Entropy vs. SOC of the 18650 type lithium ion call at 20°C.

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Mn Surface Doping for Improved Thermal Properties of Ni-rich Layered $LiNi_{0.82}Co_{0.12}Mn_{0.06}O_2$ Cathode for Lithium Ion Battery

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Ni-rich layered cathode, $LiNi_xCo_yMn_zO_2$ (NCM, $x > 0.6$, $x + y + z = 1$) has been considered as promising cathode materials for EVs (EV, PHEV, HEV) because of its high capacity resulted from high Ni content in transition metal site. However, the essential limitation of using Ni-rich NCM is rapid capacity fading during cycling due to material degradation especially at high temperature. It is supposed that structural instability is increased with increasing Ni portion, which will lead poor cycle performance of Ni-rich NCM. Thermal stability is also decreased by high nickel content because of weak Ni-O bonding in framework. Ni dissolution from cathode surface by undesirable side reaction between electrode and electrolyte have been usually discussed as main reason of material degradation. To overcome these negative features, surface doping would be effective way to improve thermal properties of Ni-rich NCM materials.

In this study, Mn surface doping was designed in order to construct more stable surface structure by reinforcing metal-oxygen bond in Ni-rich NCM. To achieve effective Mn surface doping, surface of $LiNi_{0.82}Co_{0.12}Mn_{0.08}O_2$ (NCM) was coated with Mn using Mn acetate as coating source by wet process. Mn coated NCM was then heat treated. Finally Mn surface doped NCM (Mn-NCM) was prepared. The electrochemical as well as physico-chemical characteristics of pristine NCM and Mn-NCM were investigated using various analytical techniques. No impurity and lattice parameter change were observed by XRD measurement. Higher Mn content was obtained at surface of Mn-NCM by cross-section TEM-EDS analysis, where surface composite of Mn surface coated NCM was $LiNi_{0.71}Co_{0.10}Mn_{0.19}O_2$. As shown in Fig. 1, TEM-EDS linear mapping indicates Ni content is increased from surface to center of NCM particle while Mn and Co contents are decreased. The depth of Mn doping depth is about 150 nm. Particle hardness was measured, and is found to improve from 51 MPa to 110 MPa as a result of Mn surface doping. High temperature (60°C) cycle performance indicates the enhanced cycle performance was obtained for Mn-NCM. Even capacity retention after 50 cycle was 31% for pristine NCM, that of Mn-NCM was maintained up to 61%. DSC curves for charged cathode show that main exothermic peak is increased from 214°C to 231°C by Mn surface doping. This result emphasizes that a surface doping is effective to improve thermal stability of NCM. The detail results will be discussed at meeting.

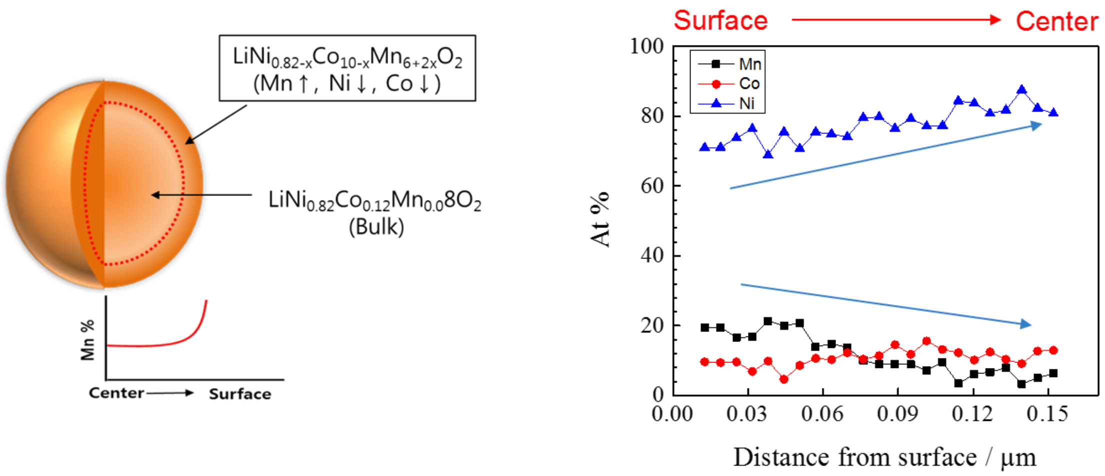

Fig. 1. Schematic draw of the surface doping and cross-section TEM-EDS linear mapping results of Mn surface doped $LiNi_{0.82}Co_{0.12}Mn_{0.08}O_2$

Dependence of adsorbed CO on electrode potentials and Electrolytes for electrocatalytic reduction of CO_2 on Pd nanoparticles

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In light of the ever-increasing energy demands due to a growing population and a constant rise in living standards, the accumulation of greenhouse gas, CO_2, in the atmosphere causes a severe challenge for the human society and leads the global worming pressing issue. The electrochemical reduction of CO_2 into useful fuels is one of the main methods for reducing CO_2 accumulation, which has attracted great attention due to some advantages including the control of the reaction rate and product selectivity.

In this work, the electrochemical reduction of CO_2 was studied using gas diffusion electrodes (GDEs) with Pd nanoparticles/carbon black as the electrocatalyst. We study the electrochemical properties, faradaic efficiency of CO generation, onset potential of CO_2 reduction, and electrolyte effect for various metal catalysts in order to develop desired catalysts with high activity and good product selectivity. Here $KHCO_3$, K_2SO_4, K_2HPO_4, KCl, and $K_2C_2O_4$ were employed as the supporting electrolytes. $KHCO_3$ has been found to facilitate the electrochemical reduction of CO_2 meanwhile the Faradaic efficiency of CO generation and current density of CO_2 reduction can be up to 95% and -7.8 mA cm^{-2} at -0.8 V vs. RHE, as shown in Figure 1.

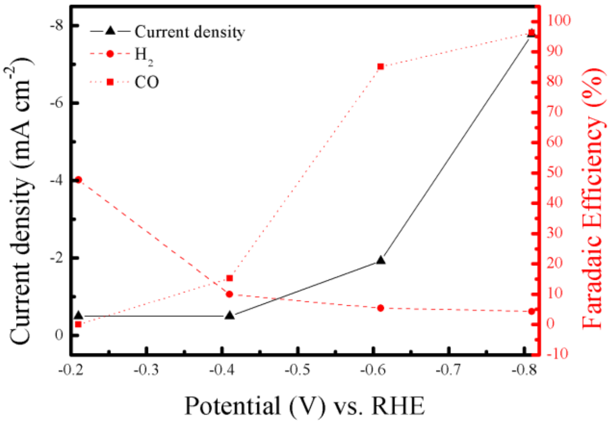

Figure 1. Total current density and Faradaic efficiency of H_2 and CO generation on the Pd/XC72-coated gas diffusion electrode for 1-h electrolysis.

Keywords: Pd nanoparticles, gas diffusion electrode, carbon monoxide, CO_2 reduction

High Selectivity Reduction of CO_2 to CO on Fe/N/C Catalyst with Excellent Tolerance to Metal Impurities

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Electrocatalytic reduction of CO_2 (CO2RR) is considered as a potential strategy to solve energy problem. However, CO2RR catalysts suffer from a large overpotential and low selectivity, thus rational design of efficient electrocatalysts is crucial. Here, we reported a novel Fe/N/C catalyst for CO2RR with high CO selectivity (99%) at a moderate overpotential of 0.44 V (Fig. 1A). It has been demonstrated that the high selectivity stemmed from the high micropores structure facilitating CO_2 to take up the active sites of Fe/N/C catalyst and leading to high CO selectivity on the basis of strong CO_2 adsorption capacity (Fig. 1B).

High tolerance to metal ion contaminant is also important for CO2RR catalysts, since this reaction occurs at a relatively low potential, where metal ions in electrolyte can be deposited easily on electrode surface and accelerate the side reaction—hydrogen evolution. Herein, the prominent tolerance to metal impurities was observed on the as-prapared Fe/N/C catalyst. Upon introducing 0.67 mM $NiCl_2$, the Faradaic efficiency (FE) for CO only dropped from 99% to 84% on the Fe/N/C catalyst (Fig. 1C). In contrast, on the oxidized Ag foil, the FE of CO sharply dropped to near zero, followed by the increase of H_2 FE near to 100% (Fig. 1D).

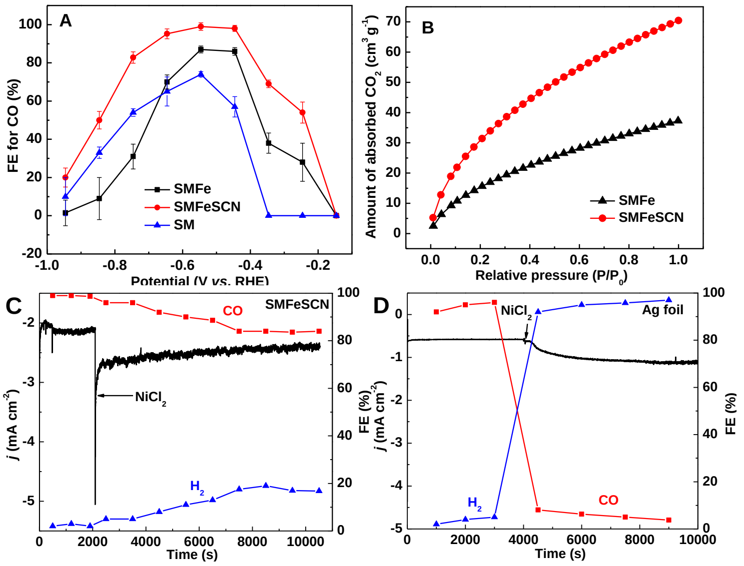

Fig. 1 (A) Faradaic efficiency of CO versus potential. (B) CO_2 adsorption isotherms. (C, D) Current-time (i-t) curve in 0.1 M $NaHCO_3$, 0.67 mM $NiCl_2$ was introduced during the test. Total current density *vs* time (left axis), FE for CO and H_2 production *vs* time (right axis).

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Morphologic Evolution of Gallium Nitride Wafer during Photoelectrochemical Etching

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Due to wide band gap and high thermal conductivity, gallium nitride (GaN) has been generally considered as one of the third generation semiconductor materials[1]. Nevertheless, the current technologies of chemical/electrochemical etching do not apply to the GaN wafer because of its high chemical inertness. It has been demonstrated that photoelectrochemical (PEC) etching enables the fabrication of the GaN wafer, but the etching mechanism still is ambiguity. In this report, the effects of water or hydroxide anions were investigated, respectively. The experimental results demonstrated that the reactions of the holes with water or hydroxide anions occurred at the different anodic potentials (Figure 1) in deep eutectic solvents (DES). With the increasing of anodic potential, water and hydroxide anions would have different influence on the morphologic evolution of GaN wafer. The mechanism of PEC etching of GaN wafer was suggested.

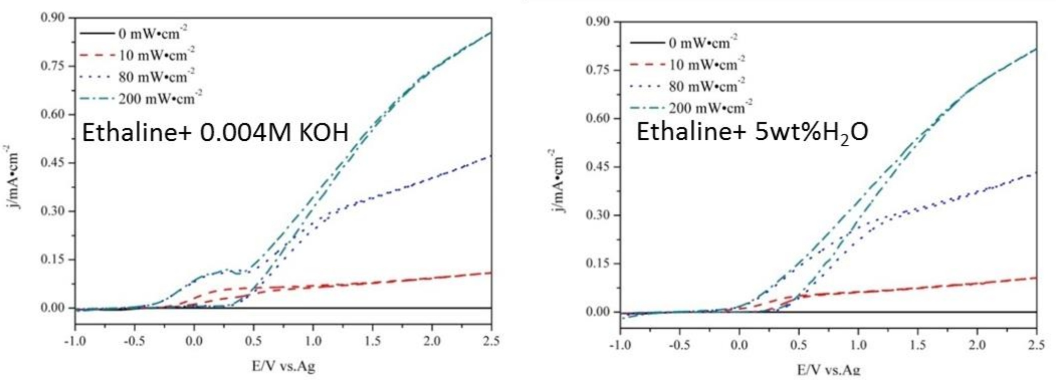

Figure 1. CVs of Ga-polar GaN at a scan rate of 20 mVs.

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Acknowledgments:
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Evaluation of cell performance at -5 to -80°C: NiMH and Li-ion cells

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Origin of low temperature phenomena are still under debate (*e.g.* Zhan, 2003). For our first approach, we developed a simple measurement system equipped temperature controller for testing performance of NiMH and Li-ion cells in low temperature range. The developed system consists of digital multimeter, freezer, insulation box, temperature logger, mechanical relays, heaters, fans and control PC as shown in Figure 1. A test cell is installed in an insulation box and set in the freezer. Heaters, fans and thermocouples are also installed in the insulation box and used for a precise temperature control. Measurements of (1) voltage of cell, (2) intensity of current through the circuit and (3) cell voltage connected to the circuit were carried out. Those were measured individually by using digital multimeter under the relays control. One set measurement is defined to be the following sequence: initially (1), then 5 times repeat of (2) and (3), and finally (1). For the one-set measurement, connection time of cell to the circuit is less than 10 seconds in order to avoid for reducing the capacity of the cell. Target temperature is changed from -80 to -30 degree C and -30 to -5 degree C with 5 degree C step by 90 minutes interval. The temperature changes of the cell were two ways, cooling (-5 to -30 and -30 to -80 degree C) and heating (-80 to -30 and -30 to -5 degree C). The one-set measurement was carried out for every 10 minutes. After keeping the temperature for 80 minutes, the cell temperature is considered to be the same as that of the insulation box, and the measurements of (1) (2) (3) values at the 80 and 90 minutes were selected for evaluation at each temperature. In this experiments, we used AA type NiMH and new Li-ion cells individually. Results of the used NiMH cell are shown in Figure. 2. Cell performance increases with temperature rise. It also shows hysteresis for (2) and (3) around -50 to -30 degree C. In the cooling way, a higher voltage and a higher current intensity are seen. The hysteresis was not found for the new Li-ion cell. We doubt cell inside temperature did not reach insulation box temperature. Therefore, next experiments are carried out by extend temperature change interval for 180 and 300 minutes. Temperature range was focused from -60 to -5 degree C where the hysteresis is appeared. The hysteresis feature also appeared both extend time intervals. Temperature dependent phenomena such as chemical reaction rate and elastic deformation of cell shape cannot explain the hysteresis. For further interpretation of the hysteresis phenomena, we will perform further experiment using other resistance of the circuit and impedance measurement of cells.

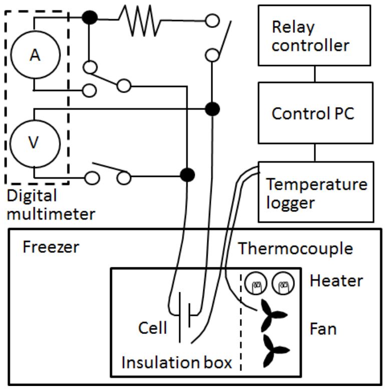

Figure 1. Developed system for cell performance evaluation.

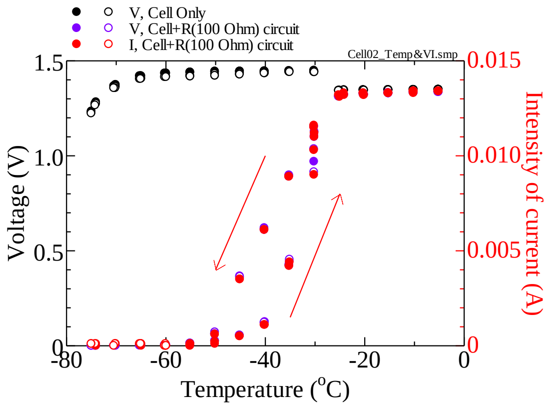

Figure 2. Performance of the used NiMH cell.

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Bridging Nano and Micro Scales to Model Transport Processes in PGM-free Electrodes in Polymer Electrolyte Fuel Cells

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Polymer-electrolyte fuel cell (PEFC) is a promising energy conversion technology with high thermodynamic efficiency, power density and zero-emission. Due to their low cost and material abundancy, PGM-free electrodes are promising candidates for meeting 2020 cost targets set by U.S. Department of Energy (DOE) [1]. However, to compensate the lower volume-specific activity, these catalyst layers are about an order of magnitude thicker compared to conventional Pt-based electrodes. Due to larger thickness, mass-transport and Ohmic losses can be significant within these PGM-free electrodes. Furthermore, water management is even more important than in conventional electrodes due to larger time and spatial scales. Understanding and optimizing morphology of PGM-free electrodes is critical in reducing mass-transport and Ohmic losses, as well as water flooding. Previous modeling efforts treated catalyst layer as a porous media with effective properties obtained with imaging methods (FIB-SEM, X-ray tomography). Although these studies improve on standard volume-averaged approaches, they lack in capturing through-thickness morphology inhomogeneity. To better understand the influence of the electrode microstructure on the transport processes, we bridge micro and nano-scales obtained with X-ray computed tomography (CT) to model the transport processes in the PGM-free electrodes.

Three novel iteration algorithms for modeling scale-bridging between imaged morphology with micro-CT and nano-CT are presented. The nano-CT model with higher resolution serves as a powerful tool to characterize the meso and nano-scale, which cannot be captured by micro-CT due to imaging resolution limits. In all three algorithms, the micro-scale domain is discretized into a grid, where boundary conditions of each grid cell are obtained with nano-scale model. In this first model implementation, we couple two models along several electrode locations (y-axis). In the first algorithm, micro-scale model generates Dirichlet boundary condition on boundary 1 of node 1 and Neumann boundary condition on boundary 2 of node 2 for nano-scale model to compute the Dirichlet boundary condition on boundary 2. Then this Dirichlet boundary condition is fed back into micro-CT model to renew the Neumann boundary condition until solution convergence is reached. In the second algorithm, micro-scale model generates Dirichlet boundary conditions on both sides for nano-scale model to compute the Neumann boundary condition on boundary 2. Then this information is fed back into micro-scale model to renew the Dirichlet boundary condition on boundary 2 until the solution converges. The third algorithm bridges the two models using mortars. [2] First, piecewise finite-element basis functions are assigned to nano-scale models with initial guess of the unknown coefficients. Then the interface properties are calculated and the jump in fluxes across the interfaces is determined. Then the Jacobian is constructed along with the equation system. Finally, the equation system is solved and the coefficients are updated. Transport processes in idealized geometries with designed boundary conditions are calculated to study the convergence rate of these three algorithms and to assess the algorithms' effectiveness. The most effective scale-bridging method is selected to study the transport processes in the PGM-free electrode of the PEFCs. Species diffusion, ions and electrons conduction, electrochemical reactions are resolved in the coupled model.

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Composite Films of Two-dimensional Black Phosphorus Nanoflakes and Graphene supported Pd nanoparticles for ethanol electrooxidation enhancement

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ABSTRACT: Preparing composite films ~~is~~ is an effective way~~a good way~~ to improve the catalytic performance of electrocatalysts in fuel cells. In this paper, Black Phosphorus nanoflakes and Graphene (BP-G) composites films were prepared on a large scale via ball milling method and served as the support for Pd loading targeted for efficient ethanol electro-oxidation. The synthesized BP-G-Pd catalysts were characterized by TEM, XRD, XPS and many electrochemical methods. The results showed that the BP-G-Pd composites films ~~Pd nanoparticles were uniformly loaded on BP-G and~~loaded with Pd nanoparticles uniformly~~ the~~ ~~BP-G-Pd~~ could exhibit~~ed~~ ~~much~~ enhanced electrocatalytic activity and stability compared with pure Pd/C.

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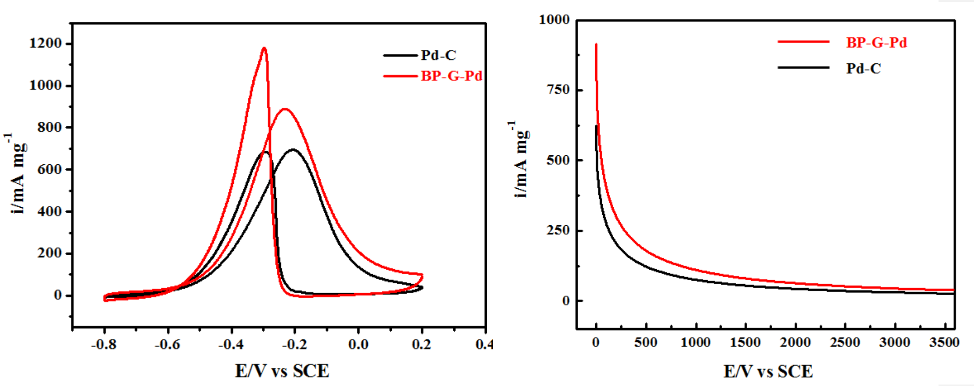

Fig.1 1.0 M NaOH + 1.0 M C_2H_5OH solution at the scan rate of 50 mV s^{-1} and chronoamperometric curves for the Pd-based catalysts in 1.0 M NaOH + 1.0 M C_2H_5OH solution at 0.20 V.

Key words：ethanol electrooxidation, black phosphorus, graphene

The research on preparation of superhydrophobic surfaces of pure copper by hydrothermal method and its corrosion resistance

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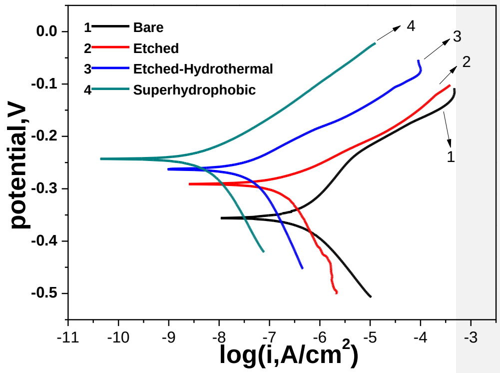
ABSTRACT: In this paper, the superhydrophobic film was constructed via the combination method of chemical etching and high-temperature hydrothermal on copper surface. Copper was etched by the NH_3 solution. And the copper was put into the autoclave filled with sodium hydroxide solution for some time at high temperature, in which the surface could be oxidized to construct a micro-nano-scale surface structure. And finally surface was modified with stearic acid. The results showed that superhydrophobic film prepared by hydrothermal method had good corrosion resistance in simulated sea water. The highest corrosion rate can reach to 99.81% with the contact angle up to 157.7°, and its superhydrophobic film structure had a lot of thin strip-like structures. In addition, this study explored the changes on the surface morphology of the as-prepared samples in the alternating wet and dry environments (simulated coastal atmosphere) for 60 days, and it were nearly unchanged to verify the outstanding performance and stability for the as-prepared supuerhydrophobic copper.

~~Figure 1 EIS and Tafel plots of bare cooper, superhydrophobic cooper, etched and etched-hydrothermal treatment cooper in 3.5 wt. % NaCl solution~~



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~~**Key words:** superhydrophobic, corrosion and protection, copper,hydrothermal method,electrochemical, micro and nano~~

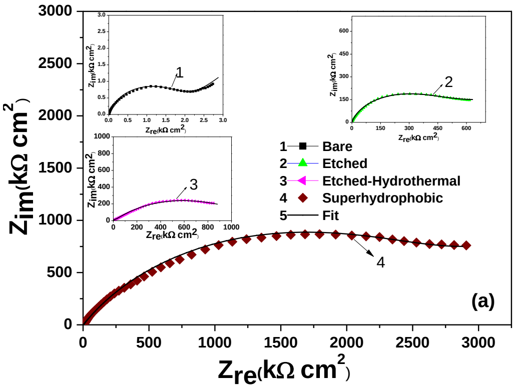

Figure 1 EIS and Tafel plots of bare cooper, superhydrophobic cooper, etched and etched-hydrothermal treatment cooper in 3.5 wt. % NaCl solution

Fabrication and electrochemical studies of solid electrolyte and cathode composite for all solid lithium secondary battery

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Recently, lithium ion batteries with high working voltage, high energy density and good cycle ability have been widely adopted as the most promising portable energy source in electronic devices. However, lithium secondary batteries have some safety problem due to using the liquid electrolytes. Solid electrolytes are one of the very important keys to realize all-solid-state secondary batteries with high safety and high energy density. The garnet structure solid electrolyte is great candidate solid electrolyte in all solid lithium ion battery. It is better than others in terms of electrochemical stability and high ionic conductivity. In this studies, garnet LLZO was doped with a different elements via. coprecipitation method in order to increase the ionic conductivity and structure stability. Bare LLZO powder with tetragonal structure was changed into cubic structure when the chemical elements were doped. Especially, the best doped LLZO showed an excellent crystallization with a high intensity peak, indicating the highest ionic conductivity of 7.11×10^{-4} S/cm due to the excellent sinterability.

Nitrogen-doped porous carbon derived from residuary peanut shell: an excellent electrode material for supercapacitors

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Porous carbon has been commonly used as electrodes material in electrochemical double layer capacitors (EDLC) supercapacitors due to large surface area, good electronic conductivity, excellent electrochemical stability and low price.[1,2] In particular, nitrogen-doped porous carbon (NPC) exhibits an improved capacitive performance in a hybrid capacitor (combination with EDLC and pseudo-capacitance).[3] Herein, a new type of NPC derived from carbonized peanut shell was prepared by a series of processes of ball-milling, carbonization, activation with melamine and KOH. The obtained NPC sample has a high nitrogen-doping content (13.82 atomic %), a large specific surface area (1294 $m^2\ g^{-1}$) and a hierarchical porous nano-architecture with micropores size below 2 nm, mesopores size of 2-5 nm and macroporous frameworks. In a typical two-electrode system assembled with this new NPC electrodes, a maximum specific capacitance of 309 $F\ g^{-1}$ can be obtained at a current density of 1 $A\ g^{-1}$, while it shows a good capacitance retention even at a high current density, for example, 297 $F\ g^{-1}$ at 10 $A\ g^{-1}$. More importantly, the as-fabricated supercapacitor possess a maximum energy density of 42.9 $Wh\ kg^{-1}$ with a power density of 500 $W\ kg^{-1}$ and keep an excellent cycle stability after 5000 cycles, which makes it a potential candidate in application for EDLC or hybrid supercapacitors.

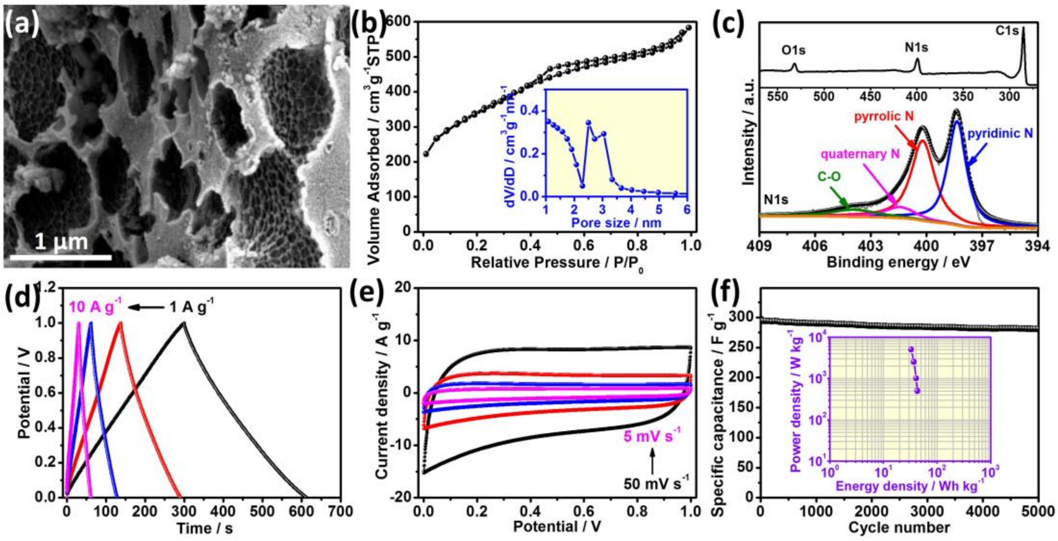

Figure. The characterizations of NPC: (a) SEM image; (b) Nitrogen adsorption-desorption isotherms (inset: pore size distribution); (c) High-resolution XPS spectra of N1s. All the electrochemical measurements were carried out in 6 mol L^{-1} KOH aqueous solution: (d) galvanostatic charge-discharge curves at different current densities; (e) cyclic voltammetry curves at various scan rates; (f) cyclability at a current density of 10 $A\ g^{-1}$ over 5000 cycles (inset: Ragone plot).

Acknowledgement

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Electrochemical Properties of FeS_2 Thin Film Cathode for Thermal Batteries

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Pyrite (FeS_2) is currently used as cathode materials for thermal batteries because of its high specific energy density, environmental non-toxicity and low cost. Powder compaction technology is widely used for the preparation of thermal battery components. This method, however, limits the diameter above 150 mm, thickness below 0.25 mm and the geometry of the battery components. This limitation leads to an excess in cell capacity, overweight, and higher cost of the pellets, resulting in the decrease of the specific capacities and the delay of the activation time of thermal batteries [1-3]. FeS_2 thin film cathodes were fabricated by tape casting to improve the specific capacity. The residual organic binder of the FeS_2 thin film cathodes was decreased with the temperature of the heat treatment, which resulted in the improvement of the specific capacity due to the lower resistance. FeS_2 thin film cathode with excellent specific capacity as well as good handling robustness was obtained by optimized heat treatment. FeS_2 thin film cathode (130 ㎛ thick) showed considerably high specific capacity of 2,502.7 A·s g^{-1}, compared with a specific capacity of 998.9 A·s g^{-1} of pellet cathode (400 ㎛ thick). It is also found that specific capacities of the FeS_2 thin film cathodes decreased due to the more residual binder and the restrictive reaction of active materials with molten salts as the thickness increases. This excellent electrochemical performance suggests that the tape casting process is a promising technology for improving the specific capacities of FeS_2 cathode in thermal batteries.

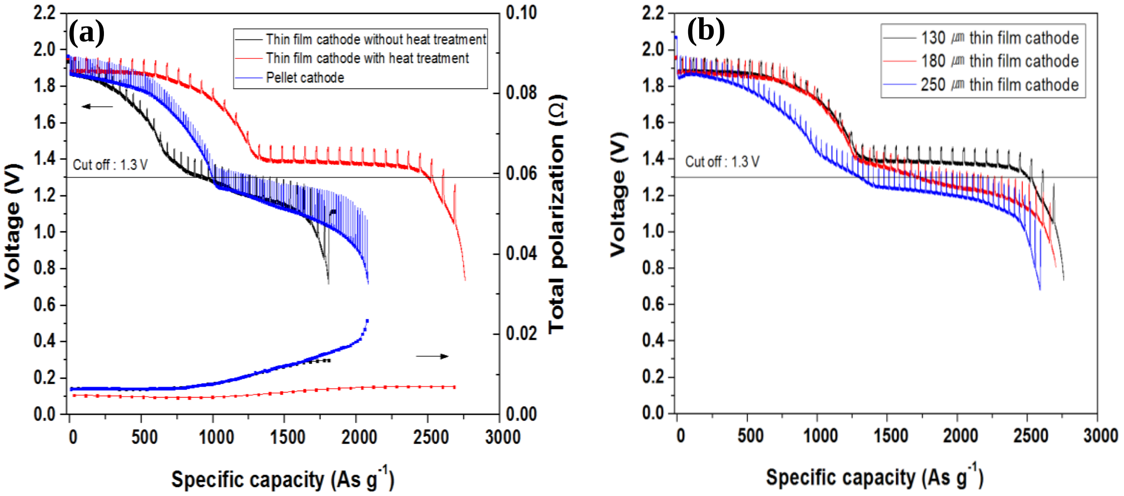

Fig 1. Discharge performances of single cell with FeS_2 thin film cathode and pellet cathode; (a) with heat treatment temperature and (b) with thickness

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Effects of Processing on the Capacitive Performance of Onion-like Carbon

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Onion-like carbons (OLC), which are formed from many concentric fullerene shells, are promising materials for electrode materials for energy storage devices that are required to operate at fast charging and discharging rates (e.g. supercapacitors). The high conductivity, nanoscale dimensions, and unique spherical shape of OLC enables facile electrolyte access to the OLC surface as well as rapid ion transport upon electrode polarization [1, 2]. These properties also make OLC a promising material for use as a conductive additive or for use as the active component of functional inks, but the tendency for individual OLC particles to form large agglomerates (isolated OLC particles are typically 5-10 nm in diameter with agglomerates reaching several hundred nanometers [3]), which tend to flocculate in solution, makes forming stable, colloidal OLC suspensions challenging. Previous attempts at producing stable OLC suspensions in aqueous media by functionalizing their surfaces with hydrophilic surface functionalities required purification techniques that resulted in an extended synthesis procedure [4]. Investigations into the oxidation of other carbon nanomaterials using acid treatments showed that the products of the oxidative process had highly functionalized surfaces which not only improved the stability of the carbon nanomaterials in solution but also increased the specific capacitance of the carbon materials through pseudocapacitive contributions by the oxygen-containing surface functionalities [5].

Herein, we report on how the combination of attrition milling, acid treatments, and probe sonication can reduce the particle size of OLC agglomerates and also functionalize the OLC with hydrophilic surface groups which prevent sedimentation by stabilizing the OLC particles in solution. The resulting OLC suspensions are stable in solution for months without any observable sedimentation and when used as electrode materials for aqueous supercapacitors, the processed OLC shows a 3-fold increase in capacitance at low scan rates (while having similar performance to untreated OLC at high rates) due to the activation of the surfaces of the OLC particles during the milling and oxidative treatments [6]. As a result, this process has proven successful in creating stable, colloidal aqueous suspension of onion-like carbons with improved capacitive properties that can be used directly as a functional ink or as conductive additives for composite materials.

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Combining Complementary Techniques to Control and Understand the SEI Formation on Silicon Alloys

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The combination of organic electrolytes, reactive Li metal, and ions, and of alloying and intercalation reactions with associated volume changes render Li-ion batteries (LIBs) complex electrochemical systems. A potential development of a new Li-ion battery system needs to fulfill severe requirements, among others progress in specific capacity and energy density as well as in cycle life, reliability and safety. Future lithium-ion batteries are considered for a broad range of applications beyond the initial use in consumer electronics, from electric vehicles (EV) to off-grid or home energy storage for example in combination with photovoltaic systems. Advanced characterization techniques can help the development and allow deep insights in acting mechanisms – preferably at the atomic or low-nanometer scale and performed in-situ1,2. As a matter of fact electrochemical interfaces are controlled by (applied) potentials and may significantly change at open circuit conditions. They are also buried in electrolyte and may quickly react in contact with other media. These latter facts make electrochemical research both challenging and interesting at the same time. Techniques based on synchrotron-light such as in-situ X-ray Diffraction (in-situ XRD) or Hard X-Ray Photoelectron Spectroscopy (HAXPES) can complement electrochemical testing for battery research, but also lab-based methods as for example Atom Probe Tomography (APT) or Surface Force Apparatus (SFA) measurements [1] offer unprecedented insights. I will describe recent applications of the latter techniques [2] for our research on Si and Si-alloy interfaces and solid electrolyte interphase (SEI) formation. By using HAXPES the influence of the new formula of electrolytes has been investigated comparing the electrochemical performance and SEI formation between Si and Si-alloy half-cells cycled with modified electrolytes.

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The influence of the synergistic inhibition between suppressor and halide ion for void-free filling in micro via filling

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Electrodeposition of copper has been used for fabricating the wires of printed circuit boards (PCBs) and integrated circuit (IC) applications in electronic industry. The interconnection between different layers is developed by the metallization of micro via or through hole [1]. To ensure the reliability and stability of the interconnects, the micro via has to be fully filled without voids and seams through the reported process of "superfilling", or "bottom-up filling".

In order to obtain the superfilling, several additives are added in the copper plating solution. The accelerator and suppressor increase and decreases the Cu electrodeposition rate, respectively. The leveler selectively inhibits Cu deposition on the protrusion of the rough surface, making a planarized surface [2]. The influence of counter anion with a leveler has been studied in previous studies [3]. M. J. Kim et al. announced recently that iodide indicated the strong inhibition among halogen ions as a counter anion of leveler [4] and enhanced the suppression of suppressor [5]. The TSV-scaled trenches are filled with a combination of accelerator, suppressor, and halide ion.

In this study, we performed the micro via filling by applying the halide ion into Cu electroplating solution. The electrochemical analyses are conducted to study the relation between suppressor and halide ion. Micro via is fully filled with the addition of accelerator, suppressor, and halide ion as shown in Fig. 1. The halide ion indicated the weak inhibition at the low concentration as shown in Fig. 2 (a). The current profile remained unchanged according to rotating speeds. The suppressor represented the reduced current by the strong inhibition effect without the difference according to rotating speeds as shown in Fig. 2 (b). However, when the suppressor and halide ion are dissolved into Cu electroplating solution, the current decreased additionally and the time reaching at the saturated current is reduced by increasing the rotating speed as shown in Fig. 2 (c). This behavior is resulted from the convection-dependent adsorption of the synergistic inhibition between suppressor and halide ion.

We will introduce the synergistic effect between the suppressor and halide ion in micro via filling and electrochemical behaviors. The convection-dependent adsorption of a complex between suppressor and halide ion will be discussed with various suppressors. The adsorption mechanism is suggested through the impurities of Cu film and EQCM measurement. Furthermore, the reduction of filling time is studied by the suggested mechanism.

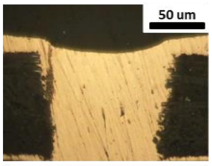

Fig. 1. Cross-section image of micro via

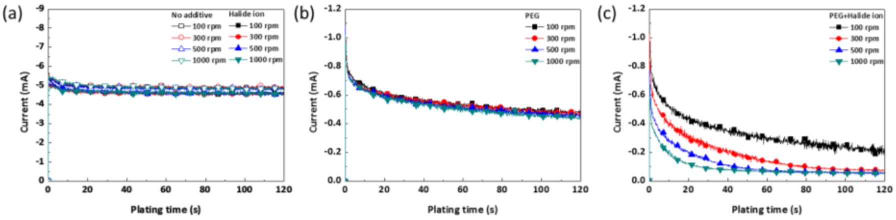

Fig. 2. Current profiles with differently grouped additives of suppressor and halide ion

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Highly active and stable CuO catalyst embedded in TNTs for the photoelectrochemical reduction of carbon dioxide

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In this work, CuO catalyst with nanostructure was fabricated on anodized titanium dioxide (TNTs) by pulse electrodeposition of Cu in an acidic copper sulfate solution and the subsequent thermal oxidation process. TNTs carrier was pretreated at 450 ℃ for 2h before use, which could facilitate the deposition of Cu nanoparticles into the pore space of TNTs. The micro-morphology and phase composition of as-prepared CuO/TNTs electrodes as well as its photoelectrocatalytic properties were investigated detailedly. Selected electron diffraction and HRTEM indicates that the deposits is transferred into CuO by heat treatment. The pulse current affects the electrodeposition way of copper, and nanostructured CuO/TNTs composited electrode can be obtained at current density between -3 mA/cm^2 and +3 mA/cm^2. Effects of deposition charge were particularly studied. Combined the photocurrent-potential curves with the SEM images, it is found that the CuO/TNTs electrodes with 300 mC deposition charge showed a relatively higher photocurrent as excessive deposits will lead to the blockage of nanotube and destroy the nanostructure. The stability of CuO/TNTs during photoelectrochemical reduction of CO_2 was also investigated, which was greatly affected by the applied potentials. When the applied potential was around -0.4 V, the initial photocurrent of electrode reached a maximum of 0.8 mA cm^{-2} and the current decline was much slower compared with that at -0.6V or more negative potentials. Photoelectrocatalytic reduction of CO_2 using the CuO/TNTs were conducted under visible light and potential of - 0.4V, in which the synthesis of methanol reached 1.13 mg in 100 ml electrolyte after 3h.

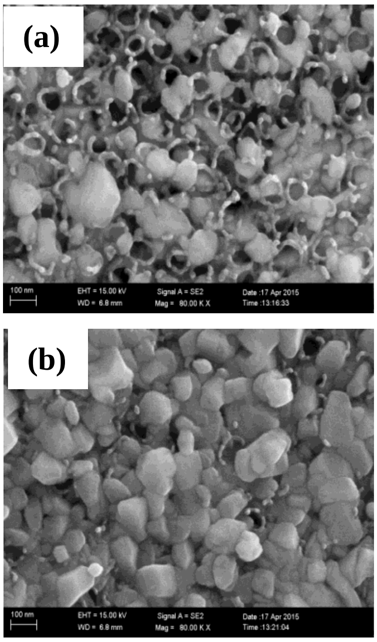

Fig. 1 Top-view of CuO/TiO$_2$ electrodes with deposition charge of 300 mC (a) and 400 mC (b)

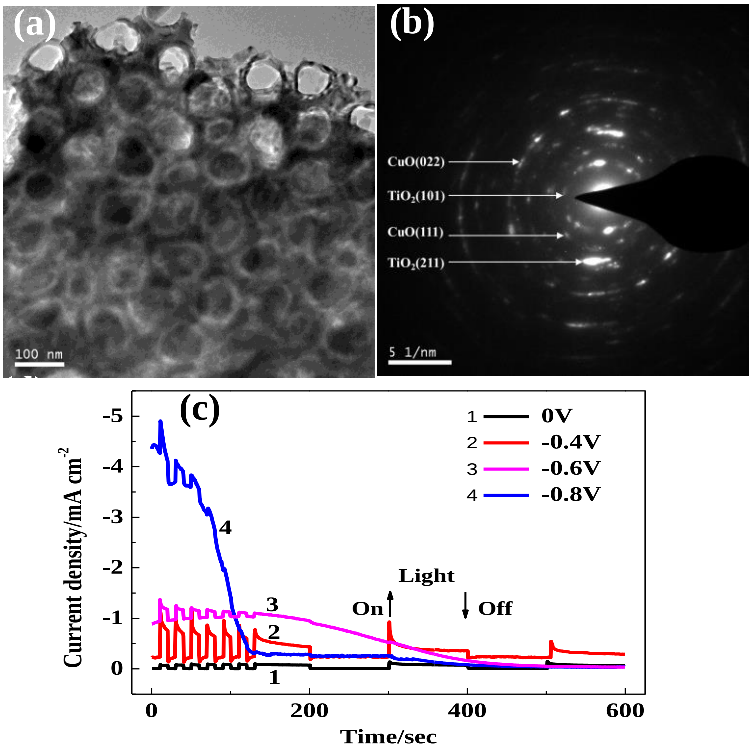

Fig.2 (a) TEM images, (b) selected electron diffraction of CuO/TiO$_2$ electrode and (c) photocurrent-time curves in 0.1 M $NaHCO_3$ electrolyte at different potentials

Electrochemical Detection of Nitric Oxide Release from Normal and Stressed cells

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Nitric oxide (NO) plays important roles in myriad biological processes and is considered as a biomarker of cardiovascular disease, hypertension, symptoms of vaginitis, and cancer. Sensitive detection of NO molecules is vital toward the understanding of cell functionality and pathology as well as to the diagnosis of disease, drug discovery, and biological research [1-3]. Here, we report on a facile and environmentally compatible strategy for the construction of an advanced NO electrochemical sensor based on reduced graphene oxide (rGO) and AuPt bimetallic nanoparticles.

In the present work, a facile two-step electrochemical process was employed to prepare an AuPt-rGO modified glassy carbon electrode (GCE). Firstly, a 5 µL suspension of GO (0.3 mg mL^{-1}) was cast on a GCE and allowed to air dry. Subsequently, the cast GO was electrochemically reduced to a rGO film via cyclic voltammetry scanning for 20 cycles in a 0.1 M Phosphate buffer saline solution, which was carried out in the potential range between 0.0 and -1.5 V vs Ag/AgCl at a scan rate of 50 mV s^{-1}. Secondly, the AuPt nanoparticles were in situ electro-synthesized on the rGO/GCE by applying -250 mV for 500 s in an aqueous solution of 0.1 M H_2SO_4 that contained different Au/Pt molar ratios. The resulting electrode was subsequently rinsed with water and used for surface characterization.

The prepared nanocomposites were further employed for the electroanalysis of NO using differential pulse voltammetry (DPV) and amperometric methods. The dependence of AuPt molar ratios on the electrochemical performance was investigated. Through the combination of the advantages of the high conductivity from rGO and highly electrocatalytic activity from AuPt bimetallic nanoparticles, the AuPt-rGO based NO sensor exhibited a high sensitivity of 7.35 µA μM^{-1} and a low detection limit of 2.88 nM. Additionally, negligible interference from common ions or organic molecules was observed, and the AuPt-rGO modified electrode demonstrated excellent stability. Moreover, this optimized electrochemical sensor was practicable for efficiently monitoring the NO released from rat cardiac cells, which were stimulated by L-arginine (L-arg), showing that stressed cells generated over 10 times more NO than normal cells. The sensor developed in this study may serve as an important and cost-effective tool for the study of cellular stress responses in biological processes and for medical diagnostics.

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Investigation of DNA Single Nucleotide Polymorphism by Electrochemical *In Situ* Fluorescence Microscopy

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Single nucleotide polymorphism (SNP) is the variation of a nucleotide at a single position in a DNA sequence among individuals. The detection of SNPs is of utmost importance as SNPs are associated with various human diseases. New detection methods, faster and less expensive than the existing ones are continuously sought after.

In this work, we investigate a detection methodology based on the electric-field assisted denaturation of DNA. The employed technique couples electrochemical measurements with *in situ* fluorescence microscopy in real time. Electrochemistry is used to induce the denaturation of DNA, while fluorescence measurements are employed to detect the associated melting events. For this purpose, fluorescently labeled DNA sequences are immobilized at gold electrodes as self-assembled monolayers (SAMs), the probe being thiolated and the complementary strand bearing a fluorescent label, in both instances at the 5'- extremity. Because the fluorescence is heavily quenched by the bulk metal electrode, in a distance-dependent way, the denaturation as well as the desorption of the double-strand give rise to strong fluorescence bursts when the potential is swept in the negative direction. We present the results of a comparative study of perfect match and SNP-containing target sequences (e.g. SNP 309T>G of the human *MDM2* gene). The presence of a mismatch in a sequence significantly reduces the stability of the DNA duplex, therefore making it more susceptible to electric-field induced denaturation. Fluorescence measurements allow us to observe the potential induced melting of double stranded DNA in the case of target sequences bearing the mismatch, and the influence of various parameters, such as the immobilization conditions, ionic strength or nature of the substrate, on the fluorescence vs. potential curves is presented.

Dissolution of Pt during Oxygen Reduction Reaction Produces Pt Nanoparticles

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The loss of Pt during the oxygen reduction reaction (ORR) affects the performance and economic viability of fuel cells and sensors. Our group previously observed the dissolution of Pt nanoelectrodes at moderately negative potentials during the ORR. Here we report a more detailed study of this process and identify its product. The nanoporous Pt surface formed during the ORR was visualized by AFM and high-resolution scanning SEM, which also showed Pt nanoparticles on the glass surface surrounding the electrode. The release of these nanoparticles into the solution was confirmed by monitoring their catalytically amplified collisions with a Hg microelectrode used as the tip in the scanning electrochemical microscope.

The Electrical Double Layer in 'Water-in-Salt' Electrolytes: Theory and Molecular Dynamics Simulations

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One challenge in developing the next generation of lithium ion batteries is the replacement of organic electrolytes, which are flammable and most often contain toxic and thermally unstable lithium salts, with safer, more environmentally friendly options. Water-in-salt (WIS) solutions are a promising class of electrolytes that have been recently developed to overcome this challenge.[1] The emergence of WIS electrolytes spawns the necessity to understand the underlying physics that governs their behavior in electrochemical systems and bestows upon them their desirable properties as battery electrolytes. Here, we develop a simple modified Poisson-Boltzmann theory that can be used to describe the electrical double layer (EDL) structure of WIS electrolytes. The model explicitly takes into water polarization in external electric fields, as in the spirit of [2] and [3], as well as the specific interactions of water with ionic species. Additionally, our theory is able to model electrostatic correlations between ions using theory developed in [4], and it accounts for steric effects using a four component (water, cations, anions, and vacancies) asymmetric Bikerman lattice gas model. We apply our modified Poisson-Boltzmann theory to model the EDL of a WIS electrolyte, and then validate our continuum results against a series of molecular dynamics simulations. In addition to modeling the EDL, our theory and atomistic simulations can provide further insight into the enhanced electrochemical stability window of this promising new class of electrolytes.

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Preparation and characterization of ITO/TiO_2 electrodes doped with Ni or Co and its use in the Picloram degradation

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Picloram (4-amine-3,5,6-trichloropiridine-2-carboxilic acid), is an organic molecule usually used as a herbicide for the control of broadleaf weeds in grasses and pastures, wheat, barley, oats, and for woody plant species [1]. Pichloran, which has a recalcitrant nature, presents a risk for water sources. Consequently, the aim of this work is to develop a photo-electro-system in order to reach better rate of degradation for Picloram.

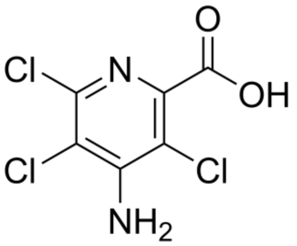

Figure 1: Picloram Structure

In order to do this, we prepared electrodes based on an ITO glass slide coated with a paint of TiO_2 nanoparticles, doped with Ni-or Co-hydroxide. The M-TiO_2 particles were characterized by XPS, X-ray diffraction, FTIR-ATR and SEM-EDS, whereas the electrochemical behaviour of the electrode by cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS), both in dark and with UV irradiation. Characterization techniques indicate that Co species have a structure like hydroxides, being homogeneously dispersed at the TiO_2 surface. It is important to note that in the presence of cobalt the TiO_2 particles are less aggregated.

A comparison between CVs obtained under different experimental conditions in order to show the effect of the irradiation of the system using two lamps, 365 and 254 nm in wavelength are shown in Figure 2. The results indicate that the PCL oxidation increases in the presence of UV light, and that this increases in currents is higher at 365 than 254 nm using ITO/Co-TiO_2 electrodes in a pH 11 electrolyte. The results using Ni-TiO_2 electrodes (not shown) did not show activity for PCL oxidation.

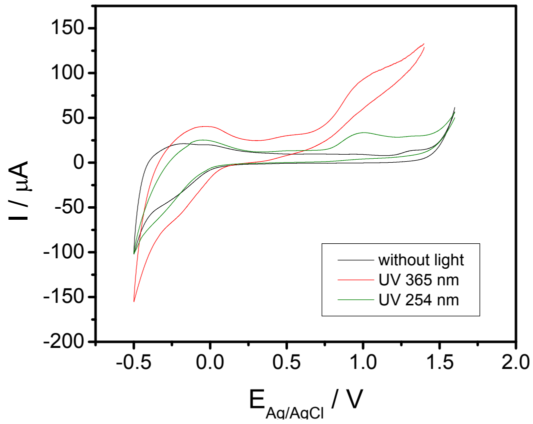

Figure 2: Effect of the UV-radiation in CVs at 10 mV s^{-1} in PCL 430 mg L^{-1} in pH 11 electrolyte using ITO/Co-TiO2 electrodes.

Acknowledgements We thank CONICYT-CHILE through the grant FONDECYT 1140207 and MINEDUC-CHILE for the grant USA1498.17 and for the recruitment of Dr. Francisco Fernández

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Light-Induced Design of Fluoropolymers as Efficiency and Stability Booster for Perovskite Solar Cells

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Photovoltaic (PV) technology has evolved rapidly in the past few decades and now encompasses a large variety of materials and device structures. A key aspect to be taken into account in any PV technology is the operational durability of these systems in outdoor conditions. Clearly, loss of performance during operation represents a significant drawback and limitation for their commercialization. In this context, the large compositional flexibility of polymeric materials as well as their proven easy processability may be of great help in imparting improved durability to PV systems.

Organometal halide perovskite solar cells have demonstrated high conversion efficiency but poor long term stability against ultraviolet irradiation and water. We show that rapid light-induced free-radical polymerization at ambient temperature produces multifunctional fluorinated photopolymer coatings that confer luminescent and easy-cleaning features on the front-side of the devices, while concurrently forming a strongly hydrophobic barrier toward environmental moisture on the back contact side. The luminescent photopolymers re-emit ultraviolet light in the visible range, boosting perovskite solar cells efficiency to nearly 19% under standard illumination. Coated devices reproducibly retain their full functional performance during prolonged operation, even after a series of severe aging tests carried out for more than 6 months.

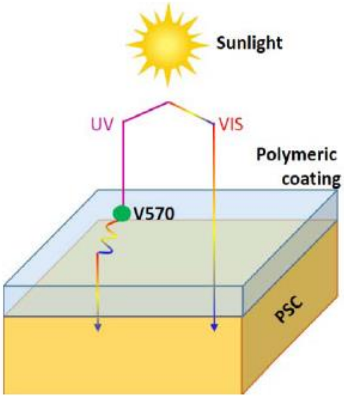

Fig. 1 - Scheme of the UV-coating operating principle.

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Degradation of Chlorophenols on electrodes based on Graphite M-exchanged Zeolite with M= Mo and/or Co

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Pollution of the environment in general and water in particular is today one of the most important global problems as a result of population growth, over consumption of natural resources and industrial development. Special attention has been dedicated to chlorinated phenols, in particular 2,4,6-trichlorophenol (TCP) due to this compound being widely used for decades as a fungicide in agriculture, the treatment of wood and bleaching of wood pulp.

In a previous study we determined the effect of zeolites on chlorophenol degradation [1]. Now in this work we have developed new electrodes based on a mixture of graphite and Mo- and/or Co-exchanged zeolites supported on a glassy carbon disc electrode. For this, three zeolites with different hydrophobic/hydrophilic characters have been exchanged with Mo and/or Co species and characterized on their surface by different physical and chemistry techniques. The characterization agrees with the presence of a very small amount of Co with very little particles, whereas Mo is mainly as a Mo(VI), both exchanged and deposited onto the zeolites forming different structures depending on the different kinds.

Working on a pH 3 electrolyte saturated in molecular oxygen, the better results of 2,4,6-trichlorophenol degradation were obtained by eletrolyses at the potential of oxygen reduction with some differences between the zeolites. In Figure 1 the results for ZY are shown. The study was developed in dark and in UV-vis illuminated systems, increasing both the chlorophenol degradation and the formation of a quinone, in the latter.

These results can be attributed to a synergy between the effect of the UV light to the chlorophenol radical reaction, the OH radical that can be formed from the hydrogen peroxide produced at the interface and to the Mo-species that can generate a photocurrent when it is irradiated. By GC-mass/mass it has been possible to detect different final products depending on if the system is irradiated or not.

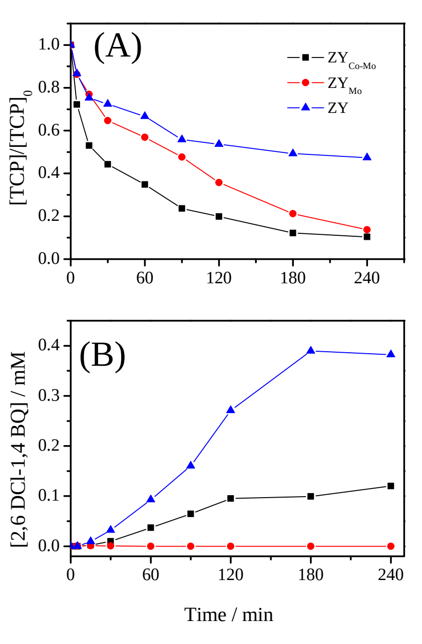

Figure 1: Abatement curve of 2,4,6-trichlorophenol (A) and generation of 2,6-dichloro, 1-4 benzoquinone during the electrolysis time using GC electrodes modified with M-exchanged ZY zeolite at pH 3

Acknowledgements We thank CONICYT-CHILE through the grant FONDECYT 1140207 and MINEDUC-CHILE for the grant USA1498.17 and the recruitment of Dr. Francisco Fernández

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Utilizing *in situ ec-S/TEM* to Study Electrochemical Nucleation of Copper

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Electrochemical nucleation of metals have long been investigated using chronoamperometry[1], cyclic voltammetry[2], and electrochemical impedance spectroscopy[3]**.** The current/potential time transients from these methods are used as basis for models for various proposed nucleation mechanisms such as instantaneous and progressive nucleation[4]. Physical insight has been primarily inferred from the current/potential time transient models and ex situ analysis of the deposit thereafter. However, surface restructuring is known to occur ex situ. *In situ* methods, such as *in situ* STM[5] *and in situ* AFM[6], avoid surface restructuring; however, the time resolution of these methods are lacking[7]. Thus direct correlation between the nucleation processes and electrochemical measurements have not been studied in great detail due to the present lack of *in situ* characterization methods that permit the simultaneous acquisition of electrochemical measurements with high spatial resolution imaging *and* high time resolution processing within the electrolyte.

Recent advances in liquid cell *in situ* electrochemical scanning/transmitting electron microscopy (*ec-STEM*), mitigates this issue[7, 8]. *In situ e*c-STEM can acquire and analyze time-resolved images of the nucleation and growth process at the nanometer-scaled spatial resolution while quantitative electrochemical measurements are concurrently performed. Therefore, this technique can also provide clarity between nucleation growth and classical electrochemical nucleation models such as the Scharifker and Hills[4] model and the Sluyter-Rehbach[9] model.

Recent advances in an all-copper flow battery has created a renewed interest in copper electrodeposition from a high halide electrolyte[10]. Here, we apply the *in situ* ec-STEM approach to investigate the electrochemical nucleation of copper from different electrolytes. Copper electrodeposition from a high halide electrolyte differs from that of a sulfate electrolyte in that the copper (I) oxidation state is stabilized whereas in a sulfate electrolyte the common oxidation state is copper (II). This combined with the nodular nature of copper deposited from a high halide electrolyte[11] is indicative of a possible difference in nucleation mechanism from that of copper sulfate. This presentation compares the electrochemical nucleation of copper from a sulfate and from a high halide electrolyte, discusses the nuances of *in situ* liquid cell ec-S/TEM, and compares the observed *in situ* growth with electrochemical nucleation models.

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Superior Conducting Polymer Materials for Passive and Active Measurements of Neural Activity

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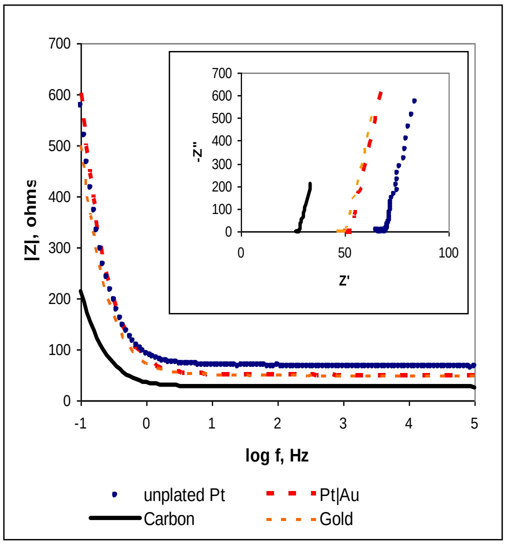


Significant strides in improving electrodes modified with conducting polymers (CPs) to enhance performance for sensing, stimulation, and electroanalysis have been made by our group.

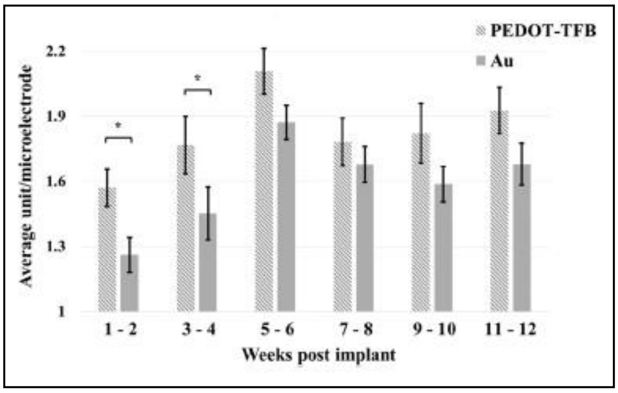
Previous results using small counterions for doping of CPs showed that these polymers exhibited a very different impedance signature than the more commonly studied PEDOT:PSS and that the general behavior was independent of the substrate for deposition, as shown in the figure on the left.

When the fabrication process was adapted for deposition on acute (Microprobes for Life Science, Gaithersburg, MD, PT/IR metal microelectrodes) and chronic neural probes (Neuronexus, Ann Arbor, MI, Model CM16), the same reduced impedance over a broad frequency range was seen.

The electrodes proved to be robust over prolonged testing in solution studies under accelerated aging conditions and in a stimulation/sensing study in a rat model, as shown in the figure on the right.

Recent efforts have focused on fabrication of electrodes based on other CP/anion combinations and development of electrodes for in vivo analytical applications.

Results from the sensing/stimulation studies as well as the more recent studies will be summarized.



Electrodes Electrochemically Modified with PEDOT Nano-wires. Assay in Photovoltaic Cells Based on Conducting Polymers

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Since its discovery in 1979, conductive polymers have attracted widespread attention because of their electronic properties, which have been useful for use in different devices, such as: fuel cells, biosensors, energy accumulators, photovoltaic cells, among others. However, and in spite of their excellent properties, in the field of energy conversion there is an important difference in it efficiency with respect to devices based on inorganic compounds, Which lies mainly in the recombination of the electron-hole pair, because the formation mechanism differs mainly in the distance that the exciton must travel to the donor-acceptor interface, before the formation of the electron-hole pair. It is recommended that this should be between 3 to 10 nm, before recombining and decreasing its efficiency [1]. For this reason, many authors have pointed out that in order to improve these energy conversion devices, a morphological modification of the surfaces must be carried out, that is to say, to use nano-structures capable of generating an increase in the efficiency of these devices [2].

From this background and considering the methodology that we have reported to prepare poly (3,4-ethylenedioxythiophene), PEDOT-nw nanowires, using only electrochemical techniques [3], a photovoltaic cell is constructed from the modification of a conductive glass (ITO) prepared by depositing TiO_2 by potentiostatic technique (at E = -1.2 V for 300 s), etching 33.3% of its surface and then undergoing treatment of 500 ° C for 1 h. Thus, X-ray diffractograms, XRD, show anatase crystallographic formation (101). It is then impregnated with ruthenium II (N3)-cis-bis-(isothiocyanato)-bis-(2,2'-bipyridyl-4,4'-dicarboxylate) dye for 24 h. A thin PEDOT film is deposited on this, then the template and, finally, the PEDOT nano-wires, according to the previously described electrochemical method [3].

The photovoltaic measurements were performed in the absence and presence of light, comparing devices prepared with PEDOT-bulk (ITO|TiO_2|N_3|PEDOT-bulk) and PEDOT-nw (ITO|TiO_2|N_3| PEDOT-nw). For this, a solar simulator, with a power of 100 mW cm^{-2}, is used after depositing 100 nm of Al by physical vapor deposition, PVD, for contact of the device.

From the transients j-V (Fig. 1) it is possible to verify that the current densities by using PEDOT-bulk and PEDOT-nw are similar, however, there is an important effect when the polymer is nano-structured, since the % of efficiency increases from $4.86 \cdot 10^{-4}$ to 10^{-3}. This increase of almost two orders of magnitude is promising, considering that it can be optimized according to the dimensions of the nano-wires and this is feasible with the methodology that we have designed, whose main advantage is the use of electrochemical techniques, which allows to control the working conditions, directly deposit the nano-wires on the electrode surface and thus ensure the high reproducibility and stability of the modified electrodes.

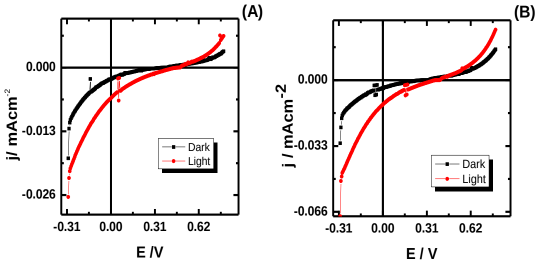

Figure 1. J-V responses of ITO|TiO_2|N_3|polymer. Polymer is: (A) PEDOT-bulk, and (B) PEDOT-nw.

Acknowledgments

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Copper(II) Determination with Modified Carbon Nanotubes Electrodes using Dyes as Ligands

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Copper is an essential trace element that plays a central role in the biochemistry of humans. The electronic structure of copper allows it to serve as co-factor in redox reactions of enzymes, such as cytochrome c oxidase, lysyl oxidase and superoxidase dismutase, the latter ~~is~~ enzyme being directly involved in the detoxification of reactive oxygen species.[1] Copper promotes angiogenesis, the growth of blood vessels that nourish with oxygen and nutrients an expanding tumor.[2] Tumor cells cannot grow more than 1-2 mm in diameter without angiogenesis.[3] Several reports in literature have shown that copper levels in cancer patients are significantly elevated compared to ~~that~~ those found in healthy subjects. The studies showed that while the zinc, iron and selenium concentrations w~~h~~ere significantly lower in cancer patients, the copper concentrations ~~were~~ usually elevated 2-3 fold.[4]

Pyrogallol red (PR) is a triphenylmethane dye, usually used as reagent in protein determination.[5] Alizarin Red S (ARS) is an anionic, sulfonated dihydroxo anthraquinone dye, used as a staining agent in textiles or mineralized bones of biological specimen.[6] In electrochemistry, these dyes have~~s~~ been employed as ligands for voltammetric analysis of several metals in solution.[7]

Mis en forme : Justifié

We modified glassy carbon electrodes (GC) by drop casting a suspension of multiwall carbon nanotubes (CNT) in toluene, and ARS and RPG were adsorbed on these surfaces~~ ARS and RPG were adsorbed~~. These electrodes were use as platforms for stripping copper determination. Linear sweep (LSV) and square wave voltammetries (SWV) in addition to differential chronopotentiometry, were studied as well as time and potential of stripping, pH value and interference of several cations.

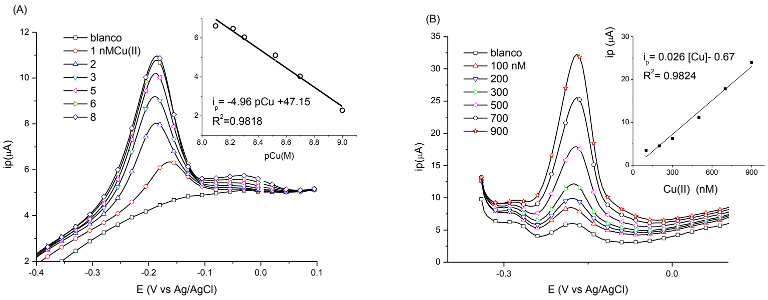

Figure 1. Calibration curve of modified electrodes with CNT using A) Red Pyrogallol with LSV, inferior limit of linearity range (ILoL) 0.5 nM B) Red Alizarin S using SWV, ILoL= 50 nM

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Landfill Leachate Treatment by Electrooxidation Method Using Pt Coated Ti Anode

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In this study, landfill leachate treatment by electrooxidation method was studied for reducing Chemical Oxygen Demand (COD). Operations were carried out using Platinum (Pt) coated Titanium (Ti) anode and iron cathode. Both anode and cathode had same dimensions with 100 x 50 x 2 mm. The effects of operating parameters like initial pH (2, 4, 6, 8, 10), current density (25, 35, 45, 55, 65 mA/cm^2), type of supporting electrolyte (NH_4Cl, NaCl, KCl, K_2SO_4) and operation time on overall removal efficiency and energy consumption were determined.

The initial concentration of 4100 mg/L COD was reduced to 1000 mg/L corresponding to the removal efficiency of 76% at initial pH of 4 and current density of 65 mA/cm^2. Also, 97.2% of color reduction was achieved at the total operation time of 480 minutes. The energy consumption in the first 60 minutes of operation was 162 kWh/m^3. As a results of experiment it can be said that electrooxidation with Pt coated electrode is effective for the treatment of landfill leachate

Keywords: COD, Electrochemistry, Electrooxidation, Landfill Leachate

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Generalized Nernst Layer model for ion transport. Bromate reduction.

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It is well known since the development of the Levich theory for the convective diffusion of a single transporting species to/from a solid surface that the diffusion layer thickness, z_d, of the Nernst stagnant layer model is determined by competition of the convective and diffusional components of the flux. It leads to dependence of z_d on the diffusion coefficient of the transporting species, D.

The situation is evidently more complicated for systems containing ***several*** transporting species because of difference in their diffusion coefficients since it is not clear which of these diffusion coefficients should be used as *D*, e.g. in the Levich formula for z_d for the rotating disk electrode. For such systems we have proposed a simple calculation scheme (called as ***Generalized Nernst layer model***, GNL), which enables one to take into account the above effect of the difference between the diffusion coefficients of the transporting species, without explicit introduction of the convective-diffusion terms into equations.

This approach has been tested for bromate reduction process [1], where one uses the ability of bromine, Br_2, to be reduced quasi-reversibly into bromide anion, Br^-:

$Br_2 + 2\ e^- \rightleftarrows 2\ Br^-$ on the cathode (1)

which in its turn is subject to the irreversible (for high acidity of the solution) comproportionation reaction:

$BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$ in the catholyte (2)

The GNL model introduces ***individual diffusion layer thicknesses for all species***, z_{dA}, z_{dB}, z_{dC} or z_{dH} for A (BrO_3^-), B (Br^-), C (Br_2) or H (protons) species, correspondingly. Approximate analytical expressions for all characteristics of the system have been derived for any set of the possible values of parameters of the system [2-4]. In particular, the maximal current within the framework of the GNL model (line D in Fig.1) for the diffusion-limited conditions has turned out to depend on the ratio of the diffusion layer thicknesses for H^+ and Br_2. As a consequence, these results cannot be reproduced correctly by the conventional Nernst layer model for any choice of the *D* value (lines A, B, C and H in Fig. 1).

On the contrary, our comparison of predictions based on the ***GNL model*** and the ***convective diffusion theory*** for the bromate system have shown their proximity for both the concentration distributions inside the (thin) kinetic layer and the maximal current density

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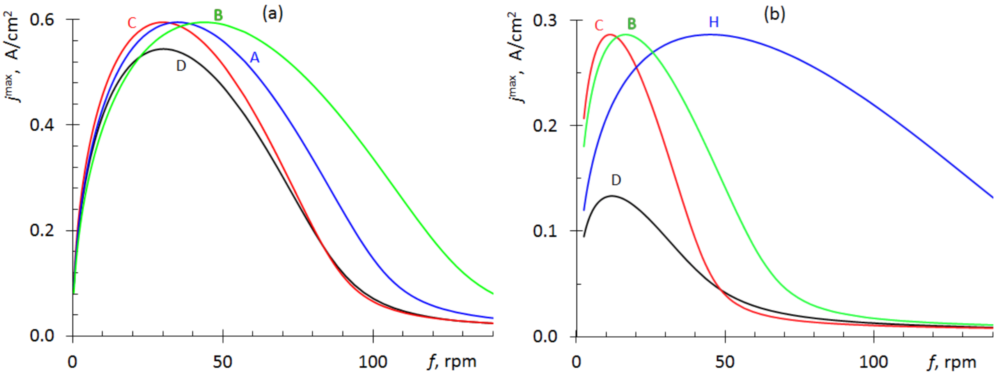

Fig. 1. Dependence of the maximal current density, j^{max}, of the RDE frequency, f. Line D: GNL model [2-4]. Lines A, B, C and H: Nernst-layer model [5]. (a) Proton excess, H° » A°, (b) Bromate excess, A° » H°.

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Very strong current regime for bromate reduction.

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Electroreduction of the non-electroactive bromate (BrO_3^-) anion at uniformly accessible electrode (such as rotating disk electrode) has been studied. This process can be carried out via a catalytic cycle composed of the reversible redox couple, Br_2/Br^-, and the comproportionation reaction between BrO_3^- and Br^- inside solution generating Br_2:

$Br_2 + 2\ e^- \rightleftarrows 2\ Br^-$ (1)

$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3H_2O + 3Br_2$ (2)

The radically new feature of this reaction compared to conventional redox catalysis is the accumulation of Br_2 and Br^- as a consequence of the BrO_3^- transformation, making it an ***autocatalytic*** one (EC" mechanism) [1].

In our analysis, transport of the components in solution has been described within the framework of the Nernst stagnant layer model. Numerical calculations carried out recently [2,3] for this system confirmed the validity of our previous approximate analytical approaches for the weak current and thin kinetic layer regimes [1] for small and moderate values of the principal parameters of the system: ratio of the diffusional and kinetic layer thicknesses, $x_{dk} = z_d / z_k$, for the whole range of possible currents. At the same time these numerical results [3] showed a pronounced change of the calculated concentration distributions, compared to predictions of the thin kinetic layer model [1], for strong currents which can pass for very large values of this parameter, x_{dk}.

A new theoretical analysis performed in this study [3,4] has provided approximate analytical expressions for the concentration distributions under conditions of a **very strong current** exceeding the bromate diffusion-limited one. They have demonstrated that the passage of such currents results in the **cardinal change** of the kinetic layer structure, compared to that for moderate currents. The comproportionation reaction took place mostly inside a layer near the electrode surface (corresponds to x = 0) for moderate current densities (Fig. 1, red line $x_{dk} = 6$), while for strong currents a BrO_3^--free layer is formed near the surface so that the reaction is localized within a narrow "**reaction zone**" displaced from the electrode surface (Fig. 1, black line $x_{dk} = 200$).

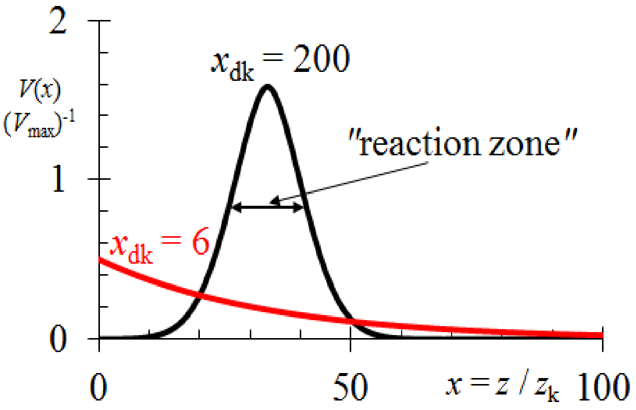

Fig. 1. Dependence of the normalized local rate of the comproportionation reaction $V(x) / V_{max}$ as a function of dimensionless coordinate x, normal to electrode surface (x = 0) for moderate ratio of the diffusional and kinetic layer thicknesses ($x_{dk} = 6$) and very strong current regime for very thin kinetic layer ($x_{dk} = 200$).

Acknowledgement: This work is supported by the Russian Science Foundation (grant № 15-13-20038).

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Electrochemical Reduction Aqueous of CO_2 on Electrode Coated with Redox Active Nano-Metallopolymer of Nickel(II)-Salen

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In an ideal situation, the CO_2 produced must be balanced with what is consumed to maintain environmental stability. The electrochemical reactions of CO_2 are of interest for the synthesis of chemicals and for approaches to decrease global warming. *Schiff*-based complexes are well known for their ability to catalyze chemically different reactions, where acid-base (bifunctional) sites present in metal complex may play an important the role of interaction with CO_2.

In this work, we study self-assembly strategies to construct of the nano-metallopolymer by electrodeposition of the [2,2'-[ethylenebis(nitriloethylidyne)]diphenolato]-nickel(II) complex (Ni(II)-Salen) on platinum surface and its electrocatalytic properties in the carbon dioxide reduction in aqueous medium. In order to determine a potential region of CO_2 reduction on coated electrode, cyclic voltammetry measurements were first performed. The electrode coated with nano-metallopolymer of Ni(II)-Salen are cycled (0.0 V to -0.95 V *vs.* SCE) in saturated solution of CO_2 in 0.5 mol L^{-1} KCl. Reduction of CO_2 can be observed from Figure 1 (curve a) by noting that the CO_2 curve drops faster that the curve for electrolyte solution saturated N_2. Under the N_2, the current density is found to be 0.311 mA/cm2 whereas, under CO_2 saturation, it shows current density of 0.769 mA/cm2 at −0.9 V *vs.* SCE. The increased current density under CO_2 saturated condition shows that the metallopolymer is catalytically active in the electrochemical reduction of dioxide carbon. The peaks at -0.48 V and -0.20 V present when the electrode is cycled under N_2 are correspondent the redox pair Ni(I)/Ni(II) of the polymer. The increase of current on the peaks under CO_2 condition is indicative of the intermediates formation during the cycles of carbon dioxide reduction.

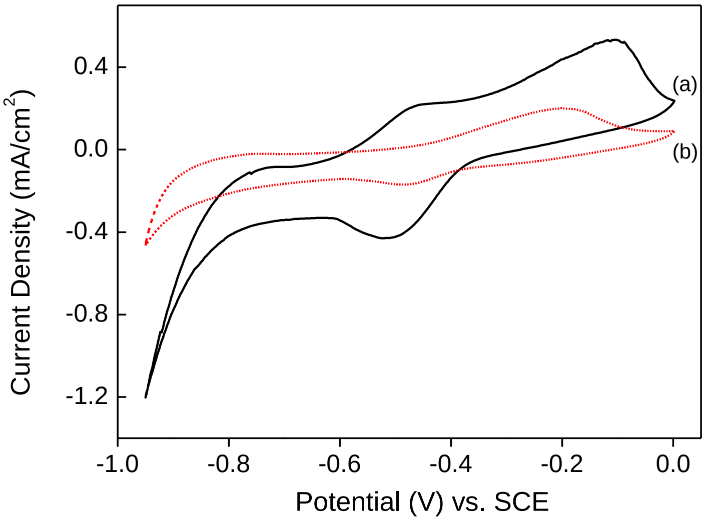

Fig.1. (a) CV of electrode coated metallopolymer in CO_2 saturated solution in 0.5 mol L^{-1} KCl solution. (b) CV of electrode coated metallopolymer in N_2 saturated solution in 0.5 mol L^{-1} KCl solution. Scan rate = 25 mV s^{-1}.

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Fuel cell operando IR/Raman spectroscopy

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Operando IR and Raman micro-spectroscopy of the membrane electrode assembly (MEA) of a fully operating hydrogen/oxygen Nafion electrolyte fuel cell is described including the cell and sample compartment designs for spectroscopy of fuel cells with flowing anode and cathode streams. Stark-tuning IR plots of CO vibrational bands will be discussed in the context of co-adsorption. Raman micro-spectroscopy is used for coarse depth profiling of the fuel cell system determine appropriate positioning of the micro-spectroscopy laser focal point for MEA catalytic layer spectroscopy. Visualization of density functional theory calculated normal mode eigenvector animations enabled assignments of Nafion side-chain vibrational bands in terms of the exchange site local symmetry: C_1 and C_{3V} modes correlate to the sulfonic acid and sulfonate forms respectively. These local symmetry based assignments are used to interpret operando IR and Raman spectra of fuel cells.

Effects of proton transport limitations in bromate reduction process

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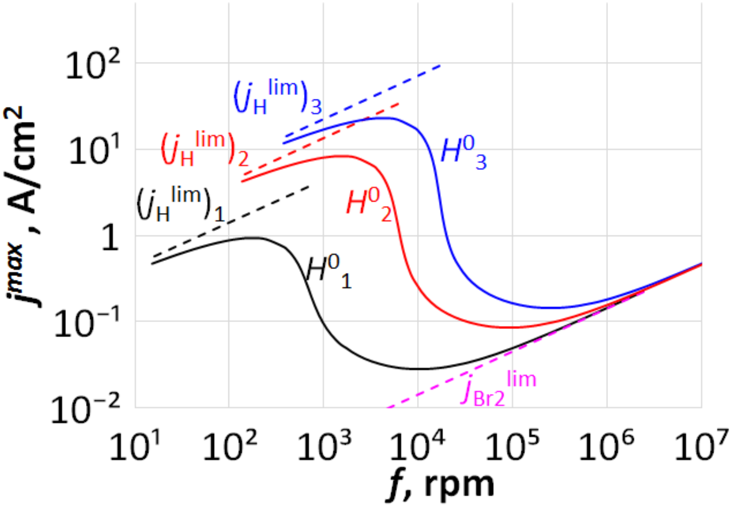
Process of the bromate anion reduction in the presence of a very low bromine concentration from an acidic solution for the one-dimensional transport under steady-state conditions has been analyzed theoretically. Bromate being non-electroactive in the potential range under consideration, its transformation takes place via the redox cycle: $Br_2 = 2Br^- + 2e^-$, $BrO_3^- + 6\,H^+ + 5\,Br^- = 3\,Br_2$. Its specific feature compared to the conventional EC' mechanism is progressive increase in the overall amount of the redox components, Br_2 and $2Br^-$, due to consumed bromate. As a result, this novel EC" mechanism possesses autocatalytic properties so that even a trace amount of bromine in the bulk solution may result in very high current densities, up to the those limited by diffusion of the principal solution components, bromate and protons.



Unlike our previous study of this system carried out for excess of protons compared to bromate [1] we consider an opposite situation where ***bromate is in great excess compared to protons*** so that it is the proton transport across the diffusion layer which limits the maximal current [2-5]. Approximate analytical formulas have been derived for characteristics of the system which describe the process for all possible values of its parameters.

Behavior of the system depends crucially on the relation between the diffusion layer thickness, z_d, and the kinetic layer thickness, z_k (determined by the rate of the homogeneous reaction). As a result, the theory predicts a complicated behavior of the maximal current j^{max} as a function of the diffusion layer thickness (or of the disk rotation rate, f, for the RDE technique), with a maximum and a minimum (where j^{max} is comparable with the diffusion limited currents for protons, j_H^{lim}, or for bromine, j_{Br2}^{lim}, respectively) separated by the range of an anomalous variation: rapid increase of the maximal current for larger diffusion layer thicknesses, or for lower RDE frequencies (Figure).

In particular, for sufficiently thick diffusion layer thicknesses, $6\,z_k < z_d$, the amounts of the accumulated redox-couple components inside a thin kinetic layer near the electrode surface become so high that the maximal current j^{max} is limited by the proton transport from the bulk solution into the kinetic layer, i.e. by its diffusion limited current, j_H^{lim} (Figure).

Since its value is proportional to the bulk-solution concentration of protons, H^0, it may reach very high values for strongly acidic solutions. Figure demonstrates the plots, j^{max} vs. f, for three different concentrations of protons: $H^0_1 = 1M$, $H^0_2 = 3M$, $H^0_3 = 5M$).

Acknowledgement: This work is supported by the Russian Science Foundation (grant № 15-13-20038).

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The Effects of Electrolyte Additives on $Li_4Ti_5O_{12}$ and How they Impact Gassing

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Batteries consisting of $Li_4Ti_5O_{12}$ (LTO) anodes do not require the formation of a solid electrolyte interface to deliver robust high-rate performance at room temperature, however performance suffers at elevated temperatures due to gassing. Research has linked this gassing to the instability of the electrolyte on the surface of charged LTO at elevated temperatures.[1-3] If this is the case a passivation layer which prevents the electrolyte from coming into contact with the charged surface of LTO should hinder gassing. Several classes of electrolyte additives have been investigated in $Li_4Ti_5O_{12}/LiMn_2O_4$ coin cells and pouch cells. ATR-FTIR and X-ray photoelectron spectroscopy has been used to gain an understanding of the surface films formed with different additives while in-situ gas measurements based on Archimedes' principle and gas chromatography have given insight into how the implementation of these additives affects gassing. The results from this study enable the selective design of surface films for LTO anodes, which impedes gassing at elevated temperatures without sacrificing performance.

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Strirring nanoparticles: electrochemical behaviour of suspended Prussian Blue nanoparticles

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The electrochemistry of suspended nanoparticles received recently some attention [1,2]. This research was oriented towards recording of single electrochemical events, evaluation of nanoparticles reactivity and determination of their size and concentration [3]. Typical experiments were performed in quiescent conditions, when diffusing nanoparticles collide with the ultramicroelectrode. When the electrode is set at appropriate potential electrons are transferred from or to the nanoparticles and electrocatalytic [1], electrodissolution [2] or redox reaction [4,5] is enabled. The two latter examples are related to redox transformations of organic [4] or metal oxide nanoparticles [5].

Recently we have demonstrated that electrochemical response of catalytic nanoparticles can be obtained in forced convection conditions [6,7]. Injection of gold nanoparticles suspension into glucose solution resulted in characteristic step like current-time characteristics obtained with "noncatalytic" rotating disc electrode (RDE), due to electrocatalytic oxidation of glucose [6]. Injection of carbon nanoparticles suspension into flow system filled with ascorbate solution, with electrochemical wall jet detector, results in peak shaped characteristics obtained due to electrocatalytic oxidation of ascorbate [7].

Here we would like to show that suspended redox active nanoparticles may exhibit electrochemical reactivity of under hydrodynamic conditions on the example of citrate stabilized, cubic shape (size 20-30 nm) Prussian Blue (PB) nanoparticles (PBNPs) at RDE. The cyclic voltammograms recorded in PBNPs suspension exhibits similar features to that obtained with PB modified electrode [8]. Subsequent injections of citrate stabilized PBs suspension into aqueous electrolyte solution with RDE potential set to the value corresponding to reduction (0.0 V) or oxidation (1.0 V) of PB result in characteristic current steps resulting from reduction or oxidation of PBNPs. The role of adsorption of nanoparticles in this precess will be discussed. The results of attempt of electrocatalytic application of suspended PBNPs to H_2O_2 will be also presented.

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Anodic TiO_2 Nanocavity Arrays for the Fabrication of Au-WO_3-TiO_2 Photocatalysts

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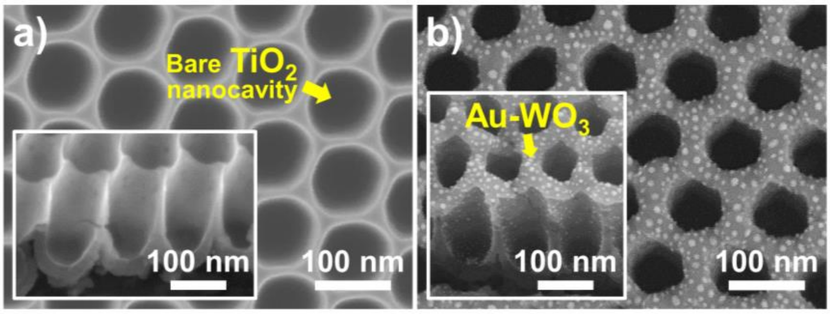
Effective strategies to improve the photocatalytic performance of TiO_2 are the coupling with a suitable semiconductor (*e.g.* WO_3[1,2]) and the surface modification with a charge-transfer co-catalyst (*e.g.* Au[3]).

We explore the use of highly-ordered arrays of TiO_2 nanocavities for the synthesis of Au-WO_3-TiO_2 structures for photocatalytic H_2 generation. The TiO_2 nanocavities are grown by electrochemical anodization of Ti in a hot H_3PO_4/HF electrolyte.[4] The resulting structures are hexagonally-packed and have individual diameter and depth of some 100 nm (Fig. a). We coat the TiO_2 nanocavities with sputter-deposited thin metal films, namely W and Au films with nominal thickness of ~ 1-30 nm. Then, a suitable thermal treatment simultaneously leads to *(i)* crystallization of TiO_2, *(ii)* formation at the TiO_2 surface of crystalline WO_3 by W thermal oxidation and *(iii)* morphological evolution of the Au films into nanoparticles by solid-state dewetting.[5] Key feature of this fabrication approach is that the sputter-coating and dewetting conditions (*e.g.* sequence and amount of sputtered metals) can be adjusted to tailor the formation of different Au-WO_3-TiO_2 structures (Fig. b).



TiO_2 surfaces decorated with minimal amounts (*e.g.* 1 nm-thick layers) of both Au and W are significantly more active towards photocatalytic H_2 evolution than their counterparts synthesized by depositing larger amounts of sputtered metals. The results of various characterization techniques (SEM, XRD, XPS, TEM) and electrochemical measurements (EIS) suggest that a synergistic effect towards high H_2 generation efficiencies is achieved by formation of WO_3 nanocrystals at the TiO_2 surface necessary for charge carrier separation,[6] and by the placement of Au nanoparticles at the surface of both WO_3 and TiO_2, which favors electron trapping-transfer to the redox species in the environment. The used fabrication pathway is crucial for controlling the photocatalyst morphology, and can be extended to other case-studies for rational photocatalyst design.

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Electrosynthesis of valeric acid

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Valeric acid (pentanoic acid) is produced industrially via hydroformylation (oxo-process) of 1-butene and 2-butene followed by oxidation of valeraldehyde and isovaleraldehyde to the corresponding acids (Figure 1).

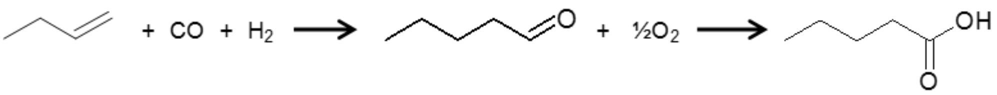

Figure 1: Hydroformylation of 1-butene and subsequent oxidation of valeraldehyde to valeric acid

Valeric acid has a market size of ~20 ktons annually and is used as synthetic lubricant, plasticizer, extractant, fragrance and flavour amongst others. The hydroformylation process for valeric acid is based on raw materials derived from fossil resources and therefore non-renewable. Levulinic acid, or 4-oxopentanoic acid, is one of the renewable platform chemicals and be derived from lignocellulosic biomass via acid catalysed hydrolysis (Isikgor *et al.*, 2015). Chemical conversion of levulinic acid to valeric acid by hydrogenation proceeds through subsequent formation of γ-valerolactone, pentenoic acid and then valeric acid with possible deactivation of the precious metal catalyst by polymerisation products (de Maria, 2016). Electrochemical reduction of levulinic acid to valeric acid was already discovered in 1911 by Tafel and Emmert at lead and mercury cathodes (Figure 2) and has advantages over the chemical conversion such as utilisation of non-precious metals and ambient reaction conditions.

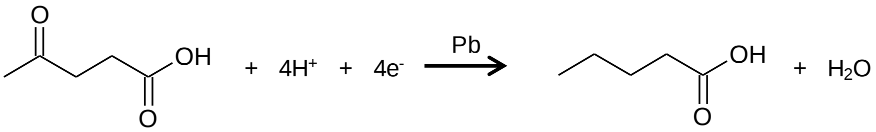

Figure 2: Electrochemical reduction of levulinic acid to valeric acid

The electrochemical reduction mechanism involves the formation of the hydroxymethyl radical, organometallic and subsequently hydrolysis to yield the hydrocarbon (Eberson *et al.*, 1970). Other studies have validated the findings of Tafel and Emmet and have obtained higher current efficiencies, yields and high selectivities (Chum, 1982; Nilges et al., 2012; Xin et al., 2013; Dos Santos et al., 2015). Copper, iron, nickel and carbon materials resulted in low yields, current efficiencies and selectivities.

In our study we focussed on the applicability of other materials having a high overpotential for the HER and influence of the formation of a second phase on product and reactant distribution due to reduced solubility of valeric acid.

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Electrochemical synthesis of furandicarboxylic acid

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Lignocellulosic biomass is abundant, cheap, and many platform sugars can be derived from it. 5-(Hydroxymethyl)furfural (HMF) can be produced from the C6 sugars and can be further oxidized to furandicarboxylic acid (FDCA). The latter can serve as a monomer for bio based polymers, such as polyethylene furanoate (PEF) [1] and is considered one of the twelve building blocks of the future for the production of bio-based chemicals and plastics [1]. So, far no commercial process of HMF to FCDA is available yet. Most of the approaches for production of FDCA are thermocatalytic or bio-catalytic conversions which often are energy demanding and require harsh process conditions (aggressive solvents, toxic oxidants, high O_2 or air pressures, elevated temperatures) and expensive noble metal catalysts, e.g. based on Pt, Au, and Pd [2].

Electrochemical oxidation allows selective and less energy demanding conversion at ambient pressures and temperatures on NiOOH electrode or on carbon based materials using mediators, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) [1]. Our research focused on scaling up towards more industrially relevant conditions such as increased HMF concentrations (up to ~10wt% HMF), utilization of an industrial type of plate-and-frame electrolyser together with the construction of a bench-scale system which includes integrated product separation. TNO has tested direct oxidation on NiOOH foam electrodes. The oxidation was performed continuously in 0.1 M Na_2SO_4 (pH 12) at 0.8 V vs Ag/AgCl with subsequent FDCA recovery, and both selectivity and current efficiency achieved were >85 % (Figure 1).

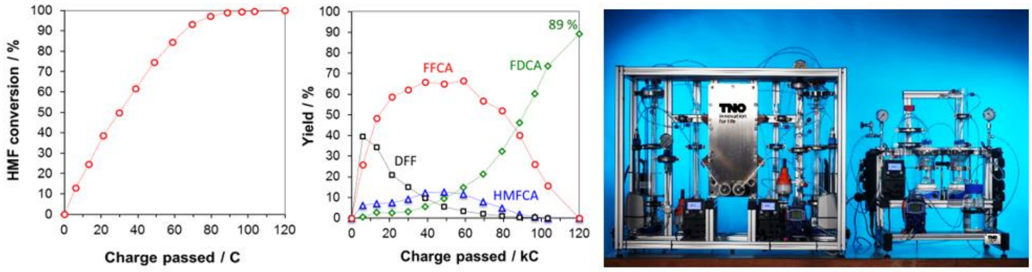

Figure 1: Conversion of 10 wt% HMF to FDCA in 0.1 M Na_2SO_4 (pH12) at 0.8 V vs Ag/AgCl (left image). Yield of FDCA and HMF oxidation intermediates (middle image). A bench scale continuous electrolyser setup with DSP (right mage).

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Enhanced Photoelectrochemical Performance of Cuprous Oxide/ Graphene Nanohybrids

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One of the biggest challenges of the 21th century is to consume environmentally friendly energy instead of the conventional non-renewable ones. Our largest available renewable energy source is sunlight, which might be harnessed using the gained knowledge in the field of photoelectrochemistry in the past 45 years.

Photoelectrodes can help to utilize solar energy in different ways: solar energy is either converted into electricity with photovoltaic solar cells, or stored in the form of chemical energy utilizing different photoelectrochemical (PEC) processes. This latter strategy, which relies on chemical reactions initiated at the semiconductor/electrolyte interface by photogenerated charge carriers, offers a viable avenue for direct hydrogen evolution and carbon dioxide reduction to useful fuels.

There are several requirements that a photoelectrode must fulfill: it has to be (1) stable, (2) insoluble in the test medium, (3) resistant to photocorrosion; but in the meantime, it is expected to (4) have a broad optical absorption, and (5) to show good charge separation-, and transfer behavior. One single material, however, according to our current knowledge, cannot meet all these criteria. For this reason, the attention shifted to composite materials, which contain several different components. These components are selected to tackle each individual task (e.g., co-catalyst, or light absorbers, etc). Design and preparation of an effective composite photoelectrode material is a major undertaking – hence, it has become one of the main research projects in the field of photoelectrochemistry.

In this study, we investigated the reasons behind the improved PEC performance of nanocarbon based photoelectrodes. For this purpose, various nanostructured electrodes were prepared, including carbon nanotube (CNT) networks, spray-coated graphene films (using exfoliated few-layer platelets), and 3D graphene foams. Variable amounts of p-Cu_2O was loaded on their surface via a controlled, carefully designed, multiple-step electrochemical deposition protocol. By comparing and contrasting the PEC behavior of these hybrid photocathodes, we investigated the effects of various nanocarbon scaffolds, with primary focus on graphene. (Photo)electrochemical measurements (including photovoltammetry, electrochemical impedance spectroscopy, photocurrent transient analysis) revealed better performance for the 2D graphene containing photoelectrodes, compared to the bare Cu_2O films, if the geometrical area of the electrodes is considered. After taking into account the actual surface area of the nanostructured photoelectrodes (which is vastly different for each carbon substrate), it was found that the 3D graphene based hybrids outperformed their counterparts. This could be rationalized by its interconnected structure, which facilitated effective charge separation and transport, leading to better harvesting of the generated photoelectrons.

These structure-property relationships can be exploited in general for the rational design of hybrid photoelectrodes, to obtain potentially attractive candidates for PEC energy conversion schemes, such as water splitting or CO_2 reduction.

Investigation of CO_2 Reduction Products in Lithium Ion Batteries

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Lithium ion batteries (LIBs) are essential to renewable energy development and are consistently being used in more numerous applications. It is known that during cycling and especially at elevated temperatures, LIBs tend to form gaseous reduction products which cause performance degradation as well as unsafe intracellular pressure. With cycling, carbonate containing electrolytes decompose into CO_2 and SEI components and vary in concentration. Here, we present preliminary NMR, IR, and GC-MS results of model studies performed on solid sodium and lithium with CO_2 gas.

Infiltrated porous oxide monoliths as high lithium transference number electrolytes

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High lithium transference number (t_{Li^+}) electrolytes are greatly beneficial as they could solve the problem of ion concentration gradients within the lithium cell which limit its lifetime and practical energy density. In “soggy sand” electrolytes (insulating oxide nanoparticles dispersed in typically organic lithium salt solution), lithium conductivity is enhanced (and anion conduction depressed) in the space charge zones due to the coupled effects of anionic adsorption and association-dissociation equilibrium.[1] When mesoporous silica particles are used as a solid phase, lithium can be efficiently transported through the interconnected pores.[2] A convenient way of circumventing particle network reproducibility and stationarity issue is infiltration of solid mesoporous silica pellets (sol-gel synthesis, ≈0.5 mm thick, S_{BET}≈500 m^2 g^{-1}) with liquid electrolyte, for example lithium triflate/poly(ethylene glycol) dimethyl ether. Such composite liquid/solid electrolytes exhibit high lithium transference numbers (t_{Li^+}≈0.9) linked with high ionic conductivities (σ_m=0.5-0.8 mS cm^{-1}) and remarkably stable solid electrolyte interphases.[3] Charge carrier chemistry at liquid/solid interface will be discussed in terms of various silica surface modifications.

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Hydrogen embrittlement of martensitic high strength steels: relationship between microstructure and hydrogen diffusion and segregation

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In many industrial applications, increase of the mechanical properties is required due to the severe exposure conditions and solicitations. So high strength steels with a martensitic microstructure are widely used. But when mechanical characteristics are increased, hydrogen susceptibility has also to be considered. In contact with hydrogen environments either during manufacturing steps such as surface treatments or in service when subjected to corrosion phenomena, these steels could be subjected to Hydrogen Embrittlement (HE). For Quenched and Tempered Martensitic steels (QTM) our different studies have suggested that the hydrogen diffusion and segregation is strongly dependent on the metallurgical parameters [1-5]. Especially, Electrochemical Permeation (EP) experiments combined with Thermal Desorption Spectroscopy (TDS) analyses were recently used in order to evaluate the hydrogen diffusion and segregation in different materials [4].

We have used the both techniques in order to characterize the hydrogen diffusion and segregation for different quenched and tempered martensitic steels QTM with an ultimate tensile strength (UTS) varying from 1200 to 1500 MPa. The parameters extracted from the modeling of the permeation test are correlated with the metallurgical features of the QTM steels. A specification attention has been provided to desorption kinetic during the electrochemical permeation to evaluate the maximum of the hydrogen flux.

Charging conditions were also used in order to determine the maximum content of hydrogen absorbed in the materials without internal damage and a desorption kinetics at 20°C were characterized using TDS and compared to the electrochemical permeation data. The redistribution of hydrogen during the baking period is discussed and compared through the evolution of the mechanical properties during a tensile test. We illustrate that the damage processes depend on the hydrogen flux more than the hydrogen concentration.

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Electrokinetic Preconcentration and Electrochemical Detection of Silver Nanoparticles

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Electrochemical detection of individual analyte species has become increasingly attractive in the electrochemical community. Current examples of analytes being detected include single nanoparticles, emulsion droplets, vesicles, biological macromolecules, and single ions.[1-9] Of interest is the direct oxidation of silver nanoparticles at the surface of an indicator electrode. Silver nanoparticle oxidation has been used in detection of E. coli bacteria, and the influenza virus.[7,8] Currently the detection is done at room temperature by applying constant (dc) potentials. Here we present a different approach. A high frequency alternating (ac) waveform is applied to the indicator electrode in addition to the dc potential. This results in two phenomena in solution, the dielectrophoretic force, and electrothermal flow. To date dielectrophoresis has been used primarily in particle sorting.[10] Here we present its use in the electrochemical detection of silver nanoparticles. We show that, by applying ac signal, an increase in the frequency of silver nanoparticle collisions with the surface of the indicator electrode is observed. Further development of this approach will lead to the improvement of the detection limits in electrochemical experiments.

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A Wireless, Portable, and Inexpensive Open-Source Potentiostat

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The detection and quantification of trace components in complex samples is essential for various applications, leading to the development of several sensitive and reliable analytical techniques. However, factors such as high instrumentation cost, extensive sample preparation, and limited selectivity reduce the efficacy of these methods. Thus, there is a clear need for portable, autonomous, and inexpensive electrochemical instruments. We propose an open-source wireless potentiostat to address this need.

The proposed potentiostat contains the following blocks: a custom analog front-end (AFE) including a digital-to-analog converter (DAC) and an analog-to-digital converter (ADC); a low-cost commercial microcontroller board (Arudino 101); a wireless module (Adafruit Bluefruit LE SPI Friend); and a small single-board computer (Raspberry Pi 3). The Arduino is pre-programmed by the Pi to send arbitrary digital samples to the DAC through a serial peripheral interface bus (SPI), which then converts them to the analog output voltage waveforms required for voltammetry. A low-noise transimpedance amplifier in the AFE senses the current in the analyte as the voltage between reference and working electrode varies. The sensed voltage is amplified, digitized by the ADC, sent to the Arduino over SPI, and finally wirelessly transferred to the Pi through a Bluetooth low energy (BLE) link. Note that the system is completely autonomous once the Arduino has been pre-programmed with the voltammetry waveform; "on-air" updates of the waveform are also possible. Moreover, wireless communication with the Pi can be maintained for distances >100m.

Another innovative contribution is to compensate the inaccuracy caused by staircase voltammetry (SCV). SCV has been widely used in electroanalytical chemistry. However, as has been documented in the literature, situations do arise where the use of SCV can yield results quite different than those that would be obtained by conventional analog scan voltammetry (LSV) [1]. Hai et al. theoretically compared the electrical response of a series RC equivalent circuit (including a voltage-dependent capacitor) to SCV and LSV [2]. They also provided a method to compensate for SCV step-size effects, which is to integrate the current over the entire duration of the step to yield the total charge injected, which is then divided by the step time to yield an average current over the length of the step. This method is utilized in the proposed potentiostat system: multiple data points are acquired per step and stored on the Pi text files, which are further processed locally to compensate for SCV.

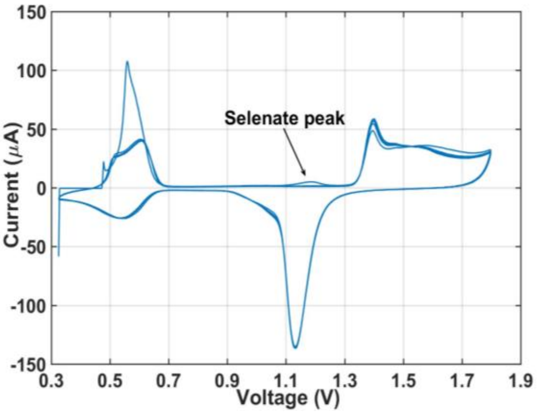

Figure 1: Experimental detection of selenate.

The proposed potentiostat has been used to test several analytes, including selenate, ruthenium hexamine, and ascorbate. In general, performance is similar to much more expensive benchtop instruments. Figure 1 shows successful detection of 50 nM selenate using anodic stripping voltammetry (ASV). Table 1 quantifies the improved performance of our device compared to another low-cost potentiostat [3].

Table 1. Comparison between the proposed device and the Cheapstat [3]

Parameters	Cost ($)	Sampling rate (Hz)	Sweep range	Detection range	SCV compensation	Wireless transmission
Proposed	~120	1-1500	±2.5V	50 nA – 800 μA	Yes	Yes
Cheapstat	~80	1-1000	±0.99V	100 nA – 50 μA	N/A	N/A

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Effects of Alkali Metal Ions on the SEI Formation at Graphite Anode in Propylene Carbonate Based Electrolytes

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Lithium ion batteries (LIBs) are widely used in portable electronic devices for the last few decades and have currently expanded to electrical vehicles and other high density power applications as well as large scale energy storage stations. Ethylene carbonate (EC) is an essential component in commercial LIBs electrolyte due to its excellent passivation of the graphite anode. However, the high melting point of EC (36.4°C) limits the low temperature battery applications. Propylene carbonate is an attractive electrolyte solvent because of its wider working temperature range which can not only enable the LIBs to operate at extreme temperature conditions but also improve the safety of the batteries. However, PC co-intercalates into graphite with lithium ions, leading to exfoliation of the electrode, which results in rapid capacity decay[1,2]. The cycling performance of graphite anode in PC electrolyte has been reported to be improved by incorporating salts and additive such as LiBOB and VC which generates a stable SEI. Recently, Xiang et.al and Zhang et.all reported that the addition of small amounts of Cs^+ into PC electrolyte inhibit the co-intercalate of PC into graphite, resulting in the improved cycling ability[3,4]. However, the mechanism is not yet fully understood.

In this study, we have systematically investigated the effects of alkaline metal ions including Na^+, K^+ and Cs^+, to the cycling performance of graphite anode in PC -based electrolyte (1M $LiPF_6$ + EC: PC: EMC 5:2:3). As shown in figure 1, Li^+ and Na^+ containing electrolyte show high irreversible capacity, and reversibility is comparatively higher for cells containing K^+ and Cs^+ additives**.** These cells show low or negligible PC reduction ~ 0.7V as opposed to the ones that contain Li^+, Na^+ additives. In order to understand the mechanism of the improvement, we have characterized the SEI formation at the graphite electrode, utilizing x-ray photoelectron spectroscopy (XPS), attenuated total reflectance fourier transformation infrared spectroscopy (ATR-FTIR) transmission electron microscopy (TEM) and inductive coupled plasma mass spectrometry (ICP-MS). The detailed results will be discussed in the meeting.

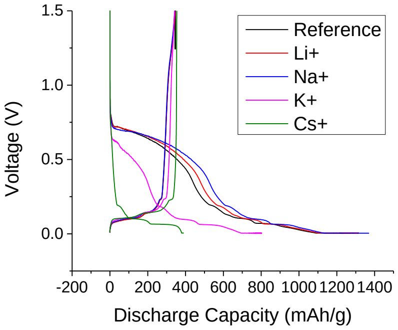

Fig. 1. Voltage profiles for the first cycle of graphite anode in the presence of different alkaline metal ions.

Acknowledgements
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In-situ monitoring the electrodeposition of silver nanoplates and its catalytic applications

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Single-crystal metal is an important material as a model catalyst in catalytic science. It has provided an important insight into understanding of the structure–property relationships. Much effort has been devoted to synthesis of single-crystalline metallic nanostructures in recent years.[1,2] However, it is still a great challenge to obtain surfactant-free silver single crystal surface. Here we develop a simple, controllable electrochemical method to synthetize single-crystal silver nanoplates and characterize the chemical reaction occurring on the surface.

In this work, the electrochemical dark-field technique was used to monitor the growth of silver nanoplates and to understand the growth mechanism. A large single crystal plate free of surfactant can be easily prepared by potential step techniques. As shown in Fig. 1a left, the silver nanoplates are of both hexagonal and triangular shapes and size of the plate is about 20 µm. The crystalline nature of the silver nanoplates was confirmed through X-ray diffraction (XRD) pattern and SAED pattern, as shown in Fig. 1a right, which clearly reveals the high quality Ag (111) structure. The size and thickness of the silver nanoplates can be finely tuned by varying the deposition potential. More interesting, we observed a clear layer stacking growth pattern in Ag nanoplates for the first time, and the upper layer has the same thickness as the bottom layer shown in Fig. 2. The nanoplates were used as substrates for studying the photocatalytic activity in tip-enhanced Raman scattering, which forms a good comparison for Au single crystal in the plasmon-assisted reduction of 4-nitrothiophenol (4-ATP) to p,p'-dimercaptoazobenzene (DMAB) reaction.[3]

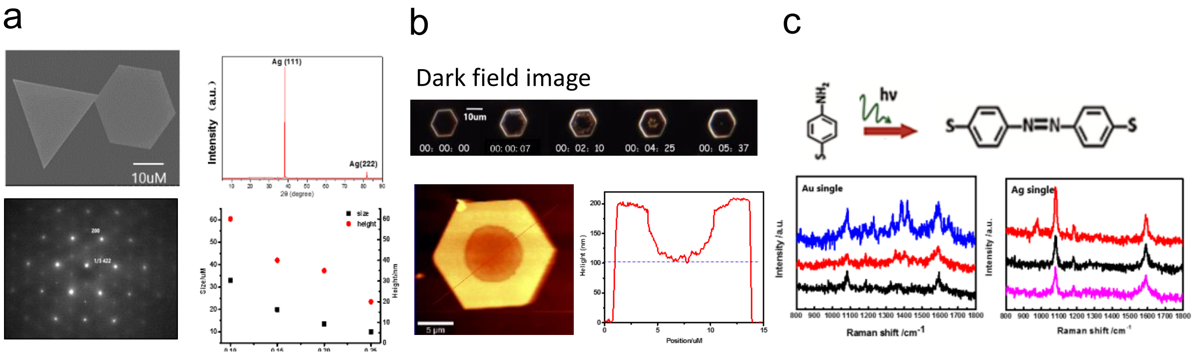

Fig. 1(a) Characterization of silver nanoplates. (b) Layer stacking growth pattern. (c) Application of silver nanoplates

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Voltammetric determination of anti-hypertensive drug hydrochlorothiazide using screen-printed carbon electrodes modified with L- glutamic acid

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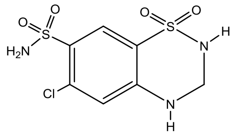

Figure 1: Hydrochlorothiazide structure

Hydrochlorothiazide (HCTZ, figure 1), 6-chloro-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide, is a drug widely used to hypertension treatment. HCTZ acts on the kidneys inhibiting sodium and chloride ions reabsorption into nephron contoured tubules and also preventing water reabsorption, which results in a decrease in blood pressure [1]. Moreover, HCTZ is also used in the treatment of renal tubular acidosis, diabetes insipidus, edema, and prevention of kidney stones. The determination of this drug in different matrices is currently carried out by means of different analytical techniques, like as high performance liquid chromatography (HPLC), which is the analytical technique indicated by the United States Pharmacopeia [2], spectrophotometry, capillary electrophoresis, among others. Nevertheless, these techniques have some disadvantages such as high initial investment (equipment), need of sample pre-treatments, time-consuming procedures, expertise required and high cost of consumables.

Electroanalytical methods are a very notable alternative for the determination of pharmaceuticals as HCTZ [3]. The modification of electrodes increases the level of determinations of different species. Glutamic acid (GA) is a modifier with easy manipulation and good performances. Carbon electrodes modified with L-PolyGA have been used for the determination of different analytes in solution such as drugs and metabolites [4].

In this work, new electroanalytical methodologies using screen-printed carbon electrodes modified with L-AG by both, electropolymerization (SPCE/L-PGA) and electrografting (SPCE/L-EGA) modifications were developed.

The modification of SPCE with L-GA monomers by electropolymerization was optimized and performed for the subsequent determination of HCTZ by differential pulse voltammetry. Electropolymerization modification conditions: 0.02 M L^{-1} AG in 0.04 M hydrochloric acid solution, scanning 5 voltammetric cycles at 180 mV s^{-1} vs $Ag/AgCl_{(sat)}$. The modification by electrografting is based on a previous optimized procedure [5]. Figure 2 shows the calibration plot obtained using this electrode. It can be observed a symmetric and well-defined signal in each HCTZ addition, and a lineal relationship between current peak oxidation and HCTZ concentration, in the range from $8x10^{-6}$ y $1x10^{-4}$ mol L^{-1}. The electroanalytical methodologies were applied in HCTZ determination in two commercial pharmaceuticals.

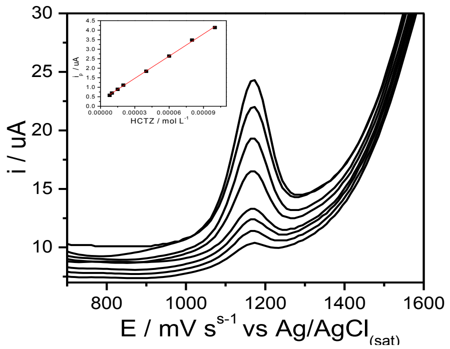

Figure 2 calibration plot to HCTZ using SPCE/L-EGA

Acknowledgements PhD Scholarship from CONICYT N° 21130071, FONDECYT GRANT 1170352 and Generalitat of Catalunya (Project 2014SGR269)

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Modification of electrodes with nanostructured materials for the detection of hydroquinone

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In the recent years, nanostructured materials (NSM), such as carbon nanotubes (CNT) and gold nanospheres (AuNS), have been widely used to modify electrode surfaces because they increased the sensitivity of electrochemical sensors [1-3].

In the present work, different NSM: multiwalled carbon nanotubes (CNT), CNT functionalized with carboxylic acids and amine groups (CNT-COOH and CNT-NH_2 respectively), and gold nanospheres were used to modified a glassy carbon electrode. The electrochemical oxidation of hydroquinone (HQ) was studied with the modified electrodes with NSM. A 3-electrode cell was used: NSM-modified glassy carbon electrode as work electrode, a Ag/AgCl as reference electrode and a platinum wire as a counter electrode.

When a modified electrode was used with the different nanotubes, the capacitive current and the redox process current (HQ/Q) increased. The most defined and high response was obtained using CNT-COOH and CNT-NH_2 (Fig. 1).

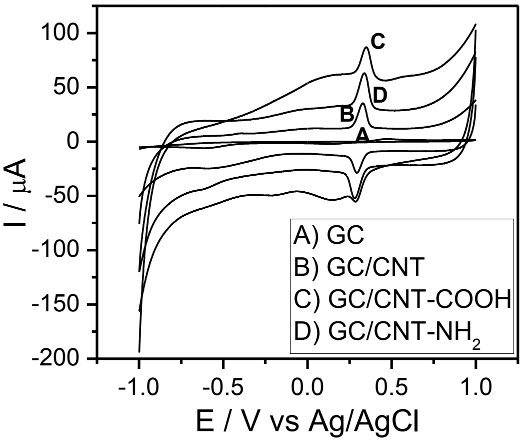

Fig. 1. Effect of the different carbon nanotubes on the oxidation of HQ.

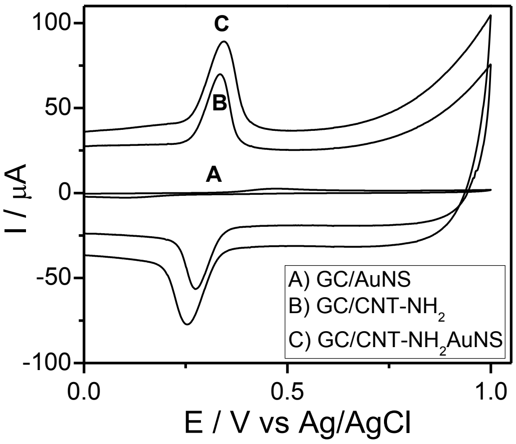

Fig. 2. Effect of the AuNS on the oxidation of HQ.

The presence of AuNS increased the current response for the oxidation of HQ, obtaining higher currents using GC/CNT-NH_2-AuNS electrode (Fig. 2). GC/CNT-COOH-AuNS and GC/CNT-NH_2-AuNS surfaces were characterized by SEM.

Finally, this electrode was used for the simultaneous determination of the HQ in the presence of its structural isomers catechol and resorcinol, achieving well defined and separated peaks.

Acknowledgments:

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Combination of Anaerobic Digestion and Solar Photo Electro-Fenton processes to remove organic matter from a synthetic slaughterhouse wastewater.

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Anaerobic Digestion (AD) is a very interesting process due to the production of methane during the degradation of organic compounds [1]. However, AD does not remove the bio-resistant organic compounds present in some wastewater.
On the other hand, electrochemical advanced oxidation processes are an excellent alternative for the elimination of persistent pollutants from wastewater, being Solar Photo Electro-Fenton (SPEF) process, the most promising, clean and low-cost method in the removal of organics [2].

In this work, the treatment of 2.5 L of two different initial concentration of synthetic slaughterhouse wastewater (1700 (sample A) and 3500 (sample B) mg COD/L each one) in a UASB reactor (Upflow Anaerobic Sludge Blanket) was performed. The continuous treatment was followed during 15 days with a hydraulic retention time (HRT) of 10 h. During this first stage it is possible to highlight the removal of chemical oxygen demand (COD) was 90% for sample A and 60% for sample B after 15 days.

After 15 days in the UASB reactor, the post-anerobic treatment wastewater was conducted to an electrochemical pilot plant. The electrochemical cell contains a DSA anode and an Air-difussion cathode coupled to solar photoreactor. The removal of was studied. 5 L of post-aerobic treatment solutions were treated by SPEF process to remove the bio-resistant substances applying two different currents.

A complete mineralization of organic matter was obtained by AD-SPEF processes at the end of electrolysis, showing the application of combination processes to the treatment of slaughterhouse wastewater.

Acknowledgments:
CONICYT Doctoral Scholarship Project 21140248 and FONDECYT Grant 1170352

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sp^3/sp^2 ratio in BDD electrodes: effect on the degradation of Aniline and the generation of oxidant species.

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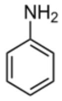

Figure 1. Aniline structure

The electro-oxidation (EO) process depends strongly of the chemical nature of the anodic material used. In this sense, the most commonly used anode for this process is the boron doped diamond electrode (BDD), which is mainly synthesized by the chemical vapour deposition method (CVD). By CVD, has been possible to obtain BDDs supported on niobium, silicon and titanium, using different concentrations of boron, and with different sp^3/sp^2 proportions of carbon. Recent studies have shown that the conversion or combustion (mineralization or transformation to CO_2) of an organic compound present in solution, depends of the sp^3/sp^2 carbon ratio of a BDD electrode, since a higher sp^3/sp^2 ratio could favour the generation of hydroxyl radicals ($^{\bullet}OH$) above the oxygen evolution reaction[1]. In the present work the degradation of aniline (Fig. 1) and the generation of oxidant species (H_2O_2 and $S_2O_8^{2-}$) were studied using $BDD_{sp3/sp2}$ electrodes with different sp^3/sp^2 ratios (BDD_{154}, BDD_{190}, BDD_{220}, BDD_{252}, BDD_{303}) by electro-oxidation process. The electrolysis were performed in a non-divided electrochemical cell at room temperature (25 °C) using the previously mentioned anodes and a stainless steel electrode as cathode, both immerse in Na_2SO_4 0.05 M. Aniline removal was followed by both, the decay of the concentration and chemical oxygen demand (COD) abatement. On the other hand, the generation of oxidant species were quantified too.

A complete degradation of aniline is achieved using the five anodic materials without high differences (Fig. 2a). However, the mineralization has a direct relationship with the electrode: a higher sp^3/sp^2 ratio (BDD_{252} and BDD_{303}) allows obtaining a high mineralization (Fig. 2b). The difference in the mineralization of aniline could be related with different electrogenerated oxidant species as persulfate anion and hydrogen peroxide. During the electrolysis both, persulfate anion and hydrogen peroxide are continuously generated on all BDD electrodes (Fig. 3a), and the accumulation of their depends on the sp^3/sp^2 ratio.

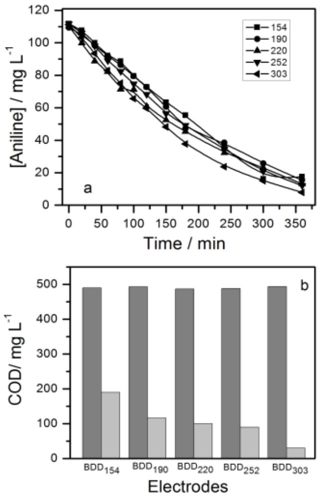

Figure 2. (a) Concentration and (b) COD decay.■=t_0, □ =t_{360}

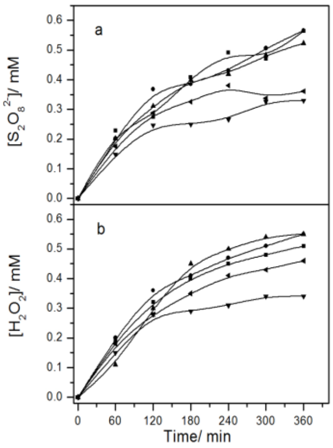

Figure 3. Generation of oxidants with respect to electrolysis time. (a) Persulfate anion, (b) hydrogen peroxide. BDD_{154}= ■, BDD_{190}=•, BDD_{220}=▲, BDD_{252}= ▼ BDD_{303}= ◀

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Electrochemical and Optical Effects of Chalcogenide Doping on Organo-metal Halide Perovskite

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Abstract:

Organometal halide perovskite solar cells have evolved in an exponential manner in the two key areas of efficiency and stability. The power conversion efficiency (PCE) of such materials reached 20.1% two years ago. Organo-lead halide perovskites are one of the most promising candidates for use in the production of next-generation solar cells. The generic perovskite structure, ABX_3, allows the synthesis of a broad range of perovskite materials by the simple modification of the building blocks A, B, and X (A = organic group, B = metal and X = halide). The preparation of solar cell materials based on methylammonium lead halides, $CH_3NH_3PbX_3$ (X = Cl, Br, and I), has been reported. These mixed halide systems are solution-processable and have tuneable optical properties. The optimal bandgap for single-junction solar cell materials is known to be between 1.1 and 1.4 eV. However, the bandgaps of methylammonium lead trihalide ($CH_3NH_3PbI_3$ or MALT) perovskites are beyond this range. In this study the bandgaps of MALT perovskites were modulated by the incorporation of chalcogenide (S, Se and Te) ions into the perovskites. The electrochemical, electronic and band-gap properties of the chalcogenic MALT perovskite nanomaterials were studied by cyclic and square wave voltammetries, ultraviolet/visible spectroscopy and photoluminescence spectroscopy. The microscopic properties of the materials were interrogated by high resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM); while the composition, particle size and structure of the materials were confirmed with X-ray diffraction (XRD) measurements.

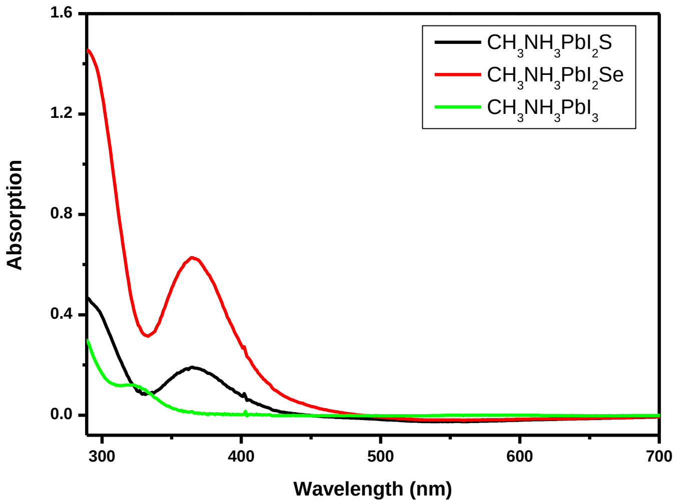

Fig 1: Ultraviolet-visible of undoped (green) and doped with Sulfur (black) and Selenium (red) Perovskites.

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Scale up of the electrokinetic treatment assisted with a biological permeable reactive barrier of an herbicide-polluted soil.

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In this study, the remediation of a pesticide-polluted soil using an electrochemical biological combined technology is assessed in a 32 m^3-prototype [1-3]. The polluted soil was subjected to an electrokinetic (EK) treatment with a biological permeable reactive barrier. The biological barrier placed in the soil was a microbial consortium adapted for 2,4-D (selected as model of polar herbicide) and oxyfluorfen (selected as model of non-polar herbicide) degradation. The electrodic configuration selected was a fence of alternating anodes and cathodes surrounding the main contamination point (Fig 1). To evaluate this technology, a 40-day test was conducted using an electric potential gradient of 1.0 VDC cm^{-1} (between consecutive electrodes). Temperature, pH, conductivity and pollutant and nutrient concentrations were monitored during the treatment in electrolytic wells and in different sample-points located along the cell. Moreover, at the end of the test, a post-analysis characterization of the soil section was performed. Results are compared to those obtained in absence of biological permeable reactive barrier in order to clarify the main mechanisms involved in the removal of pollutants.

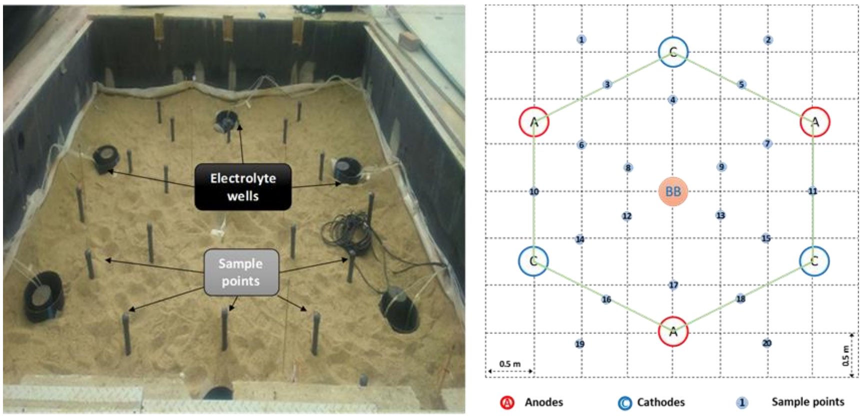

Figure 1. Electro-bioremediation Prototype.

Acknowledgements: The Spanish Ministry of Economy, Industry and Competitiveness and the European Union through the project CTR2016-79197-R is also gratefully acknowledged.

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Electrochemical detection of graphene oxide in flow

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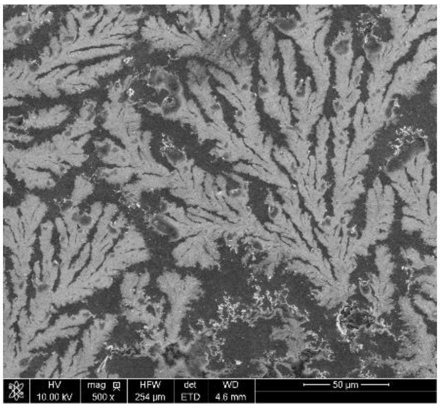
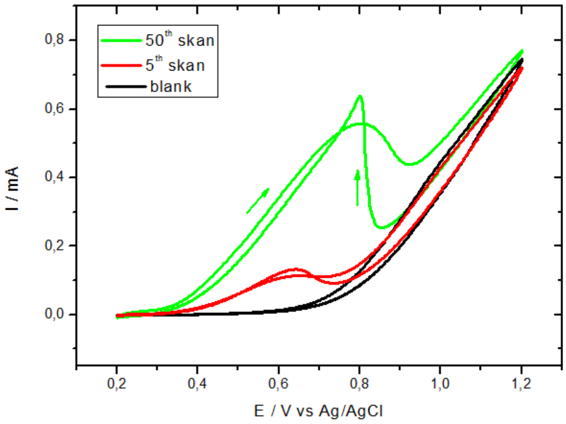
The nanoobjects have already found a numerous applications as a results of their unique electronic, optical, thermal, and chemical properties [1,2]. Not surprisingly their global production increases every year [2], and the development of methods of nanoobjects detection is highly desirable. Comparing to other techniques like TEM, AFM or XPS electrochemical detection is cost-effective, simple and fast [3].

Until to date researchers were focused on electrochemical detection of various types of nanoparticles in quiescent conditions [3-5], but recently, intensive efforts have been devoted to demonstrated that it is also possible in flow [6-8]. Here we will present results of our research on electrochemical detection of graphene oxide (GO) in a fluidic system. It is well known that graphene oxide with C/O ratio 2:1 is an insulator [9]. However, reduction process produces conductive reduced graphene oxide (rGO) with larger C/O value. There is plenty of compounds capable to reduce GO like hydrazine, ascorbic acid, hexamethylenetetramine, Al, $NaBH_4$, or sulphur derivatives [5]. In our work we have used Na_2SO_3 as a substrate because GO can be reduced by SO_3^{2-} [10] and this anion can be oxidized at the working electrode. Therefore, it is useful to track an electrocatalytic properties of obtained material.

We will demonstrate that we were able to detect GO in flow in a few ways. The hydrodynamic cyclic voltammetry allows us detect GO due to electrocatalytic oxidation of SO_3^{2-}. This methodology also is suitable for the flow injection system where the samples of GO are injected and the significant increase of anodic current at the working electrode is observed. Moreover, the direct electrochemical GO detection is possible at the electrode, earlier used for electrooxidation of SO_3^{2-}. An interesting fact is that during the flow experiment dendritic structure is formed at the working electrode.





It seems that flow injection analysis system will allow continuous, fast and simple graphene oxide detection in width range of concentration and with good limit of detection.

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Electrochemical studies of methanol electro-oxidation on Pt/RuO_2/TNTs nanocomposite thin film electrodes

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Poisoning devitalization of Pt catalyst caused by the absorption of carbon monoxide is an important issue in direct Methanol Fuel Cell (DMFC). This work introduce a novel nano-structured Pt catalytic electrode, in which RuO_2 modified TiO_2 nanotube arrays (TNTs) was used as a carrier for the loading of Pt nanoparticles. RuO_2/TNTs support was prepared via coating method, herein the $RuCl_3$ sol was filled into the voids of TNTs under vacuum condition followed by thermal decomposition to form RuO_2. Pt particles were located on the RuO_2/TNTs support by pulse potential electrodeposition in 2 mmol/L H_2PtCl_6 solution. Catalytic property for methanol oxidation and resistance of CO-poisoning with this Pt/RuO_2/TNTs nanocomposite electrode were studied intensively by cyclic voltammetry and electrochemical impedance spectroscopy measurements. Experimental results show that the catalytic performance of Pt/RuO_2/TNTs enhances remarkably as the deposition time of Pt increases to 3000s, after which the electrode performance tends to be stable due to that the active surface area has reached a constant level. It is found that the methanol oxidation current on Pt/TNTs is much smaller than that on Pt/RuO_2/TNTs, what's more, the rate of current delay on Pt/TNTs is rapid with the scan cycle increasing. Among the electrodes, the Pt/RuO_2/TNTs electrode prepared by coating RuO_2 for 11 times presents the most stable performance, indicating a strong effects of RuO_2 in anti CO poisoning. In Nyquist diagrams, one capacitance arc representing the action of deprivation of H atom appeared in the first quadrant and one inductance arc representing the action of deprivation of CO appeared in the fourth quadrant. From the fitting results, the reaction resistance R_o and inductance L decreased with the coating times increasing under bias potential of 600 mV, and in this case CO oxidation is the rate controlling step.

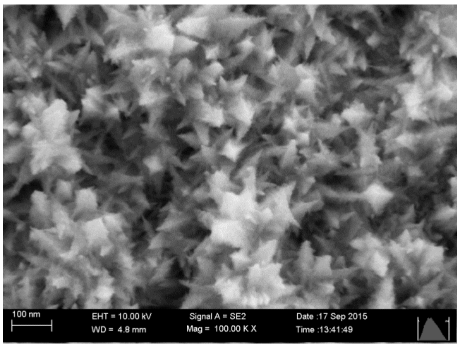

Fig. 1 SEM image of Pt/RuO_2/TNTs prepared by coating RuO_2 for 5 times and depositing Pt for 2000 s

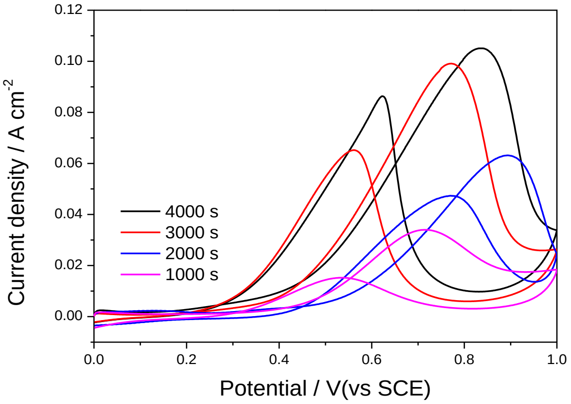

Fig. 2 Cyclic voltammetric curves of Pt/RuO_2/TNTs electrode with different deposition time of Pt, at scan rate of 50 mV/s.

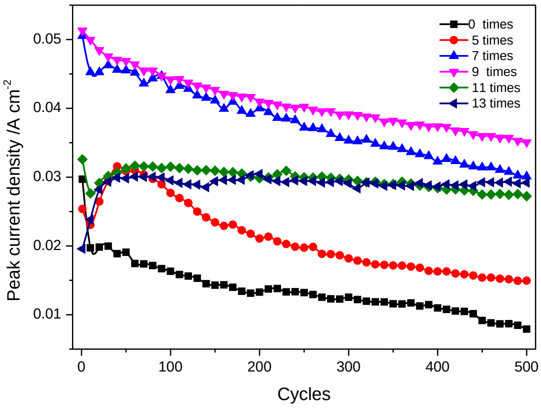

Fig. 3 Peak current density varied with scan cycles for Pt/RuO_2/TNTs electrode with different coating times of RuO_2, measured in 1 mol/L H_2SO_4+0.5 mol/L CH_3OH solution

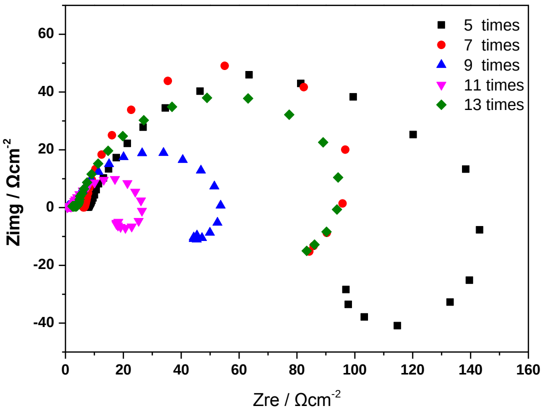

Fig. 4 Nyquist plots of Pt/RuO_2/TNTs electrode prepared with different coating times of RuO_2, measured at bias potential of 600 mV.

Single and Multiplexed Detection of Cytokines in Urine, Saliva and Serum using Disposable Electrochemical Immunosensors

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We present three immunosensing configurations for the determination of cytokines involving screen-printed carbon electrodes (SPCEs) as the electrochenical scaffolds.

The first amperometric immunosensor for quantification of urinary TGF-β1(transforming growth factor-β1), a cytokine proposed as a biomarker for renal disease, was prepared. The specific anti-TGF was covalently immobilized onto carboxylated- magnetic microparticles supported onto SPCEs using Mix&Go® polymer, and a sandwich-type immunoassay with biotin-anti-TGF and conjugation with peroxidase-labeled streptavidin (poly-HRP-Strept) polymer for signal amplification, was performed (Fig 1a). Amperometric measurements were carried out at -0.20 V by adding H_2O_2 solution onto the electrode surface in the presence of hydroquinone (HQ). The calibration plot allowed a range of linearity extending between 15 and 3000 pg/mL TGF-β1 which is adequate for the determination of the cytokine in urine and plasma.The limit of detection, 10 pg/mL, is notably improved with respect to those from ELISA kits. The usefulness of the immunosensor was evaluated by analyzing urine spiked with TGF-β1 at pg/mL levels.

“Click” chemistry by means of copper(I) catalyzed azide-alkyne cycloaddition was also used to develop an immunosensor for TGF-β1. IgG-alkyne-azide-MWCNTs conjugates were prepared and, after a blocking step with casein, anti–TGF were immobilized and the target cytokine was sandwiched with biotinylated anti-TGF labeled with poly–HRP-labeled streptavidin (Fig 1b). The affinity reaction was monitored amperometrically as above, using the H_2O_2/HQ system. Calibration plots for TGF-β1were linear between 5 and 200 pg/mL which is a suitable range for application to clinical samples, A limit of detection of 1.3 pg/mL was achieved. The immunosensor was applied to the analysis of spiked human serum samples at different concentration levels with excellent recoveries.

Dual screen-printed carbon electrodes modified with 4-carboxyphenyl-functionalized double-walled carbon nanotubes (HOOC-Phe-DWCNTs/SPCEs) were also used as scaffolds for the preparation of multiplexed immunosensors for simultaneous determination of interleukin-1β (IL-1β) and factor necrosis tumor α (TNF-α) cytokines. Anti-IL-1β and anti-TNF-α were immobilized in an oriented form using Mix&Go® polymer, and sandwich-type immunoassays with amperometric detection involving H_2O_2/HQ system and poly-HRP streptavidin, was implemented (Fig 1c). The ranges of linearity extended between 0.5 and 100 pg/mL and from 1 to 200 pg/mL for IL-1β and TNF-α, respectively, these ranges being adequate for the determination of the cytokines in clinical samples. The achieved limits of detection were 0.38 pg/mL (IL-1β) and 0.85 pg/mL (TNF-α). l as negligible cross-talking. The dual immunosensor was applied to the simultaneous determination of IL-1β and TNF-α in human serum spiked at clinically relevant levels, and in real saliva samples.

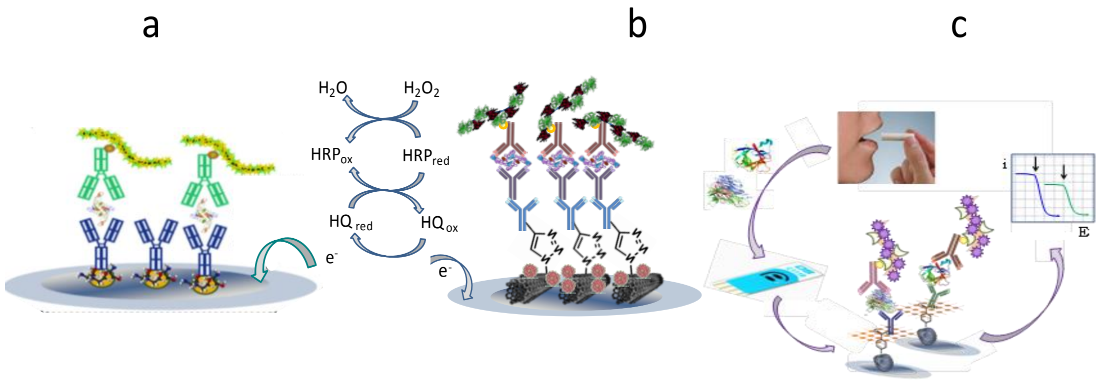

Figure 1. (a) Magneto-immunosensor and (b) “click” chemistry - based immunosensor for TGF-β1 determination; (c) multiplexed immunosensor for the simultaneous determination of IL-1β and TNF-α

Boosting up Perovskite Solar Cell Power Performance by Electrochemical Double Layer Capacitors

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Renewable energy conversion systems are now one of the most worldwide active areas of research as regards fighting the environmental impacts brought on traditional energy sources such as oil and fossil fuels. The inherent intermittency and low predictability of natural sources like wind and sun, requires high efficiency energy storage systems, like batteries and supercapacitors.

The perovskite solar cells have given rise to considerable interest among the various types of solar cell based on molecular visible-light absorbers. They are based on the photoexcitation of organic-inorganic lead halide perovskite compounds, synthesized from abundant sources with unique optoelectronic properties and electrical conductivity. [1]**.**

Electrochemical double layer capacitors (EDLCs) are extensively studied due to the increasing demand for electrical energy storage systems of long durability (over 10^6 cycles) and high specific power (higher than 10 kW/kg) [2]. EDLCs can buffer high frequency discontinuities of solar cells (DSSC) by storing the converted solar energy which is, then, delivered at high power levels. The result is an improvement of the solar energy quality. One of the key issues in the integration of EDLCs, is that EDLC leakage currents might be higher than the current generated by the harvester, thus preventing effective charge of the supercapacitor. Much attention should thus be focused on the EDLC design that has to ensure low current recharge along with high current output. A strategy is the use of high purity and electrochemically stable electrolytes, like those based on ionic liquids [3, 4].

Here it is demonstrated that by a proper design of DSSC and EDLC is it possible to simultaneously improve both the DSSC and EDLC performance and outperform the behavior of each single unit. We propose a parallel connection of perovskite DSSCs and EDLCs based on ionic liquids of different size. We demonstrate that the parallel connection arrangement offers several advantages over the series connection: i) the electronic circuitry required in sDSSC-EDLC to commute light/dark operation is not needed; ii) currents flows through an external load with same sign both under light and dark, which is useful to buffer discontinuities in solar energy conversion over relatively short time (minutes); iii) the system output current is higher than the highest current delivered separately by either the DSSC and EDLC; iv) the system features an apparent capacitance that is higher than that of the EDLC alone. The parallel connection enables a synergic interaction between DSSC and EDLC with improved current and energy storage performance with respect to those of the separate units which can be, thus, downsized. As a result, DSSC and EDLC can be independently sized according to any tailored application.

Acknowledgements

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Synchrotron Radiation Based X-Ray Absorption for Electrochemistry: New Opportunities at the SAMBA Beamline

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From a methodological point of view synchrotron based X-ray absorption techniques like X-ray Absorption Near-Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) offer the opportunity to probe the electronic and short range atomic order structure of metal electrocatalysts and, when applied to *in situ* investigations, the number of information on the metal reaction centres is tremendously amplified. Together with new development in the data analysis and modelling, X-ray absorption spectroscopy (XAS) represents a powerful site-specific tool to link the fundamental knowledge of the oxidation state (XANES) and the active site structure (XANES, EXAFS) with the electrochemical behavior. SAMBA (Spectroscopy Applied to Material Based on Absorption) is a hard XAS beamline opened to a broad scientific community spanning from physics to chemistry, surface and environmental sciences. The design of SAMBA optics is optimized in order to be very versatile and to cover the 4.5-43 keV energy range with a high flux of photons and stability, while a last generation of Ge pixelated detector (36 pixels) from Canberra provides high sensitivity for diluted specimens.[1] Recently, the beamline has been equipped with a gas distribution system with temperature and humidity control, electronic control device, and a photo-electrochemical commercial cell tested and adapted for X-ray absorption experiments with liquid electrolytes (Figure 1). A project aimed to realize a set-up for polymer-electrolyte-membrane fuel cells (PEMFC) and electrolyzers (PEMEL) working under classical operating conditions is in the pipeline, providing to the electrochemical scientific community a unique experimental station installed in-house at a synchrotron facility to fully characterize the next generation of catalysts and electrodes.

Figure 1 Example of experimental set-up for *operando* electrochemical measurements.

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Voltammetric determination of nitrophenols at a Ni(II) dimethylglyoxime complex – gold nanoparticles modified electrode

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Phenolic compounds are widely distributed in the environment due to their extensive use as intermediates in the manufacturing of pharmaceuticals, insecticides, pesticides dyes [1,2]. A large number of chloro- and nitro- phenols compounds are toxic and carcinogenic. Thus, the analysis of phenols in environmental samples is important [1,2]. This paper reports the electrochemical behaviour and detection of *o*-nitrophenol (*o*-NP) and *p*-nitrophenol (*p*-NP) with Nickel dimethylglyoxime complex ($Ni(II)(DMG)_2$) gold nanoparticles modified glassy carbon electrode (GCE/Ni(II)DMG-AuNP). The electrode was characterized using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and high resolution scanning electron microscopy (HRSEM). The results showed that Nickel(II) dimethylglyoxime complex - gold nanoparticles electrode had improved conductivity, reversibility, and electron transfer rate in selected redox probe than the unmodified GCE. The GCE/Ni(II)DMG-AuNP electrode was found to reduce the effect of phenol fouling and it was used in the determination of *o*-NP and *p*-NP in water. Under the optimal conditions, the reduction peak current varied linearly with the concentration of the phenols, with a linear regression equation of $y = -2.28153 \times 10^{-8}$ C (mol L^{-1}) x -1.3025×10^{-5} and $y = -2.139768 \times 10^{-8}$ C (mol.L^{-1}) x -7.725×10^{-6} with a correlation coefficient of 0.9910 and 0.9915 and limit of detection LOD (S/N = 3) of 5.82×10^{-7} mol.L^{-1} and 1.03×10^{-7} mol.L^{-1} respectively for *o*-NP and *p*-NP.

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Continuous Extraction of Interstitial Fluid for Diagnostic Applications by Electroosmotic Pump

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The interstitial fluid (ISF) plays an important role in transporting various nutrients, oxygen, and waste between blood vessels and cell tissues. ISF has a similar composition to blood plasma and it is regarded as an important body fluid for diagnosis. The intermittent extraction at different positions by needle with syringe[1] and 3 hours continuous extraction by ultra-filtration based on a porous membrane using a depressurizing unit[2] have been reported. We utilized a nongassing electroosmotic pump and check-valve unit and could extract ISF for 10 hours at a rate of 0.01 uL/min. The successful extraction was confirmed by measuring glucose in the extract by a glucose sensor.

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Gold nanoparticles bound to single carbon fibers via a linker derived from an aryldiazonium salt

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Gold nanoparticles (Au-NP’s) have been bound to carbon surfaces via a linker grafted from an aryldiazonium salt. Both glassy carbon and single carbon fibers have been used, with single carbon fiber electrodes exhibiting lower double layer charging current densities than the glassy carbon electrode enabling the Au-NP’s redox behavior to be more easily distinguished from the background current.

Au-NP’s were bound via a three step process, previously employed by Porter et al [1]: firstly 4-aminothiolphenol (4-ATP) was converted to the corresponding diazonium ion by addition of equimolar sodium nitrite. The thiophenyl group was then grafted to the carbon fiber surface using cyclic voltammetry, finally the carbon fiber was left in an aqueous suspension of citrate capped Au-NP’s, allowing for the spontaneous formation of gold-thiol bonds [2]. The electrochemically active surface area of the bound Au-NP’s was determined from the gold oxide reduction peak in sulfuric acid electrolyte, and was found not to significantly decrease during repetitive voltammetric cycles indicating that the bound nanoparticles were very stable. These electrodes were also used for electrocatalytic glycerol oxidation in alkaline solutions to further show that the bound nanoparticles were both active and stable.

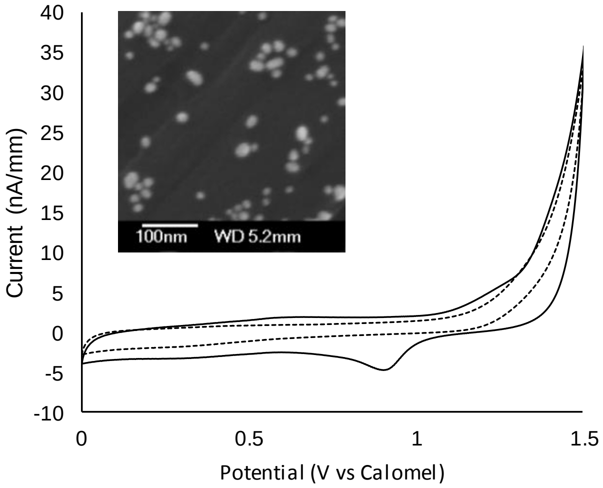

Figure 1: CV’s of single carbon fibers in 0.5M H_2SO_4 normalized by length. Dashed line indicates bare fiber, solid indicates fiber with Au-NP’s attached with loading shown by inset SEM micrograph.

By varying the grafting conditions, it is possible to vary the surface coverage of the Au-NP’s, making this a useful tool to characterize the electrochemical behavior of Au-NP’s and aspects such as the effect of spacing between nanoparticles on electrocatalytic reactions [3]. This method for producing electrodes is not confined to the binding of Au-NP’s to carbon fibers, it is possible to graft aryl groups to many conductive surfaces through aryldiazonium ion derivatives [4].

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Improved electrochemical exfoliation of graphite into high-quality graphene for supercapacitor

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Although the extensitive research efforts devoted to graphene fabrication over the past decade, the production of high-quality and large-scale graphene has remained a major challenge. In this study, an environmental friendly, economical and facile one pot method based on the controlled electrochemical exfoliation of graphite in aqueous ammonium sulfate electrolyte to produce graphene was developed to synthesize sulfur particles supported on the surface of graphene (SPG). Thiourea (CH_4N_2S), in addition to acting as a sulfur source, also regulated the radicals (e.g., HO•) and thus control the exfoliation process, resulting in sulfur particles supported on the surface of graphene (SPG). The electrochemical performance of the as-prepared SPG(1% CH_4N_2S) (Figure 1 b and d) electrode exhibited a high specific capacitance of 186 F g^{-1} at a current density of 1 mV s^{-1} compared to the graphene (112 F g^{-1}, 1 mV s^{-1}) without adding thiourea in the electrochemical exfoliation process at room temperature. Furthermore, by reducing the temperature of electrochemical exfoliation to investigate of regulation of the radicals and thus control the exfoliation process. The electrochemical performance of the as-prepared graphene by reducing the temperature electrode exhibited a high specific capacitance of 174 F g^{-1} at a current density of 1 mV s^{-1}, when the temperature of electrochemical exfoliation is reduced to 15℃. In general, this efficient and cost-effective method for electrochemical exfoliation of graphite offers great promise for the preparation of graphene that can be utilized in industrial applications to create integrated nanocomposites, conductive or mechanical additives, as well as energy storage and conversion devices.

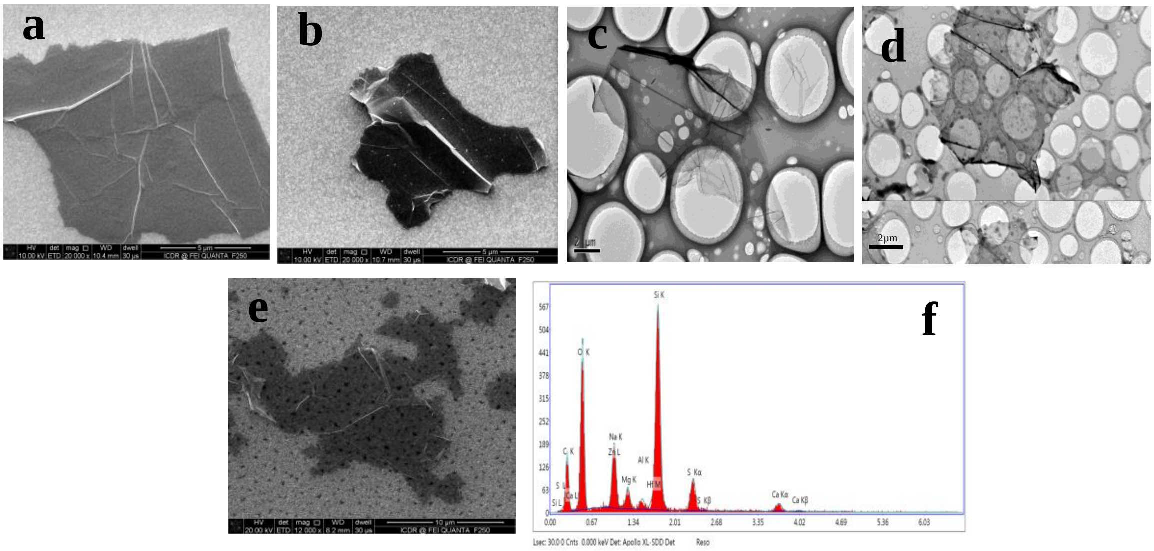

Fig 1. (a)、(b)、(e) SEM image of EG,SPG(1% CH_4N_2S) and EG(t=15℃); (c)、(d) TEM image of EG and SPG(1% CH_4N_2S); (f) EDAX of SPG(1% CH_4N_2S)

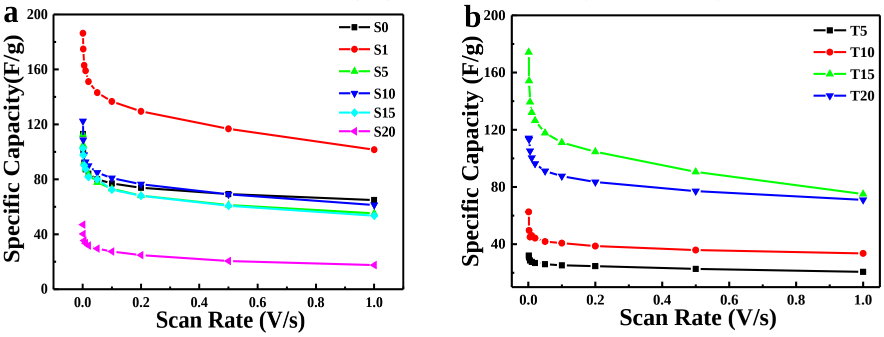

Fig 2. The specific capacitance of (a) EG and SPG (add different thiourea to the electrolyte); (b) electrochemical exfoliation at different temperature in 1 M H_2SO_4 at different current densities.

2- and 3-Dimensional Nanocomposites for Electrocatalysis

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Among the 2-dimensional substrates, graphene has a unique single-atom thick structure with sp^2-bonded carbon atoms densely arranged in a honeycomb crystal lattice. The structure and properties of graphene well meet the requirements of supports and substrates for electrocatalysts. First, graphene possesses large specific surface area, which is twice of single walled CNTs. Second, graphene has a fully conjugated sp^2 hybridized planar structure, giving rise to ultrahigh electrical conductivity, excellent mechanical properties and high thermo-conductivity. Third, graphene with interlayer structure contains lattice defects and functional groups which can anchor and immobilize metal nanoparticles on its surface. Meanwhile, with 2-dimensional metal oxide nanosheets as supports for electrocatalysts, the interaction between metal oxide and nanocrystals can enhance the catalytic performance of catalysts. In addition to 2-dimensional substrates, 3-dimensional materials can provide large surface area and fast mass transport due to the highly porous structure. On the other hand, the properties of nanomaterials are strongly dependent on their morphology, especially their exposed surface structure. Therefore, 2- and 3-dimensional material-supported metal nanostructured hybrids have attracted much attention in electrocatalysis. This presentation will cover the recent studies conducted in our group regarding the design of morphology-controlled metal nanomaterials supported on 2- and 3-dimensional substrates and their applications as efficient electrocatalysts in fuel cells. We found that 2- and 3-dimensional materials can serve as unique templates for synthesizing metal nanocrystals with well-defined structures and excellent properties. [1-6]

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A Highly Sensitiv and Simply Operated Botulinum Toxin Sensor Toward Point-of-Care Testing

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Botulinum toxin sensors for point-of-care testing(POCT) require simple operation, a detection period of less than 20 minutes, and a detection limit of less than 1 ng mL^{-1}. However, it is difficult to meet these requirements with botulinum toxin sensors that are based on proteolytic cleavage. This paper reports a highly reproducible botulinum toxin sensor that allows the sensitive and simple electrochemical detection of the botulinum neurotoxin type E light chain (BoNT/E-LC), which is obtained using (i) low nonspecific adsorption, (ii) high signal-to-background ratio, and (iii) one-step solution treatment. The BoNT/E-LC detection is based on two-step proteolytic cleavage using BoNT/E-LC (endopeptidase) and L-leucine-aminopeptidase (LAP, exopeptidase). Indium-tin oxide (ITO) electrodes are modified partially with reduced graphene oxide(rGO) to increase their electrocatalytic activities. Avidin is then adsorbed on the electrodes to minimize the nonspecific adsorption of proteases. Low nonspecific adsorption allows a highly reproducible sensor response. Electrochemical‐chemical (EC) redox cycling involving p-aminophenol (AP) and dithiothreitol (DTT) is performed to obtain a high signal-to-background ratio. After adding a C-terminally AP-labeled oligopeptide, DTT, and LAP simultaneously to a sample solution, no further treatment of the solution is necessary during detection. The detection limits of BoNT/E-LC in phosphate-buffered saline are 0.1 ng mL^{-1} for an incubation period of 15 min and 5 fg mL^{-1} for an incubation period of 4 h. The detection limit in commercial bottled water is 1 ng mL^{-1} for an incubation period of 15 min. The developed sensor is selective to BoNT/E-LC among the four types of BoNTs tested. These results indicate that the botulinum sensor meets the requirements for POCT.

Electrochemical Detection of Selenium in Water using Glassy Carbon Electrode Modified with Reduced Graphene Oxide

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Selenium (Se) is an important trace element that plays significant role in the health of humans and animals. Unfortunately, high concentrations of selenium in the body can be harmful and thus the reason for the World Health Organization limit of 10 µg/L Se in drinking water [1]. It is very important to determine the concentration selenium in different matrices owing to its biological importance. A simple electroanalytical procedure for detecting selenium in water on a reduced graphene oxide (rGO) modified electrode is described. The graphene oxide (GO) was synthesised via Hummer`s method and then reduced to rGO by using ascorbic acid. The rGO was dropped on a glassy carbon electrode (GCE) and allowed to dry at room temperature. The optimized conditions for the detection of selenium in water using square wave anodic stripping voltammetry (SWASV) were as follows: deposition potential −500 mV, pH 1, pre-concentration time of 240 s and 0.1 M nitric acid was used as the supporting electrolyte. A detection limit of 0.85 µg L^{-1} was obtained and the sensor was resistant to many interfering cationic and anionic species except Cu (II) and Cd (II). The sensor was also applied for real water sample analysis and the results obtained were validated with inductively coupled plasma optical emission spectroscopic (ICP-OES) method.

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Thermal degradation of Li/$LiCoO_2$ half-cell at moderately elevated temperature

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The market demand for lithium-ion batteries (LIBs) is expanding with an increase in the number of electric vehicles (EVs) on road. Although the normal working temperature of LIBs is about -20 to 60 ºC, the cell performance at elevated temperature is important because of EV's harsh running condition. The literatures reported that the most commonly used Li salt ($LiPF_6$) decomposes at > 70ºC, whereas the solid electrolyte interphase (SEI) on negative electrodes is damaged at >100ºC. We also found in our previous study that the surface film on a graphite negative electrode is thermally unstable at >85ºC to lose its passivation ability [1]. The previous studies on the thermal stability of surface films on the positive electrodes for LIBs are limited. The nature of surface films and their passivating ability, and their thermal stability are poorly understood, which are the primary objective of this study.

The coin-type half-cell was fabricated with $LiCoO_2$ (LCO) positive electrode and Li metal negative electrode. The used electrolyte was 1.3 *M* lithium hexafluorophosphate ($LiPF_6$) or lithium difluoro(oxalato) borate (LiODFB) dissolved in ethylene carbonate and diethyl carbonate mixture (EC/DEC=3/7 in v/v). The galvanostatic charge/discharge cycling was made at 0.1 *C* (15 mA g^{-1}) in the potential range of 3.0 ~ 4.3 V (*vs.* Li/Li^+). After 10 cycles, the cell was set at SOC0 (ca. 3.8 V (*vs.* Li/Li^+)) and stored at 60ºC or 85ºC for 24 h to assess the thermal stability of cell components. After the storage at the moderately elevated temperature, the cell was re-cycled at 25ºC to examine any degradation of cell components.

As shown in Fig. 1, when $LiPF_6$ was used as the Li salt, the capacity and Coulombic efficiency decrease after the storage, signifying that the cell components (LCO itself, surface film or electrolyte solution) are thermally degraded during the storage. When $LiPF_6$ was replaced by LiODFB, however, the cell degradation is only marginal. From these observations, we assume that the cell degradation in the $LiPF_6$-containing electrolyte is caused by the PF_5 attack on the cell components. Note that $LiPF_6$ is thermally unstable to be decomposed to generate PF_5 gas that is a strong Lewis acid. The negligible cell degradation in the LiODFB-containing electrolyte can thus be attributed to the superior thermal stability of LiODFB.

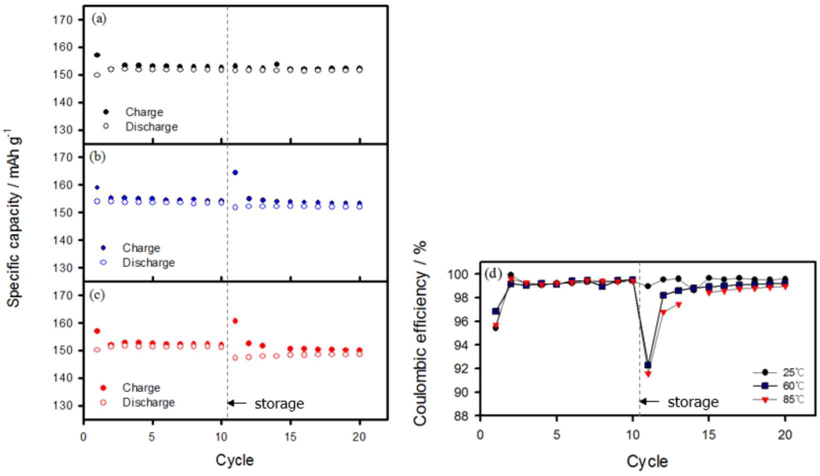

Figure 1. The capacity of Li/LCO cell traced before and after the storage: (a); without storage, (b); 60ºC storage, (c); 85ºC storage for 24 h, and (d); Coulombic efficiency of the cells (storage condition is in inset). Note that the used Li salt was $LiPF_6$.

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Ni(II)-chelated Thio-crown Complex as Single Redox Couple for Non-aqueous Flow Batteries

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The energy storage system has received a lot of interest with the expectation of energy resource moving to renewable energy. Among the energy storage systems, the redox flow batteries (RFBs) have the most attractive process; redox couples dissolved in electrolyte solutions are charged/discharged at the surface of electrodes and then stored in tanks. This property gives flexibility to design energy and power in RFBs because of spatial separation of energy storage and electrochemical reaction. Furthermore, the electrode is theoretically free from degradation because electrochemical reaction takes place at electrode surface. To take advantage of this feature, many researches have been performed for aqueous-flow batteries. In aqueous-flow batteries, acid solution is used as electrolyte and redox couples are dissolved in the acid electrolyte. Due to water electrolysis, the working voltage of cell is limited by <1.23 V in theory. In addition, acidic environment makes the electrode be corroded. Non-aqueous flow batteries are introduced as a countermeasure, which have many advantages; high working voltage, wide range of operating temperature, and liberation from corrosive acid electrolyte. However, a great part of reported redox couples do not show higher working voltage than that of aqueous system and their solubility is under 0.1 *M* [1]. Meanwhile, redox flow batteries commonly use two different redox couples for positive and negative electrolyte. It causes severe cross contamination problem; self-discharge and capacity fading. The problem associated with dual redox couple system can be relieved by using single redox couple.

In this work, Ni(II)-chelated thio-crown complex is introduced as a single redox couple for non-aqueous flow batteries. Thio-crown ligand makes metal-ligand complex stable during electrochemical reactions at both positive and negative side, such that it can play as the single redox couple. The solubility can be increased by 3 times by anion modification with no change in electrochemical stability. The high solubility and chemical stability allow a non-aqueous flow battery with energy density of 13.1 Wh L^{-1}.
Ni(II)-chelated thio-crown complex

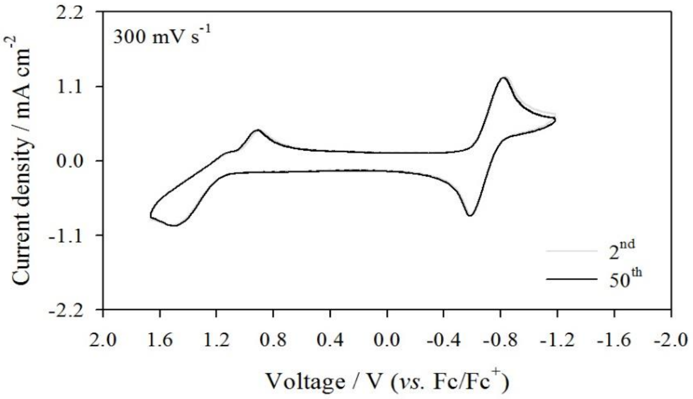

Figure 1. Cyclic voltammograms of the 2nd, 50th cycle of simultaneously scan of anodic and cathodic part of 0.01 *M* Ni([14]aneS$_4$)[TFSI]$_2$ in 1 *M* LiTFSI in EC:PC=1:1(*v*/*v*) solvent

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Measurement of gas generation in electrolytes for lithium-ion batteries

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Mis en forme : Français (France), Exposant

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Lithium-ion batteries (LIB) are one of the most popularly used energy storage systems. In this technology, the most common liquid electrolytes consist of mixtures of cyclic alkyl carbonates like ethylene carbonate (EC) or propylene carbonate (PC) in addition to linear ones like dimethyl carbonate (DMC). The lithium salt of choice remains lithium hexafluorophosphate, $LiPF_6$, which is broadly used in most commercial devices. Nevertheless those common electrolytes come with some safety concerns. During the standard utilization of the battery, some gases (CO_2, CH_4, O_2, H_2 …) are inherently generated due to undesirable side reactions at the interfaces. Moreover, $LiPF_6$ can undergo thermal decomposition beyond 60°C into LiF and PF_5. This decomposition is responsible for the formation of HF in presence of residual water, while PF_5 accelerates the decomposition of alkyl carbonates into gas. Ever since studies on the replacement of $LiPF_6$ by lithium imide salts like lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and lithium 4,5-dicyano-2-trifluoromethyl-imidazolide (LiTDI) have been conducted and show that these salts could be a good alternative since they are more stable thermally and safer. Besides, the decomposition of alkyl carbonates and electrode materials generate gases like CO_2, CO CH_4 and H_2 at anode [1] and essentially CO_2 and O_2 at cathode [2]. Accumulation of those gases inside the cell induces a rise of the internal pressure, leading to swelling and poses a potential safety risk. In this study we present the effect of lithium salt, potential, and temperature on the measurements *in operando* of gas generation in $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/Graphite cells. Volume measurements were realised via the use of pouch cells while pressure measurements were made with help of pressure cells, able to record the change of pressure occurring during cycling the battery.

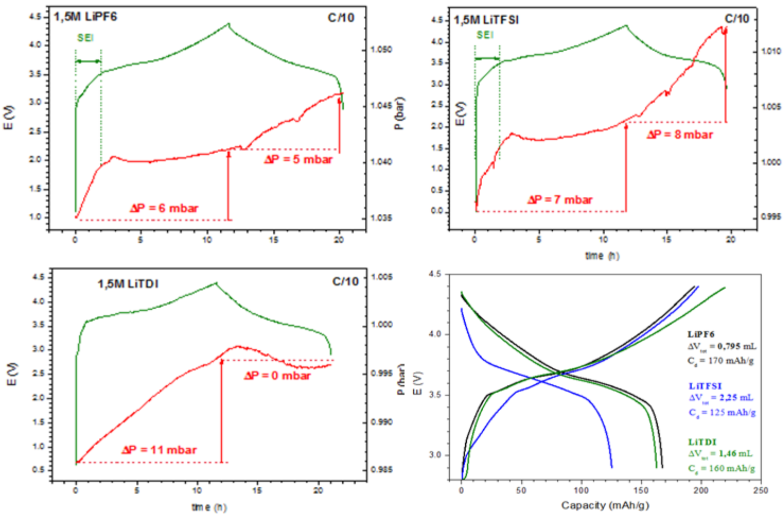

Figure 1 - Effect of 1M LiX (X=PF6, TFSI, TDI) in EC/PC/3DMC on the gas generation of NMC/Gr cells between 2.9V-4.4V vs Li+/Li

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Electrochemical oxidation of 2,4 Dichlorophenoxyacetic acid with sulfate radical generated by electrosynthesis of peroxodisulfate

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Effluents containing low concentrations of biorefractory organic contaminants require specific treatments to transform these species into biodegradable ones or into fully inorganic species like CO_2. Electrochemical oxidation is a potentially promising alternative technology for elimination of pollutants from water, in particular using a boron doped diamond anode (BDD). Using this anode, it is possible to generate hydroxyl radicals, •OH, which is a strong and unselective oxidant. In the case of halogenated organic compounds, the electrochemical oxidation using a BDD anode can lead to the formation of undesired and very toxic products such as chlorate, perchlorate and organochloride byproducts.

Thus, SO_4^{-}• based oxidation is presented as alternative oxidative treatment towards the advanced oxidation process based on •OH production. Sulfate radical has some unique features such as being a very strong electron acceptor enabling the degradation of persistent compounds which are refractory towards the hydroxyl radical. The production of this radical can be performed through the electrosynthesis of peroxodisulfate from sulfuric acid solution using a BDD anode [1].

The reactions of peroxodisulfate with organics at room temperature, is not efficient, thus peroxodisulfate has to be activated by metal reaction or by supplying energy (heat, UV…) and allows to form sulfate radicals (Eq. 1)

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-\bullet} \qquad E° (SO_4^{2-}/ SO_4^{-\bullet})=2.4\ \text{V} \qquad (1)$$

The aim of this study is to propose a process coupling the electrosynthesis of $S_2O_8^{2-}$ and the chemical reaction with halogenated-organic compounds. The chosen molecule model was 2,4-Dichlorophenoxyacetic acid (2,4 DA)which is a systemic herbicide, it is widely used as a weedkiller on cereal crops and orchards. This compound was classified as possible carcinogen.

This study is divided in 3 parts:

(i) The influence of the operating conditions on the efficiency of peroxodisulfate electrosynthesis. It has been shown that the temperature and the current density are the key parameters. More than 80% of current efficiency was reached at 9°C for i= 5 mA/cm^2 for a 2M of H_2SO_4.

(ii) The kinetics of the oxidation by sulfate radicals with 2,4-DA was found to be first order. The temperature must be higher than 50°C for the activation of peroxodisulfate in sulphate radicals.

(iii) Promising results were obtained by coupling the two steps under their optimal operating conditions.

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The Fluorescence Enhancement Mediated by High-index-faceted Pt Nanoparticles: the Roles of Crystal Structure.

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Plasmonic approaches have been considered promising to improve the detection ability of fluorescence[1]. Metal nanostructures, patterns, and collides, especially for gold and silver, have been fabricated and developed to enhance fluorescence[2]. Herein, we report that clean and ideal nano-structures, especially high-index structures, can be obtained through electrochemical synthesis and modulation, which are then utilized to investigate the importance of crystal structure in fluorescence enhancement.

Four different orientations of the Pt nanoparticles were utilized in the present fluorescence experiments to examine the contribution of the difference structure. Fluorescent solution (0.1 mM rhodamine B isothiocyanate) was homogeneously added on the nanoparticles and the four samples were detected with 532 nm laser incident on the local areas of substrate with and without nanoparticles to make a comparison. Figure1 shows the different morphology and structure of Pt nanocrystals using the SEM and the fluorescence intensity. the intensity of is similar with the background for the sphere and octahedron, but a 2.5-fold and 4.5-fold enhancement of the signals relative to background was observed for the THH and TPH respectively. We use FDTD simulation and structure characterization to explain the result. The obvious changes, including both experimental and calculational results, for those nanoparticles give the evidence to support an interesting phenomena that high-index structures, especially step atoms, may contribute to improve fluorescence signal.

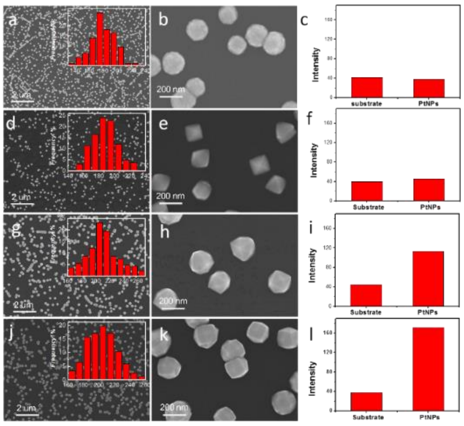

Figure 1. The SEM and the fluorescence intensity for the four difference shape of Pt nanoparticles.

Our result is worth attracting attentions as one guide in the further nanoparticle design. Even higher intensity can be observed if gold or silver can be used to fabricate those structure.

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Factors of Toluene Permeation in Proton Exchange Membrane

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Introduction

Utilization of renewable energy has been expected to establish sustainable society, because of essentially no emission. To introduce renewable energy, the large-scale transportation and storage technologies of energy has been needed to solve imbalance of energy demand and supply. The organic chemical hydride technology, which is an energy career system for hydrogen as the secondary energy and has the advantage of easy handling and low toxicity, has been attracted attention because it is a solution of the low volumetric energy density[1]. We have focused on the electrolytic direct-electrohydrogenation of toluene with a proton exchange membrane (PEM) electrolyzer in the toluene-methylcyclohexane organic hydride system. In the electrolyzer for the toluene direct-hydrogenation, the permeation of toluene from cathode to anode side through the PEM leads to the degradation of the anode.[2] However, the toluene permeability through PEMs has not been known well. In this study, we have investigated the dependency of temperature and properties of membranes for the toluene permeability of PEMs.

Experimental

Nafion®117 (*EW*=1100 g mol^{-1}, DuPont), Aquivion® E87-05S (*EW*=870 g mol^{-1}, Solvay) and E98-05S (*EW*=980 g mol^{-1}, Solvay) were used as PEMs. The cell for permeation experiment has two chambers for 1.0 M (= mol dm^{-3}) sulfuric acid and 100% toluene (Aldrich), which were separated by a PEM. The measurement was conducted at 25, 40, 50, 60 or 70°C. The permeated toluene concentration in sulfuric acid was measured by the high performance liquid chromatography (HPLC). The sampled solution for determination was stabilized with N, N-dimethylformamide (Wako) to become uniform solution with toluene and sulfuric acid in room temperature.

Results and Discussion

The permeated toluene concentration as a function of time, $C(t)$, was represented as the following equation with linear concentration profile of toluene in thickness direction of a membrane.

$$C(t) = C_{\max}\{1 - \exp(SDHt/Vd)\} \qquad (1)$$

where, S, D, H, t, V, and d are area of PEM, diffusion coefficient of toluene, distribution coefficient of toluene at sulfuric acid-PEM interface, time, volume of sulfuric acid, and thickness of PEM, respectively. The $C_{\max}$ is solubility of toluene in sulfuric acid. The apparent diffusion coefficient of toluene for PEM, defined as the product of diffusion coefficient and distribution coefficient (= DH) was determined from the $C(t)$ and $C_{\max}$ by the equation (1). Figure 1 shows the Arrhenius plots for apparent diffusion coefficient of toluene in the PEMs. The apparent activation energy for the PEMs were almost same values as about 23kJ mol^{-1}. On the other hand, DH of the Aquivion® PEMs were lower than that of Nafion®117. The DH might be affected by the EW, because the lower EW might lead to the lower toluene solubility in PEM by the higher acidity of hydrophilic region of PEM. So, lower EW might suppress toluene permeation in PEM.

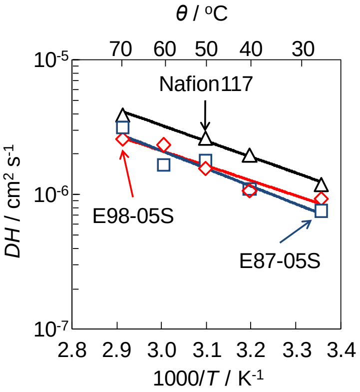

Figure 1 Arrhenius plots for apparent diffusion coefficient of toluene in Nafion117, E87-05S and E98-05S.

Acknowledgments

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Structure and orientation of enzymes used in fuel cell probe by Polarized Modulated –InfraRed Reflexion Absorption Spectroscopy and Electrochemistry

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Among alternative energies to fossil fuels, hydrogen appears as an attractive candidate because of its high energy output, and because its combustion delivers only water and heat. A few years ago, a new concept of H_2/O_2 fuel cells emerged based on biocatalysts for fuel and oxidant transformation [1]. This so-called enzymatic H_2/O_2fuel cell (EFC) is based on the specific enzymes involved in the microbial coupling for H_2 oxidation and O_2 reduction. Deciphering which parameters control the immobilization of enzymes on solid supports is essential for the development of the enzymatic fuel cells. The conformation of the immobilized enzymes and the variation of this conformation as a function of parameters such as the electric field, pH, ionic strength, covalent binding are largely unknown.

Two enzymes were used in the Lojou's laboratory to design fuel cell. [NiFe] hydrogenase from *Aquifex aeolicus* (Aa), and *Myrothecium verrucaria* bilirubin oxidase for an efficient H_2 oxidation and O_2 reduction, respectively. The enzymes were immobilized on gold electrode functionalized by a self assembled monolayer of alkane thiols, with hydrophobic or hydrophilic functions. Electrochemistry is a powerful method to follow the activity of the immobilized enzymes. Depending on the surface chemistry, the electron transfer proceeded either directly (DET) or through use of a mediator (MET), leading to conclude that the orientation of enzymes are controlled by the surface nature.

Polarized Modulated –InfraRed Reflexion Absorption Spectroscopy (PMIRRAS) can be applied for studying thin organic films (less than 100 Å) at metal air interface. PMIRRAS is carried out to give access to the conformation (secondary structure) and orientation of the enzymes adsorbed on the different functionalized gold electrode. Analysis of amide I and amide II bands allows to determine the orientation of the secondary structure element of the enzyme (α-helices, β-sheets), using the PMIRRAS selection rules. For *Aa* hydrogenase adsorption, the different amide I/amide II ratio clearly demonstrated the different orientation of the helices on the -COOH or $-CH_3$ surfaces, explaining the different electron transfer process (Figure1 A) [2]. For *Mv* BOD, although the amide I/ amide II ratio were identical (Figure 1B), electrochemistry revealed that the electron transfer pathway was DET or MET as a function of the charge of the surface [3]. On negatively charged SAM, DET decreased continuously with time, without desorption of the enzyme. A variation in the tertiary structure of the enzyme close to the active site could lead to this decrease.

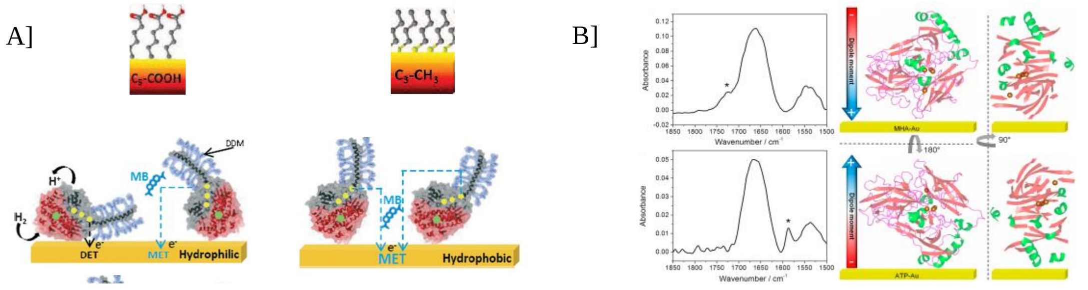

Figure 1: A] Different orientation of hydrogenase depending on SAM surfaces determined from amideI/amideII ratio, explaining the MET or MET+DET from [2], B] PMIRRAS spectra of Mv BOD adsorbed on different surfaces, indicating similar amide I/amide II ratio from [3].

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TePbPt@PbPt core shell nanowires as highly active and durable electrocatalysts for methanol oxidation reaction

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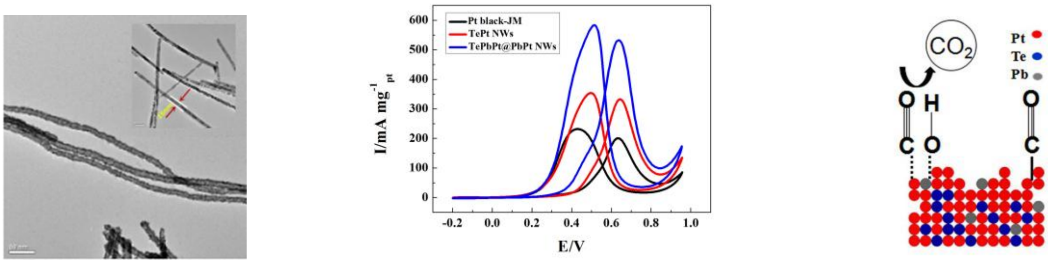
Pt based materials with nanowire structure have attracted increasing attention as a result of their high activity and durability for electrocatalysis, because of their shape anisotropy, high surface area and high electrical conductivity [1, 2]. Herein, we synthesized TePbPt@PbPt core shell nanowires through templating method. The diameter of TePbPt@PbPt nanowires was about 16 nm. The morphology and structure of TePbPt@PbPt nanowires were characterized by transmission electronic microscopy and x-ray photoelectron spectroscopy. The results reveal that a small amount of Pb atoms are exposed at the surface of the nanowires, as well as the Te exist inside of the nanawires which are protected by PbPt shell from leaching can interact with adjacent Pt atom and affect its electron structure via bi-metal/synergetic effect. These positive effects make them more active and stable towards methanol oxidation reaction (MOR) than TePt nanowires and commercial Pt black catalyst. As a consequence, the TePbPt@PbPt nanowires exhibited the mass activity of $532.35 \mathrm{mAmg}^{-1}{}_{\mathrm{Pt}}$ for methanol oxidation reaction (MOR) in acidic medium, which were 1.7 and 2.7 times higher than those of TePt nanowires and commercial Pt black catalyst, respectively. They also showed ultrahigh durability towards MOR in acidic solution. After 1000 cycles the TePbPt@PbPt catalyst exhibited 14.9% decrease of the forward peak towards MOR, while for the Pt black catalyst, the mass activity reduced 41.51% of the initial value after 1000 cycles. The core-shell nanowire catalysts are of high potential for application in methanol oxidation reaction.



(a) (b) (c)

Fig.1 (a) TEM images of the TePbPt@PbPt core-shell nanowires structure and the insert images of TePb nanowires structure. (b) MOR curves recorded at room temperature in a 0.5 M H_2SO_4+1 M CH_3OH aqueous solution at the scan rate of 50 mV s^{-1}. (c) The surface formation of Pb-OH at low potential to activate the oxidation of CO to produce CO_2.

Acknowledgments

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Effective and simultaneous removal of humic acids and Cr(VI) by electro-Fenton with H_2O_2 in-situ electro-generated on Pd loaded Fe_3O_4 nanoparticles

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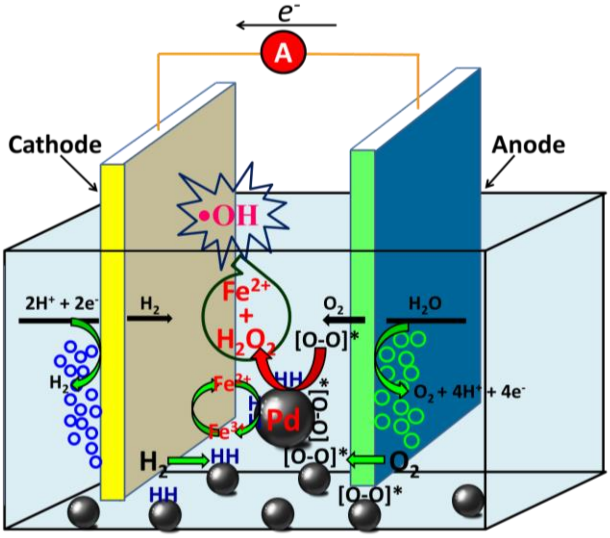
The widespread presence of humic acids (HAs) and chromium (Cr) in aquatic systems and drinking water sources is a serious threat to the environment and human being, which attracts great concerns from the protection of public health.[1,2] However, no attempts on the potential interaction and simultaneous removal of these two types of contaminants have been made. Here, an electro-Fenton process was reported for the effective and simultaneous removal of HAs and Cr(VI), where H_2O_2 was in-situ produced from the electro-generated H_2 and O_2 by the presence of Pd/Fe_3O_4 nanocatalysts and Fe(II) was provided from the support. The effects of solution pH, applied current, Pd loading, and initial concentrations of HAs and Pd/Fe_3O_4 on the removal efficiency of HAs and Cr(VI) were carefully investigated. Under the optimized electrolysis conditions (pH 3.0, 40 mA, 5.0 wt % Pd, 100 mg•L-1 HAs and 5.0 g•L^{-1} Pd/Fe_3O_4), HAs were effectively mineralized, as revealed by a total organic carbon removal efficiency of 90%, and Cr(VI) was completely reduced accompanying with 90% total Cr removal. The HAs degradation driven by the contribution of anodic oxidation was found to be important but not dominant, whereas electro-Fenton process played a fundamental role for the mineralization of HAs. The reduction of Cr(VI) was primarily attributed to the contributions from Pd/Fe_3O_4 and atomic hydrogen on the Pd catalyst surface as well as the cathodic reduction. In a similar manner, a good recycle of Fe^{3+} to Fe^{2+} was accelerated. Moreover, most chromium was removed by the deposit of chromite from the solution, which is the most common and stable mineral of chromium in the environment. Importantly, the energy consumption of this electro-Fenton process for HAs degradation was almost 2 orders of magnitude lower than those of reported electrochemical oxidation. The Pd/Fe_3O_4 nanocatalysts showed excellent removal performances for HAs and Cr(VI) after eight times repeated treatment. This work reports a cost-effective methodology for simultaneous removal of HAs and Cr(VI) and provides a new insight for efficient elimination of complex contaminants.



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Converting FeNi hydroxides into Fe-Ni phosphides as bifunctional electrodes for efficient overall water splitting

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To achieve global-scale sustainable hydrogen production, electrochemical splitting of water has been considered as a feasible strategy. Efficient water splitting requires highly active, earth-abundant, and steady catalysts, which are particularly vital to the hydrogen-evolution reaction (HER) and the oxygen-evolution reaction (OER) by lowering the dynamic overpotentials [1]. Recently, transition metal phosphides [2] are explored for HER with high activity and stability. Research shows that the introduction of phosphorus could improve the HER activity of transition-metal catalysts. For OER catalysts, Fe-Ni based composites [3] attracted great attention because of their outstanding chemisorption of OH^- and oxygen-containing intermediates. Combining the advantages of the HER and OER catalysts to get a novel catalyst is extremely beneficial for enhancing the overall electrochemical water-splitting efficiency.

Herein, we report a 3D bifunctional electrode of Fe-Ni phosphides (i.e., Ni_5P_4, Ni_2P and Fe_2P) nanosheets supported on Ni foam (Fe-Ni-P NF) via a facile hydrothermal synthesis method followed by a convenient one-step phosphorization treatment in phosphorus vapor at 500 °C. The catalytic performance of as-fabricated Fe-Ni-P NF was investigated by linear sweep voltammetry and chronopotentiometry in a standard three-electrode system. It exhibited excellent electrocatalytic performance toward both HER and OER in 1.0 M NaOH solutions, with only small overpotentials of 135 mV and 250 mV, respectively, attaining a current density of 10 mA cm^{-2}. Besides, it showed fast kinetics with a small Tafel slope of 97 mV dec^{-1} and 93 mV dec^{-1} for HER and OER successively. Using Fe-Ni-P NF as bifunctional electrodes, an alkali electrolyzer released a current density of 10 mA cm^{-2} at a low cell voltage of ca. 1.65V, and also possessed a high durability during 20 h electrolysis.

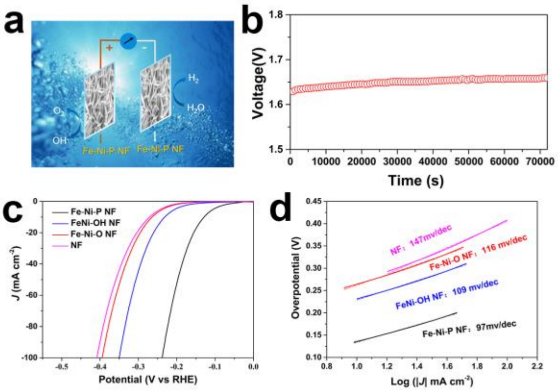

Fig. 1. (a) Schematic illustration of two-electrode cell using Fe-Ni-P NF as both anode and cathode for water splitting. (b) The stability of the two-electrode electrolyzer over 20 hours of electrolysis at 10 mA cm^{-2} in 1.0 M NaOH. (c) IR-corrected polarization curves of the Fe-Ni-P NF recorded at a scan rate of 1 mV s^{-1}, along with Fe-Ni-O NF, FeNi-OH NF, and NF for comparison. (d) Polarization curves-derived Tafel slopes for the corresponding electrocatalysts.

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The Electrochemical RTIL-Metal Interface in the Presence of Additives

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Room temperature ionic liquids (RTILs) have raised, in recent years, a lot of interest due to their unique physical properties and their possible use in various electrochemical processes and devices.
Since modifications of the double layer structure and composition may lead to important variation of the electrochemical reaction rates and mechanisms it is essential to investigate the characteristics of RTIL|metal interfaces.

RTILs are intriguing for electrochemists. Due to the solvent-free of the RTIL it is clear that the electrical double layer (EDL) can no longer be described by applying the models used for electrolytic solutions. Theoretical and numerical approaches for the description of the EDL predict various types of capacitance-potential (C-E) curves.

Besides the traditional strategy consisting in the acquisition of data characteristic of the electrode in contact with a pure RTIL, we propose an alternative way to gain insight in the double layer in the presence of RTIL through the competitive adsorption that will occur at the electrode between the ionic liquid and some selected additives. Adsorption at metal electrodes is a complex process governed by various interactions involving the additive, the electrode and the electrolytic medium. Organic additives are however commonly encountered in many electrochemical processes such as corrosion inhibition and metal electrodeposition. Moreover many intermediate species formed during electrochemical reactions may adsorb at the interface and considerably modify the kinetics and selectivity of the reactions.

Surprisingly, competitive adsorption of RTIL with other species is presently unexploited although the use of adsorption competitors has been proved in the past to be a successful route for getting a deep understanding of the metal-aqueous electrolyte solution and in particular of the behavior of water at the electrochemical interface.

Here we report on the interfacial characterization by cyclic voltammetry (CV) and ac methods particularly electrochemical impedance spectroscopy (EIS). The RTILs investigated are imidazolium based RTILs with either dicyanamide or bis(trifluoromethanesulfonyl)imide in the presence of respectively water and organic additives at Au. Bipyridine and thiouracil were chosen as additives since these compounds undergo respectively physisorption and chemisorption at a gold electrode and may thus compete differently with the RTIL. Experiments with organic additives were all carried out in a glovebox under a nitrogen controlled atmosphere while, when water is added, experiments were performed outside the glovebox. The results obtained show that the addition of water affects the electrochemical response of the electrolyte at both the negative and positive potential limits. Differential capacity measurements in the presence of the organic additives evidence the presence of the additives at the interface and their adsorption behavior is compared to that in aqueous electrolytes.

Preparation of novel polyporous graphene roll electrode for high performance supercapacitors

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As a new type of clean and environmentally friendly energy storage equipment, supercapacitors have attracted considerable interest over the past few decades because of their high power density, long cycle life, and fast recharge capability[1,2]. The specific surface area of the material is one of important factors to determine the performance of the double layer supercapacitor. Among the multitudinous electrode materials available for supercapacitors, graphene stands out and has been widely studied by domestic and international researchers, because of its unique one-atom-thick two-dimensional sp^2 carbon structure and excellent physical properties. Compared to other carbon allotropes, its excellent performance embodied in high chemical stability, electrical conductivity, surface area and a large number of interlayer structure in theory[3,4]. But due to strong π-π interaction between the graphene layers, which results in graphitic stacking[5], the specific surface area of graphene is smaller in fact. In order to overcome its force, it is necessary to make a slight change in structure of graphene.

In the work, we have successfully fabricated an aqueous, high potential symmetric supercapacitor (SSC) based on polyporous graphene roll (PGR) electrodes. Its unique structure effectively prevents the inter-sheet restacking of graphene sheets, and the large surface area of PGR is adequately utilized for energy storage. The fabricated PGR electrodes exhibit superior electrochemical properties for supercapacitor applications, including exceptionally high capacitance (319 F g^{-1} at 1 A g^{-1}) and high rate capability (222 F g^{-1} at 20 A g^{-1}) with excellent cycle stability (92% of the initial capacitance after 10000 charge/discharge cycles). As for SSC, it can be cycled reversibly in a wide potential window of 0-1.8 V and exhibits an energy density of 30.15 Wh kg^{-1} with a power density of 1.5 kW kg^{-1}, which shows superior device performance than general graphene-basic symmetric supercapacitor. It also presents stable cycling performance with 93% capacitance retention at 5 A g^{-1} after 10000 cycles. Such extraordinary electrochemical properties are exactly what we need.

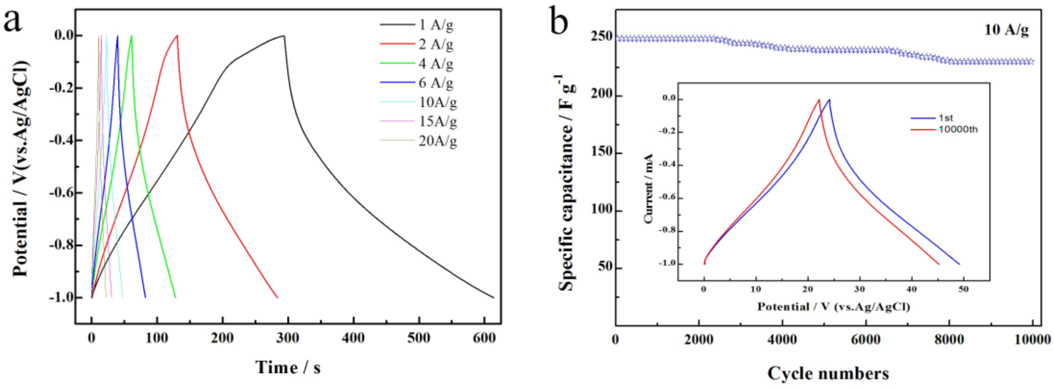

Fig. 1 (a) Galvanostatic charging/discharging of PRGs electrode at various current densities(1A/g, 2A/g, 4A/g, 6A/g, 10A/g, 15A/g, 20A/g); (b) Cycling stability of PRGs electrode at 10 A/g. The inset shows the 1st and 10000th galvanostatic charge/discharge curves.

Acknowledgments

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A Sensitive Amperometric Sensor for Determination of Ascorbic Acid Based on Network-like Carbon Nanosheets Modified Glassy Carbon Electrode

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The development of a simple and sensitive method for the determination of ascorbic acid (AA) has attracted, and is still attracting considerable attention, because AA plays an important role in biological metabolism and is usually used in large scale for the prevention and treatment of some diseases [1]. Compared to other methods, the electrochemical method has unique advantage and potential due to its high sensitivity, excellent selectivity, simplicity and low-cost [2]. However, direct oxidation of AA at bare electrode usually requires a high overpotential, which results in poor sensitivity , low selectivity and poor reproducibility [3]. Thus, it is especially important to find new materials for electrode modification, because the electrochemical performance of sensor is highly dependent on the characteristics of the electrode materials used in their fabrication.

In this work, the network-like carbon nanosheets (NCN) were prepared through a facile pyrolysis and activation using willow catkin as the precursor. The as-synthesized carbon nanosheets were first used as an enhanced electrode material for the analysis of AA. The electrochemical performance of the carbon nanosheets was investigated by cyclic voltammetry and amperometry in a traditional three-electrode system. Benefitting from the novel structure, the fabricated electrochemical sensor exhibited excellent electrocatalytic activity towards the ascorbic acid electrochemical oxidation. Besides, amperometric curve of AA on the glass carbon electrode modified with network-like carbon nanosheets showed a quick current response, a good linear relationship between peak current and concentration, a low detection limit and an excellent selectivity. Impressively, the proposed senor was successfully employed to detect AA in the commercial vitamin C injection with good recoveries.

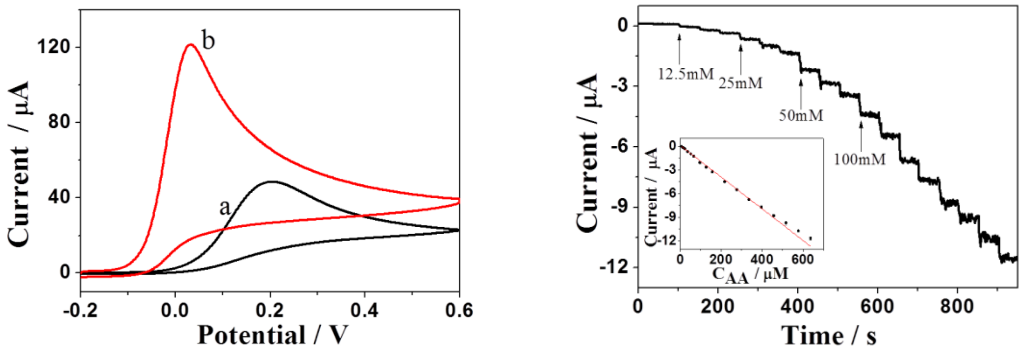

Fig. 1 CVs of 5 mM AA in 0.1 M PBS with a bare GCE (a) and a NCN/GCE (b) (left) and Amperometric plot of the NCN/GCE upon successive injection of various concentrations of AA into stirred PBS (right). Applied potential: 0.05 V. Inset: the plot of electrocatalytic current of AA versus its concentration.

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Light-Motivated pH/Thermal Multi-Sensitive ITO Glass/Polyelectrolyte Composite Electrode

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The multiple-responsive electrode derived from responsive polyelectrolytes has been greatly potential in applications of biological detection, metal ions detection, environmental sensory, and so on. In this case, we functionalized the ITO glass with a series of light/pH/thermal triple-responsive polyelectrolytes. As a result, the surface structure of the composites was characterized. And the environmental-responsive properties were measured by controlling UV/visible light exposure, pH and temperature.

The polyelectrolyte layer was synthesized by a surface-initiated reversible addition-fragmentation chain transfer radical polymerization (RAFT) [1,2]. Firstly, ITO glass was put in Piranha solution for 2h; then the fresh surface of ITO glass was modified by the RAFT initiator, 2-(dodecyl thiocarbonothioylthio) -2-methyl propionic acid (DDMAT). To synthesize the multi-responsive polyelectrolytes, pH/thermal dual-sensitive segment, 2-(dimethyl amino)-ethyl methacrylate (DMAEMA) and UV/Vis sensitive segment, N-azobenzol acrylamide (AAzo) were sequentially polymerized on the surface of modified ITO glass. Finally, the block copolymers of Poly(DMAEMA-*b*-AAzo) was functionalized.

Herein polyelectrolytes with different comonomer ratio ($M_{\mathrm{DMAEMA}}/M_{\mathrm{AAzo}}$= 99/1, 95/5, 90/10 and 80/20) were investigated by AFM, UV-Vis spectrum, ^{1}H NMR, GPC, etc. Fig. 1a showed the typical AFM images of ITO glass/Poly(DMAEMA$_{95}$-*b*-AAzo$_5$) composite. Noticeably, the copolymer brushes on the ITO glass was distributed evenly and the thickness was in a range of 20-30nm. Fig. 1b and c showed the UV-Vis spectra of ITO glass/Poly(DMAEMA$_{95}$-*b*-AAzo$_5$) composite under visible light and UV light (365 nm), respectively. It is obvious that the absorption of PAAzo block was reversible with different exposure times. Combining the AFM images, UV-Vis spectra and the ^{1}H NMR spectra (Fig. 1d), we can prove that the multi-responsive polyelectrolytes were grafted from the surface of ITO glass successfully. Fig. 1e showed the EIS of composite electrode at pH 4-10 under the UV exposure. Briefly, the *trans-cis* isomerization of azobenze group was motivated by UV/Vis exposure; consequentially affected the pH or thermal responsibility of PDMAEMA block, finally resulting environmental-responsive electrical signals.

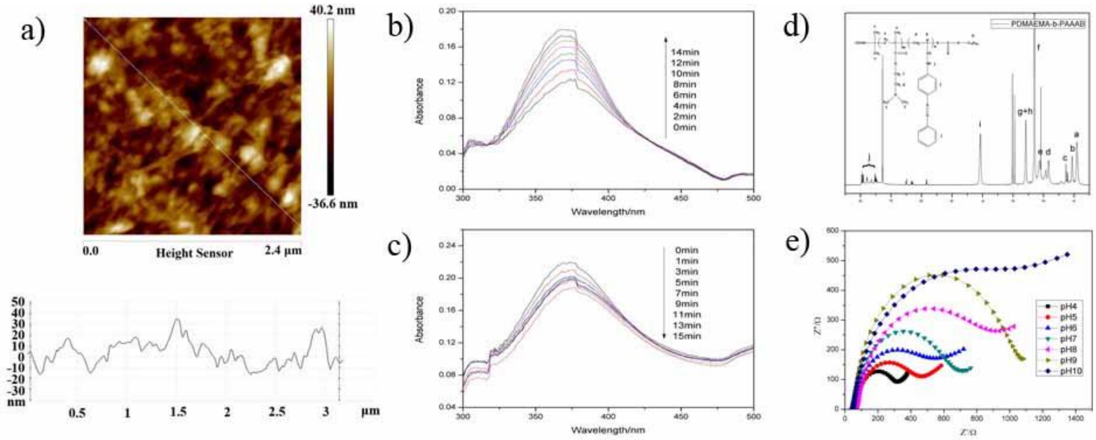

Fig. 1 The characterization and EIS property of ITO glass/Poly(DMAEMA$_{95}$-*b*-AAzo$_5$) composite electrode: (a) AFM images; (b) and (c) UV-Vis spectra with different exposure times; (d) ^{1}H NMR spectrum of Poly(DMAEMA$_{95}$-*b*-AAzo$_5$) brushes; (e) EIS of ITO glass with polymer brush at pH 4-10 under UV exposure.

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Potential Cathode Materials for Rechargeable Al Batteries

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As a trivalent metal, aluminum has long been considered as a promising battery anode owing to the high volumetric capacity (8046 mAh cm^{-3}) as well as rich abundance and low production cost. The essential reaction of an Al anode is simple, namely, Al electrodeposition/dissolution; however, the exploration of practical cathodes of modest operation voltage that allow facile transport of Al^{3+} cations is great challenging owing to strong electrostatic interactions between diffusing Al^{3+} and the host materials. An effective approach to circumvent this issue is to utilize haloaluminate ionic liquids (composed of Al halide (AlX_3) with an organic halide salt (R^+X^-)) [1]. Taking advantages of the intercalation/deintercalation or adsorption/desorption of Al-containing anionic complexes existing in the haloaluminate systems, we have demonstrated the reversible charge/discharge behavior of activated carbon fiber cloth in $AlBr_3$–1-ethyl-3-methylimidazolium bromide ([C_2mim]Br) [2].

With the aim to facilitate the identification of potential cathode materials and to provide scalable electrode production method, the compatibility of polymer binder towards chloroaluminate ionic liquids was investigated. The binder is usually employed when active materials in the powder form are evaluated, and it largely influences the resultant electrochemical behavior of a given material. To date, a variety of carbon-based materials have been evaluated as cathode materials by many research groups including us. Fairly stable cyclability and good rate capability were achieved. In addition to carbon materials, potential cathode active materials for rechargeable Al batteries with higher capacity have been reported but their properties are still far from adequate (Table 1). Our attempts to this end will be given in the presentation.

Table 1. Selected cathode materials reported for rechargeable Al batteries

Active material	Average potential (V)	Discharge capacity (mAh g^{-1})	Current rate (mA g^{-1})	Cyclability
Chloroaluminate anion intercalation				
Graphene nanoplatelets	1.80	70	2,000	Stable for 1000 cycles
Grafoil	1.80	84	100	Stable for 100 cycles
Graphitic foam [3]	1.80	60	4,000	Stable for 7500 cycles
Carbon paper [4]	1.80	90	50	Stable for 200 cycles
Chloride anion transfer				
VCl_3 [5]	1.00	76	3.33	26% remained After 10 cycles
Conversion reaction				
S [6]	1.10	1600	30	Rapid fading after 3 cycles

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Ultrasensitive Washing Free Protease Sensors Using Selective Affinity Binding, Selective Proteolytic Reaction, and Proximity-Dependent Electrochemical Reaction

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The development of a fast and ultrasensitive protease detection method is a challenging task. In here, we suggest that ultrasensitive washing free protease sensors exploiting (i) selective affinity binding, (ii) selective proteolytic reaction, and (iii) proximity-dependent electrochemical reaction. The selective affinity binding to capture IgG increases the concentration of the target protease (trypsin as a model protease) near the electrode, and the selective proteolytic reaction by trypsin increases the concentration of the redox-active species near the electrode. The electrochemical reaction, which is more sensitive to the concentration of the redox-active species near the electrode than to its bulk concentration, provides an increased electrochemical signal, which is further amplified by the electrochemical−chemical redox cycling. An indium−tin oxide electrode modified with reduced graphene oxide, avidin, and biotinylated capture IgG is used as the electrode, and p-aminophenol liberated from an oligopeptide is used as the redox-active species. The new sensor scheme using no washing process is compared with the new sensor scheme using washing process, and with the conventional scheme using only proteolytic reaction. The new scheme provides a higher signal-to-background ratio and a lower detection limit. Moreover, the increased electrochemical signal offers a more selective protease detection. Trypsin can be detected in phosphate-buffered saline and in artificial serum containing L-ascorbic acid with a low detection limit of 0.5 pg/mL, over a wide range of concentrations, and with an incubation period of only 30 min without washing process. The washing-free electrochemical protease sensor is highly promising for simple, fast, ultrasensitive, and selective point-of-care testing of low abundance proteases.

Effect of metal doping on the electronic structure of $M_2Au_{36}(SC_6H_{13})_{24}$ (M=Pt, Pd)

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Over the past decade, owing to their unique electronic structures with high chemical and thermodynamic stability, thiolate ligand-protected gold nanoclusters have been extensively studied. Recently, bimetallic gold nanoclusters have been reported, which represent an interesting system to study the change in physicochemical properties of nanoclusters by replacing gold atoms by foreign metals. In particular, bimetallic $M_xAu_{38-x}(SR)_{24}$ nanoclusters (M=Pd or Ag, SR=thiolate ligand) have been studied recently due to their different optical and electrochemical properties. In this poster, we report the stable bimetallic clusters ($[Pd_2Au_{36}(SR)_{24}]^0$ and $[Pt_2Au_{36}(SR)_{24}]^{2-}$) which show different electronic configurations, by replacing the core Au atom with Pd and Pt. The highest occupied molecular orbital-lowest unoccupied molecular gap of $[Pd_2Au_{36}(SR)_{24}]^0$ determined by voltammetry was drastically decreased to 0.26 eV, but that of $[Pt_2Au_{36}(SR)_{24}]^{2-}$ was comparable with $[Au_{38}(SR)_{24}]^0$ (0.94 eV), indicating the electronic structures could be altered upon doping of the foreign metal. This result could be explained by their different electron configurations; that is, $[Pd_2Au_{36}(SR)_{24}]^0$ cluster having 12 superatomic electrons exhibits remarkably different optical and electrochemical properties from those of the 14-electron cluster systems such as $[Au_{38}(SR)_{24}]^0$ and $[Pt_2Au_{36}(SR)_{24}]^{2-}$.

The promotion on the durability of carbon supported PtNi alloy catalyst by carbon coating and Au addition for oxygen reduction reaction

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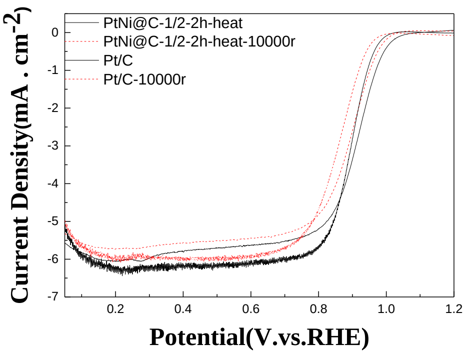
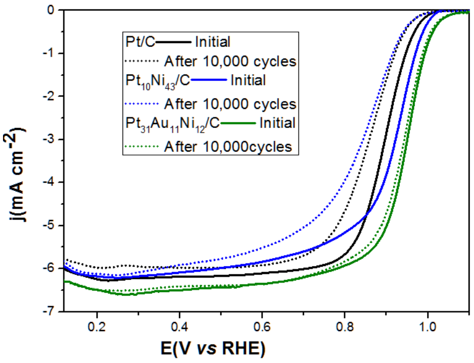
It is important to design and fabricate highly active and durable oxygen reduction reaction (ORR) catalysts for the application of proton exchange membrane fuel cells (PEMFCs). Pt-transition metal(Ni, Co, Fe, etc.) alloys demonstrate superior activity to pure Pt as a result of changes in the electronic structure of surface Pt atoms during the ORR. We have used microwave to synthesis Pt-Ni alloy catalysts, which was replicated at the nanoscale through strict control of size and composition. The binary Pt-Ni metal alloys mainly address the activity requirements. However, the nickel elements easily dissolved in acid solution, resulting in the low stability of Pt-Ni alloys. Here, we put forward two methods through carbon coating and Au addition to improve the stability.

To understand the durability of the Pt-Ni alloys with the carbon supported during the ORR process, some nanoparticles lost contact with the carbon support easily. It is commonly accepted that the destabilization of Pt-Ni alloys catalyst is associated with(1) Ostwald ripening and aggregation of the Pt nanoparticles, which were caused by the high surface energy of Pt nanoparticles and the weak interaction between catalysts and carbon supports; (2) loss of contact to support due to carbon corrosion. Herein, we report a convenient microwave synthesis of Pt-Ni alloys and carbon coating the alloys with dopamine. Through this kind of post-processing methods, Pt-Ni alloys catalyst with carbon coating exhibited higher activity. And after 10,000 potential cycles of 0.6−1.0 V, the activity decayed only about 15mV, while the direct synthesis of catalyst decayed about 65 mV. The morphological evolution of the carbon coating and direct synthesis catalysts before and after 10000 cycles was investigated by TEM. The carbon coating catalysts aggregation was not obvious，the size of the nanometer catalyst changed from 2~5nm to 2~7nm, while the catalyst by direct synthesis was from 2~5nm to 5~10nm. The carbon coating Pt-Ni/C showed the Pt mass and specific activities as high as 0.49A mg^{-1} and 0.47 mA cm^{-2}, respectively.

Because Au can fine tunes the lattice parameter and the surface electronic structure to enable activity and cycling stability. Here we investigate the oxygen reduction reaction electrocatalytic activity and the corrosion stability of ternary carbon-supported $Pt_{31}Au_{11}Ni_{12}$ alloy catalyst, which exhibit dramatically improved corrosion stability. After 10,000 potential cycles of 0.6−1.0 V, the $Pt_{31}Au_{11}Ni_{12}$/C exhibited about 7mV relatively smaller negative potential shift , which was much lower than the $Pt_{10}Ni_{43}$/C and commercial Pt/C. The $Pt_{31}Au_{11}Ni_{12}$/C showed the Pt mass and specific activities as high as 1.02 A mg^{-1} and 1.25 mA cm^{-2}, respectively.





High Performance and High CO Tolerance Nanowire Arrays as Electrocatalysts for Direct Alcohol Fuel Cells

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In this study, high performance and high CO tolerance electrocatalysts based on the vertically aligned nanowire array structure have been developed and investigated for direct alcohol fuel cell (DAFC) applications. Two alcohols, methanol and ethanol, have been chosen as the fuels, respectively, based on the different properties of the two electrocatalysts. In the first part, Pt nanowire arrays with a rough surface have been developed as the anode electrocatalyst for the methanol oxidation reaction in acidic medium. In the second part, Pd nanowire arrays have shown better electrocatalytic property towards ethanol oxidation reaction in basic medium. The modified electrodes were prepared by electrodeposition method using anodic aluminum oxide (AAO) membrane on an Ag substrate (Fig. 1A). Variation of the electrodeposition current density and deposition time led to controlled surface roughness and length of Pt nanowires;[1] Pd nanowires with controlled length were also obtained with the same method. Scanning electron microcopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray powder diffraction (XRD) were employed to characterize the morphology, chemical composition and crystal structure of the Pt and Pd nanowires. Cyclic voltammetry and chronoamperometry measurements were used to analyze the performance, CO tolerance and endurance of the nanowire array electrodes, while electrochemical impedance spectroscopy (EIS) measurements provided insights in the electron transfer resistance between the electrode and analyte. For methanol oxidation, the electrochemical results show that the rough Pt nanowire array has the best overall performance (Fig. 1B), along with a high CO tolerance, followed by the semi-rough and smooth Pt nanowire arrays. The rough nanowire array also has the highest electrocatalytic activity with the longest endurance and lowest electron transfer resistance. UV-Vis spectroscopy was utilized to measure the concentration of formic acid, which was formed during the methanol oxidation, as a function of scanning cycles, helping to elucidate the overall reaction mechanism. Similarly, from the electrochemical results, the Pd nanowire array exhibited high efficiency, high endurance, high CO tolerance, and fast diffusion rate towards ethanol oxidation. The overall reaction mechanism was probed similarly to methanol oxidation, with UV-Vis spectroscopy measuring the concentration of acetic acid, which was formed during ethanol oxidation. Both Pt and Pd nanowire array electrocatalysts showed excellent results for methanol and ethanol oxidations, demonstrating to be promising anode electrocatalysts for direct alcohol fuel cells.

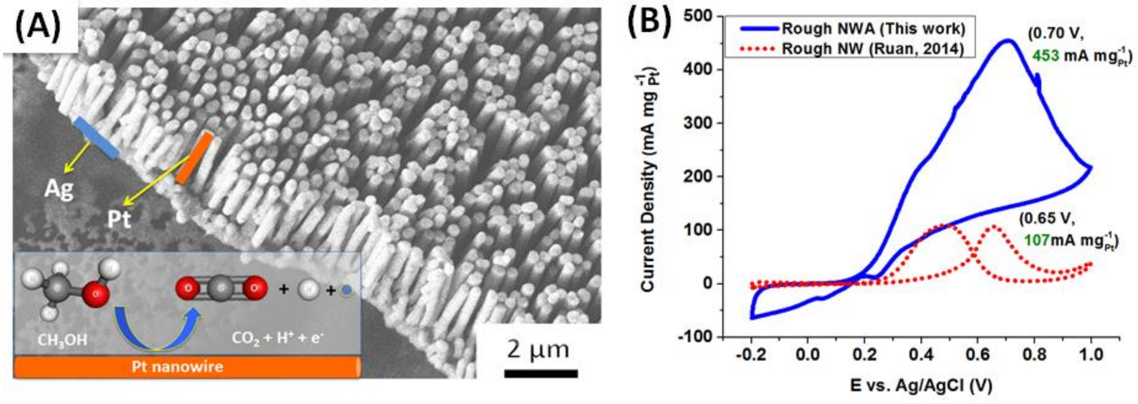

Figure 1. (a) Pt nanowire array on Ag substrate as anode electrocatalysts; (b) Cyclic voltammetry (CV) scans of rough Pt nanowire array compared to rough Pt nanowires on GCE[2].

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Galvanic Exchange Synthesis of Pt Nanoparticles Encapsulated inside Dendrimers and Their Size-dependent Catalytic Activity to Dehydrogenation of Ammonia Borane

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The size effect of nanoparticles on their catalytic activity is one of the most important issues in heterogeneous catalysis. The understanding of size-dependent activity is highly demanded for rational design of catalysts [1-2]. Synthesis of nanoparticle having well-defined sizes is thus required to study the size-dependent activity of nanoparticles, but it is still a big challenge especially in small size ranges [3]. In this study, we synthesized Pt dendrimer-encapsulated nanoparticles (DENs) using a galvanic exchange method. The synthetic method allowed synthesis of Pt DENs which are fully reduced and fairly monodisperse in size. Specifically, we synthesized size-different Pt DENs having an average from 220 to 1320 atoms. The synthesized Pt DENs exhibited size-dependent catalysis for dehydrogenation of ammonia borane.

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Spectro and electroanalytical determination of antioxidant power of “BHT like” derivatives

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Phenolic antioxidants stand as an appealing class of compounds in different areas wherever their effect is desired, from conservatives to food supplements. 2,6-di-*tert*-butyl-4-phenol, commonly known as BHT, is a synthetic antioxidant of widespread use in foodstuff products. Such products, due to their properties, display anticarcinogenic profile given the connection between cancer occurrence, radical compounds presence and inflammation, and so, the evaluation of this property is evident. In this scope, electroanalytical techniques are an excellent alternative to traditional approaches, in order to evaluate the antioxidant capacity of these organic compounds Also, regarding antioxidative properties, the main electrochemical parameters, E_p and I_p, can be explored for qualitative and quantitative approaches. Even more, E_p and I_p are thermodynamic and kinetics, parameters respectively, that can be used to estimate the reduction power of compounds. Moreover, the molecular electrostatic potential (MEP) is an information that can shed light into the antioxidant capacity of these compounds, and so, molecular modeling methods are very useful to ascertain this data. Given that molecular electrostatic properties are related to oxidation/reduction reactions within a molecule, and such properties, may vary depending on their substituents, along with the electrostatic distribution in the compound, BHT analogs could differ, in these parameters, from their precursor and, thus, display better antioxidative power. Henceforth, in this work 8 analogs (LQFM181,183,209,211-214,218), based on the 2,6-di-*tert*-butyl-4-phenol scaffold, were proposed, synthesized and evaluated, as for their antioxidant capacity, through voltammetric and spectrophotometric approaches and MEP surface analysis was performed to evaluate their most likely electroactive sites. Voltammetric experiments were carried out with a potentiostat/galvanostat µAutolab III® integrated to the GPES 4.9® software, Eco-Chemie, Utrecht, The Netherlands. The measurements were performed in a 5.0 mL one-compartment electrochemical cell, with a three-electrode system consisting of a graphite pencil electrode (GPE), a Pt wire and the Ag/AgCl/KCl 3M (both purchased from Lab solutions, São Paulo, Brazil), representing the working electrode, the counter electrode and the reference electrode, respectively. The radical scavenging activity assays were performed using 2,2-diphenyl-1-picrylhydrazyl (DPPH) reagent and antioxidant activity was expressed as EC_{50}, representing the amount (mM) of sample solution to produce 50% of DPPH discoloration relative to the blank control after five minutes of reaction. The measurements were performed in a UV–vis spectrophotometer (Quimis, model Q-798U2VS, Brasil). Moreover, in order to evaluate the differences in the molecular electrostatic potential topology between the 8 BHT analogs, semi-empiric PM6, Density Functional Theory (DFT), and ab-initio Møller–Plesset (MP2) calculations for their lowest energy enantiomorphs were performed. The 6-311+G** basis set was employed in both DFT and MP2. The well-known B3LYP exchange correlation functional was used in the DFT calculations. In order to illustrate and facilitate the analyses of the charge distributions, MEP were built for 8 analogs lowest energy enantiomorphs. DPV was performed in order to calculate the electrochemical index ($EI = \sum Ip/Ep$) and also to study the pH effect on redox processes. As expected for phenol/quinone redox systems, the E_p decrease according to deprotonation, being the slope close to the theoretical value of 59 mV / pH unite till the pKa value. Evaluating calculated values of both EC50 and EI for the analogs, it was possible to infer that improvements in overall antioxidant capacity were present in LQFM209, whereas, LQFM 212, 214 and 211 were similar, but showed inferior activity. All analogs E_p in the voltammetry were virtually the same (E_p ~0.5), from this data, it can be inferred that their oxidations sites were at least proximal. MEP topology calculated for the 2,6-di-*tert*-butyl-4-phenol scaffold lowest energy enantiomorphs, allowed the inference of each analog most likely oxidation site, moreover, each molecule displayed oxidation site(s) quantity in accordance with the voltammetry findings, i.e., number of anodic peaks. Many differences between the analogs and BHT were spotted in their electrostatic distribution, however the analogs major probable oxidation site remained similar, being the hydrogens in the ortho and metha positions of their piperazine ring. Moreover, increase in antioxidant capacity was obtained in LQFM209.

Electropolymerization of Metallophthalocyanines Carrying Redox Active Metal Centers: Electrochemical Pesticide Sensing Application

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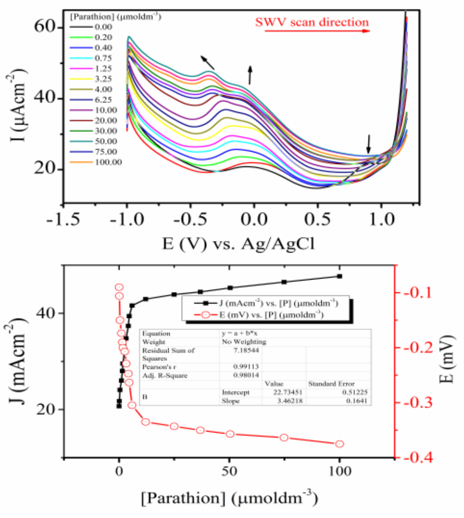
In agriculture, extensive use of the pesticides has raised serious problems regarding the healthiness, environment, and food safety. Undoubtedly, pesticide residues in crop, foods, and water cause a severe threat to human life. Therefore, the detection of trace level of the pesticides has become increasingly important [1]. Traditional analysis methods e.g. physical absorption, gas and liquid chromatography, optic methods, and mass spectroscopy are routinely carried out. Nevertheless, due to the complicated pretreatment steps, extensive labor resources and non-applicable for on-site determination, new sensing methods have been extensively studied. To solve these problems, especially the electrochemical methods were extensively preferred. With the electrochemical methods, long analysis time and extensive sample handling could be resolved with portability, rapid turnaround time, applicable for on-site determination, and cost-effectiveness [2]. One of the functional materials presently studied as the selective and stable sensors are metallophthalocyanines (MPcs). Due to the high thermal and chemical stabilities and excellent redox activities, MPcs have been extensively studied in various technological fields as well as sensor applications. Tailoring of MPc with different metal cations in the cavity of Pc and various substituents ensure synthesizing MPcs having desired properties for the target applications [2].

The synthesis, characterization, electrochemical, spectroelectrochemical and pesticide sensing properties of peripherally tetrasubstituted metallophthalocyanines (**[**CoPc(MOR-NAF)], [TiOPc(MOR-NAF)], and [Cl-MnPc(MOR-NAF)] have been reported. To increase redox activity of phthalocyanine ring (Pc), redox active Co(II), Cl-Mn(III), and Ti(IV)O metal centers were incorporated into the Pc cavity and CoPc(MOR-NAF), Cl-MnPc(MOR-NAF) and TiOPc(MOR-NAF) complexes were synthesized. Redox active and electropolymerizable 5-{[(1*E*)-(4-morpholin-4-ylphenyl)methylene]amino}-1-naphthoxy substituents on the Pc rings supplied electrochemically polymerization potential to the complexes. Voltammetry and in situ spectroelectrochemistry techniques were used for electrochemical characterizations in order to determine redox properties. Redox active and conductive GCE/MPc(MOR-NAF) electrodes were constructed with the electropolymerization of MPcs. Modified electrodes were investigated as potential pesticide sensors. Changing the metal center of the complexes significantly alters their sensing activities. While all complexes show interaction abilities for chlorophyros, fenitrothion, and methomyl. GCE/CoPc(MOR-NAF) electrode sensed fenitrothion with good selectivity and sensitivity. Although GCE/TiOPc(MOR-NAF) electrode also sensed fenitrothion with a good selectivity, the linear range of this sensing was very narrow. GCE/Cl-MnPc(MOR-NAF) electrode sensed all pesticides with similar voltammetric responses, thus its selectivity is poorer than the others, although it has good sensitivity for the pesticides.



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Insights into the Stability of Lithium-Ion Battery SEI Components in $LiPF_6$ Containing Electrolytes

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Lithium-ion batteries exhibit poor capacity retention at moderately elevated temperatures. Impedance growth and lithium-ion loss were reported to be the main factors of capacity fade.[1,2] Under such temperatures, cycles of decomposition and reformation of the SEI occur, which leads to electrolyte loss and growth of thicker SEI. Although the close connection between the capacity fade and reactions between SEI components and the electrolyte is understood, full reaction mechanisms are absent in the literature.[3] Comprehensive understanding of the underlying mechanisms will help us improve the calendar life of the lithium-ion batteries.

In this presentation, a comprehensive list of decomposition products from the LEDC, Li_2CO_3, and LMC; and proposed reaction routes will be discussed. LEDC and LMC were synthesized by reduction of EC and DMC respectively with lithium naphthalenide in high yield.[4] LEDC, Li_2CO_3, and LMC were stored in a simplified LiPF6 containing electrolyte at a moderately elevated temperature. Analysis using a combination of nuclear resonance spectroscopy (NMR), fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and gas chromatography with mass selective detection (GC-MS) yielded a comprehensive characterization of the products, which assisted in proposed reaction routes. The results will be discussed in detail.

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Electrochemical, Spectroelectrochemical, Electrocolorimetric, and Electrocatalytic Properties of Metal Phthalocyanine Compounds

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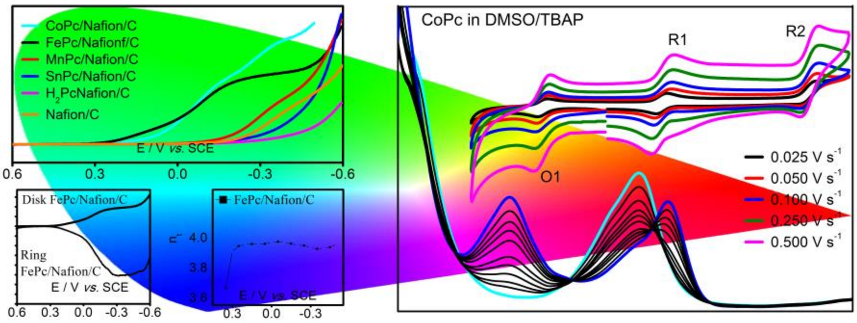
Phthalocyanines (Pcs) and their metal complexes have various advantages in the technological applications such as electrochromic materials and displays, and electrochemical energy conversion and storage systems, due to their conjugated 18π–electrons system and thus, rich redox properties [1-2]. Accordingly, these compounds have attracted considerable attention of many scientists and researchers. The redox properties of Pcs are closely and critically related to most of their industrial and technological applications. These properties can be modified in a broad scale by the metal ion in the centre and peripheral substituents. Therefore, the complete identification of these properties has vital importance for the determination of the possibility of the usage in these applications. However, it is not possible to distinguish such processes by voltammetry alone. In situ spectroelectrochemistry provide additional support for the assignment of the redox processes.

In this study, the redox properties of 2,3-dihydro-1h-inden-5-iloxy beta-substituted mononuclear metal Pcs were identified by the electrochemical techniques such as cyclic voltammetry, square wave voltammetry, and chronocoulometry. The compounds showed one-electron metal- and/or ligand-based reversible or quasi-reversible reduction and oxidation processes. The ratio of anodic to cathodic peak currents for the redox couples were usually near unity and anodic to cathodic peak separation ΔE_p ranged 60 to 100 mV, suggesting reversible to quasi-reversible behaviour. The color changes associated with the redox processes were also identified by in situ spectroelectrochemistry and in situ electrocolorimetry, with the aim of identifying the possibility of the usage of the compounds as electrochromic materials.

One of the main tasks of the current research associated with fuel cell and metal-air battery applications is the availability of efficient, stable and cost-effective electrocatalysts promoting the overall four-electron reduction of the oxygen molecule. Due to their high electrocatalytic activity in dioxygen reduction, Pc complexes have also been receiving increasing interest in the area of fuel cells and metal-air cells [2]. For this reason, the catalytic performances of the metal Pcs for oxygen reduction were also tested by dynamic voltammetry using the combined system of a rotating ring-disk electrode and a bipotentiostat, in a medium similar to fuel-cell working conditions. It was determined that the Pc complexes involving redox-active metal centers such as Co(II) ve Fe(II) have remarkably better catalytic activity towards oxygen reduction than those involving redox-inactive metal centers.



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Solubility and Coarsening of $LiAlO_2$ MCFC Matrix

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Continued particle growth and phase changes, resulting in the electrolyte redistribution and gas cross over in the electrolyte matrix fabricated from lithium aluminate (α-$LiAlO_2$), is considered as one of the leading causes of long term electrical performance degradation in molten carbonate fuel cell (MCFC) power generation systems. Solubility and coarsening of α-$LiAlO_2$ has been studied under a range of atmospheric exposure conditions to understand the role of melt chemistry and carbon dioxide/oxygen partial pressures in molten Li_2CO_3-Na_2CO_3. Phase transformation in $LiAlO_2$ has been studied by X-ray diffraction and the solubility of $LiAlO_2$ in the molten electrolyte has been studied by "pot test" technique with subsequent analysis by inductively coupled plasma mass spectrometry (ICP-MS). Under reducing atmosphere (4% H_2-3% H_2O-N_2), equiaxed round-shaped α-$LiAlO_2$ transformed to pyramid-shaped γ-$LiAlO_2$ with an increase in particle size at 650°C. The transformation from α- to γ-$LiAlO_2$ and particle growth decreased with an increase in carbon dioxide partial pressure in reducing atmosphere. Under oxidizing atmosphere (30% CO_2-70% air), phase and particle size remained largely unchanged at 650°C. Dissolution and growth processes will be discussed with emphasis on melt thermodynamics and materials modeling.

Electrochemical Sensor for the Real-Time Monitoring of Nitrogen and Phosphorous Containing Species in the Environmen

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The water circuit in the environment has implications in both the availability of clean water sources for human consumption, as well as for normal functioning of natural ecosystems. Human activity, such as industrial or agricultural processes, intervenes in this circuit and can greatly affect the quality of water resources. Nitrogen (N) and phosphorus (P)-containing compounds are essential for plant and animal nutrition. Although freely available in the atmosphere as N_2, access to fixed forms of nitrogen constitutes, in many cases, a limiting factor for plant growth. The phosphorus cycle is a slow process with implications in crops and animal growth. While phosphorus resources may be limited in certain regions, excessive presence from industrial and agricultural uses can cause algal blooms that produce extremely dangerous toxins, which are a health threat to people or animals. Managing and controlling the N- and P-cycle is essential for ensuring an overall nutrient balance and achieving equilibrium between beneficial and harmful effects. This presentation will describe development and optimization of an easy-to-use sensor for the determination of phosphorous and nitrogen-containing compounds in environmental samples. This method provides a field-deployable alternative to conventionally used approaches for detection and real time monitoring of N/P-containing species.

Electrochemical Investigation of pH-Dependent Properties of Polymer-Capped Nanoparticles

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In recent years, there has been significant research on the use of nanoparticles (NPs) for a wide variety of applications in the life sciences, energy and environmental fields. In most cases, the NPs are coated with surface ligands to ensure electrostatic stabilization and prevent aggregation. The surface coating and the characteristics of the capping agent determine many of the NP properties, most notably; stability, solubility and catalytic activity. This presentation will describe an electrochemical investigation of the pH-dependent properties of polymer-capped NPs. The work focuses on the catalytic activity and conformational changes of branched polyethyleneimine-capped silver nanoparticles (Ag-NPs). Chronoamperometric signals respond rapidly to pH-induced conformational changes of the PEI chains at the AgNP's surface. NP collision electrochemistry allows for screening and catalytic activity evaluation of the PEI-AgNPs for the decomposition of organic dyes. The results indicate that NP collision electrochemistry can be used in addition to spectroscopy and microscopy for evaluating the relationship between surface properties and catalytic activity. This study also provides fundamental information about polyethyleneimine's surface characteristics at the surface of conductive nanoparticles in various environments.

Plasmon-Enhanced Ultra-Sensitive Surface Analysis with Shell-Isolated Mode

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With nanostructured noble metal surface, optical field could be highly confined in sub-wavelength region and then the plasmon resonance is achieved. As a plasmon-based spectroscopic method, surface-enhanced Raman scattering (SERS) permeates in nanoscience, such as biological analysis, energy materials characterization, environmental contamination monitoring. However, there are two main disadvantages still limiting the applications of SERS. For example, the surface morphology needs to be nanostructured and material generality is restricted within a few free-electron like metals (e. g. Au, Ag, and Cu). In 2010, a novel methodology has been invented for plasmon-enhanced spectroscopies, which is named shell-isolated nanoparticle-enhanced Raman scattering (SHINERS).[1] The shell-isolated nanoparticle (SHIN) consists of noble metal core and ultrathin dielectric shell. Particularly, the compact isolation of core with ultra-thin shell can protect the contaminants or the contact with electrolytes while allowing the transmission of plasmon field from the metal core. *In situ* electrochemical SHINERS method has been proven effectively in monitoring the reaction processes at atomically flat Au(hkl) surfaces.[2]

Meanwhile, SHINERS method could be further applied in surface-enhanced fluorescence (SEF), with Ag nanomaterials, it is efficient to perform SEF at a wide range from 488 to 785 nm.[3] Astonishingly, in the Ag SHINs-enhanced fluorescence, an optimum de-quenced emission enhancement of more than 120,000-fold is obtained. In the presence of Ag SHINs, the single-molecule emission spectrum with high signal-to-noise ratio is acquired to probe the real-time conformational variation. Optimistically, at the electrochemical interface, Ag SHINs will pave an avenue for the monitoring of single-molecule electro-catalysis reactions.

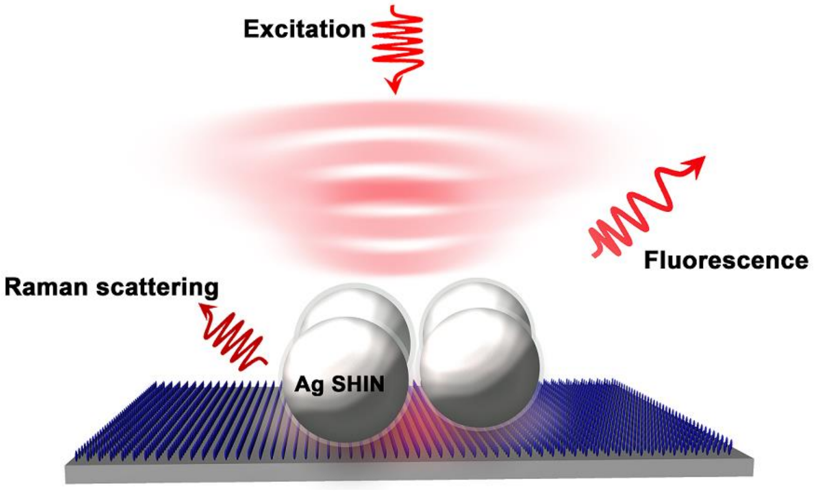

Figure 1. Schematic diagram of plasmon-enhanced ultra-sensitive surface analysis with SHINs.

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Metallic Foams as a Platform for Synthesizing Active Oxygen Reduction and Alcohol Oxidation Nanoparticle Catalysts

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Metallic foams are materials with unique properties, including high surface area, good electrical and thermal conductivity, and enhanced catalytic activity; making them good candidates as fuel cell catalysts and support for battery electrodes. When metallic foams are created with nano-sized dimensions, they are extremely fragile, and we harvest this property by using foams as a platform for creating large quantities of uniform nanoparticles for catalysis. In this work, we describe a bimetallic PtCu nanoparticle made initially from Cu nanoporous foams. This presentation will highlight recent work from our group on the tunable properties of electroactive metal foams and their effect on the electrocatalytic activity of O_2 reduction to form water or peroxide and the electrooxidation reaction of alcohols and organic acids to CO_2. In-situ methods for probing reaction intermediates for elucidating reaction mechanism will also be discussed.

Time-Resolved Nano-Impact Electrochemistry as a Sensitive Tool to Determine Diffusion Coefficient of Halides

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There are two factors that govern the Faradaic current in any electrochemical system: the kinetics of charge transfer and the diffusion of the reactant(s) towards the electrode. Classically, the diffusion coefficient D of a redox species can be determined using chronoamperometry at a microelectrode [1]. Here we present a novel electrochemical method of determining D using nano-impact electrochemistry. There, nanoparticles (NPs) in the sample impact a potentiostated electrode due to their Brownian motion, and then react undergo an electrochemical reaction that convert the NP itself into product. The associated Faradaic charge is recorded by a potentiostat, resulting in a sudden current spike on the chronoamperogram. In most of the previous work, both the shape and the duration of the current change could not be accurately resolved due to the strong filtering of the current signal [2]. Using high bandwidth measurements, this drawback can be overcome. Hence, the application of nano-impact experiments becomes more versatile. Not only the characterization of the impacting particle and the kinetics of the conversion is possible [3], but also the study of its surrounding solution.

Here, time-resolved (up to 60,000 data points per second) nano-impact analysis is employed to determine the diffusion coefficient of Cl^- in a solution, using the full oxidation of single AgNPs to sparingly soluble AgCl as the indicator reaction. At high overpotential, the reaction rate is limited by by the diffusion of Cl^- to the reacting AgNP, which is transformed to AgCl [Fig. 1 (a)]. Under these conditions and for a given concentration of Cl^-, faster diffusion of Cl^- results in a faster particle oxidation, that is a shorter spike duration in the current-time plot of the nano-impact. [Fig. 1 (b)]. According to the Stoke-Einstein equation, the diffusion coefficient D of a species depends on the solution viscosity.

Thus, it is demonstrated, that nano impact experiments allow the determination of diffusion coefficients of anions in various solutions and at different temperatures. As a proof of concept this is shown for halides using the oxidation of Ag NPs as an indicator reaction.

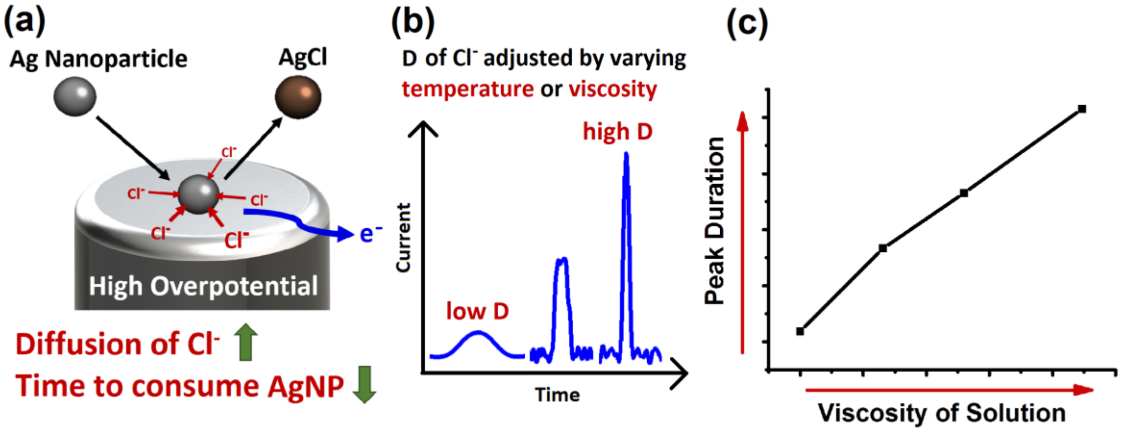

Fig. 1 (a) Oxidative nano-impact of AgNP onto a W.E. with anodic potential at high overpotential, in which the oxidation of the whole NP is limited by the diffusion of the Cl^- to the AgNP. (b and c) Narrowing (lowering of peak duration) of the impact current peaks is seen when the viscosity of the solution decreases.

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Electrochemical oxidation of cyanide on 3D Ti-RuO$_2$ anode using a filter-press electrolyzer

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The novelty of this communication lies in the use of a Ti-RuO$_2$ anode which has not been tested for the oxidation of free cyanide in alkaline media at concentrations similar to those found in wastewater from the Merrill Crowe process (100 mg L^{-1} KCN and pH 11), which is typically used for the recovery of gold and silver. The anode was prepared by the Pechini method and characterized by SEM. Linear sweep voltammetries on a Ti-RuO$_2$ rotating disk electrode (RDE) confirmed that cyanide is oxidized at $0.45 < E < 1.0$ V *vs* SHE, while significant oxygen evolution reaction (OER) occurred. Bulk oxidation of free cyanide was investigated on Ti-RuO$_2$ meshes fitted into a filter-press electrolyzer. Bulk electrolyzes were performed at constant potentials of 0.85 V and 0.95 V and at different mean linear flow rates ranging between 1.2 and 4.9 cm s^{-1}. The bulk anodic oxidation of cyanide at 0.85 V and 3.7 cm s^{-1} achieved a degradation of 94%, with current efficiencies of 38% and an energy consumption of 24.6 kWh m^{-3}. Moreover, the degradation sequence of cyanide was also examined by HPLC.

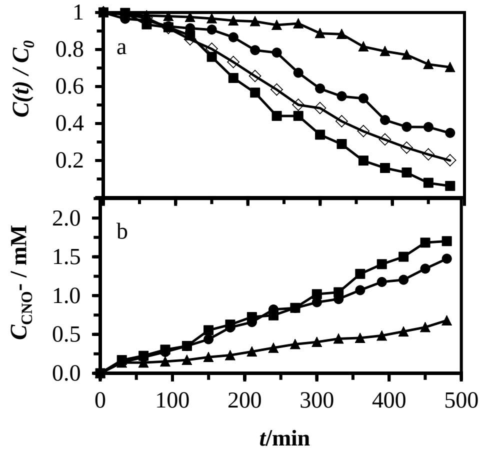

Fig. 1. Effect of hydrodynamics on (a) normalized decay of cyanide concentration, and (b) cyanate evolution *versus* electrolysis time in the filter-press electrolyzer at mean linear flow rates of: 1.2 cm s^{-1} (▲), 2.5 cm s^{-1} (●), 3.7 cm s^{-1} (■) and 4.9 cm s^{-1} (◊) at constant applied potential of 0.85 V *vs* SHE. Electrolyte: 3.85 mM (100 ppm) CN^{-} in 45 mM NaNO$_3$ at pH = 11 and T = 303 K. Area of the Ti–RuO$_2$ electrode, 98.5 cm^2.

Remote Control Electrodeposition: Patterning on Substrates without Direct Electrical Connections

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Advances in additive manufacturing technologies have been primarily driven by simple, integrated software/hardware platforms that render computer aided design files into three-dimensional objects. Simple software interfacing allows for both hobbyists and trained technicians to use highly developed technological hardware (such as 3D-printing).[1] Despite these advances in other additive manufacturing technologies, a similar trend to fully software-reconfigurable electrodeposition-based prototyping has yet to emerge. Through-mask plating, the industrial electrodeposition patterning standard, is a high cost and high waste process requiring several mask, deposition, and etch steps to fully develop patterns. More sophisticated layer-by-layer electrochemical prototyping, such as EFAB, also requires many deposition, planarization, and chemical etch steps to fabricate objects. The use of chemical etching and masks limits the reconfigurability of these technologies. However, direct-write electrodeposition methods can bridge the advantages of electrodeposition-based fabrication to software reconfigurable additive manufacturing techniques. Previously, microelectrodes and microjet nozzles have demonstrated direct-write, local electrodeposition and patterning of materials, with spatial resolution dictated by the geometry of the electrode or nozzle.[2-3] Impinging jet electroplating was further expanded by our research group by implementing full software control of electrodeposition, mass transport, and motion control with a system called Electrochemical Printing (EcP).[4]

More recently, our lab modified the EcP system to operate in a bipolar manner, enabling direct-write electrodeposition and patterning without direct electrical connections to the substrate. Bipolar electrochemistry overcomes a key limitation in traditional electrochemistry, the need to electrically connect to the substrate. Wiring to a substrate is especially difficult for micro/nano-manufactrured systems or complex three-dimensional geometries. Bipolar electrochemistry involves spatially segregated, equal and opposite reduction and oxidation on an electrically floating substrate.[5] We show that spatial and temporal control of the bipolar electrochemical couples enables patterned electrodeposition (or etching) by "remote control" without wiring to the substrate.[6] This requires more intricate electrolyte design, through the addition of an electron donating species that can undergo oxidation on the substrate concomitantly with metal reduction. We characterize local bipolar electrodeposition beneath the tip of a rastering microjet anode configuration we call a scanning bipolar cell (SBC). The fundamental interactions of thermodynamics, kinetics, and ionic transport in the SBC are explored using a range of metal reduction reactions of varying nobility and kinetic stability. Selection of the counter bipolar oxidation couple is dependent on the kinetic reversibility and thermodynamics of the accompanying metal reduction chemistry. This technology provides a platform for additive manufacturing in micro/nano-scale devices such as integrated circuits and printed circuit boards.

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Improving the Durability of Shape-controlled Octahedral Pt Alloy Nanoparticle Catalysts for use in fuel cell cathodes

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Proton exchange membrane fuel cells (PEMFCs) convert chemical energy into electricity and uses hydrogen and oxygen as fuel, which can be produced by water electrolysis from renewable energy sources. PEMFCs are currently commercialized, but further development is facing the challenge to decrease components cost. The sluggish kinetics of the oxygen reduction reaction (ORR) and harsh environment pose challenges on the development of cheap, active and stable catalysts. Shape-controlled bi- or tri-metallic Pt alloy nanoparticles have been reported to achieve extremely high mass activity in rotating disk electrode (RDE) experiments and for this reason are considered as a highly promising class of ORR catalysts.[1] Octahedral PtNi nanoparticles are a remarkable example of highly active catalysts belonging to this family. One of the principles used to explain their performance is based on their particular geometrical shape which exposes and maximizes the (111) surface. This surface has been observed to possess extraordinary high specific activity for single crystal with Pt_3Ni composition and for this reason it is desirable to recreate at the nanometer scale.[2] Despite the high mass activity, the low electrochemical surface area (ECSA), often below 50 m^2/g, is considered not optimal and possible to hinder their performance at higher current density in membrane electrode assemblies (MEA).[3] A second challenge is their morphological stability under electrochemical testing. Ni loss and other degradation processes often results in shape changes into more “rounded” or concave structures with loss of the (111) facet and lower activity (figure 1).[4]

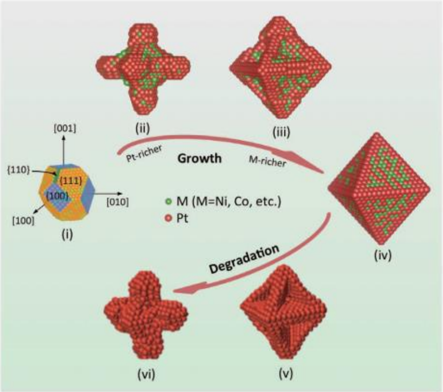

Figure 1. Life cycle of an octahedral PtNi nanoparticle showing a degradation pathway to loss of octahedral shape.[4]

In this contribution we will show our recent efforts in improving the activity and especially the durability and morphological stability of PtNi based octahedral nanoparticle catalysts. The catalysts are produced by solvothermal methods and characterized by physico-chemical techniques (ICP, XRD, TEM). Activity and stability are evaluated from RDE measurements following a protocol developed inside the INSPIRE project.[5]

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Development of Bismuth-Modified Pt Nanocatalysts for the Electrochemical Reforming of Polyols into Hydrogen and low oxidized C_3 species

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The electrooxidation of C3 alcohols (1- propanol, 2-propanol, 1,2-propanediol, 1,3-propanediol, and glycerol) has been studied in alkaline medium on Pt/C and Pt_9Bi1/C catalysts by cyclic voltammetry and in situ FTIR spectroscopy in order to better understand the reaction mechanisms. Both catalysts were synthesized with metal particle sizes below 5 nm and were characterized by TGA, AAS, and XRD. The modification of Pt by 10 at. % of Bi decreases the oxidation onset potentials of C3 alcohols down to ca. 200 mV. In situ FTIR spectroscopy measurements indicated clearly that the presence of Bi also led to avoid the C−C bond cleavage during alcohol electrooxidation reactions and, hence, to favor the formation of value-added C3 compounds. Moreover, with respect to a Pd-based catalyst, Pt_9Bi_1/C presented much higher electrocatalytic activity at low potentials. Systematic evaluation of the positions and intensity changes of absorption bands as a function of the electrode potential allowed determining reaction pathways of electrooxidation of C3 alcohols. It has been shown not only that the secondary alcohol groups are more reactive than the primary ones for all C3 alcohols, except glycerol where steric limitations due to the presence of two primary alcohol groups could be responsible of the higher oxidation onset potential. At potentials above 0.6 V, the linear 1-propanol bearing a single primary alcohol group leads to the highest activity due to lower steric hindrance of the surface compared with the other alcohols studied.

But, Pt_9Bi_1/C remains the most active catalyst for the glycerol oxidation reaction, with an oxidation onset potential as low as 0.3 V versus RHE. The hydrogen production in a direct electrolysis cell was evaluated. The Pt_9Bi_1/C anode gave a hydrogen production rate of approximately 0.11 and 0.23 sm_{H2}^3 h^{-1} m^{-2} with an electrical energy consumption of 1.3 and 1.65 kWh sm_{H2}^{-3} at 0.55 and 0.7 V, respectively. Compared with traditional water electrolysis, this corresponds to energy saving between 66 and 57 %, respectively. At low potentials, glyceraldehyde is the main reaction product and at higher potentials, glyceraldehyde and dihydroxyacetone act as reaction intermediates to the formation of carboxylates.

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New Nano-Machining Method of Electro-Regulated Chemical Etching with Distance Sensitivity

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A distance-sensitive nanomachining of the electrochemically combined chemical etching was originally developed from machine principle; the fabrication could realize large-area nanomachining without the limitation or the drawback of currently nanomachining technologies. The methodological essential is that the etchant of electrochemical generation at mold electrode diffuses to workpiece surface and then chemically etches it; and the key prerequisite of distance-sensitive etching is that the etchant diffusion must be the rate-determining step of the whole fabrication process. Experimentally, a simple and feasible strategy is to employ a redox hydrogel thin film as the etchant/precursor system, because the electron-hopping between the redox groups anchored within the hydrogel has a rather slow rate; and just relying on the self-weight of the mold electrode and the soft feature of hydrogel film, a precise parallelism between the surfaces of the mold electrode and workpiece could realize without the help of any distance-adjust equipment, which played a key role in the currently nanomachining technologies.

Multiscale carbon mold electrodes (Φ: 6-50.8 mm) of the curved surface at nanoscale were prepared by mechanical lapping and spin coating-pyrolysis methods. Employment of electropolymerization and spin coating to produce two redox hydrogel thin films (($[Ru(bpy)_2(vpy)_2]_2^+$)n and $[Ru(bpy)_2(PVP)_5Cl]^+)_n$) of controllable thickness on the mold electrode surface. The experiential results demonstrated that, when two films were employed to fabricate copper workpiece, the limited etching current density (I_{lim}) at high anodic potential (+1.0 - + 1.4 V vs. SCE) would be inversely proportional to the film thickness (δ), according with: $I_{lim}=nFDC/\delta$. (n: electron number of redox reaction; F: faraday constant; C: concentration of redox groups with the film); the etching could fabricate a completely complementary pattern of the mold profile on the copper workpiece surface with a precision around 4 nm at a rate of about 1.2 nm/min.

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New Approaches to the Design of Cathodes and Barriers for Enhanced Performance of Li/S Batteries

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Among the promising candidates for rechargeable batteries is lithium-sulfur system, which has high specific energy density, combined with the cost efficiency of sulfur due to its natural abundance [1]. However, there are several challenges with the Li/S battery, which have limited its performance. One of the main problems is the solubility of sulfur and of lithium polysulfides in battery electrolytes. The dissolved polysulfides damage the anodic solid electrolyte interphase, lead to corrosion of lithium and to the formation of shorter polysulfides. Short polysulfides, in turn, diffuse to the cathode, reoxidize and initiate a shuttle mechanism, followed by low energy-conversion efficiency. Several interesting strategies have been implemented to reduce the shuttle effects, but with limited success. Previous efforts on the subject have been focused on the sequestration of sulfur and its reduced products within the cathode by modifying the cathode structure or electrolyte. More recently, attention has moved to the design of different types of barriers, which trap polysulfide species via strong chemical bonding and feature long-term polysulfide sequestration of dissolved Li_2S_n [2].

Many of the transition-metal sulfides are electrochemically active and can undergo reversible reactions. Moreover, some sulfides are known to present much higher specific capacity than that of the intercalation compounds. Thereby using them as cathode materials for rechargeable lithium batteries can be a more effective alternative solution for the design of such next-generation batteries. Among the various transition metal sulfides, pyrite (FeS_2) is a promising cathode material for rechargeable lithium batteries because of its high theoretical capacity (894 mAh/g), low cost and near-infinite natural abundance. Therefore, as a model for cathode materials, FeS_2 has recently been widely investigated. However, progress in developing a viable Li/FeS_2 battery has been hampered by the poor cycleability of the FeS_2 cathode, high open-circuit voltage and a sharp ohmic drop observed during the initial discharge [3].

In the current work, we studied the effect of mixed conducting composites based on transition-metal sulfides and metal particles as barriers on the electrochemical performance of Li/S batteries. Modification of cell configuration by the insertion of different types of barriers between the cathode, separator and anode, improved the utilization of the active material and increased the reversible discharge capacity and coulombic efficiency. In addition, we evaluated compounds $Li_xM_yFeS_2$ (M=Cu, Co, Mo), obtained by mechanochemical synthesis, as a new type of cathode material for rechargeable lithium batteries with lithium anode and different electrolytes. Cells with modified lithiated chalcopyrite-based cathodes provide 600 to 1200mAh/gS with over 98-99% faradaic efficiency and enable more than 200 reversible cycles.

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Microfluidic Ionic Circuits Powered by RED (Reverse Electrodialysis) as a Full Iontronic System

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An enormous development of solid-state electronics as an information processing interface has offered lots of fast, miniaturized, cost-effective and highly efficient electronic devices. However, their usages cannot simply be expanded into biological information processing for several reasons. Biological system like the nervous system uses ions or molecules as signal carrier in aqueous condition unlike electronic circuits do. Instead, ionic circuits composed of electrolyte, water, polyelectrolyte gels have been widely utilized as an alternative for handling ionic signals. This concept is referred to as 'iontronics' [1], where there have already been numerous researches containing ionic diode[2], polyelectrolyte junction field effect transistor[3] in microfluidic chip and some logic circuits[4, 5]. The problem is that all these kinds of ionic signal processing devices have relied on electronic power source like potentiostat or battery. It has been inevitable to use metal electrodes, e.g. Ag/AgCl electrode and metal wires to connect the power source to the ionic circuit. Further bio-related researches like biological integration of ionic information processing circuits couldn't have been feasible even if there had been certain iontronic systems mimicking in-vivo ionic signaling processes as there weren't an ionic, non-faradaic and potentially biocompatible power source.

Here, we present ionic circuits driven by the voltage generated from RED (Reverse electrodialysis. RED is an ionic power source that converts the free energy of mixing two different salt solutions, e.g. seawater and river water that are inexhaustible resources at estuaries. The two solutions are alternately located between cation and anion exchange membranes. Any arbitrary potential can be obtained by adjusting the number of IEMs (Ion-exchange membrane) and the salinity ratio of two salt solutions. Microfluidic ionic diode and logic circuit worked normally by simply connecting them to RED through commercial plastic tubes filled with electrolyte. In addition, the voltage applied to the circuit can be switched on and off, or adjusted to a certain value by tightening and releasing the flexible connection tube. The substitution of the power source into RED is important because a full iontronic interface where the entire system operates in an ionic fashion including the voltage source can be developed.

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Surface Structure Role in Selectivity of Photo-electrochemical Water Splitting

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Photo-electrochemical water splitting represents one of the key processes needed for successful utilization of renewable energy sources for distributed generation, storage and use of energy[1]. The research related to the electrochemical and photo-electrochemical splitting of water is primarily motivated by electricity storage in hydrogen. The overall process itself, however, is limited by the kinetically sluggish oxygen evolution reaction (OER). Primary effort was therefore focused on a development of new oxygen evolution catalysts based on rational design approach combining the DFT screening with target synthesis.

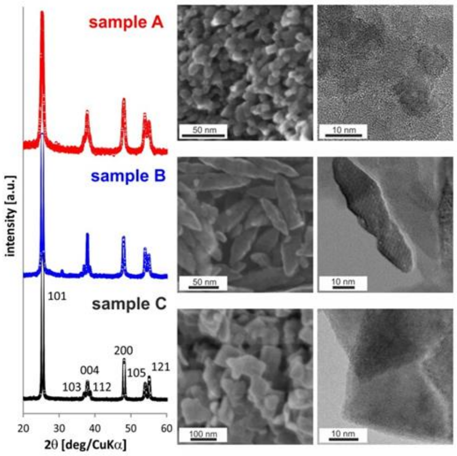

Figure 2 Powder X-ray diffraction patterns (left) and SEM images (middle) and HRTEM images (right) of anatase samples differing in the nanocrystal shape. The sample assignment is given in the Figure annotation. The SEM images were taken on the catalysts attached to the electrodes; the HRTEM images correspond to as prepared catalysts after calcination

This paper compares selectivity of different surface orientations of the most common TiO_2 allotropes – rutile, anatase and brookite nanocrystals exposing different facets. The titania nanocrystals were oriented by analysis of the high resolution TEM micrographs as shown on an example of anatase in Fig. 1. The selectivity of different titania surface structures in photo-electrochemical water splitting was investigated by means of on-line mass spectroscopic detection (DEMS). The relative amount of oxygen normalized by the passed charge shows significant variation depending on the particular TiO_2 surface structure (see Fig. 2). The significant differences in the amount of the produced oxygen on different surface structures is attributed to a competition between electron and hole charge transfer at the semiconductor/electrolyte interface The observed tendencies can be rationalized with help of the DFT calculation assuming the nanocrystalline electrode behaves electronically as macroscopic object [2] (i.e. the formation of SC layer is not hindered by the dimensions of the individual nanocrystals).

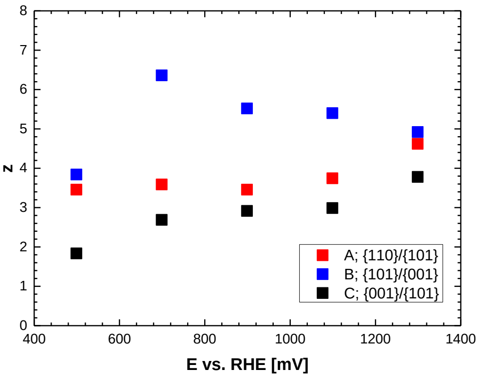

Figure 1 DEMS based average number of electrons needed to evolve one molecule of oxygen as a function of the applied potential on different anatase photocatalysts illuminated in acid (pH=1) electrolyte solution The sample colour coding is the same as in Figure 1.

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Boosting the performance of Pt/C catalysts for the oxygen reduction reaction through modification with hydrophobic ionic liquids

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Low temperature fuel cells are predicted to have a great potential for future energy applications. But so far a broad commercialization is hindered by high costs of the platinum-based electro catalysts, combined with unsatisfying oxygen reduction (ORR) kinetics and catalyst durabilities.[1]

Within this work we could demonstrate that the activity and stability of a conventional Pt/C catalyst could be effectively boosted by modifying the catalyst with inexpensive, small amounts of hydrophobic ionic liquid (IL, $[C_4C_1Im][NTf_2]$). We could show that this highly scalable modification technique can accelerate the ORR kinetics by preventing Pt sites from being oxidized, which results in a record in mass activity for Pt/C (1.01 A mg^{-1}_{Pt} @0.9 V).[2] The effect of IL on the performance of the catalyst can be manipulated by variation of the catalysts pore filling degree.[3]

The IL modified Pt/C samples were comprehensively characterized by TEM, ICP-OES, FTIR, N_2-sorption and electrochemical CO-stripping techniques. The catalytic performance towards ORR was investigated by applying the thin film rotating (ring) disk electrode method (R(R)DE) and compared to the as-received Pt/C. Cyclic voltammetry (CV) measurements revealed, that the introduction of $[C_4C_1im][NTf_2]$ leads to a negligible site blocking effect of the Pt surfaces (EAS: 94.6 vs 99.0 m^2 g^{-1}_{Pt}), but more interestingly to a significant suppression of the formation of oxygenated species (OH_{ad}). Furthermore, from Tafel plots, it can be seen that the pristine Pt/C catalyst has a Tafel slope of 63 mV dec^{-1} at 0.9 V, whereas the IL-modified sample offers a slope of 96 mV dec^{-1}, which is closer to the intrinsic Tafel slope of ORR on clean Pt surface (120 mV dec^{-1}). These results disclose, that the IL effectively helps to protect the Pt sites from oxygenated species. To control the influence of IL on the adsorption behavior of Pt surfaces, CO stripping experiments were conducted. It could be proved that the IL selectively locates on the defect sites and therefore protects the catalyst from oxidation reactions. At the same time the Pt surface becomes more reactive to the reagents, which can be seen as a breakthrough in ORR catalysis. As a result, the IL modified catalyst samples showed impressively enhanced ORR activities compared to the pristine Pt/C without IL. The intrinsic specific activity for Pt/C-$[C_4C_1im][NTf_2]$ could therefore be increased by 3.1 times from 0.34 to 1.10 mA cm^{-2}_{Pt}. Moreover, the mass specific activity (MSA) reached a value of 1.01 A mg^{-1}_{Pt}, which is significantly above the mass activity target of 0.44 A mg^{-1}_{Pt} set by the US Department of Energy (DOE) for 2017-2020.

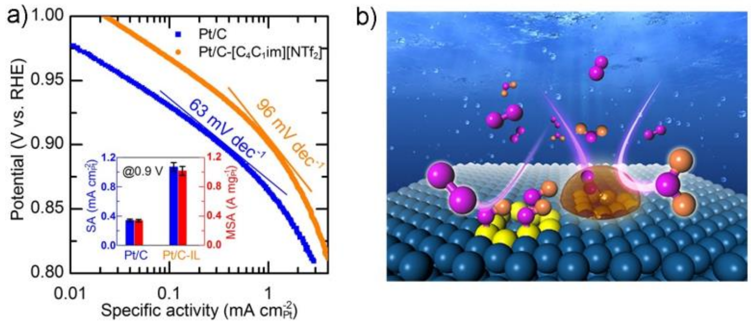

Figure 1. a) SA of Pt for ORR as a function of potential. The inset shows the activity comparison of the Pt/C catalysts before and after IL modification. b) Scheme illustrating that the hydrophobic IL would help to protect low coordinated Pt sites from being oxidized by repelling water molecules.

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A combined DFT and Experimental Approach forProbing Metal-Support Interaction in Pt nanoparticle supported on Nitrogen Functionalized Mesoporous Carbon

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Proton exchange membrane fuel cell (PEMFC) wide spreading is still hindered by the bottleneck of the oxygen reduction reaction (ORR). Actually, large amounts of precious Pt metal are required to promote the sluggish kinetics, causing the PEMFCs to be economically uncompetitive with conventional technologies. One way to reduce the metal loading while increasing the metal nanoparticles (NPs) catalytic activity is to support them on activated surface able at triggering their activity by increasing the number of active sites or by electronic interaction.[1] Pt NPs on nitrogen functionalized mesoporous carbon (NMC) have proved to be interesting materials for oxygen reduction reaction (ORR).[1]

In this paper we employed a new synthetic route for the simultaneous Pt NPs deposition and carbon support doping by using a platinum precursor bearing a nitrogen containing ligand such as 1,10-phenantroline or 2,2’-bipyridine. Metals NPs (average size 3 nm) were successfully synthesized by thermal solid state reduction on a commercial carbon. XPS analysis confirmed that during the treatment the ligand degrades and the nitrogen is embedded in the mesoporous carbon structure obtaining a surface modification of the carbon support, preserving the bulk conductivity and thermal stability.[2]

Electrochemical characterization revealed superior mass catalytic activity towards ORR in those catalysts showing higher Pt-N interaction expresses as B.E. shift of nitrogen components (Fig.1a). Pyridinic, pyrrolic and graphitic functional groups were considered in a DFT computational investigation for discriminating the interaction with a single Pt atom and nitrogen defects. DFT analysis confirmed that the interaction between Pt and nitrogen depends on the number and different types of nitrogen functional groups so that the most stable structure is observed when Pt interacts closely with 4 pyridinic groups (Fig.1b).

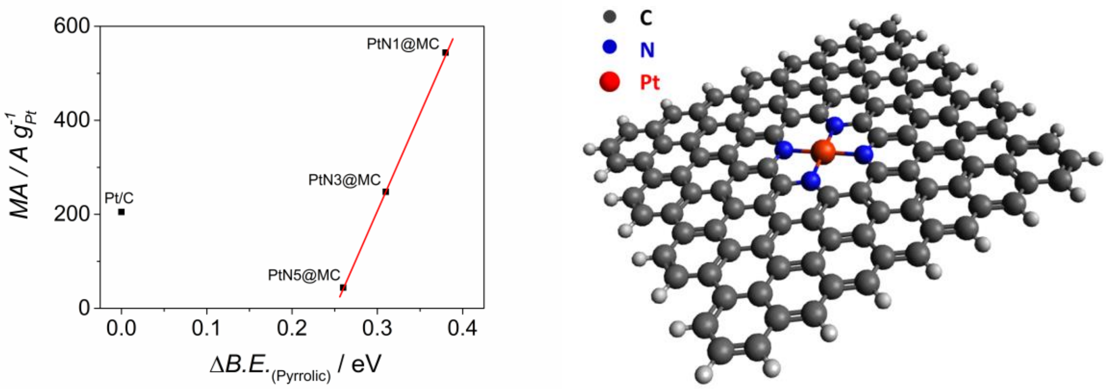

Figure 1. a) correlation between pyrrolic B.E: shift and mass activity towards ORR, b) DFT optimized structure Pt atom on NMC.

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Flexible Boron-Doped Diamond (BDD) Electrodes for Plant Monitoring

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Detecting the bio-potential changes of plants would be useful for monitoring their growth and health in the field [1]. A sensitive plant monitoring system with flexible boron-doped diamond (BDD) electrodes prepared from BDD powder and resin (Nafion [2] or Vylon-KE1830 [3]) was investigated. The properties of the electrodes were compared with those of small BDD plate-type electrodes by monitoring the bioelectric potential of potted *Aloe* and hybrid species in the genus *Opuntia*. While flexible BDD electrodes have wide potential windows, their cyclic voltammograms are not identical to those of the BDD plate. Further, the potential gap between a pair of electrodes attached to the plants changes as the plants are stimulated artificially with a finger touch, suggesting that the bioelectric potentials in the plant also changed, manifesting as changes in the potential gap between the electrodes. The BDD electrodes were assessed for their response reproducibility to a finger stimulus for 30 days. It was concluded that the plant monitoring system worked well with flexible BDD electrodes. Further, the electrodes were stable and as reliable as the BDD plate electrodes in this study. Thus, a flexible and inexpensive BDD electrode system was successfully fabricated in this study for monitoring the bioelectric potential changes in plants.

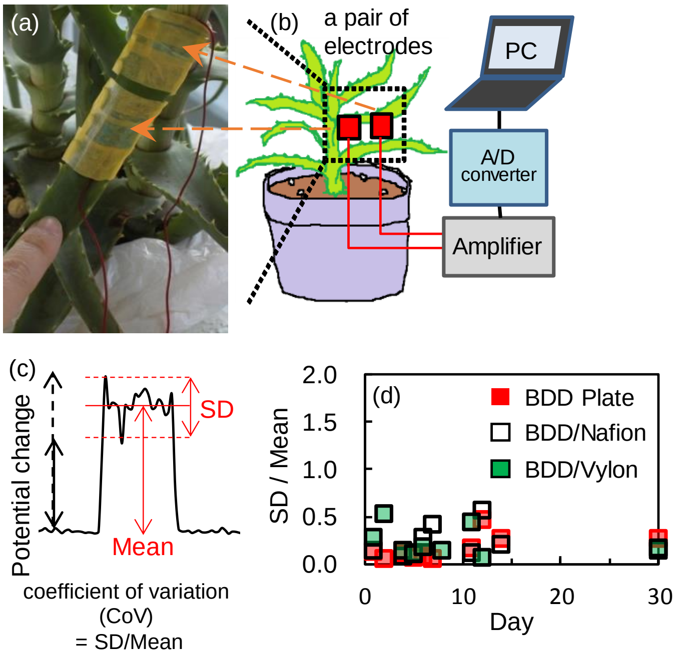

Fig. 1 (a) Finger touch on a leaf of a potted *Aloe*. (b) Schematic of the measurement system for plant monitoring. (c) Potential changes between a pair of electrodes on potted *Aloe* and statistical analysis. (d) SD/Mean (coefficient of variation) for the potential changes measured with each electrode.

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Effects of pH and electrolytes on the stability of the ZnO nanorods photoanode for the photoelectrochemical water splitting

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Nanostructured ZnO has high activity and wide band gap for photo-electrochemical water splitting. However, their application has been limited by the susceptibility of ZnO towards photocorrosion in aqueous electrolytes. This study aims at optimizing the electrolyte solution to improve the long-term stability of ZnO photoanodes. The results indicate that the long-term stability of ZnO nanorods is visible in the borate and carbonate buffers compared to the non-buffered electrolytes (pH 10.5) during the photoelectrochemical water oxidation. Furthermore, the optimal pH for ZnO photoanodes is between 9.0 and 13.0 in the borate electrolyte and from 9.5 to 12.0 in the carbonate buffer. The morphology of ZnO nanorods was not significantly changed in the solutions of pH = 10.5, which demonstrated that the lifetime of ZnO could be increased when the borate or carbonate were existed in aqueous electrolytes. The water splitting process of ZnO were tested in both borate and carbonate buffers under AM 1.5G simulated sunlight. The results exhibited the highest stability when tested in a pH 10.5 borate and carbonate buffers. In this case, 80% of the initial photoactivity was preserved after a 12-h test, indicating that the lifetime of the electrode could be increased by over an order of magnitude compared to the standard testing conditions in neutral, non-buffer electrolytes.

Keywords: Zinc oxide, borate buffer, carbonate buffer, water splitting.

Li-O_2 battery based on electrospinning PVDF/PET/PVDF nanofiber non-woven membrane and perovskite $La_{0.5}Ce_{0.5}Fe_{0.5}Mn_{0.5}O_3$ bi-functional catalyst

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Abstract

This work is studied the electrochemical performance of the Li-O_2 battery based on electrospinning PVDF/PET/PVDF nanofiber non-woven membrane and perovskite $La_{0.5}Ce_{0.5}Fe_{0.5}Mn_{0.5}O_3$ (denoted as LCFMO) catalyst. The perovskite oxide catalyst for the air cathode was prepared by using a simple wet chemical co-precipitation method. The PVDF/PET/PVDF nanofiber non-woven membrane was synthesized by an electrospinning (EP) method. The novel cathode slurry inks for the air cathode was prepared by using as-prepared $La_{0.5}Ce_{0.5}Fe_{0.5}Mn_{0.5}O_3$ oxide catalyst with two carbons support, Ketjen Black (KB) carbon black and graphene (GNS). It was found that the optimal composition of the air cathode is based on the slurry composition of oxide catalyst:GNS:KB=7:2:1) on electrospray on Ni-foam matrix. The discharge capacities of the Li-O_2 battery can be achieved about 300 mAh g^{-1} (controlled maximal discharged capacity at 300 mAh g^{-1}) at 0.1 mA g^{-1} rate at least 190 cycles without apparent capacities decay. It also found that the Li-O_2 battery with the as-prepared $La_{0.5}Ce_{0.5}Fe_{0.5}Mn_{0.5}O_3$ oxide catalyst and the as-prepared PVDF/PET/PVDF composite nanofiber membrane showed excellent cycling stability. It is due to the excellent performance of LCFMO bi-functional catalyst. It can markedly reduce the both the charge over-potential and the discharge over-potential. Another reason may be due to the composite nanofiber non-woven membrane. It has the optimal pore size, higher porosity, and ionic conductivity for the composite non-woven membrane. It was also found that the he Li-O_2 battery showed much lower the interfacial charge resistance (i.e., lower R_{ct}) by AC impedance analysis. It was found that those novel materials can be used on Li-O_2 battery systems to improve their. electrochemical properties.

Keywords: Li-O_2 battery, $La_{0.5}Ce_{0.5}Fe_{0.5}Mn_{0.5}O_3$ catalyst, Electrospinning, PET nonwoven polymer membrane, Wet chemical process

Development of toluene direct hydrogenation electrolyzer for energy carrier technology

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Introduction

The utilization of renewable energy has been expected as an energy system of low CO_2 emission adapted to the global environment. The large-scale transport and storage system of hydrogen has been considered the important technology to solve the local imbalance of energy supply in global scale. We have studied the high-efficient electrolytic direct-hydrogenation of toluene with water decomposition for the organic hydride system[1, 2]. This method has the advantages of small theoretical decomposition voltage and no exothermic heat loss compare with the conventional 2-step hydrogenation with the water electrolysis. In this study, we aimed to improve electrochemical property with the development of the cathode flow field, diffusion layer and anode structure in the toluene electrohydrogenation electrolyzer.

Experimental

A conventional or fine mesh DSE® electrode for the oxygen evolution (De Nora Permelec ltd), a carbon paper (35BC or 10BC, SGL carbon ltd.) applied Pt-Ru/C (TEC61E54, TKK) catalyst with ionomer, and Nafion 117® were used for the anode, the cathode, and the proton exchange membrane (PEM), respectively. The carbon paper as the diffusion layer was loaded the Pt particles for 0.02 $mg_{\text{-Pt}}$ cm^{-2} by the impregnation method. The cathode was hot-pressed on the PEM at 120 °C and 10 kgf cm^{-2} for 3 min to fabricate a membrane cathode assembly. The cathode flow fields were parallel for the 35BC of the carbon paper or no flow path for the 10BC. During the operation of the electrolyzer, the anode and cathode compartments were circulated 1 mol dm^{-3} H_2SO_4 at 10 ml min^{-1} and 10% toluene – methyl cyclohexane at 10 ml min^{-1}, respectively. The electrochemical measurements were conducted for the linear sweep voltammetry (LSV), the electrochemical impedance spectroscopy (EIS), and the current efficiency measurement.

Results and discussion

Figure 1 shows the cell voltage and the current efficiency for conventional anode with parallel and developed fine mesh anode without flow path electrolyzer at 60°C. The fine mesh anode electrolyzer without cathode flow path had much smaller cell voltage and higher current efficiency than those of the conventional anode electrolyzer with parallel flow field. The loading of Pt particle into the diffusion layer would improve current efficiency by the enhancement of mass transfer to the catalyst layer by suppression of side reaction of hydrogen generation. The fine mesh DSE® would reduce overvoltage anode and internal resistance with uniform contact with the membrane and the cathode. All these improvements decreased cell voltage from 2.11 to 1.80 V at 0.4 A cm^{-2} and also increased the current density at 95% of the current efficiency from 0.09 to 0.30 A cm^{-2}.

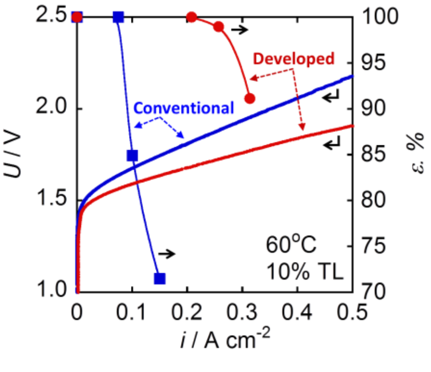

Figure 1 the cell voltage and the current efficiency for conventional and developed electrolyzer with 10% toluene concentration at 60°C.

Acknowledgements

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Identification of Copper(II)–Lactate Complexes in Alkaline Aqueous Solutions for Cu_2O Electrodeposition

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Cuprous oxide (Cu_2O) is known as a p-type semiconductor, and has attracted increasing attention as a solar cell material. The electrodeposition of Cu_2O from alkaline aqueous baths containing copper(II) salts and lactate as complex former was first reported by Rakhshani and co-workers [1] and further developed by the groups of Switzer [2], Izaki and Shinagawa [3]. Dissolved copper(II) complex(es) in the alkaline lactate baths, however, still remained undetermined. In the previous meeting [4], we have reported that the most likely Cu(II)-lactate complex in strong alkaline region is $CuL_2(OH)^-$ judging from a conventional continuous pH titration curve. Some time after that, however, we found that the Cu(II)-lactate complexation is very slow to achieve equilibrium and, therefore, the continuous titration underestimated the equivalent point. A time-dependent change in visible absorption spectra for a Cu(II)-lactate baths indicated that it takes more than one day for the equilibrium. In response to the finding, we have acquired a revised "titration" curve in an alternative way without using automatic burette. Here, we prepared dozens of airtight sample solutions containing 0.4 M $Cu(ClO_4)_2$ – 3.0 M lactic acid (HL; $L^- = CH_3CH(OH)COO^-$) and added different amounts of NaOH to each. Several days after the NaOH addition, the pH values of each solution were measured to assemble a well-equilibrated "titration" curve. The equivalent point appeared in the revised curve clearly showed that the *final* Cu(II)-lactate complex is $Cu(H_{-1}L)_2^{2-}$ ($H_{-1}L^{2-} = CH_3CH(O^-)COO^-$) formed by the reaction: $Cu^{2+} + 2HL + 4OH^- \rightarrow Cu(H_{-1}L)_2^{2-} + 4H_2O$. A set of refined absorption spectra (Fig. 1a) beyond pH = 6 gave two different couples of isosbestic points and concomitant blue shift with increasing pH, implying that there are two different complexation equilibria in this region: $CuL_2 + OH^- = Cu(H_{-1}L)L^- + H_2O$ and $Cu(H_{-1}L)L^- + OH^- = Cu(H_{-1}L)_2^{2-} + H_2O$. In order to observe the $Cu(H_{-1}L)_2^{2-}$ complex directly, mass spectra for the solution were measured by employing novel probe electrospray ionization [5,6]. The spectra successfully gave a sequence of signals attributed to $[Cu(H_{-1}L)_2{\cdot}Na_3](NaL)_x^+$ where x = 0–11 at m/z = 308, 420, 532, … 1540 (Fig. 1b), which clearly substantiated the presence of $Cu(H_{-1}L)_2^{2-}$ species at pH 7–11. Since such deprotonation of α-hydroxyl group ($L^- + OH^- \rightarrow H_{-1}L^{2-} + H_2O$) could never happen for free uncoordinated lactate ions, the formation of $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ is due to a strong Lewis acidity of Cu^{2+} ions and/or some specific interaction between d^9 Cu^{2+} ion and the ligands, especially in a concentrated solution with relatively high ionic strength. We actually observed the formation of $Cu(OH)_2$ precipitate, when the solutions were diluted.

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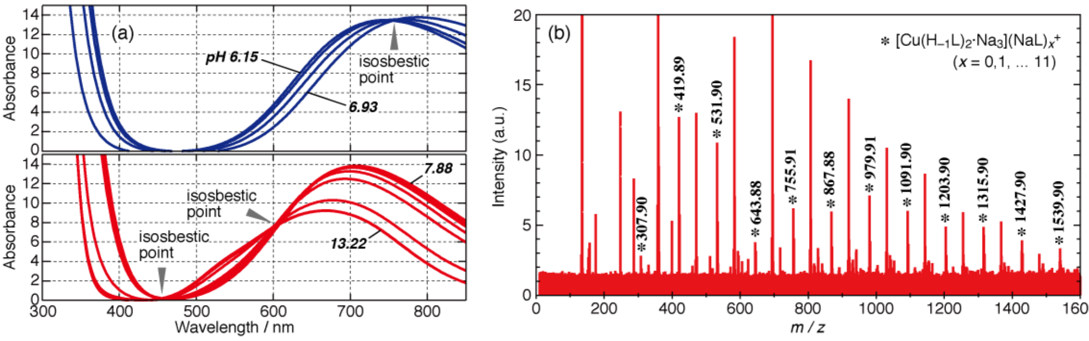

Figure 1. (a) A set of visible absorption spectra for Cu(II)-lactate solutions, collected using a quartz cell with 1 mm path and converted to the absorbance values for standard 1 cm path, and (b) probe electrospray ionization mass spectrum (positive ion mode) for the solution of pH 9.5.

Facile Synthesis and Electrochemical Performance of Porous N-C/Co_3O_4 Nanocomposite

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Recently, with the rapid development of the electronic and information industry, lithium ion batteries (LIBs) have been widely used in mobile phone, notebook, and hybrid electric or all electric vehicles owing to the advantages of high specific capacity, long cycle life and large energy density. However, the main commercial graphite as anode material possesses low theoretical specific capacity (372 mA h g^{-1}) and poor ratio performance, which are far below the needs of large-scale energy application and limit the development of LIBs. Therefore, there is an urgent need to replace the graphite anodes using advanced electrode materials with high specific capacity [1-3].

Herein, the porous nitrogen doped carbon (N-C)/Co_3O_4 nanocomposite was prepared successfully by using waste bamboo leaves as templates and reactants. The prepared method is facile and simple. The Co_3O_4 nanoparticles obtained with the average diameter of 150 nm were distributed on the surface of N-C fibers derived from bamboo leaves. This method exhibits recycling of resource and turning waste into treasure in an eco-friendly way. And the N element doped in carbon can enhance the conductivity of the product and provide more active sites, which benefits for improving the electrochemical performance. The discharge specific capacity of the N-C/Co_3O_4 composite is 887 mA h g^{-1} after 100 cycles at the current density of 100 mA g^{-1} and also exhibits a capability of 415 mA h g^{-1} at the high specific current density of 1 A g^{-1}, showing a high reversible specific capacity and good rate capability. With these outstanding performances, the as-synthesized N-C/Co_3O_4 composite may be a promising candidate anode material for LIBs..

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Asymmetric supercapacitors consisting of functional electrospun carbon nanofiber/manganese oxide electrodes with high power and energy densities

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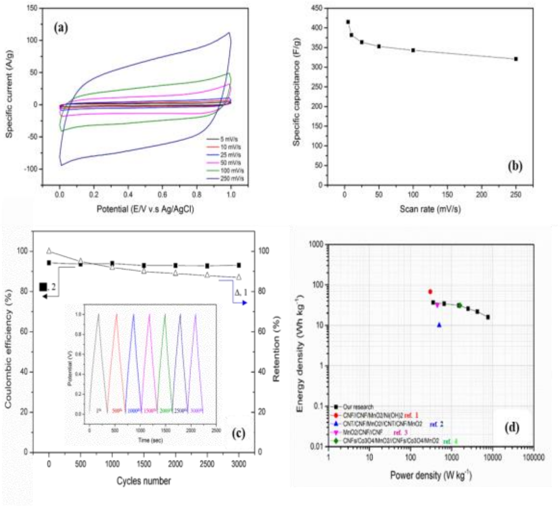
Carbon nanofibers modified with carboxyl groups (CNF-COOH) with good wettability and high porosity are homogeneously deposited with amorphous manganese dioxide (a-MnO_2) by potentiodynamic deposition for the application of asymmetric supercapacitors (ASCs). The acidic treatment successfully enhances the hydrophilicity of carbonized polymer nanofibers and facilitates the access of electrolytes within the CNF-COOH matrix. This modification favors the deposition of a-MnO_2 and improves the electron transport between a-MnO_2 and CNF-COOH. In this composite, a-MnO_2 homogeneously dispersed onto CNF-COOH provides desirable pseudocapacitance and the CNF-COOH network works as the electron conductor. The composite of CNF-COOH@MnO_2-20 shows a high specific capacitance of 415 F g^{-1} at 5 mV s^{-1}. The capacitance retention of this composite is 85% in a 3000-cycle test. An ASC cell consisting of this composite and activated carbon as positive and negative electrodes can be reversibly charged/discharged to a cell voltage of 2.0 V in 1 M Na_2SO_4 with specific energy and power of 36.7 Wh kg^{-1} and 354.9 W kg^{-1}, respectively (based on the total mass of two electrodes). These encouraging results make CNF-COOH@MnO_2 be promising for the ASC application.

Keywords: Carbon nanofibers, modified, amorphous manganese dioxide, asymmetric supercapacitors.



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Comparison different preparation methods for FeF_3/C composite cathode materials and its performance investigation

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Abstract

The work reported two different preparation methods for synthesizing $FeF_3 \cdot 0.33H_2O$/C composite cathode material. In order to further improve electrochemical performance of FeF_3, we add extra 15wt.%V_2O_5 and 5%carbon black additive into FeF_3, then sintered at 180°C for 12h to obtain the composite materials. The FeF_3 cathode materials were prepared by using $Fe(NO_3)_3$ and NH_4F raw materials via a ball-milled method and a solvothermal process. The characteristic properties were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffraction lighting spectroscopy (DLS), micro-Ramam spectroscopy, the galvanostatic charge-discharge method and the AC impedance method. It was found that the discharge capacity of ball-milled BM-FeF_3/C composite is 145.08 mAh g^{-1} at a 0.1C rate; in contrast, it is 192.22 mAh g^{-1} for Solvo--FeF_3/C composite prepared via a solvothermal process. It was discovered that the charge retention rate of BM-FeF_3/C composite and Solvo--FeF_3/C composite are 83.25% and 95.63%, respectively. It is due to the much smaller particle size and higher specific surface area. The AC impedance results also indicated the charge transfer resistance of Solvol--FeF_3/C composite (R_{ct}=103 ohm) shows much lower than that of BM-FeF_3/C composite (R_{ct}=179 ohm) after 30 cycle charge/discharge testing. The experimental results demonstrate here that our solvothermal process can be applied on FeF_3 material for the mass production. It also found that Solvo--FeF_3/C composite material is a promising high-capacity cathode material for Li-ion battery application.

Keywords: FeF_3, Solid-state method, Solvothermal process, Lithium ion battery, cathode material

Palladium Nanoparticles Immobilized Mesoporous Silica Spheres: An Electrochemical Sensor for Real Time Detection of Cancerous Cells via Hydrogen Peroxide sensing

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Studies associated with the development of efficient diagnostic techniques and curative remedies for cancer are of extreme significance owing to the elevated mortality rate caused by the disease. Early stage screening of this disease can help to put a check on troubles caused by it. Concerned to this, recent researches have affirmed the generation of reactive oxygen species (ROS) from cancerous cells and cancer associated fibroblast. Thus by tracking cellular ROS one can get an insight of various intracellular processes. Hydrogen peroxide (H_2O_2) is the quintessential non radical ROS prevailing in the cellular surroundings. Thus quantitative determination of cellular H_2O_2 by a sensitive and reliable technique can provide a clear idea of its role in cellular physiology and also provide a faster, reliant diagnostic assay for cancer. Herein this work we report the synthesis and fabrication of a non-enzymatic, amperometric H_2O_2 sensor, which can be employed to detect H_2O_2 released from cancerous cells. For this purpose palladium nanoparticles immobilized on sulfonic acid functionalized mesoporous silica spheres (Pd-SO_3H-MSS) is successfully synthesized and characterized using various physicochemical and electrochemical techniques. Further glassy carbon electrode modified with a thin film of Pd-SO_3H-MSS (GC/Pd-SO_3H-MSS) is employed for electrochemical reduction of H_2O_2 using amperometry technique with extremely low limit of detection (14 nm) and wide linear range (25 nm to 1 mM). Moreover, GC/Pd-SO_3H-MSS also proves its fruitful utilization for the real time detection of H_2O_2 released from human cervical cancer cells (HeLa).

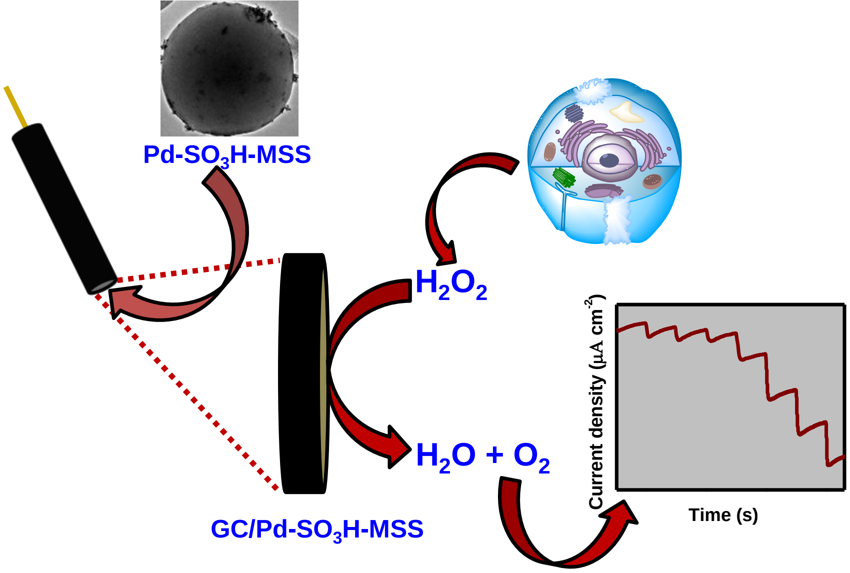

Figure: Schematic representation for the electrochemical detection of H_2O_2 released from cancerous cells

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N-type Amorphous Silicon Thin Film on 3D Current Collector as Negative Electrode for Li-ion Batteries

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Amorphous Si with n-type dopants is a promising candidate as anode for Li-ion batteries (LIBs) due to its high theoretical capacity of 4200 mAh/g, low potential *vs.* Li^+/Li and a possibility to enhance the electrochemical performance of LIBs due to increased electrical conductivity . Flat Si thin films with a thickness of more than 200 nm show a rapid capacity fade due to the film delamination from a current collector and further loss of electrical contact [1]. 3D structured Si anode has a large surface area and allows decreasing the thickness of the film without negatively affecting the areal mass loading of the electrode. However, development of 3D structure for Si material is doomed to failure since significant volume change upon operation of this anode any patterns experience destruction upon repeated cycles of charge/discharge [2-4]. Deposition of Si film on 3D current collector could solve these issues more effectively.

Herein, we reporte on a facile and cheap venue to prepare well performing Si thin film anodes with a possibility to scale up. The present study we focus on investigation of electrochemical performance of 400 nm thick n-type amorphous Si thin film anode deposited on Cu nanowires and graphene coated Ni foam 3D current collectors using magnetron sputtering. Si thin film on polished and rough Cu foils was studied as a reference. Raman spectroscopy, atomic force, transition and scanning electron microscopy accompanied the investigation in order to track the structure and morphology changes of Si anode. Both 3D anodes have exhibited similar performance with a high initial capacity of around 4000 mAh/g and a reversible capacity of around 2000 mAh/g upon 150 cycles at a voltage range of 0.1 – 1.5 V *vs.* Li^+/Li and 0.2 C rate. The detailed electrochemical results (rate capability, charge/discharge profiles, cycling voltammogram, impedance spectra) as well as synthesis routes and characterization details will be presented at the conference.

Acknowledgements
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Electrochemical Pesticide Sensors Based on Electropolymerized Metallophthalocyanines

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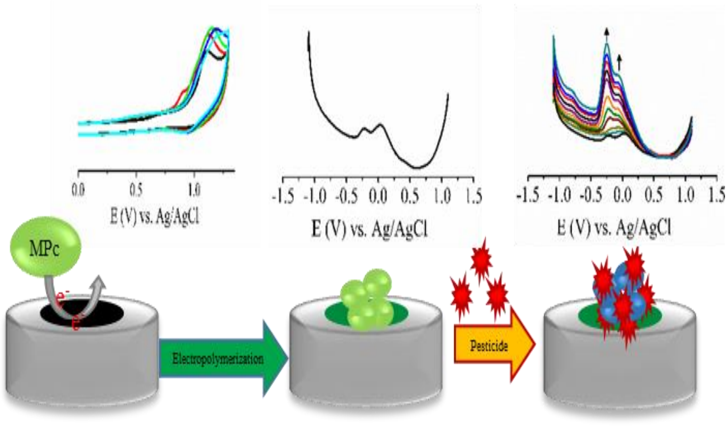
The rapid detection of pesticides in the environment, public places, or workplaces and the monitoring of individual exposures to chemical warfare agents is crucial for human health. For these purposes, numerous pesticide sensors working with different techniques were published. Among the techniques such as gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), optical approaches, and etc., the electrochemical methods were extensively preferred due to the one of the solution for disadvantages of the analyses at centralized laboratories, requiring extensive labor and analytical resources, and often results in a lengthy turnaround time [1-3]. With the electrochemical methods, long analysis time and extensive sample handling could be resolved with portability, rapid turnaround time, and cost-effectiveness. One of the functional materials presently studied as the selective and stable sensors are metallophthalocyanines (MPcs)[2,3] Due to the high thermal and chemical stabilities and excellent redox activities, MPcs have been extensively studied in various technological fields as well as sensor applications. Tailoring of MPc with different metal cations in the cavity of Pc and various substituents ensure synthesizing MPcs having desired properties for the target applications.

In this study, new metallophthalocyanines (MPcs) bearing redox active metal centers were synthesized. To increase redox activity of phthalocyanine ring (Pc), redox active Co(II), Cl-Mn(III), and Ti(IV)O metal centers were incorporated into the Pc cavity and CoPc(ma), Cl-MnPc(ma), and TiOPc(ma) complexes were synthesized. Redox active and electropolymerizable [2-(4-{[(1*E*)-(4-morpholin-4-ylphenyl)methylene]amino}phenyl) ethoxy] substituents on the Pc rings supplied electrochemically polymerization potential to the complexes. All complexes gave metal based reduction processes in addition to the Pc based processes. Moreover, redox active and conductive GCE/MPc(ma) electrodes were constructed with the electropolymerization of MPcs. Modified electrodes were investigated as potential pesticide sensors. Changing the metal center of the complexes significantly alters their sensing activities. While all complexes show interaction abilities for chlorophyros, fenitrothion, and methomyl. GCE/CoPc(ma) electrode sensed fenitrothion with good selectivity and sensitivity. Although GCE/TiOPc(ma) electrode also sensed fenitrothion with a good selectivity, the linear range of this sensing was very narrow. GCE/Cl-MnPc(ma) electrode sensed all pesticides with similar voltammetric responses, thus its selectivity is poorer than the others, although it has good sensitivity for the pesticides.



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Rhenium Complexes Based on 2-Pyridyl-1,2,3-Triazole Ligands: a New Class of CO_2 Reduction Catalysts

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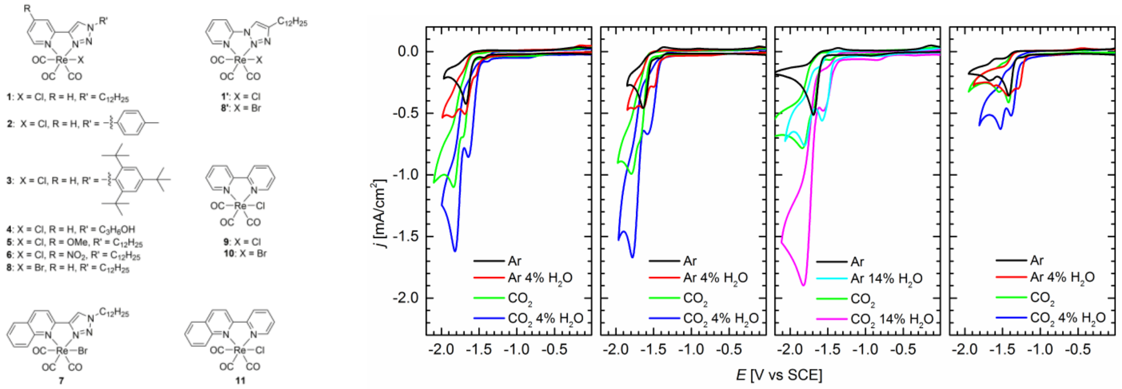
A series of $[Re(N^\wedge N)(CO)_3(X)]$ ($N^\wedge N$ = diimine and X = halide) complexes based on 4-(2-pyridyl)-1,2,3-triazole (pyta) and 1-(2-pyridyl)-1,2,3-triazole (tapy) diimine ligands have been prepared and electrochemically characterized. The first ligand-based reduction process is shown to be highly sensitive to the nature of the isomer as well as to the substituents on the pyridyl ring, with the peak potential changing by up to 700 mV. The abilities of this class of complexes to catalyze the electroreduction and photoreduction of CO_2 were assessed for the first time. It is found that only Re-pyta complexes that have a first reduction wave with a peak potential at around -1.7 V vs SCE are active, producing CO as the major product, together with small amounts of H_2 and formic acid. The catalytic wave that is observed in the CVs is enhanced by the addition of water or trifluoroethanol as a proton source. Long-term controlled potential electrolysis experiments gave total Faradaic yield close to 100%. In particular functionalization of the triazolyl ring with a 2,4,6-tri-tert-butylphenyl group provided the catalyst with a remarkable stability.



(Right) : Structure of rhenium complexes synthesized and investigated in this study. (left) : cyclic voltammograms of 1 mM of compounds 1, 2, 3, and 1’ (left to right panels) in MeCN with 0.1 M Bu_4NPF_6 under argon or CO_2 and with or without water recorded at 0.1 V·s^{-1} at a glassy carbon disk electrode at room temperature.

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Improved electrochemical performance of $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ cathode materials by ruthenium oxide surface modification

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Abstract

This work reported a simple solid-state method to prepare $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ composite materials by using LiOH、MnO_2、$Ni(OH)_2$、D-Tartaric Acid. The Tartaric Acid was used as a complex agent. The Ruthenium oxide (RuO_2) was used to modify $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ material via a simple sol-gel method. The characteristic properties were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), TEM, micro-Raman spectroscopy, the AC impedance method, and galvanostatic charge-discharge method. The 2032 coin half-cell was assembled to examine the electrochemical performance at various rates, i.e., 0.2C-10C. It was found that the discharge capacities of pristine $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ material is around 241.48 mAh g^{-1} at 0.1C rate; 178.59 mAh g^{-1} at 1C rate. In contrast, it was revealed that the discharge capacities of $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ cathode material coated with 4 wt.%RuO_2 shows 255.15 mAh g^{-1} and 210.01mAh g^{-1}at 0.1C and 1C rate, respectively. In addition, the long-term cycling performance for RuO_2 surface-modified Li-rich oxide composite was conducted at 0.1C rate for 30 cycles and 1C rate for 100 cycles; it was found that the charge retention ratio of 0.1C and 1C rates are 88.63%/cycle and 84.56%/cycle, respectively. The reason for higher discharge capacity and stable long-term cycling performance, it is due to the RuO_2 layer prevent the active material direct contact with electrolyte and excellent electron conductivity of RuO_2. It was found that RuO_2-coated $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ composite material shows a promising candidate for high capacity Li-ion battery application.

Keywords: $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$, composite cathode material, Solid-state method, D-Tartaric acid, Li ion battery, Ruthenium oxide

Corrosion behavior of thermally treated black Ni-P coatings

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In this work, Ni-P coatings have been deposited onto carbon steel substrates from a nickel sulfate electroless bath, as a source of nickel and sodium hypophosphite as a reducing agent. Electroless black nickel surfaces were obtained through etching of electroless nickel-phosphorous deposits with an oxidizing acid solution. EDX studies suggested that the coatings were constituted by 7% phosphorous. Surfaces predominantly covered by NiO were identified through XPS. This work aims to study the effect of the thermal treatment of hardening done to a black Ni-P coating on the corrosion resistance. These black surfaces are intended for absorption in solar concentrators. The heat treatment applied was a tempering carried out by heating the material at 500 °C and a subsequent sudden cooling with water. The procedure was repeated for three cycles. Corrosion resistances of black electroless nickel-phosphorus coatings with and without heat treatment were investigated by polarization measurements and electrochemical impedance spectroscopy (EIS) in 0.5M NaCl solutions at room temperature and without stirring. The equivalent circuit for electrochemical impedance measurement, on the corrosion resistance of black electroless Ni-P deposits, consisted of the following elements: resistance of solution (Rs), the charge transfer resistance of the coating (Rct) and a constant phase element. The results of these studies show an increase of corrosion resistance when the black Ni-P coating has been thermally treated.

Keywords: electroless, black Ni-P, Tafel plot, Electrochemical Impedance Spectroscopy.

Electrochemical Oxidation of effluents from desalting crude oil

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Water from the crude oil desalination process contains high concentrations of chlorides (>1200 ppm) and highly toxic aromatic hydrocarbons such as benzene and phenolic compounds, among others. In this paper, we present the use of electrochemical technology employing boron-doped diamond deposited on a silicon substrate (Si/BDD) electrode, to solve the problem of inadequate disposal of these effluents. Alternatively, the use of metal oxide electrodes has been evaluated to offer a technology through electrochemical oxidation via highly efficient active chlorine [1] and with the possibility of industrial scaling.

The evaluated samples were characterized using physicochemical methods, GC-MS and ICP. The analysis of $^{\bullet}OH$ was performed by spectroelectrochemistry, and the validation of the formation of such reactive species was carried out by fluorescence spectroscopy. Electrolysis at different pH values and current densities were performed in galvanostatic mode, and the efficiency of the process was evaluated by physicochemical and total organic carbon (TOC) analyses. Physicochemical analyses, GC-MS and ICP, indicated the presence of highly toxic organic and inorganic compounds, exceeding the maximum limits of concentration established by Mexican regulations.

The analysis of the radical $^{\bullet}OH$ showed a significant influence during the process of oxidation and transformation of chlorides to highly reactive chloro radical species. The results obtained showed that the organic pollutants were successfully destroyed, through a synergy of both the electrochemical incineration process and the active chlorine-mediated oxidation process.

To identify the effect of each process, the use of tertbutyl alcohol (50 mM) ($k = 6 \times 10^8\ M^{-1}S^{-1}$) [2] as a $^{\bullet}OH$ scavenger was implemented, finding out that the action of $^{\bullet}OH$ is minimal comparatively to generated electroactive chlorine species. With the optimal operating conditions ($pH = 8.5$, $j = 100\ mAcm^{-2}$, $t_r = 3$ h) a 98.2% mineralization rate was achieved on TOC, with the electrochemical mediated oxidation being the main reaction path and responsible for the degradation efficiency obtained. Electrochemical oxidation via active chlorine of effluents from the crude oil desalination process is technically feasible.

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Engineering Binary Ru-Sn Oxides as Bi-functional Catalysts for the Air Electrode of Rechargeable Zinc-air Batteries

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For rechargeable zinc-air batteries, the most important issue is to develop excellent catalysts for both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) on the air electrode. RuO_2 nanoparticle is one of the best OER catalysts in either acidic or alkaline solutions[1,2]. However, RuO_2 shows a poor activity in the ORR. In order to obtain a high-performance bifunctional catalyst for both the ORR and OER and to reduce Ru content to lower the cost, binary Ru-Sn oxides in various compositions are synthesized via a facile hydrothermal process. Ru-Sn oxide nanoparticles have been characterized by X-ray diffraction, transmission electron microscopic images, and N_2 adsorption-desorption isotherms analysis. From the TEM images, the particle size of Ru-Sn oxide nanoparticles is less than 10 nm. The electro-catalytic activities were measured by linear sweep voltammetry using a rotating ring-disk electrode. As shown in Figure 1, the full cell test under the air supply demonstrates that the peak power density has 100 mW cm^{-2} at current density is 190 mA cm^{-2} in alkaline media. The results of this study strongly support that binary Ru-Sn oxide nanoparticles are a promising bifunctional catalyst for the air cathode of rechargeable zinc-air batteries.

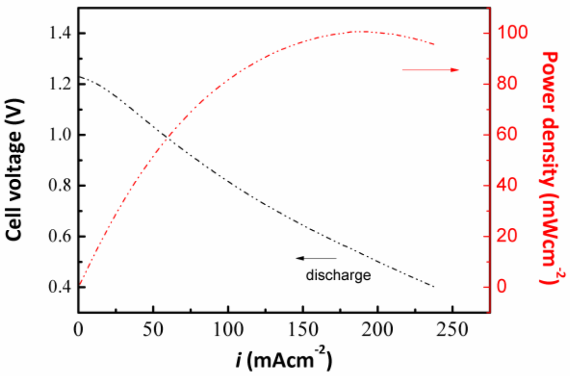

Figure 1. The full cell discharge curve and power density against the discharge current density measured in 6 M KOH + 0.2 M zinc acetate under an ambient air atmosphere.

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Highly Stable Carbon-Free Cathodes for Li-Air Batteries with Aqueous Alkaline Electrolyte: Electrochemical and Structural Investigations

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The operation of a secondary Li-air battery requires to run the battery in oxygen reduction reaction (ORR) as well as in oxygen evolution reaction (OER). OER represents the charge reaction and requires a sufficient catalyst for oxygen evolution. Currently carbon materials are widely used in cathodes of aqueous alkaline Li-air batteries due to their high electronic conductivity, stability, relatively low costs and catalytic activity towards oxygen reduction reaction (ORR) [1,2]. However, carbon-based cathode materials are non-stable in the potential range of OER as they start to corrode at potentials higher than open circuit voltage (OCV) [3,4]. Corrosion leads to high degradation corresponding to successive capacity loss and ultimately destruction of the cathode. To improve long-term stability and reduce side reactions such as H_2 and CO_2 evolution carbon-free bifunctional cathodes for aqueous alkaline Li-air batteries are of need [5,6]. In this poster we present cathodes with a combination of Ag or Ni as conductive additive and Co_3O_4. Those were prepared with a dry-processed and solvent-free preparation method [7]. Electrocatalytic activity regarding both ORR and OER was investigated by cyclic voltammetry (CV) for up to 300 cycles in half-cells (Fig.1). In addition structural and surface characteristics of the Ag/Co_3O_4 were investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). These combined measurements give new insights in the materials' oxidation states and the stability of Ag oxides in Ag/Co_3O_4 cathodes throughout a complete battery cycle [8]. Cathodes with the combination of Ag and Co_3O_4 show high activity for both reactions ORR and OER and a significant improvement in performance compared to both pure Ag and pure Co_3O_4 cathodes. Long-term tests show superior stability of the bimetal cathodes [6].

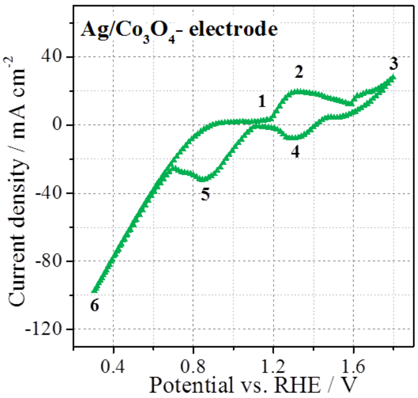

Fig.1: CV carried out in half-cell, 1 M LiOH solution, 25 °C

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Inherent electrochemical activity and stability of amorphous MoS_x films for the hydrogen evolution in the 0.6-13 pH range

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Transition metal dichalcogenides (TMDs) have attracted significant attention in the last decade in the electrocatalysis community as promising earth-abundant candidates to replace platinum group metal catalysts for the hydrogen evolution reaction (HER) in polymer electrolyte membrane electrolysers. A pioneering study demonstrated that the HER activity of TMDs only occurs at the edge sites, leaving the basal planes catalytically inactive.[1] As a result, several synthetic strategies have been proposed to obtain edge-abundant nanostructures.[2-5] Recent studies reported a one-step, substrate insensitive electrodeposition method to obtain amorphous MoS_x thin films with tunable stoichiometry from a $(NH_4)_2MoS_4$ aqueous solution.[6,7] While initial investigations have focused on the elucidation of the MoS_x electrodeposition mechanism and stoichiometry, critical aspects in catalysts benchmarking such as durability and long-term stability remain unexplored. Several reports not only have confirmed the influence of pH in the inherent electrochemical activity of TMDs[8] but also its effect in the long-term stability under operating conditions.[9] Herein we will present a comprehensive study of MoS_x thin films deposited on Si/Ti/Au substrates across the 0.6-13 pH range. Growth rate studies coupled with profilometry measurements enable the preparation of MoS_x films with controllable thickness. Plotting of the MoS_x redox peak potentials vs. operating pH demonstrates a correlation between the inherent MoS_x redox mechanisms and the final HER activity. Accelerated durability tests on several voltage windows monitored with ex-situ X-ray photoelectron and Raman spectroscopies inform of the electrochemically induced morphology and stoichiometry changes in the MoS_x films. Finally, stability tests (3000 cyclic voltammograms, maximum current density output= 10mA cm^{-2}) benchmark the optimum pH operation range for the prepared MoS_x films.

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Critical Roles of Electron Transporting Layer in Perovskite Solar Cells

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Organic-inorganic hybrid perovskite solar cells have attracted great attention due to their high power conversion efficiency (PCE) and low cost. To further improve the PCE and long term stability, interfacial engineering is very critical, especially for improving the property of electron transporting layer. Meanwhile, an anomalous hysteresis effect still exists, especially with the n-type TiO_2 as the electron extraction layer, which is typical in the perovskite solar cells. Herein, we focus on the optimization of the TiO_2 electron transporting layers including the compact layer and mesoporous layer. Considering the poor conductivity and charge extraction ability of TiO_2, we use Atomic Layer Deposition (ALD) technique to prepare compact layer and treat the mesoporous layer with $TiCl_4$ and Li salts. In detail, we prepare two kinds of TiO_2 compact layers using ALD and Spin-Coating (SC) methods and compare their influences on the hysteresis effect. By AC impedance spectroscopy study, we find that the ALD prepared compact layer is ultra-thin with uniform morphology and show small interfacial capacitance, C_{eff} and large recombination resistance, R_{rec}, meaning reduced charge accumulation and accelerated electron transport, which would relief the hysteresis effect. On the other hand, $TiCl_4$ treating is found to be necessary to enhance the connectivity of the TiO_2 nanoparticles as well as the between the compact and mesoporous layers. The $TiCl_4$ treating also ensures a continuous and dense compact layer after high temperature annealing of the mesoporous layer. Li salts treating is found to effectively improve the conductivity and charge extraction ability of TiO_2, thus enhancing the PCE and decreasing the hysteresis effect. Finally, using the improving electron transporting layer, we can get a best PCE of 19.9% in the reverse scanning and 19.1% in the forward scanning with scanning rate 250 mV/s. [1, 2]

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TiO_2 Single Crystal electrodes for in-situ SERS Investigation of TiO_2/N719 Interfaces

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Semiconductor−molecule interfaces are an important class of systems where light absorption and charge separation can take place. Although this interface has been intensely investigated for promoting its photovoltaic performance, most of the employed electrodes are polycrystalline nanoparticle films with irregular morphology and ambiguous defects[1-2]. Single crystal electrodes, with well-defined surface structure, are more suitable for investigation of detailed interfacial interactions. However, for a wide bandgap semiconductor such as TiO_2, the enormous bulk resistance of large-size single crystalline electrodes hinders their large-scale application.

In this work, we adopt an argon sputtering−annealing method to prepare rutile(110) single crystalline surface with sufficient conductivity for electrochemical experiments by creating bulk oxygen vacancies and increasing charge carriers. This semiconductor single crystalline electrode was used to investigate the TiO_2/N719 interface, which is the most important interface in dye-sensitized solar cells (DSSCs). Surface enhanced Raman spectroscopy (SERS) under electrochemical condition, utilizing the electromagnetic enhancement of Au@SiO_2 core−shell nanoparticles, is employed to detect the adsorption configuration and conformational change of the N719 molecule.[3] Comparative investigations are carried out on nanoporous P25 TiO_2 electrodes. The potential-dependent Raman shift of ν(N=C=S) at rutile (110)/N719 interface suggests that the binding of the SCN group of N719 to the TiO_2 surface is the intrinsic nature of the TiO_2−N719 interaction. Hydrogen bonding between COOH and the TiO_2 appears to be more favorable on the atomic flat rutile TiO_2(110) surface than on the surface of nanoporous P25 as revealed by the stronger Raman shift of ν(C=O) (COOH) on the former. The volcanic type potential dependent Raman intensity of the charge transfer sensitive C-C inter ring stretching mode reveals that photo induced charge transfer (PICT) occurs for both P25 and rutile(110) ignoring surface morphology, and the potential to achieve PICT resonance depends on the band structure of the semiconductor as supported by the Mott-schottky results. This work demonstrates that the large-size single crystalline TiO_2 can be used as electrodes in electrochemical investigations, EC-SERS studies and semiconductor/dye interfacial studies.

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In Situ Raman Spectroscopic Studies on Lithium Electrode/Electrolyte Interfaces Based on Different Plasmon-Enhancement Strategies

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Interest in the study of metallic lithium (Li) is rapidly increasing during the recent years because of its potential applications in the secondary batteries. Li is thermodynamically unstable, which makes the Li/electrolyte interfaces very complex. It is widely believed that a solid electrolyte interphase (SEI) film formed on the surface of Li plays important role in the electrochemical behavior of Li electrodes in the Li-based batteries[1]. Hence, understanding the evolution processes of the Li/electrolyte interfaces is important to enhance the performances of Li-based batteries. Due to the ultra-high detection sensitivity, surface enhanced Raman spectroscopy (SERS) has been one of the powerful spectroscopic techniques for the investigation of the electrode/electrolyte interfaces[2]. However, for the existing reports in Li-based batteries, only a few of *ex situ* SERS have been used to detect the Li/electrolyte interfaces[3,4], which is lack of dynamic and comprehensive analysis for the interface evolution processes and leads to obtaining the partial and oversimplified information. Herein, with emphasis on methodology, we develop three plasmon-enhanced strategies based on different plasmonic sources, including surface plasmon resonance (SPR) from Li itself or other SERS-active metals, for *in situ* SERS study on the Li/electrolyte interfaces.

First, nanostructured Li is expected to support SERS effect, which can be directly used to detect the interface processes without introducing extra SPR-active metals. The nanorod Li arrays prepared by electrodeposition of Li on Cu in $LiPF_6$-containing esters electrolyte with trace H_2O additive appear to be effective for obtaining the SERS effect[5], providing a convenient *in-situ* method to follow the SEI evolution process. However, the strength of SPR for Li is closely correlated with the shape and size of the nanostructures, while Li electrodes with flat surface offers advantages over the counterpart with nanostructure when used in Li-based batteries. Hence, the obtained spectroscopic information from Li electrode/electrolyte interfaces based on the SPR of Li itself are not yet representative. Second, noble metal, such as Au and Ag, is one of the high SERS-active materials with an average SERS enhancement factor of 10^5–10^7. By means of the SPR effect of Ag, *in situ* SERS studies on the formation process of SEI film was performed before and after Li deposition on the Ag nanoparticles-modified Ag electrode surface in esters electrolyte. Nevertheless, the identification of the SEI compositions can be easily done only before the Li deposition on Ag surface. Once the Li deposition happened and Li–Ag alloys were formed, the characterized peaks of SEI film disappeared immediately and the evolution of SEI after Li deposition could not be detected, which is ascribe to the dielectric constant change of Ag after the lithiation. Third, since not subject to the substrate generality, shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) is a more effective technique for SEI investigation[2]. The SERS-active Au or Ag nanoparticles were coated with an inert shell of either SiO_2 or Al_2O_3, and spread them as a Raman signal amplifier over a Li anodes. The ultra-thin coating isolates the inner nanoparticles and prevents them from direct contacting with the electrolyte. In this way, the evolution of the SEI on the Li surface could be precisely detected in real time. The above-mentioned three methods complement each other, which is highly desirable for revealing the formation mechanism of SEI on the Li surface.

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A new probe of the electrochemical interface: surface magnetism

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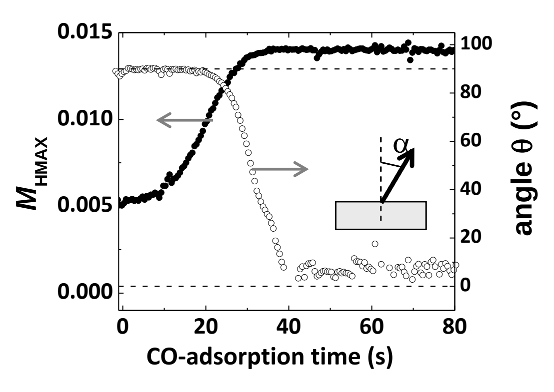
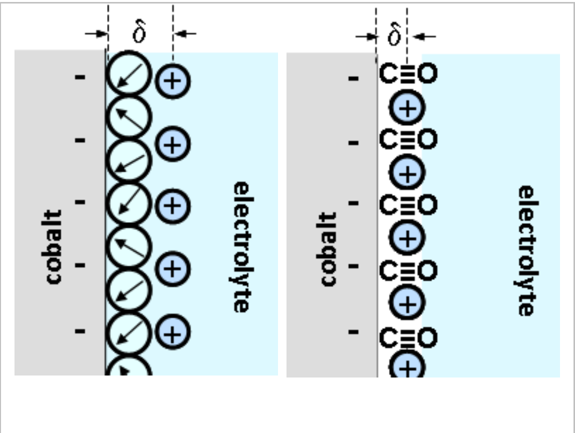
We present a new method to probe electrode surface chemistry and double layer structure at the electrochemical interface [1]. This method is based on the high sensitivity of the magnetism to the surface chemistry of magnetic electrodes. For this purpose, we designed a new setup where the magnetic properties (magnetization amplitude and orientation) can be measured in-situ on electrodes in an electrochemical flow cell. The measurement time resolution is ~0.5 s and its sensitivity is a small fraction of chemically modified electrode surface.

We will give several examples in the case of Co/Au(111) electrodes showing the insights into the electrochemical interface provided by this powerful probe. In the first example, we probe the adsorption of CO on Co. Since CO adsorption induce a 90° change of the magnetization orientation of the Co electrode, the CO adsorption kinetic could be measured as shown in the plot of the Figure below. We will also show that this probe is sensitive to the initial step of Co oxidation in alkaline electrolytes [2]. In the second example, we demonstrate that the magnetic properties are strongly modified by the hydrogen evolution reaction (HER) at CO-covered Co electrodes. We exploit this correlation to study the HER reaction mechanism. In the third example, we take advantage of the sensitivity of this probe to the electric field present at the electrochemical interface to unravel the structure of the double layer at H- and CO-covered Co electrodes (see drawing below) [3].





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Carbon composite bipolar plate for redox flow battery

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Redox flow battery (RFB) is electrochemical energy conversion and storage system by the oxidation and reduction reaction of electrolyte active materials. In recent years, much attention has been focused upon the research and development of redox flow battery because of its low cost, long cycle life, deep-discharge capability, greater energy efficiency and less impact on environment. In addition, this battery employs the same electrode and bipolar plate on both sides of the cell. Like other batteries, electrodes and bipolar plate are the key components of RFB. The bipolar plate plays role as a substrate for electrode. Therefore, the bipolar plate material for RFB should have low bulk resistivity as well as good flexibility to increase the electrochemical activity. The cycling performance of RFB also depends on strongly the electrochemical properties of electrode and bipolar plate materials. In this work, we prepared carbon composite bipolar plate using graphite powder, carbon black and polypropylene. This carbon composite bipolar plate showed a high electrical conductivity and good flexural strength. Therefore, it is expected that this bipolar plate can be used to increase power density and energy efficiency of redox flow batteries.

Determination of the Working Potential Windows of Electrode Materials for Capacitance Deionization and Invert Capacitance Deionization

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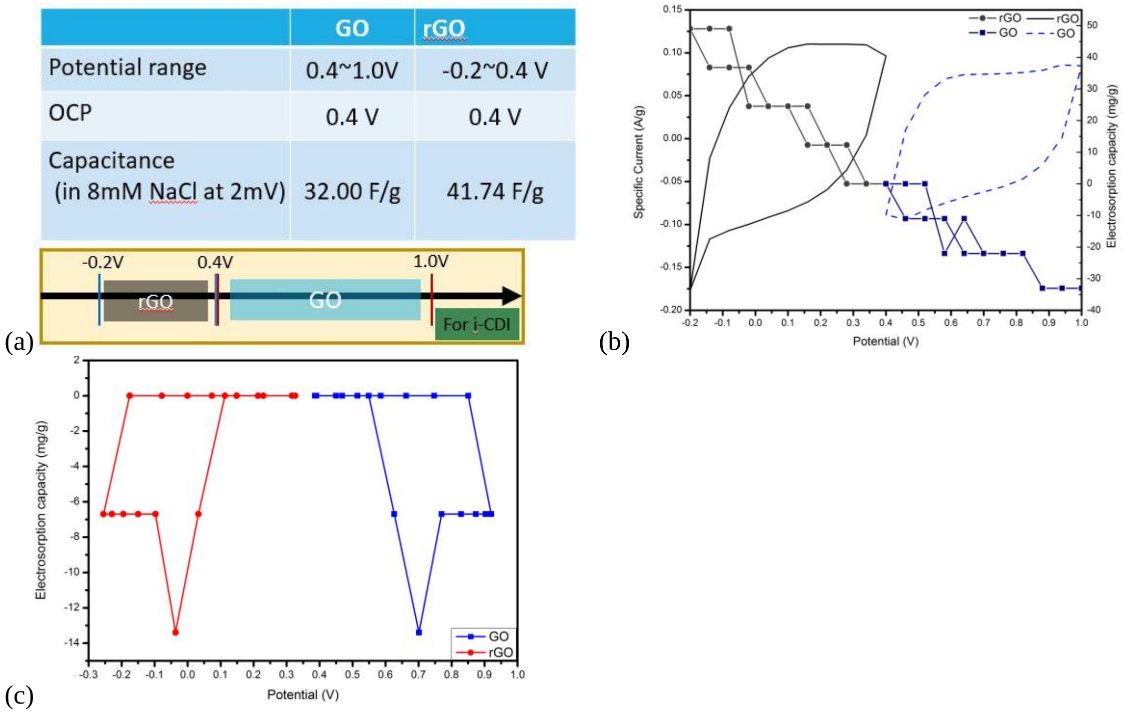
Abstract

Capacitive deionization (CDI) is an alternative and new technology for desalination, which is based upon reversible salt adsorption–desorption at porous carbon electrodes, such as activated carbons and graphene. Surface modification of graphene oxide and reduced graphene oxide electrodes can shift their potential of zero charge for ion adsorption/desorption. When the material surface provides a negative charge, its potential of zero charge (E_{PZC}) will be positively shifted, which is good for ion adsorption. Such unique characteristics can be employed for the invert capacitive deionization (i-CDI) operation [1]. To investigate the effects of surface properties and capacitance on the performance and stability of deionization, understanding what kind of materials [2] suitable for the anode and cathode is very important in the CDI and i-CDI applications.

However, there is no suitable strategy to judge the operating potential window for electrode materials of CDI and i-CDI systems. In this work, a novel reference electrode is designed to determine the potential window of operation and to gain the understanding of anions and cations adsorption/desorption in different potential windows. Finally, the most suitable potential windows of positive and negative electrodes for CDI and i-CDI applications were determined for different electrode materials.



	GO	rGO
Potential range	0.4~1.0V	-0.2~0.4 V
OCP	0.4 V	0.4 V
Capacitance (in 8mM NaCl at 2mV)	32.00 F/g	41.74 F/g

Figure 1. (a) The potential windows of GO/rGO against a reference electrode for the i-CDI system. (b) A plot of electrosorption capacity and specific current as a function of potentials for graphene oxide and reduced graphene oxide. (c) A plot of electrosorption capacity as a function of potential for the asymmetric capacitor consisting of graphene oxide and reduced graphene oxide as the cathode and anode for the i-CDI operation.

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Visible-Light-Driven Water Oxidation at Polarized Liquid-Liquid Interfaces

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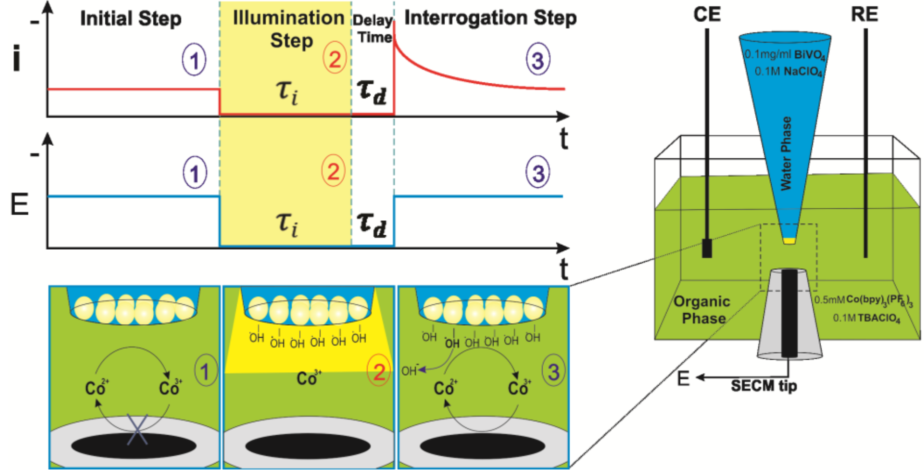
Interfaces between two immiscible electrolyte solutions (ITIES) are a promising model mimicking some functional biomembranes in nature (charge carrier separation by two interacting photocenters - z-scheme) and offer novel opportunities for catalyst regeneration or exchange at the interfaces of liquids [1].



We studied O_2 evolution by hyperbranched nanocrystaline $BiVO_4$ dispersed in water phase. The driving force of this photo-induced ET reaction can be controlled easily by the chemically polarization of the L/L interface, which then clearly influences the efficiency of the parallel reaction of photo-generated hole-driven water oxidation by increasing the O_2 evolution rate [2]. $[Co(bpy)_3](PF_6)_3$ is used as an electron-acceptor compound in organic phase dramatically inhibiting fast unfavorable electron-hole recombination, analogous to the functionality in the electron transport chain between PSII and PSI 3]. The high surface area of nanosized $BiVO_4$ crystals with a specific hyperbranched structure [4] along with the defect free liquid/liquid (L/L) interface could overcome the inherent poor electron transport properties of $BiVO_4$ materials and minimize the interfacial recombination of photo-excited electrons-hole pairs by rapidly transferring them to reactants in the adjacent liquid phases. This systems also allows to interrogate the photoelectrochemical reaction by oxidation of $[Co(bpy)_3]^{2+}$ at a detector microelectrode (ME in the organic phase) in a scanning electrochemical microscope (SECM).

The study of such systems is particularly efficient with a co-linearly arranged micropipette mechanically stabilizing the L/L interface and a microelectrode for detection. Firstly, the micropipette can be prepared with orifices much smaller than the Au ME so that very high collection efficiencies for $[Co(bpy)_3]^{2+}$ is attained. Secondly, the capillary can also be used as a wave guide for an approximately homogeneous illumination of the L/L interfaces. Thirdly, such a micro L/L interface can be used as substrate for the surface interrogation mode of SECM (SI-SECM) enhanced by new experimental routines to allow pulses of different signals (potentials, light source, switches). This mode allows quantitative assessment of adsorbed hydroxyl radicals ($OH^\bullet$) at the surface of nanocrystaline $BiVO_4$ substrate as previously demonstrated on solid-liquid interfaces [5]. In the interrogation step, the ME-generated titrant (Co^{2+}) reacts with adsorbed hydroxyl radicals.

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Preparation of graphene oxide coated $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ by self-assembly process and its electrochemical properties study

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Abstract

The work reports the preparation of high-capacity $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (Li-rich oxide) composite cathode material by a solid-state ball-milled method. The as-prepared Li-rich oxide was further carried out by a surface modification using graphene oxide. $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$/graphene oxide (GO) composite material was synthesized via an electrostatic self-assembly process. The characteristic properties were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), Transmission electron microscopy (TEM), micro-Raman spectroscopy, the galvanostatic charge-discharge method and the AC impedance method. It was found that the discharge capacities of pristine $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ material are 217.80, 215.85, 204.07, 173.31, 134.38, 115.81, and 84.27 mAh g^{-1} at 0.1C, 0.2C, 0.5C, 1C, 3C, 5C, and 10C, respectively. In contrast, it was revealed that the discharge capacities of 1wt.%PDDA-3wt.%GO-coated $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ composite material show 253.10, 226.84, 211.01, 195.18, 166.35, 144.61 and 97.35 mAh g^{-1} at 0.1C-10C, respectively. In terms of the long-terms cycling properties, we found that the discharge capacities at 0.1C start at 253.23 mAh g^{-1}, then decline to 216 mAh g^{-1} after 30 cycles. It shows excellent charge retention rate (ca. 93.6%). Moreover, it was found that the discharge capacities at 1C start at 178 mAh g^{-1}, then gradually decline to 169.55 mAh g^{-1} after 100 cycles. It shows excellent charge retention ratio (ca. 94.84%). The results demonstrate here that our solid-state method and GO self-assembly method can be applied on Li-rich oxide material for the Li-rich oxide composite mass production. In summary, itt also found that GO-coated $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ composite material is a promising high-capacity cathode material for Li-ion battery application.

Keywords:

$Li_{1.2}Ni_{0..2}Mn_{0.6}O_{2,}$ Composite cathode material, Solid-state method, Surface-modified, Electrostatic self-assembly, Graphene oxide (GO), Li ion battery

Aluminium Micromachining via Mass-Transfer Limited, Electrochemical Dissolution in Phosphoric Acid

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Aluminium is widely used as a substrate for the micromachining of gas-phase microreactors due to its high thermal conductivity, easy machinability and the possibility to form surface layers of highly ordered, porous aluminium oxide, which act as support layers for the deposition of noble metal catalysts [1,2]. Combining wet electrochemical etching and photolithography, so-called Through-Mask Electrochemical Micromachining (TMEMM), is seen as a way to fabricate microreactors in large quantities at low cost [3]. Concentrated phosphoric acid is a suitable electrolyte for TMEMM of aluminium, because mass-transfer limited, electrochemical dissolution at elevated temperatures leads to a reflective surface with sub-micrometer roughness [4]. However, at present few studies exist [5,6], in which the influence of TMEMM process parameters such as applied potential and mass transfer conditions on the resulting depth, width, shape profile and uniformity of machined microchannels is investigated and how variations therein affect the performance of microreactor devices.

In this work, aluminium discs were electrochemically dissolved through photoresist masks in 85% H_3PO_4 at 75°C using a custom-made rotating disc electrode setup. The influence of applied potential, cumulative passed charge and rotation rate on the dimensions, shape profile and uniformity of the resulting microchannels was studied and compared with a shape evolution model based on diffusive mass transfer [7]. The channels and cross-sections made thereof were characterized via scanning electron microscopy (SEM), light microscopy and optical profilometry. The experimental and model results agree well with each other in terms of the ratio of vertical to lateral material removal, the resulting channel dimensions and the overall shape profile. However, SEM images show slightly more undercutting than is expected, possibly due to the presence of an initial air-formed oxide film between the substrate and the photoresist mask. Nonetheless, preliminary results on the machining of complex microfluidic structures demonstrate that TMEMM of aluminium is a feasible alternative to other micromachining techniques (Figure 1).

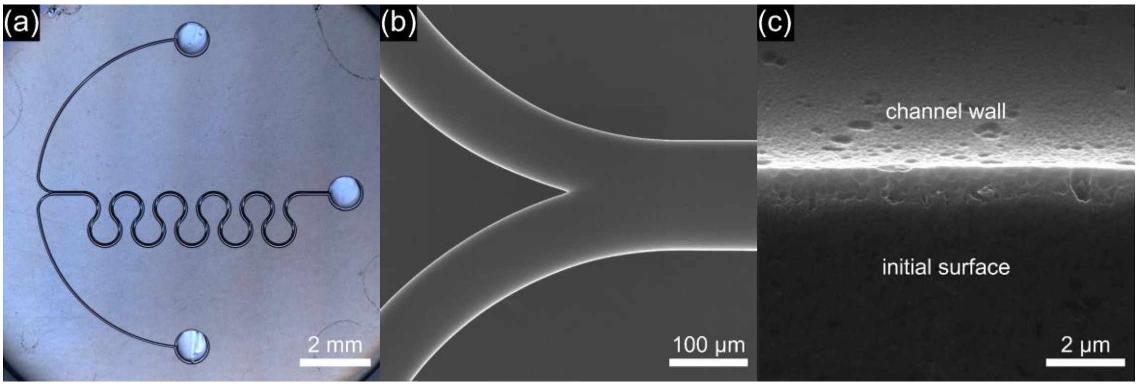

Figure 1: (a) Exemplary microchannel structure consisting of two inlet channels, a y-mixer tee and a serpentine channel, (b) SEM image of the y-mixer tee, (c) SEM image showing the channel edge.

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Electroanalytical Method for Isoprocarb Pesticide Using a Boron-Doped Diamond Electrode

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Isoprocarb (2-Isopropylphenyl methylcarbamate, IPC) is a carbamate insecticide used worldwide since 1970 in agricultural and cotton spraying [1]. In this work an electrochemical method to quantify IPC by Differential Pulse (DP) voltammetry using a Boron-Doped (BDD) sensor pre-treated cathodically (+3 V for 5 s followed by –3 V for 300 s) is proposed. The IPC exhibits a single oxidation signal around 1.7 V vs. Ag|AgCl|KCl(3 mol L^{-1}), as shown in Fig. 1A. The influence of pH over the IPC oxidation process was evaluated using cyclic voltammetry from 2 to 5 and no dependence was observed, Fig. 1A. The Fig. 1B shows the DP voltammograms recorded for successive aliquots addition of an 1.00 mmol L^{-1} IPC stock solution in acetate buffer solution (pH 5) and the peak current values were used to plot the analytical curve (inset Fig. 1B). The DP voltammetric parameters used were 8 mV step potential, 70 mV amplitude potential and 50 mV s^{-1} scan rate. The linear range obtained was between 2 to 167 µmol L^{-1} (R^2 = 0.9986), the detection and quantification limits were calculated as 1.0 and 3.3 µmol L^{-1}, respectively. This proposed method is the first electroanalytical method for directly quantification of IPC without the need of a derivatization process or the use of a biosensor showing that this method is a very promise for routine analysis.

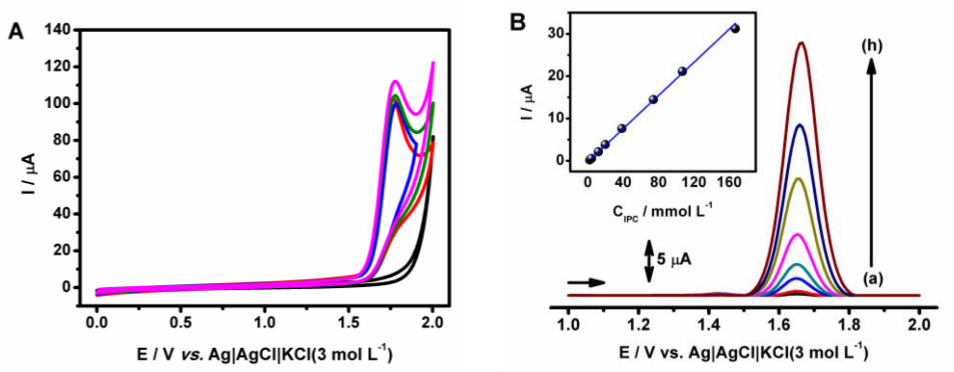

Fig. 1. (A) Cyclic voltammograms recorded in the presence of 0.5 mmol L^{-1} IPC solution in 0.1 mol L^{-1} phosphate buffer, pH 2 (—) and pH 3 (—); 0.1 mol L^{-1} acetate buffer (I = 0.1 mol L^{-1}), pH 4 (—) and 5 (—) and in the absence of IPC, pH 5 (—); scan rate = 100 mV s^{-1}. (B) DP voltammograms for successive additions of a 1.00 mmol L^{-1} IPC stock solution in 0.1 mol L^{-1} acetate buffer (pH 5): 2.00 (a); 3.98 (b); 11.9 (c); 19.6 (d); 38.5 (e); 74.1 (f); 107 (g); 167 (h) µmol L^{-1}. The DP voltammetric parameters: step potential = 8 mV, amplitude potential = 70 mV and scan rate = 50 mV s^{-1}. Inset: analytical curve.

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Non-enzymatic Acetylcholine Sensor Based on the Low Energy Nitrogen Ion Beam Irradiation on Tungsten Trioxide Thin Films

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Acetylcholine (ACh), the first identified excitatory neurotransmitter, and is involved in neurotransmission for the central and peripheral nervous systems. It plays an important role in brain cholinergenic system which affects attention, learning and memory, sleep, and arousal. The unstable regulation of ACh concentrations causes some neuropsychiatric disorders such as Parkinson's and Alzheimer's diseases, myasthenia gravis, progressive dementia and schizophrenia. Therefore, more sensitive and accurate measurement methods of ACh have received remarkable importance in neuronal cholinergic system research. Among various traditional methods for ACh detection, electrochemical non-enzymatic ACh sensors can allow for simple preparation and storage, afford good stability against denaturation, and provide effective enzyme-like catalysis over a wide pH and temperature range [1]. Metal oxides nanostructures have recently aroused tremendous interests in a broad range of functional studies and technological applications. Among nanostructured oxides of metals, tungsten trioxide (WO_3) is a n-type semiconductor with a wide band-gap energy range and possesses distinctive features of structural flexibility, functional biocompatibility, enhanced electron-transfer kinetics, non-toxic properties, outstanding chemical stability, low cost and size and shape dependency of reactivity, high specific capacitance, enhanced electrochemical activities [2-4].

In the present work, a novel non-enzymatic ACh sensor was developed based on low energy nitrogen ion beam (100 keV N^+) irradiated on WO_3 thin films modified indium tin oxide (ITO) electrode. WO_3 thin films deposited on ITO substrates by spin coating technique was subjected to low energy ion beam irradiation under different fluences ($1x10^{14}$ to $1x10^{17}$ ions/cm^2) and the products were characterized by powder XRD, FESEM, PL and Hall Effect measurements. The optimum fluence of N^+ ($1x10^{15}$ ions/cm^2) irradiated WO_3 thin films exhibit enhanced crystallinity, enriched surface defects and mobility with kidney-shaped morphology. The negatively charged N^+ ion irradiated on the surface of WO_3/ITO electrode showed comparative studies on the attraction towards $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$ electrolyte by cyclic voltammetry studies. Compared with pristine and other irradiated WO_3/ITO, the optimum fluence of N^+ ($1x10^{15}$ ions/cm^2) irradiated WO_3/ITO displayed higher electrocatalytic activity towards ACh detection in 0.1 M KOH solution. The diffusion coefficient and catalytic rate constant involved in the electro-oxidation of ACh at the active sites of N^+ irradiated tungsten species were reported. The fabricated sensor showed a high sensing performance with a sensitivity of 60.57±0.62 mAM^{-1}cm^{-2} over a wide linear range of 0.1-8000 µM and lowest detection limit of 23 nM. The proposed Ach sensor showed an excellent selectivity, long-term high stability, good reproducibility with satisfactory recoveries.

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Evaluation of the redox status of the human placenta using electrochemical microdevices

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The knowledge of the human placenta development is of major importance because it allows to improve the early screening and the care of major pregnancy pathologies associated with placental dysfunction and fetal growth restriction (FGR). During the development of the human placenta, important modifications of the placenta environment occur including a rise of the dioxygen levels from about 20 to 60 mmHg during the first pregnancy trimester[1]. This modification can induce variations of the redox status of the placenta leading to harmful pathologies. It is therefore interesting to evaluate in real time the impact of dioxygen on the redox status of the placenta and to explore this impact in pregnancy pathologies.

Our strategy relies on the conception and implementation of electrochemical sensors in cell culture platforms and microfluidic devices, to finely control the environment of biological cells and mimic biological conditions. The evaluation of the redox status of the placenta was achieved by designing electrochemical miniaturized sensors that selectively detect targeted analytes: reactive oxygen and nitrogen species (ROS/RNS). This approach helps in bringing close information on the extra cellular diffusion and dynamics of secreted analytes as soon as they are formed from one particular part of the cell culture. In addition, the electroanalytical techniques allow to monitor in real time the flux and the quantities of the targeted analytes[2,3].

We report here on the design and implementation of miniaturized sensors inside cell culture wells and also integrated inside micro channels for the detection of both nitric oxide (NO) and hydrogen peroxide (H_2O_2) (Fig. 1) that will be used as biological markers of the redox status of the placenta. Two types of electrode surface modification were developed and optimized to get sensitive and selective amperometric detection of both analytes *in vitro*. Then, the performances of both sensors were evaluated in cell culture medium. Finally, NO and H_2O_2 biocompatible sensors were optimized for the simultaneous and real time detection of both analytes in explants of human placenta and in cell culture models.

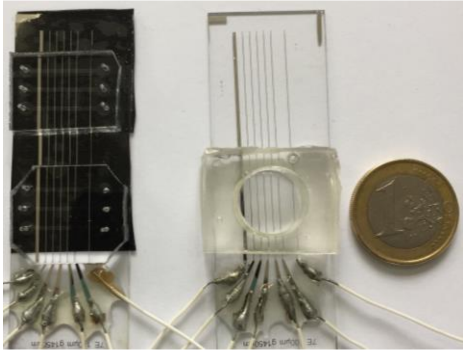

Figure 1. Photo of PDMS-glass assembly for ROS/RNS in vitro detection, in a well cell culture (a) and a micro channel of a microfluidic device (b) implemented with arrays of microband electrodes screened in the bottom of the vessels.

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Oxygen Reduction Reaction Activity for Vacuum-Deposited Pt-Monolayers on Metal Single Crystal Substrates

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M@Pt (M = Pd, Au, etc.) core-shell catalyst is one of the promising cathode electrode materials for polymer electrolyte fuel cell (PEFC) from the view-points of a great potential to reduce Pt usage and to enhance the oxygen reduction reaction (ORR) activity of Pt. ORR activity enhancement could be derived from electronic state changes induced by surface lattice strain of Pt, so-called strain effect and Pt-shell on metal or alloy cores depict volcano-shape activity plot depending on type of core-elements [1]. However, we have recently reported that activity of Pt-monolayers on core-metals is significantly affected by the Pt-shell surface and core-shell interface structures. Therefore, well-defined Pt-epitaxial layers on single crystal core substrates should be needed for clarifying genuine activity of the core-shell structures [2]. In this study, we investigate ORR activity of vacuum-deposited Pt-monolayers on various metal single crystal substrates and discussed effect of core-metal elements on the activity.

Deposition of Pt-monolayers were conducted by molecular beam epitaxy (MBE) in ultra-high vacuum (UHV). We used M(111) (M=Pd, Rh, Ir) as single crystal substrates. After surface cleaning by repeating cycles of Ar^+ sputtering and subsequent annealing, 2 and 4ML-thick Pt was deposited onto the substrates by an electron-beam evaporation method at 573 K (Pd) or 673 K (Rh, Ir). The resulting surface structures were verified with reflection high-energy electron diffraction (RHEED), scanning tunneling microscope in UHV (UHV-STM), and low-energy ion scattering (LEIS). Then, the prepared samples were transferred without being exposed to air to an electrochemical system set in a N_2-purged glove box. Cyclic voltammogram (CV) of the samples were recorded in N_2-purged 0.1 M $HClO_4$, and, then, linear sweep voltammetry (LSV) was conducted by using a rotating electrode (RDE) method after saturating the solution with O_2. The ORR activities were estimated by kinetic-controlled current density (j_k) at 0.9V vs. RHE by using Koutecky-Levich plots.

Fig.1 summarizes ORR activities for *n*ML-Pt/M surfaces. Although all the Pt/M surfaces show much higher activity than Pt(111), the activity enhancement factors are highly depend on core-elements. Order of the enhancement factor is as follows irrespective of Pt-shell thickness.

Pt/Rh > Pt/Ir > Pt/Pd > Pt

Especially, 2ML-Pt/Rh shows j_k values of 21 mA/cm^2 at 0.9 V which is ca. 31 times higher than Pt(111). On the other hand, degree of lattice mismatch between Pt and M substrate completely follow to the above activity order. Therefore, the result indicate that the activity enhancement of the single crystal Pt/M catalysts strain mainly stem from compressive strain in Pt derived from the lattice mismatch and the strain in well-defined Pt/M core-shells interface lead to the unusual activity enhancement.

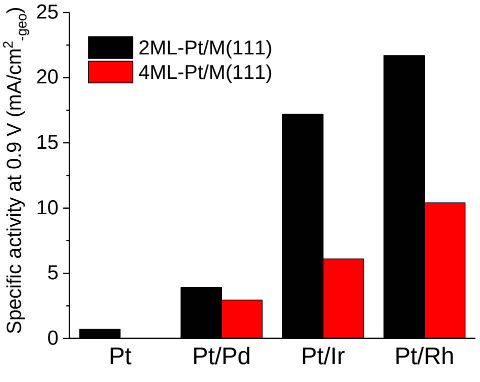

Fig.1 ORR activities of *n*ML-Pt/M(1111) surfaces

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Novel Alkaline Bifunctional Polymer Electrolytes for Supercapacitors

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In this study, the sticky copolymer polyurethane-polyacrylic acid (PU-PAA) which can act not only as an electrolyte in supercapacitor but also as a binder for both electrodes has been successfully synthesized from polyacrylic acid (PAA) backbone cross-linked by polyurethane (PU). PAA chains act backbone in the copolymer, which increases the density of carboxyl groups and promotes segmental motion. Increasing the content of carboxyl groups enhances the water absorption capability to increase the ionic conductivity. The cross-linked agent, PU chains, not only improves the water retention to avoid the release of water but also provides the sticky property to act a binder for both electrodes. The cross-linked PU-PAA copolymer gel electrolyte exhibits an ionic conductivity greater than 10^{-2} S cm^{-1} in various alkaline supporting electrolytes. According to electrochemical analysis, the carbon paper electrodes after acidic treatment with PU-PAA copolymer in 1 M KOH gel electrolyte system demonstrate an excellent electrochemical behavior. Its areal specific capacitance can reach 223 mF cm^{-2} at 10 mV s^{-1} and 232 mF cm^{-2} at 1 mA cm^{-2}. In the electrochemical impedance spectroscopy analysis, the carbon paper supercapacitor with our PU-PAA copolymer gel electrolyte demonstrates a lower contact/charge-transfer resistance (0.78 Ω) than those using a commercial PAA polymer (3.5 Ω).

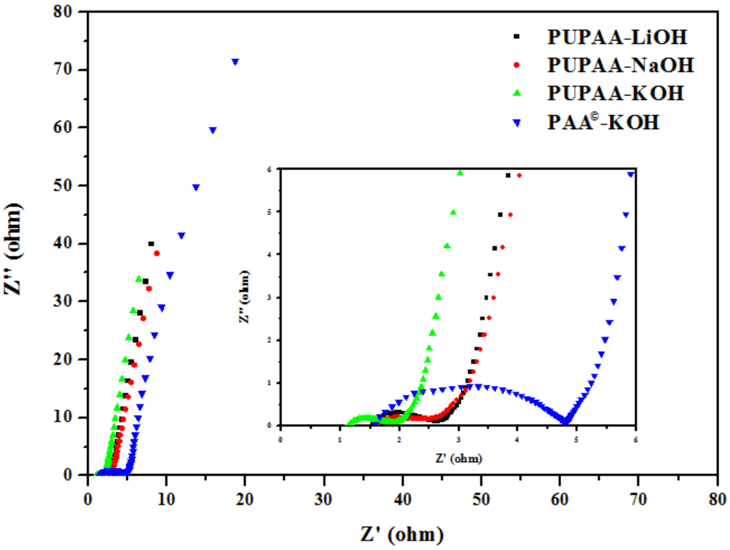

Figure 1. Nyquist plots of a symmetrical cell in various polymer electrolytes.

Influence of Cu contents on electrochemical behavior of 600MPa grade HSLA steel FCAW weld metal

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The effects of Cu additions on the properties of a 600MPa grade HSLA steel weld metals (WM) by flux-cored arc welding (FCAW) in the laboratory were investigated in this work. The 600MPa grade HSLA steel FCAW joints were fabricated by the as-prepared flux-cored wires with different Cu contents from nil to 1.0 wt.% in a M21 mixed gas protection environment. The relationship between the micro-structural factors, mechanical properties and electrochemical impedance behavior of the weld metal (WM) was studied by means of full metallographic, mechanical and electrochemical on the specimens cut transversely to the weld beads. The best combination of microstructure and tensile properties was obtained in the weld metal contained 0.5% Cu. With more increasing of Cu content, the microstructure has changed from a mixture of acicular ferrite, grain-boundary ferrite, bainites and proeutectoid ferrite to a mixture of proeutectoid ferrite, grain-boundary ferrite, intergranular richments and inclusions. It is found that Cu addition could improve the tensile strength of WM, with the maximum value of 727MPa by 0.5% Cu addition. The mechanical strength fluctuated significantly and the toughness descent with the increasing Cu addition, due to such micro-alloys as Ni, Mo et. al enriched in the inclusions by weakening the microalloying effect. The electrochemical impedance behavior of each WM in a 3.5wt% NaCl solution was investigated. Proper Cu addition in WM would improve its anti-corrosive properties, indicated by the larger EIS circles of WM within 0.5~0.89% Cu addition, seen Fig.1. Lower or higher Cu addition barely improve the WM's EIS behavior. In conclusion, an optimal addition of Cu in the flux-cored wire offer better conditions for uniform microstructure with improved mechanical property and corrosive resistance behavior.

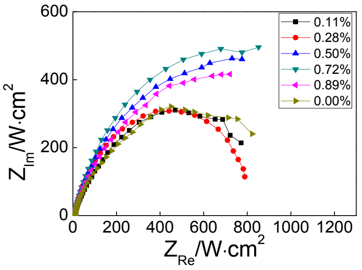

Fig.1 EIS curves of Cu added WMs in 24h

Keywords: 600MPa grade HSLA steel, microstructure, potentiodynamic polarization, electrochemical impedance spectroscopy

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Influence of the nature of the alkaline electrolyte on the durability of platinum-based carbon-supported electrocatalysts for direct liquid alkaline fuel cells

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Direct liquid alkaline fuel cells (DLAFC) are competitors to H_2-fed proton-exchange membrane fuel cells for portable or automotive applications [1]. Because many metals and metal oxides are stable at high pH [2], it is commonly accepted that electrode materials of DLAFC will be stable in operation. However, this common belief was proven wrong for carbon-supported Pt and Pd nanoparticles (NPs), which undergo severe electrochemical surface area losses even for a very mild potential cycling procedure in 0.1 M NaOH [3, 4]. Identical-location transmission electron microscopy (ILTEM) experiments revealed pronounced detachment of the Pt (and Pd) NPs from the carbon support, but minor degradation phenomena for the Pt (and Pd) NPs and the carbon support itself.

Additional experiments made by varying the nature of the alkaline electrolyte (LiOH, NaOH, KOH, CsOH, NH_4OH – see Fig. 1) and using *in situ* Fourier-transform infrared spectroscopy enabled to shed light on the mechanism of such particle detachment: it is linked to carbonates formation by local corrosion of the carbon support assisted by the Pt (or Pd) nanoparticles.

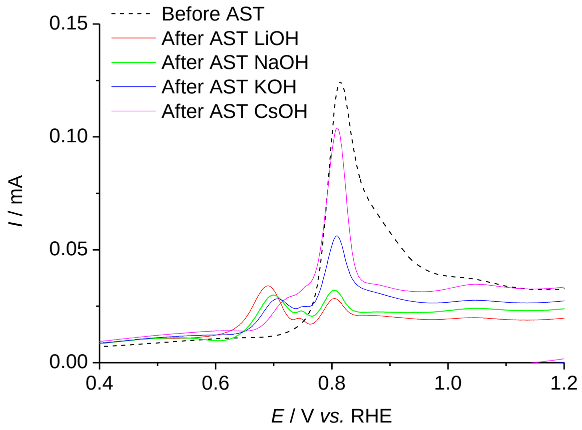

Figure 1: CO-stripping voltamperograms of the Pt/C electrocatalysts measured in H_2SO_4 prior/after 150 potential cycles in the range $0.1 < E < 1.23$ V *vs.* RHE at $T = 25°C$ in various 0.1 M MOH electrolytes (M = Li, Na, K, Cs), for which the propensity of solid M_2CO_3 formation increases in the sequence Cs, K < Na << Li.

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Photoelectrochemical Reduction of CO_2 with Black Titanium Dioxide Nanotube Arrays as Photoanode and Aqueous Ionic Liquids as Electrolyte Solution

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CO_2 is known as the main greenhouse gas that can induce some undesirable environmental changes, such as global warming, desertification, ocean acidification, etc.[1] Capture and subsequent utilization of CO_2 provide the opportunities to solve this problem.[2] Because CO_2 is the highest existing form of carbon, the conversion of CO_2 must consume energies. To close the carbon circle, the consumed energies should be provided by renewable energy resource. In various methods of conversion of CO_2, photoelectrochemical (PEC) reduction that introduces renewable solar energy is one of the prospective and potential ways to produce solar fuels and chemicals.[3] Parallelly, in recent years ionic liquids (ILs) have been widely adopted as electrolytes in electrochemical conversion of CO_2, due to their unique physicochemical property.[4]

In this work, PEC reduction of CO_2 was carried out by using black titanium dioxide (TiO_2) nanotube arrays as photoanode and aqueous IL (1-ethyl-3-methylimidazolium tetrafluoroborate, $[EMIM]BF_4$) as electrolyte solution in the two-electrode system and in a typical proton exchange membrane reaction configuration (Figure 1). TiO_2 nanotube arrays were synthesized through method of anodization, and then were reduced by high temperature hydrogenation to obtain black TiO_2 nanotube arrays. The scanning electron microscope characterization show that the TiO_2 nanotube arrays (Figure 2) with regular arrangements, smooth tube walls and clean nozzles can be successfully prepared, when electrolyte solution containing 5% volume content of water, voltage of 30 V and sonicating in ethanol for 30 min was applied as the preparation conditions. The incident photon-to-current measurement shows that the photocurrent density of black TiO_2 nanotube arrays can reach as high as 1.258 mA/cm^2 under the applied potential of 1.23 V (vs RHE).

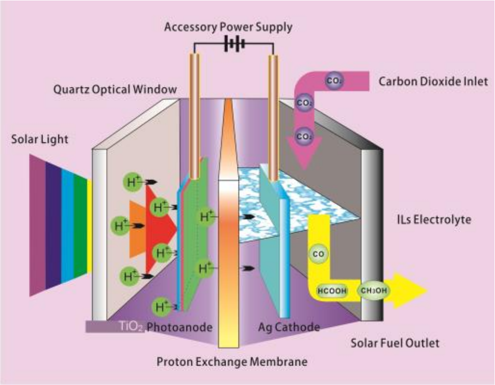

Figure 1 scheme of a PEM reaction cell.

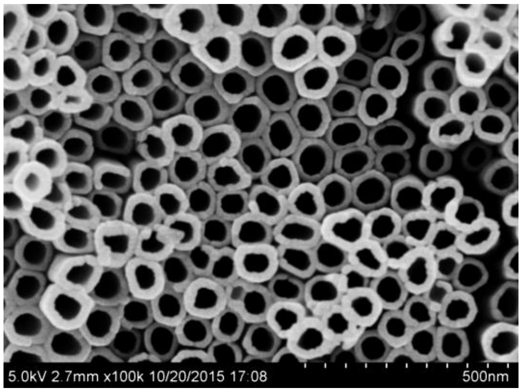

Figure 2 SEM image of TiO_2 nanotube arrays.

The PEC reduction results show that in this IL-assisted PEC reduction strategy for CO_2, the Faradaic efficiency of CO was as high as 90.6% at the applied voltage of 1.7 V, and the photon-to-chemical efficiency was 0.12% at the applied voltage as low as 1.2 V.

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A Novel 3D Graphene-Fe_3O_4-Polyaniline Nano-Composite for Supercapacitor Electrodes

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ABSTRACT Environmental and energy issues, the two hottest topics today, have drawn great interest and made quick development in renewable and sustainable sources. Various functional materials have been constructed and applied for supercapacitors. As important energy-storage devices, super-capacitors have attracted considerable attention in recent years by virtue of their high power density, excellent cycle efficiency, and quick charge/discharge rates. In the report, a promising candidate for high-performance supercapacitor electrodes, Graphene-Fe_3O_4-Polyaniline (rGO/Fe_3O_4/PANI) 3D ternary composite, was designed and prepared via in-situ hydrothermal and oxidation polymerization methods. Their structures and properties were characterized and evaluated by powder X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and ultraviolet-visible (UV-vis) absorption spectroscopy, the electrochemical properties. The enhanced mechanism for supercapacitor electrodes were investigated in detail. Due to the synergistic effect among uniformly distributed Fe_3O_4 and PANI nanostructures on rGO sheets by strong interaction to form 3D configuration, the electrochemical properties of rGO/Fe_3O_4/PANI-based electrode were improved greatly. For example, the specific capacitance increased from 299.1 Fg^{-1} for PANI, to 371.1 Fg^{-1} for rGO/PANI and further to 486.5 Fg^{-1} for the resultant rGO/Fe_3O_4/PANI. Importantly, even after 1500 cycles, the resultant electrode showed very well stability and significant enhanced effect of specific capacitance stability compared to PANI. The enhancement mechanism of specific capacitance stability was investigated in detail.

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Thermally responsive polymer films on electrodes – verification of the switching process and influence of peptide coupling

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This study is concerned with a thermally responsive, polymer-based electrode. Such systems are interesting with respect to the design of switchable reaction schemes on sensing electrodes. The core component is a temperature-responsive poly(oligoethylene glycol) methacrylate (poly(OEGMA)) type polymer containing photoreactive benzophenone- and carboxy group- side chains.
First, turbidimetry measurements have been applied to investigate the responsive behavior of the polymer in aqueous solution at different pH values. Second, the polymer is fixed on gold exploiting chemisorption of the photoreactive 2-(dicyclohexylphosphino)benzophenone (DPBP) and subsequent photocrosslinking. Third, the electrochemical behavior of the resulting polymer electrode has been investigated in buffered ferri-/ferrocyanide solution at room temperature and under temperature variation by cyclic voltammetry (CV). The CV experiments demonstrate that the redox couple behaviour is similar to a microelectrode. With raising temperature structural changes of the polymer layer are indicated. This can be mainly seen from the maximum current values. Repeated heating/cooling cycles analyzed by CV measurements and pH changes analyzed by quartz crystal microbalance with dissipation monitoring (QCM-D) reveal the reversible nature of the restructuring process.
The immobilized films are further modified by covalent coupling of two different small biomolecules - a hydrophobic peptide (HA-TAG) and a more hydrophilic one (FLAG-TAG). These attached components influence the hydrophobicity of the layer in a different way - the resulting change of the temperature behavior has been studied voltammetrically. It can be clearly concluded that the hydrophobic peptide has a more pronounced effect on the temperature-induced voltammetric current changes.
Consequently, the study confirms a previous investigation, which shows that the binding of a hydrophilic antibody only slightly shifts the responsive behaviour [1]. For a sensorial application this means that significant changes of the film can be expected when a bimolecular recognition reaction changes significantly the hydrophilicity-hydrophobicity balance on the surface.

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N-doped Graphene/α-Fe_2O_3 Modified Photoanode for Enhanced Pyridine Degradation in Integrated Bioelectro-photocatalytic System

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Nitrogen is frequently present in micropollutants, since many biologically active compounds, e.g., pharmaceuticals or pesticides, contain aromatic and aliphatic amino groups [1]. Due to their potential ecological and health risks, a polishing treatment of municipal wastewater treatment plant effluents is needed to minimize the discharge of micropollutants to receiving waters. Biological approaches are useful for removal of pyridine and nitrogen from wastewater, though their application for water environmental remediation is limited, due to the challenges of performance maintenance and secondary pollution associated with carbon source supply and the pathogen concerns [2]. In comparison, photocatalytic method presents a more environmentally-benign option, which enables efficient removal of pyridine and nitrogen without introducing any chemicals or bacteria and requiring any post-treatment. In particular, α-Fe_2O_3 attributed to its excellent optical and electronic properties, chemical stability, nontoxicity, and low cost, has been extensively investigated for such purposes. However, α-Fe_2O_3 is not an ideal photocatalytic material because of its low quantum efficiency which is ascribed to the short hole diffusion length and the low conduction band position of Fe_2O_3 [3]. It is demonstrated by many researches that the N-doped graphene layer could serve as a charge transfer medium, which may significantly reduce the charge recombination rate and accelerated charge transfer [4]. In addition, due to the low reaction selectivity, harmful by-products may be generated during the photocatalysis processes. These limitations highlight the needs for more selective, cost-effective and sustainable photocatalytic processes to transform pyridine to N_2 completely.

In this study, we reported an integrated bioelectro-photocatalytic system by equipped with a N-doped graphene/α-Fe_2O_3 modified anode and a biocathode. In this integrated bioelectro-photocatalytic system, the harvested photo-electrons derived from photoanode would be delivered to the biocathode via an external circuit for cathodic reduction. The successful coating of N-doped graphene/α-Fe_2O_3 on the electrode surface was verified by scanning electron microscopy, Raman spectrum and XPS. As shown in Fig.1, fin-like structure of N-doped graphene/α-Fe_2O_3 composite was fabricated onto graphite brush electrode through electrodeposition. This bioelectro-photocatalytic system synergically utilized both bioenergy and photoenergy for efficient and complete pyridine degradation, and had a promising future for water environmental remediation.

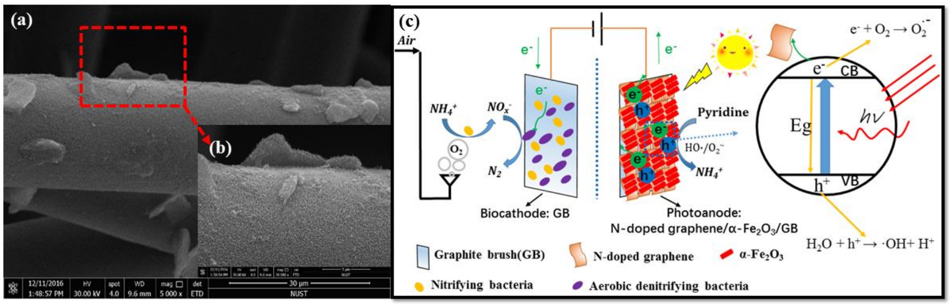

Fig. 1. SEM images of modified electrode with a magnification of (a) 5000×, (b) 20000×, and schematic process for simultaneous removal of pyridine and nitrogen in bioelectro-photocatalytic systems (c).

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Low cost of tubular porous electrode reactor for electrochemical treatment of anticancer drugs wastewater

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ABSTRACT:

Application of electrochemical reactor for industry wastewater treatment was limited by high cost due to the inefficient mass transfer of molecule [1]. For this case, a newly electrochemical reactor equipped tubular porous electrode was designed in order to enhance the mass transfer. The electrode was fabricated by loading a RuO_2 layer onto porous titanium tube by sol-gel, vacuum induction and thermal decomposition method, its pore size and porosity were 0.98 μm and 27%, respectively. The micro-pores of the electrode could facilitate a vertical flow between the anode and cathode with the present of pump which can not only enhance the mean mass transfer coefficient but also achieve more uniform the mass-transfer distribution along the electrode length [2]. Moreover, in the view of microscopic texture, porous structure also contributed to an improvement of specific surface area so as to enlarge electrochemical active area. Electrochemical property experiments of cyclic voltammetry and normal pulse voltammetry were studied to prove the foregoing benefits [3]. Due to these results, electrochemical treatment of anticancer drugs wastewater suggested that the reactor removed 84.1% of COD and 100% of target contaminate under low current density of 5 mA cm^{-2}, meanwhile the biodegradability was enhanced and toxicity was reduced. Particularly, the electric energy consumption and operating cost of the reactor were only 1.5 kWh kg^{-1} COD and $ 0.78 per ton, indicating the reactor was cost saving.

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Facile Morphology Controllable Synthesis of PtPd Dendritic Nanorods on Graphene-Multiwalled Carbon Nanotube Hybrid Support as Efficient Electrocatalyst for Oxygen Reduction Reaction

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Hybrid Graphene-Multiwalled carbon nanotube (G-M) (Fig. 1a) synthesized by a novel one-pot modified Hummers method followed by thermal annealing is explored as an efficient oxygen reduction reaction (ORR) catalysts support. PtPd alloy dendritic nanorods were deposited on the hybrid through a facile and convenient approach at room temperature. The as-prepared nanocatalyst PtPdNR/G-M (Fig. 1b) is investigated and discussed about their ORR activity in comparison with PtNR/G, PtNR/G-M and commercial JM40 (Pt/C) catalysts. It is found that the MWCNT could expand the graphene sheets, which is beneficial for the utilization of PtPd dendritic nanorods. Although the electrochemical active surface areas (ECSA) of dendritic nanorods catalysts are smaller than JM20 catalyst, they demonstrate a discernible positive shift in the formation of absorbed hydroxyl species, accelerating the ORR. The ORR polarization curves (Fig. 2b) further confirm the results reflected in the cyclic voltammetry (CV) (Fig. 2a). Impressively, the PtPdNR/G-M catalyst exhibits the best ORR activity which is attributed to the following reasons: (i) the positive alloy and morphology effect, (ii) the better hybrid G-M support, and (iii) strongly coupled PtPd dendritic nanorods and hybrid support. It is of great potential for the application of PtPd/G-M as the ORR catalysts in proton exchange membrane fuel cells (PEMFCs).

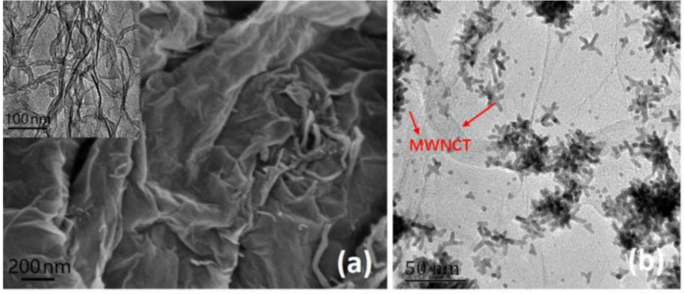

Fig. 1. FESEM image for (a) G-M, inset shows the TEM image of it; TEM image for (b) PtPdNR/G-M.

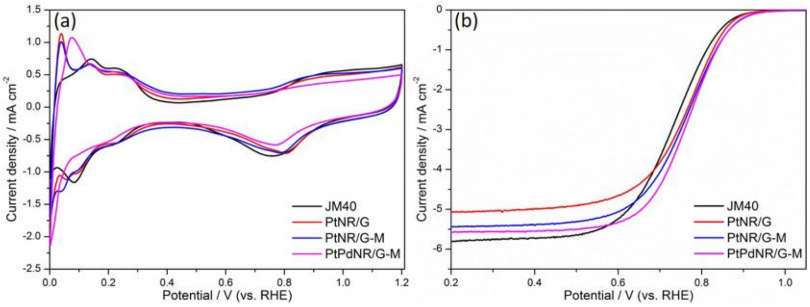

Fig. 2. CV curves for (a) JM40, PtNR/G, PtNR/G-M and PtPdNR/G-M in 0.1 M $HClO_4$ with a potential scanning rate of 50 mV s^{-1}; ORR polarization curves for (b) JM40, PtNR/G, PtNR/G-M and PtPdNR/G-M in 0.1 M $HClO_4$ with a potential scanning rate of 5 mV s^{-1}.

KEYWORDS: PtPd Dendritic Nanorods, Graphene, Multiwalled Carbon Nanotube, ORR.

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Photogalvanic Cell Consisted of Photo-activated Flavin Mediated Oxidation of NADH and Reduction of Hydronium Ion

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Enzymatic biofuel cells are expected to be alternative energy sources. Although much effort has been devoted to developing better ones, the cells are required to have a greater output for practical use. As a promising strategy, we tried to accelerate the oxidation of the soluble coenzyme nicotinamide adenine dinucleotide (NADH), which is a key process for the discharge, and the enzymatically active NAD$^+$ is the product. Because the direct electro-oxidation of NADH requires an extremely high overpotential [1], we used both flavinmononucleotide (FMN) as a redox mediator and light irradiation.

We employed a one-compartment glass cell containing an unglazed cylindrical vessel. The glass cell was filled with pH 7 McIlvaine buffer solution containing NADH/FMN as the anolyte and the unglazed vessel was filled with an aqueous H_2SO_4 solution as the catholyte. The platinum gauze was used as the anode and the platinalized Pt plate was used as the cathode. A schematic depiction of the cell is shown in Fig. 1.

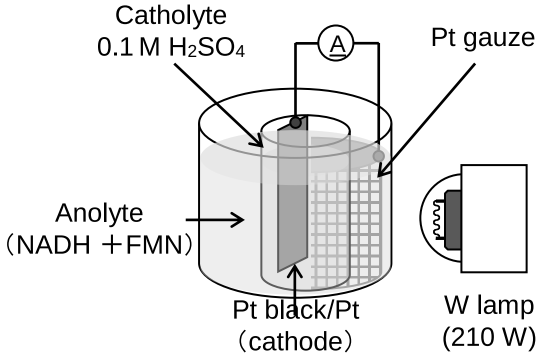

Fig. 1 Schematic depiction of the photogalvanic cell.

When the cell was irradiated by a 210 W tungsten lamp, the cell current was clearly observed, implying that this system acts as a photogalvanic cell. On the other hand, hydrogen evolution was seen on the cathode. Figure 2 shows the change in the cell current with time during light irradiation. The current significantly increases by the irradiation, then gradually decreases to a steady value. The anodic cell reaction is the oxidation of the reduced FMN produced by the photocatalyzed redox reaction with NADH, and the cathodic cell reaction is the reduction of the hydronium ion.

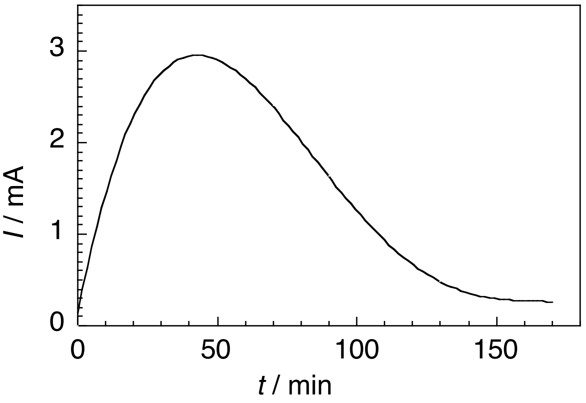

Fig. 2 Change in the cell current *vs*. the irradiation time. The anolyte is pH 7Mcllvaine buffer solution containing 1 mM FMN and 2mM NADH as the electrolyte.

The concentrations of both FMN and NADH + NAD$^+$ are roughly constant during the discharge, implying that FMN acts as the redox mediator and NADH is quantitatively converted. Moreover, the fact that the total charge was the same regardless of the concentration of FMN supported the quantitative conversion.

The wavelength dependence on the cell reaction was examined. The results showed that a low current was observed when the light whose wavelength was less than 545 nm was irradiated. On the other hand, the current was evident when the light at a wavelength was less than 400 nm was irradiated. Taking the maximum absorption wavelength (455 nm for FMN and 356 nm for NADH) into consideration, the excitation of FMN is necessary for the cell reaction to proceed. We are now investigating the reaction mechanism.

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Novel Conducting, Biocompatible and Biodegradable Copolymer PEDOT-*co*-PLLA for cell growth and differentiation

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Poly(L-lactic acid) (PLLA) is a biodegradable polymer, suitable for short term applications, and biocompatible with living tissue widely used in biomedical applications such as implants, sutures, drug encapsulation, etc.[1] Particularly, conducting polymers (CPs) such as polypyrrole (PPy), polyaniline (PANi) and polythiophene (PT) have been investigated as electroactive substrates for the culture of especially electrically excitable cells. They have been proved to play an important role with electrical stimulating in proliferation, adhesion or differentiation of various cell types.[2] Join both properties, electrical and biodegradable, in the same biomaterial is very desirable. However, there are some approaches which try to create blends or composites between CPs and biodegradable polymers [3,4], but there are some problems with heterogeneity and lack biodegradability of conducting part of the biomaterial. In 2007, the first conducting and biodegradable polymer was reported, based on aniline pentamer (AP) and reaching a copolymer triblock PLA-*b*-AP-*b*-PLA (PAP).[5] In spite of this, polyaniline presents a well known cytotoxicity which limits its use in biomedical applications.[6] To overcome this problems, a copolymer based on poly(3,4-ethylenedioxythiophene) (PEDOT) covalently linked to poly(L-lactic acid) (PLLA) with conductive and biodegradable properties, was prepared. Such strategy allows changing the amount of EDOT or PLLA monomers, obtaining different conductivity, biodegradability and biocompatibility. Their properties were characterized by different techniques and the biocompatibility was tested using embryonic stem cells to induced nerve cells differentiation.

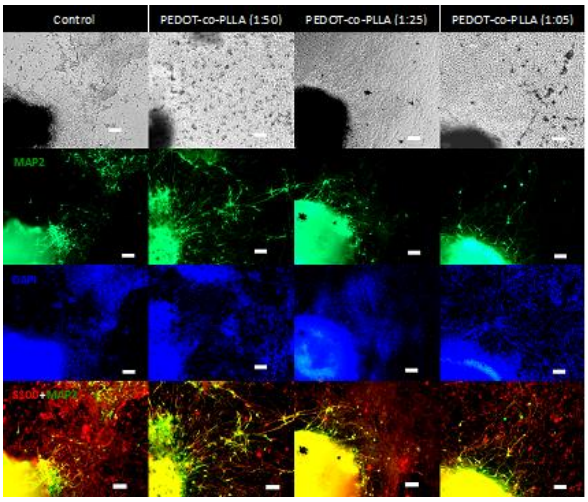

Figure 1 – Characterization of embryonic stem cells differentiation of the E14tg2a on polymeric scaffolds. Photomicrography in phase contrast showing cell morphology differentiated for 14 days on commercial plastic plate (control) and on PEDOT-co-PLLA in different proportions. Immunostaining for mature neurons with anti-MAP2 (green), cell nuclei (blue) and glial cells with anti-S100 (red). Calibration bar 100μm.

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Bioelectrocatalytic Ethanol Oxidation through the Immobilization of Dehydrogenase Enzymes in Cascade on a C8-LPEI Matrix

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The goal of this investigation was the preparation of enzymatic bioanodes aiming the bioelectrocatalytic oxidation of ethanol through the immobilization of dehydrogenase enzymes in cascade on the surface of a carbon support. For enzyme immobilization, the hydrophobically modified linear polyethylenimine (LPEI) containing octyl groups (C8-LPEI) was chosen as the polymeric matrix, in which the enzymes are anchored by the cross-linking agent ethylene glycol diglycidyl ether (EGDGE).

In the first stage of the bioelectrocatalytic oxidation of ethanol using only the enzyme alcohol dehydrogenase (ADH), it was observed that the C8-LPEI/EGDGE polymer matrix requires sensitive optimization in terms of the amount of the cross-linker agent (Figure 1A). Under concentration of the cross-linker maintained at 5 %, the maximum current and power density values obtained was about 150 ± 17 μA cm^{-2} and 12.5 ± 1.4 μW cm^{-2}, respectively. In the second stage of ethanol bioelectrocatalytic oxidation, the addition of the second enzyme to the system requires another optimization step between the amount of enzyme now used and the C8-LPEI/EGDGE matrix. In this second stage, although the results show an increase in the power density values obtained (in the best conditions evaluated, 20.0 ± 2.3 μW cm^{-2}), the expected 2-fold increase from the mono-enzymatic system was not reached (Figure 1B). Finally, in the third stage of the bioelectrocatalytic oxidation of ethanol, even under high concentration conditions of both the cross-linker agent and the polymeric matrix C8-LPEI, it was observed a decrease in power values when compared to previous steps. Overall, we concluded that the immobilization of all the enzymes responsible for ethanol bioelectrooxidation is not a sterically favorable task for the chosen immobilization system, which although it is quite elegant, presents limitations when a large number of enzymes molecules are required.

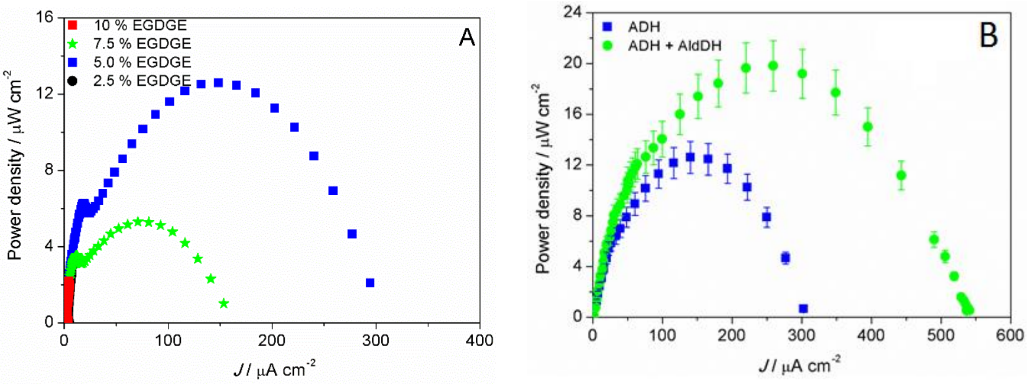

Figure 1. Power curves obtained in ethanol/O_2 biofuel cell tests with the bioanode prepared in different EGDGE ratio containing only the enzyme ADH (A). Power curves obtained in ethanol/O_2 biofuel cell tests with the bioanodes prepared with both ADH and AldDH in optimized C8-LPEI/EGDGE concentrations of 20 mg mL^{-1} and 10 % respectively (B). Phosphate/citrate buffer solution pH 7.2, 1.9 mmol L^{-1} NAD$^+$, and 0.02 mol L^{-1} ethanol.

Electron Transfer at Tunneling Nanoelectrodes

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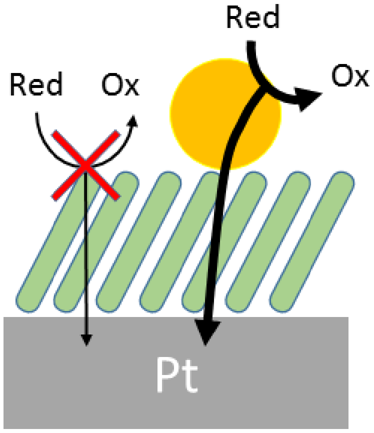

Figure 1. (A) Schematic of possible electrochemical reactions occurring at a tunneling electrode made with a metal nanoparticle/alkane-thiol/metallic electrode junction.

A tunneling electrode (Fig. 1A) consists of a metallic electrode (e.g. Pt disk microelectrode, grey rectangle) covered by a dielectric layer (e.g. SAM of alkane thiol, green rods) and a conducting layer (e.g. metal nanoparticles, noted NP, orange sphere). According to recent theory electrochemical transfer may occur normally on the NP while it is blocked at the surface of the insulating layer.[1] With a proper adjustment of the thickness of the dielectric layer and the particle size, the tunneling exchange current with the particle can be indeed several orders of magnitude greater than the tunneling exchange current with molecules at the surface of the dielectric. In such a situation the tunneling electrode behaves like a bare metal electrode.[2 3] This concept was exploited by the groups of A. Bard and S. Chen to produce spherical Pt and flat carbon nanoelectrodes, respectively. These electrodes are produced by depositing stochastically individual Pt nanoparticles or graphene sheets on passivated electrodes.[4,5]

In the present communication we attempt to test the latest theories on tunneling nanoelectrodes [6] by studying the electrochemical response of a "model" electrode composed of individual NPs stochastically deposited on a blocked microelectrode. Relevant parameters like the size of the NP and the surface density of NP are explored.

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PtFe Alloy Catalyst Supported on Porous Carbon Nanofiber with High Activity and Durability for Oxygen Reduction Reaction

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To reduce the high cost of oxygen reduction reaction (ORR) catalyst and improve the performance of the proton exchange membrane fuel cell (PEMFC), low-Pt or non-Pt catalysts have been studied in recent years. In this paper, PtFe alloy nanoparticles are loaded on porous carbon nanofiber (PCNF) via one-step modified glycol reduction method by adjusting solution pH. On the surface of PCNF, PtFe alloy nanoparticle can be uniformly dispersed with a narrow particle size distribution (Fig 1). In this PtFe alloy series, the catalyst PtFe alloy nanoparticle prepared in pH=7 solution with PCNF as carbon support exhibits better ORR performance(Fig 2(a)), which shows even higher onset potential than that of commericial catalyst Pt/C (Johnson Matthey, JM20). Moreover, comparable durability is also obtained through ADT test after 2000 cycles (Fig 2(b-c)). The excellent performance of PtFe-PCNF catalyst may attribute to the structural and electronic effects of transition metal in the PtFe alloy. The rough surface and porous structure of PCNF is also supposed to be beneficial for performance improvement.

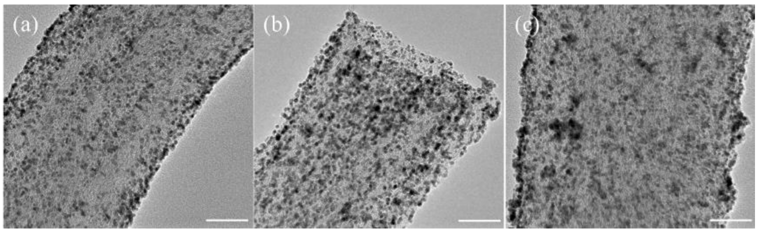

Fig 1. TEM pictures of selected samples: (a) pH 7 PCNF support; (b) pH 9 PCNF support; (c) pH 11 PCNF support. Scale bar=20 nm

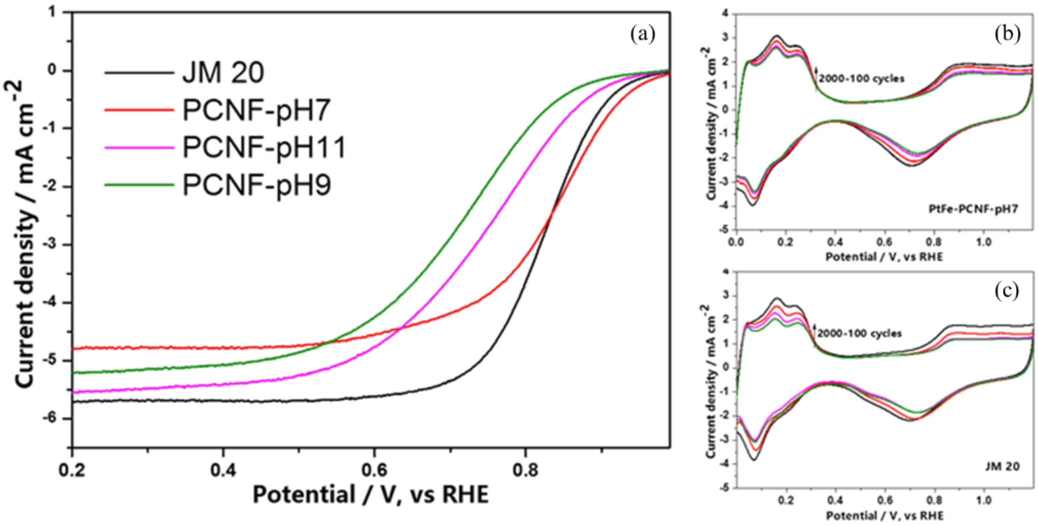

Fig 2. (a)LSV curves of catalysts; (b) ADT tests of PtFe-PCNF-pH 7; (c)ADT tests of JM 20;

KEYWORDS: Porous carbon nanofiber (PCNF), Pt-alloy, Oxygen reduction reaction (ORR), Fuel cell

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Electrochemical sensor based on an ionic liquid and carbon black for the determination of nanomolar levels of the Allura Red colorant

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The combination of ionic liquids and carbon-based nanomaterials for the design of highly sensitive electrochemical sensors is an interesting approach explored in the last years by electroanalytical chemists [1, 2]. In this work, we will present the first electrochemical sensor based on low-cost carbon black (CB) nanoparticles and an ionic liquid (IL) to enhance the voltammetric determination of the Allura Red (AR) colorant. For the preparation of this sensor, a glassy carbon electrode (GCE) was modified with CB (VXC72R) and IL (1-butyl-3-methylimidazolium tetrafluoroborate) within a crosslinked-chitosan (CTS, crosslink agent: epichlorohydrin) film. SEM micrograph of the surface of the IL-CB-CTS/GCE electrode showed the presence of spherical shaped CB nanoparticles covered by the IL-CTS matrix (Fig. 1a). The cyclic voltammetric response of AR on different electrodes is presented in Fig. 1b. As can be seen, a significant increment of the analytical signal was attained with the IL-CB-CTS/GCE electrode, which could be related to its higher electroactive surface. All experimental parameters related to the sensor preparation and the AR determination via square-wave adsorptive anodic stripping voltammetry (SWAdASV) were systematically optimized. The SWAdAS voltammograms recorded for different AR concentrations are presented in Fig. 1c, whose inset presents the obtained AR analytical curve. The analytical features included a linear range of 3.98×10^{-8} to 9.09×10^{-7} mol L^{-1}, limit of detection of 9.21×10^{-10} mol L^{-1}, and excellent repeatability of measurement (inter- and intra-day). The proposed sensor was successfully applied for AR determination in soft drink powder samples, with results statistically equivalent (at a confidence level of 95%) to those attained through a UV-vis comparative method.

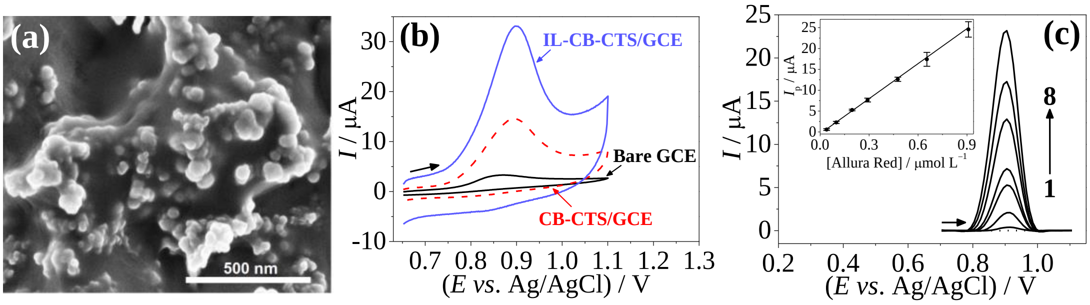

Fig. 1. (a) SEM micrograph of the surface of the IL-CTS-CB electrode. **(b)** Cyclic voltammograms (v = 50 mV s^{-1}) for a 50 μmol L^{-1} AR in 0.2 mol L^{-1} phosphate buffer solution (pH 4.0) recorded with bare GCE, CB-CTS/GCE, and IL-CB-CTS/GCE electrodes. **(c)** SWAdAS voltammograms recorded with a IL-CB-CTS/GCE electrode for different concentrations of AR: (1) 0.00 (blank solution), (2) 3.98×10^{-8}, (3) 9.90×10^{-8}, (4) 1.96×10^{-7}, (5) 2.91×10^{-7}, (6) 4.76×10^{-7}, (7) 6.54×10^{-7}, and (8) 9.09×10^{-7} mol L^{-1} in 0.2 mol L^{-1} phosphate buffer solution (pH 4.0). Parameters: $E_{pc} = 0.0$ V, $t_{pc} = 180$ s, $f = 10$ Hz, $a = 70$ mV, and $\Delta E_p = 10$ mV.

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High Voltage Performance of Lithium Ion Cells with EC-Based and EC-Free Electrolytes

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The demand for high energy densities and high operating voltages in lithium ion batteries (LIBs) necessitates exploring bottlenecks of cell performance. While the commonly employed layered transition metal oxide cathodes and graphite anodes show good performance, the electrolytes are the limiting component during high voltage operation. Conventional organic electrolytes contain ethylene carbonate (EC), which is known to undergo oxidative decomposition reactions at high voltages. Recent reports in literature suggest that cells with EC- free electrolytes show longer life and implicate EC as the component responsible for accelerated performance degradation.[1]

In order to investigate these performance loss mechanisms, we conducted extensive tests with 2032-type coin cells and reference electrode (RE) cells; results from these tests and our interpretation of the data will be reported during this presentation. Our cells contained a $Li_{1.03}(Ni_{0.5}Co_{0.2}Mn_{0.3})_{0.97}O_2$ - based positive electrode (NCM523) and a graphite- based negative electrode (Gr).[2] Cell electrolytes examined included the following compositions: 1.2 M $LiPF_6$ in EC:EMC (3:7 w/w), 1.2 M $LiPF_6$ in EMC and 1.2 M $LiPF_6$ in FEC:EMC (5:95 w/w). The 3-4.4 V cycling followed a standard protocol, which included formation cycles and aging cycles at 30 °C; pulse-power impedance and AC impedance measurements were made periodically during the cycling.[3] The coin cell measurements provide valuable information on the parameters, such as cycle life, capacity retention, and impedance changes. The RE cells provided information on electrode potential and electrode impedance changes during cycling.

Our data show that cells containing electrolytes with EC: EMC (3:7 w/w) and FEC: EMC (5:95 w/w) solvents have similar performance, while the cells with 100% EMC as solvent have lower capacity retention and higher impedance rise. The mechanisms responsible for similarities and differences in performance between the various electrolytes will be highlighted at the meeting. Our mechanistic understanding of the capacity fade and impedance rise in these cells provides guidelines for the development of electrolyte systems for high-voltage lithium-ion cell operation.

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One-step Preparation of Carbon and Fe3O4 Nanospheres Coated Fe3O4 for Lithium Ion Batteries

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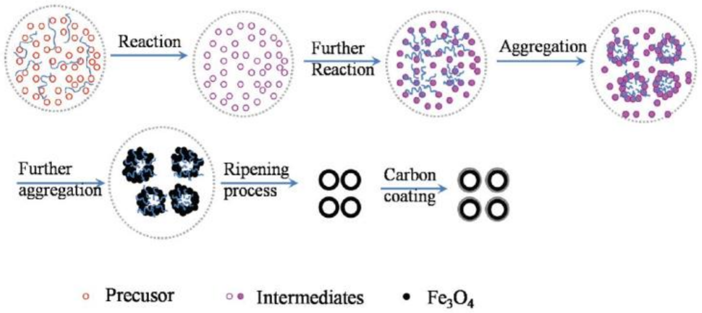
Fe3O4 nanospheres are synthesized by a solvothermal method with the assistance of surfactant. The nanospheres are further modified with glucose to obtain Fe3O4/C nanospheres. The crystalline structure and surface morphology are investigated by a combination of X-ray diffraction, transmission electron microscopy and scanning electron microscopy. The results suggest that cubic Fe3O4 nanospheres are achieved, with a diameter the coating process, ~5 nm carbon layer is uniformly formed on the surface of Fe3O4 spheres. The electrochemical performances of synthesized Fe3O4 and Fe3O4/C nanospheres as anode materials for lithium-ion batteries are conducted via galvanostatic discharge/charge measurements and cyclic voltammetry. Under a current density of 100 mA g-1, the Fe3O4/C nanospheres exhibit a delithiation capacity of 767.2 mAh g-1 over 100 cycles with excellent capacity retention of 98.2 % and improved rate capacities. This work demonstrates that the prepared Fe3O4/C is a promising anode material for lithium ion batteries[1-3].



Scheme 1 Illustration of the formation procedures of Fe3O4 and Fe3O4/C nanospheres

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SPEEK/ZnO Nanocomposite films for electrochemical detection of dopamine

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Abstract

A modified electrode was fabricated by drop casting method of sulphonated polyether ether ketone/zinc oxide (SPEEK/ZnO) nanocomposite on the gold electrode towards electrochemical oxidation of dopamine.The SPEEK/ZnO nanocomposite was characterized by using Fourier transform infrared (FT-IR), Uv-vis, and the surface morphology were assessed by scanning electron microscopy (SEM). Electrochemical oxidation of dopamine on a gold electrode (Au) modified with SPEEK doped with zinc oxide nanoparticles was examined by cyclic voltammetry in 0.1 M phosphate buffer solution PBS at pH 7. The result obtained at Au/SPEEK/ZnO modified electrode was compared with those obtained at the bare Au and Au/SPEEK nanocomposite modified electrodes. All electrodes were conditioned by potential cycling at a potential of 0.2V (vs Ag/AgCl, sat'd KCl) in 0.1 M PBS solution. It was found that the zinc oxide nanoparticles increased the electroactivity of SPEEK for dopamine oxidation. For the quantitative analysis of dopamine (DA), the Au/SPEEK/ZnO electrode exhibited good linear properties in the concentration range from 5.4×10^{-14} to 1.9×10^{-14} µM with a sensitivity of 217.4 $\mu A\ mM^{-1}\ cm^{-2}$ and a limit of detection of 0.85 nM. The interference study also revealed no AA interference signal at AA concentration one thousand times that of DA. The prepared electrode exhibited satisfactory stability and long shelf life when stored at ambient conditions. It has been demonstrated that the Au/SPEEK/ZnO modified electrode can be successfully used for the assay of dopamine in some real samples.

Keywords: SPEEK; Zinc oxide; Gold electrode; Dopamine; Cyclic voltammetry; Square wave voltammetry.

In-situ reduced petal-shaped Co/Co_3O_4 supported on Ni foam: a new catalyst for H_2O_2 electroreduction

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Recently, H_2O_2 as both fuel and oxidant for fuel cell has received a lot of notice due to its high energy density, easier storage and handling than gaseous oxygen. These advantages make H_2O_2 to be widely applied to various low-temperature liquid-based fuel cells [1]. Since the electrochemical reduction rate of H_2O_2 at cathodes has a critical influence on the performance of fuel cells, searching for suitable cathode catalysts has become a significant mission to improve the performance of fuel cells. Transition metal oxides have been widely used recently and also demonstrated to be high-performance electrocatalysts for H_2O_2 electroreduction [2]. Among those transition metal oxides, Co_3O_4 is a significant material for electrochemical energy storage, sensors, and catalysis [3] and also exhibited excellent activity and good stability for H_2O_2 electroreduction in alkaline solution. However, the low electronic conductivity of Co_3O_4 highly restricts its electrocatalytic property. In recent years, some reports have revealed that the Co_3O_4 decorated with metal particles could increase the conductivity and further improve its electrochemical performance, but the metals applied are always noble metals, which will increase the cost of electrodes.

To reduce the cost of electrode, in-situ chemical reduction method has been used in this work to form a rough Co layer which is a kind of base metal with good conductivity from the as-prepared Co_3O_4 petals supported on Ni foam to build a Co/Co_3O_4 petals (Co/Co_3O_4 Ps) electrode toward H_2O_2 electroreduction. The Electrochemical performance of H_2O_2 electroreduction on the Co/Co_3O_4 Ps is explored by cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectrometry (EIS). In a solution of 3 mol L^{-1} NaOH and 0.5 mol L^{-1} H_2O_2, the current density of H_2O_2 electroreduction on Co/Co_3O_4 Ps is 440 mA cm^{-2} at -0.8 V, higher than that on Co_3O_4, which make the obtained Co/Co_3O_4 Ps an excellent alternative catalyst for H_2O_2 fuel cell.

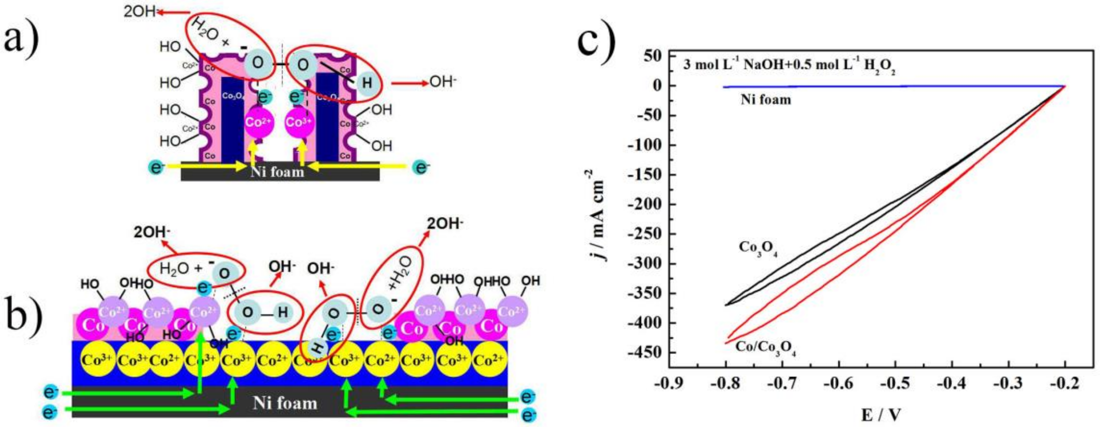

Fig. 1 Schematic diagram depicting the mechanism for H_2O_2 electroreduction on Co/Co_3O_4 Ps electrode (a,b) and comparison of CVs (scan rate: 20 mVs^{-1}) of Ni foam, Co_3O_4 and Co/Co_3O_4 Ps .

Acknowledgments

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Modifier-Free Microfluidic Electrochemical Sensor for Heavy Metal Detection

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Heavy metals are widely used in manufacture of batteries, pigments, alloys, electroplating and coating *etc.* [1, 2]. However, mining, pouring, casting, processing and inappropriate disposal of heavy metals have made them hazard pollutants to the environment [3], posing severe threat to ecological systems and presents a great challenge for global sustainability. Their toxic and non-biodegradable nature also impose severe risks to the human health. Therefore, researchers have been striving to develop simple, cost-effective and also portable sensing devices for fast and point-of-care analysis of heavy metal pollution in the environment, especially in developing countries and areas with insufficient infrastructures.

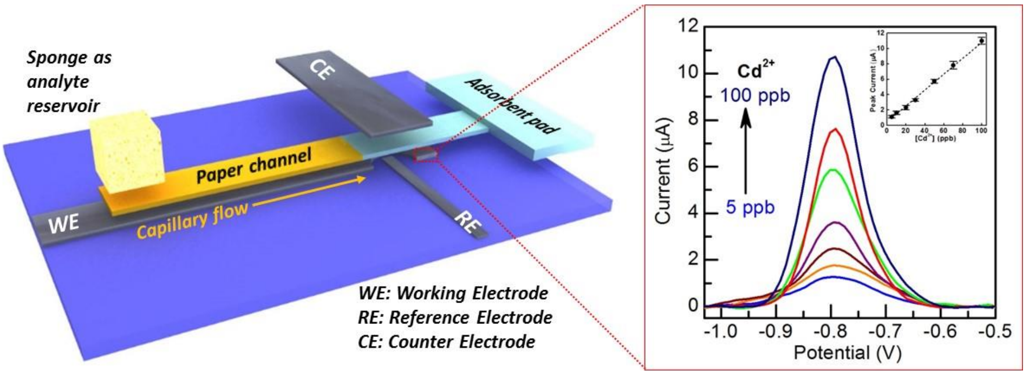

Figure 1. Scheme for the μCS (left panel), representative square wave voltammograms for Cd^{2+} (right panel) in 0.1 M acetate buffer over the μCS and the associated calibration plot.

Herein, a highly sensitive, robust and low-cost microfluidic electrochemical carbon-based sensor (μCS) for detection of trace heavy metals is presented. The miniaturized μCS devices are based on a microfluidic paper channel combined with a novel 3D layout with working and counter electrodes facing each other and analyte flowing along the microfluidic channel between these two electrodes (Figure 1). Pristine graphite foil free of any surface modifier is not only used as the electronically conductive pad but also directly employed as the working electrode for fabricating the μCS. The resulting simple and portable device was applied in Cd^{2+} and Pb^{2+} detection by using square wave anodic stripping voltammetry. As shown in Figure 1, the peak current of Cd^{2+} increases linearly with concentration from 5 to 100 ppb. Detection limits down to 1.2 ppb for Cd^{2+} and 1.8 ppb for Pb^{2+} can be achieved over the μCS based on the 3σ method. The μCS devices are also found highly robust for heavy metal detection, the sensing performance of a single μCS device being reproducible for up to 10 repetitive measurements. From the SEM analysis we noticed that the graphite foil consisting of abundant of edge-plane sites which could favor the metal ion deposition, thus enabling graphite foil to be a simple block material for an electrochemical sensor. We believe these findings would have significant implications in developing other fast and cost-effective detection platforms, such as clinical diagnosis and security inspection [4].

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Preliminary Study on Electrochemical Reduction of Ammonium Metaborate to Indirectly Generate Ammonia Borane

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Ammonia borane (NH_3BH_3), a kind of crystalline complex hydride with the highest hydrogen content (19.6 wt.%) ever found to date, can controllably liberate hydrogen gas (H_2) via hydrolysis by virtue of suitable catalyst under mild condition, and has thus become one of the most compelling hydrogen storage material[1]. The hydrolytic reaction of ammonia borane follows: $NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2$, generating the byproduct of metaborate with no higher-value industrial use, which greatly influences the practice cost of ammonia borane as hydrogen source. Hence, seeking effective and feasible technical route to transform ammonium metaborate to more valuable other materials, especially revert back to ammonia borane, is surely worthy of expectation[2].

Our serial preparing experiments regarding ammonia borane have already verified that ammonium borohydride (NH_4BH_4) could exist as an unstable intermediate in the synthesizing process, and thermally decompose to form ammonia borane. This suggests us to firstly transform the hydrolytic product (NH_4BO_2) to NH_4BH_4, and next to NH_3BH_3, just as the recycling strategy of its congener ($NaBO_2$). As per thermodynamic calculation, the electrochemical reaction $BO_2^- + 6H_2O + 8e \rightarrow BH_4^- + 8OH$, or conversion of metaborate into borohydride, should be able to carry out at an appropriate voltage and current[3], which implies the high possibility for electrochemical synthesis of ammonia borane.

In this work, a H-type glass cell was employed as electrolytic cell with Nafion cation exchange membrane as cell divider. The anolyte and catholyte were, respectively, 1.0 M H_2SO_4 solution and (1.0M TMAH + 0.2M ammonium metaborate + 1~5% TU) mixed aqueous solution. Pb rod or glassy carbon rod (ϕ6.0mm) served as anode; porous composite electrode ($NiB/MnO_2/Ti$) acted as cathode, and alkaline Hg/HgO was used as reference electrode. A rectangular wave pulse power source were employed to overcome electrostatic repulsion of the borate anion from the cathode. To avoid oxidation loss of the resulting BH_4^- intermediate the cathode compartment should be fully filled with inert gas. Cyclic voltammetry measurements by using three electrode system was performed to test for the presence of borohydride in the catholyte solutions after electrolysis, with a sweep rate of 100 mV/s over the range of −2.0V to +0.3 V. In addition, the ion chromatography and iodometry (iodide back-titration method) were also applied to quantitatively analyze the borohydride concentration. Upon finishing electrolysis the resultant mixture was carefully transferred out of cathode chamber under inert gas protection and low temperature (around zero degree), followed by addition of some amount of organic solvent with continuous agitation for some time. The target product ammonia borane could be obtained via rotarily evaporating the upper clear liquid that was separated from centrifugation of the electrolysis mixture.

The research results show that under the given conditions the ammonia borane sample could be successfully prepared through electrochemically cathodic reduction. The current efficiency for the entire electrolytic process could reach to 40~60%.

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Size dependency of electrocatalyst-support interaction of Pt supported by two-dimensional Ti_3C_2 in oxygen electrocatalysis

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We studied on the effects of catalyst particle size on electrocatalyst-support interaction to ultimately affect the kinetics and durability of oxygen electrocatalysis. Pt, the best catalyst for oxygen reduction reaction (ORR), was used as the electrocatalyst. Two-dimensional titanium carbide (2D-Ti_3C_2, belonging to the MXene group) was used as the support alternative to popular carbon materials. The 2D-Ti_3C_2, characterized by its corrosion-resistance and electric conductivity, donated electrons to Pt nanoparticles supported by it. The electron donation by 2D-Ti_3C_2 was confirmed by the binding energies (BE) of Pt in Pt/2D-Ti_3C_2 more negative than that of Pt/C. The electrocatalyst-support interaction became stronger as the Pt particle size decreased. The size dependency was confirmed by the BE shift (|ΔBE|) of 2 nm Pt larger than that of 4 nm Pt: the negative BE shift from the BE of Pt/C (ΔBE) = -0.35 eV for 2 nm Pt supported by 2D-Ti_3C_2 (2nm-Pt/2D-Ti_3C_2) versus -0.25 eV for 4nm-Pt/2D-Ti_3C_2. More electron-rich Pt induced by its smaller dimension resulted in faster ORR kinetics by encouraging desorption of ORR products. The size-interaction-electroactivity relationship was described by a dimensional parameter representing the size of Pt nanoparticles. It was assumed that Pt atoms at the interface between Pt and 2D-Ti_3C_2 were more negatively charged than Pt atoms in bulk, showing higher electroactivities.

Hydrogen-Hypobromite Flow Battery

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The old but earlier abandoned H_2-Br_2 flow batteries[1] experience a renaissance these days, as several research groups around the World [2] are developing this technology for stationary energy storage, and companies in Israel[3] and Netherlands[4] are attempting their commercialization. However, H_2-Br_2 flow batteries present a severe hazard due to the presence of large amounts of concentrated acidic bromine solution, as well as face corrosion and anode poisoning due to bromine crossover. Recently we proposed[5] flow batteries employing highly soluble neutral solutions of halogen oxoanion salts as Aqueous Multielectron Oxidants. While we are pursuing the development of $LiBrO_3$ –based flow batteries for Fully Electric Vehicles, for stationary energy storage we chose NaBrO oxidant.

When pressurized hydrogen is used as the reducer, the protons required for the electro- reduction of hypohalate (1) are generated (2) on the negative electrode and transferred through a cation- selective membrane, which simultaneously prevents the internal short-circuiting via the reduction of the halate on the negative electrode.

In the positive electrode: $XO^{-} + 2H^{+} + 2e^{-} \leftrightarrow H_2O + X^{-}$ (1)

On the negative electrode: $H_2 - 2e^{-} \leftrightarrow 2H^{+}$, (2)

In one type of such flow batteries both discharge and charge occur at high current densities without the use of precious metal electrocatalysts on the positive electrode by taking advantage of a pH-dependent solution-phase com/dis-proportionation (3) coupled to a fast electrode process (4) (X=Cl, Br)

In the posolyte: $X^{-} + XO^{-} + 2H^{+} \leftrightarrow H_2O + X_2$ fast (3)

On the positive electrode: $X_2 + 2e^{-} \leftrightarrow 2X^{-}$, fast (4)

and of reagent- and waste-free OIMALF ™ process for changing the pH of the oxidant fluid between acidic during discharge and alkaline during charge in order to reverse the direction of (3).

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New Methods for the Electrochemical Synthesis of 3,3´,5,5´-Tetramethyl-2,2´-biphenol

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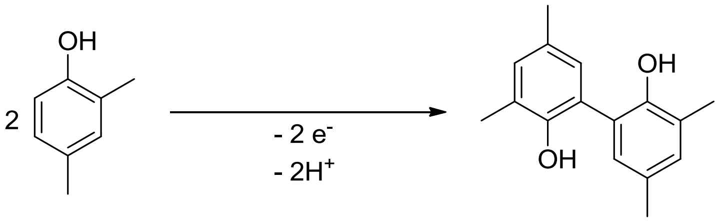
3,3´,5,5´-Tetramethyl-2,2´-biphenol **1** is of high interest since it exhibits superior application as ligand building block for the transition metal catalysis.[1] The biphenol **1** is accessible by direct electrochemical oxidation of 2,4-dimethylphenol **2**.[2] However, the synthesis of this rather simple molecule is challenging because over-oxidation and side reactions resulting in a diversity of by-products, oligomers and polymers.[3,4] Therefore, novel concepts and methods for the electro-synthesis of 3,3´,5,5´-tetramethyl-2,2´-biphenol **1** will be presented in detail.



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Theory and Simulations for the Electron-Transfer/Ion-Transfer Mode of Scanning Electrochemical Microscopy in the Presence or Absence of Homogenous Kinetics

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The electron-transfer/ion-transfer (ET/IT) mode of scanning electrochemical microscopy (SECM) was developed recently and applied to studies of heterogeneous reactions at the substrate surface. The charged products or intermediates are detected by measuring the ion-transfer current of the species across the liquid/liquid interface supported at the tip of a nanopipette.

In this research, we developed the theory for this technique and explore its potential advantages and limitations [1]. By using the COMSOL Multiphysics package, the approach curves were simulated for three commonly encountered experimental situations, that is, the surface-generated ionic species is either chemically stable or participates in a first- or second-order homogeneous reaction. The simulation results are generalized in the form of analytical approximations derived under limiting conditions.

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Electrolyte in Na-ion batteries systems: towards an improvement of safety and lifetime

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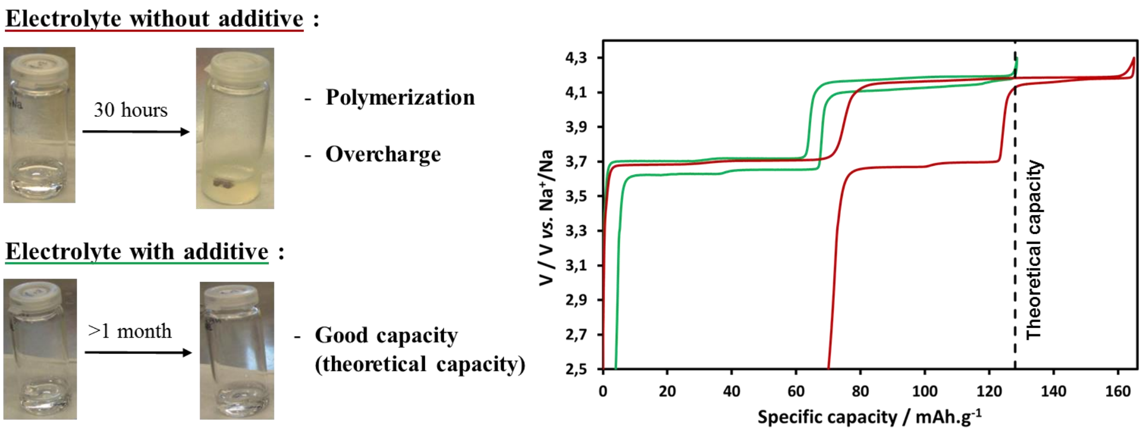
Electrolyte is a crucial point for the safety and the lifetime of lithium-ion batteries (LIBs). The electrolyte decomposition must be avoided in order to guarantee LIBs development in the future. It's also the case for post-lithium systems as sodium-ion batteries (NIBs). Today, organic carbonates are the predominant electrolyte base used in the best LIBs and NIBs.

In this study, we determine and quantify the formation of the main byproduct of Na-ion system: ethylene glycol bis-(methyl carbonate) (EGMC)[1,2] utilizing liquid GC/MS (Gas Chromatography/Mass Spectrometry). EGMC resulting from the degradation of the commonly used electrolyte: 1M $NaPF_6$ in EC:DMC (1:1). The effect of an additive, fluoroethylene carbonate (FEC), on electrode passivation and electrolyte decomposition is also investigated. A well-known positive electrode materials for Na-ion battery was chosen for the study: a fluorophosphate ($Na_3V_2(PO_4)_2F_3$).
Moreover, two types of half-cell designs were used and compared with different amount of FEC using galvanostatic charge-discharge and cyclic voltammetry methods.[3]

Finally, a third design of cell was realised and studied with the optimized amount of FEC to show the effect of this additive in full system prototypes.



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Adhesion Control Mediated by Organic Molecules at Metal/Non-metal Interface

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It is important to control interfacial properties between metal and non-metallic substrates such as polymer and ceramics to obtain high performance of semiconductor chips and electronic/electric devices as well as energy conversion systems. Various attempts have been engaged to get intimate adhesion between heterogeneous interfaces through depositing metallic layer on non-metallic substrate followed by pressing both substrates at high temperature and high pressure conditions. In any methodology, the main issue is to form stronger metallic layers on the non-metallic layers to make electric pathway of devices withstand at more stringent conditions.

For this purpose, we formed an organic molecule layer, (3-Aminopropyl)triethoxysilane, on the surface of silicon wafer dissolved in the organic solvents, toluene, at moderate temperature in the humidity controlled chamber. Then it was catalyzed with Pd/TiO_2 nuclei and sintered, which resulted in more robust adherence between metal and silicon wafer substrate. Then, we chemically and electrochemically deposited nickel and copper layers on it, and measured the mechanical and electrical characteristics between two parallel layers. Now, this technique is also applied other materials such as glass, silicon wafer, silicon nitride layer and polyimide film.

Metal Oxide Nanoparticles / Pani Nanocomposite Modified Glassy Carbon Electrode for the Detection Of Dopamine

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Abstract

A chemically modified electrode constructed based on chemically synthesised polyaniline (PANI) doped with nickel, zinc and iron oxide nanoparticles coating on glassy carbon electrode (GCE) to give GCE-PANI-NiO, GCE-PANI-ZnO and GCE-PANI-Fe_3O_4 is reported in this study. The nanocomposites obtained were characterized with field emission scanning electron microscopy (FE-SEM), FTIR, UV–vis spectroscopy, XRD, EDX, TEM, cyclic voltammetry and electrochemical impedance (EIS) techniques. The electrochemical response of dopamine on the modified electrode was determined using square wave voltammetry (SWV) at physiological pH 7. The dynamic range for the dopamine determination was between 2 x 10^{-8} µM to 9.9 x 10^{-2} µM with detection limits 1.15 x 10^{-10} M, 6.33 x 10^{-10} M and 3.14 x 10^{-6} M for GCE-PANI-ZnO, GCE-PANI-NiO and GCE-PANI-Fe3O4 sensors respectively. The LOD value reveals that the best electrode is GCE-PANI-ZnO. The common metabolites such as ascorbic acid and serotonin do not interfere over this range of concentrations which show the selectivity of the proposed sensors. The prepared electrode exhibited satisfactory stability when stored at ambient conditions. It has been demonstrated in this study that the GCE-PANI-ZnO modified electrode can be successfully used for the assay of dopamine in real samples.

The Importance of Cannizzaro-Type Reactions during Electrocatalytic Reduction of Carbon Dioxide

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The electrocatalytic reduction of CO_2 has been the subject of research activities for more than half a century, because of its promising potential to produce fuels and commodity chemicals and to alleviate anthropogenic CO_2 emissions. However, there are still significant hurdles to overcome before it will be industrially viable. The major bottlenecks are a poor product selectivity, competition with hydrogen evolution, catalyst stability and high overpotentials. Recently, the focus has been on the formation of liquid products or hydrocarbons, leading to many recent publications on CO_2 reduction electrocatalysts forming useful products with remarkable current efficiencies. Nevertheless, the formation pathways of many of the (by-)products are still unclear from a mechanistic point of view and typical product distributions are often observed such as the concomitant formation of methanol and formic acid or ethanol and acetic acid.

In this work we show the crucial importance of the effect of local pH changes during CO_2 reduction on product distribution [1]. We demonstrate the involvement of disproportionation reactions leading to product distributions which should be distinguished from direct CO_2 reduction. These reactions are promoted by the local pH (changes) during CO_2 reduction, as shown in Figure 1. A supposedly inactive electrode, Boron Doped Diamond, is primarily studied in this work, with an interesting activity for the reduction of CO_2 or CO to methane, which to our knowledge has not been reported before. Importantly, formic acid and methanol are formed which we prove to be the result of Cannizzaro-type reactions promoted by OH^- ions near the electrode, as a result of the simultaneous hydrogen evolution reaction. The importance of this phenomenon is illustrated by generalizing to C_2 and C_3 aldehydes and to different electrode materials. Moreover, it is found that this phenomenon is strongly influenced by the electrolyte pH and buffer capacity. In the recent literature about electrocatalytic CO_2 reduction product distributions involving acids and alcohols are often unaccounted for or generally ascribed to direct CO_2 reduction. Our work shows that they may be the result of base-catalyzed disproportionation reactions.

Our findings reveal important new insights for CO_2 electroreduction, which may explain mechanistic aspects of liquid product distributions often found for a variety of catalysts [2-4]. Moreover, the intriguing activity of BDD for CO_2 reduction towards methane should be taken into account, especially when used as substrate for catalysts for CO_2 reduction. Our study contributes crucial new knowledge to the on-going electrocatalytic CO_2 reduction research and other electrochemical reactions in general.

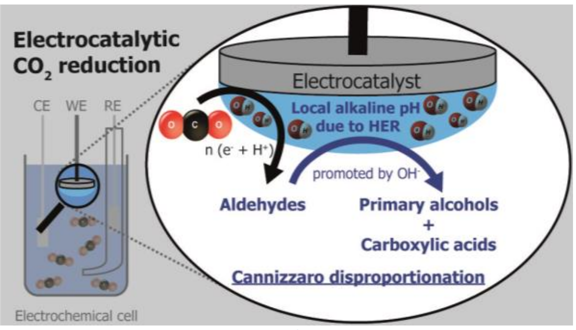

Figure 1 Cannizzaro type reactions for Electrocatalytic CO_2 reduction

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Design of modular filter for treatment of air used as an oxidant in the mobile APU based on PEM fuel cell

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PEM type fuel cell represents promising technology for efficient conversion of chemical energy of fuel into electrical energy. It possesses several important advantages, like a high efficiency, flexibility, process intensity, nontoxic reaction products and silent operation. Silent operation is caused by fact, that fuel cells don't involve any moving parts. Only ventilators for air supply and valves are sources of noise in this case. Products of reaction are only pure water, heat and electrical energy. This fact allows application of fuel cells also in areas sensitive to exhalations, e.g. mobile medical beds or in field hospitals. Other potential applications represents power source for speleologist, rescue operations or reserve power source for firefighters and police. Mobile PEM fuel cell unit can also be used as temporary power source for telecommunication transmitters or meteorological stations. All these applications require construction of suitable mobile management system for PEM fuel cell stack.

APU weight should not exceed upper weight limit of 15 kg, excluding pressurized gas cylinders. Logical solution is to use ambient air as an oxidant in order to reduce complexity (and weight) of the entire system. Main problem in this case represent air contaminants. They can reduce lifetime of the fuel cell. Solid impurities, like dust or pollen, can deposit on cathode surface and in combination with produced water form a sludge blocking distribution channels and gas distribution layers of the fuel cell. Also platinum nanoparticles used as a catalyst can be poisoned by the various pollutants often presented in the air in industrial agglomerations. Most dangerous is dihydrogen sulfide and other sulfur compounds, which are strong poisons for platinum catalysts. Regeneration of the catalyst poisoned by hydrogen sulfide is impossible. Last group of potentially dangerous air pollutants are organic compounds like benzene or toluene. These compounds, if adsorbed, can block the catalyst surface. In this case catalyst can be regenerated by applying external voltage pulse. The consecutive adsorbed pollutants oxidation is non-selective. Due to this fact it is not possible to fully regenerate catalyst poisoned by organic compounds. Moreover, certain degradation of the catalyst support based on the carbon black may occur.

Filters for removal of mechanical particles with diameter down to 0.2 µm are today commercially available. For removal of chemical impurities active carbon is typically used. Promising approach to air treatment thus represents utilization of the mechanical filters with interlayer of active carbon. Important parameter in this respect represents pressure drop over the filter, because it is directly related to the overhead consumption of electrical energy produced by the APU.

First target of this study was to characterize and different commercially available filters. Investigated parameters were pressure drop, ability to capture model pollutants, dimension and final price. On the base of these data, filter suitable for operating fuel cell was selected when accounting for the typical air pollutants and desired fuel cell lifetime. Second target of this work was to improve ability of selected filters to capture gaseous impurities. This can be achieved on different ways, e.g. by adding extra layer of active carbon to increase their capacity for individual pollutants removal, by combining filter with special sorbents in different form or by adding extra honeycomb filter with high specific selectivity. On this way it is possible to produce filters optimized for different environments, e.g. for industrial areas, highways, plantations, mines, sandpits and others.

This work was supported by Ministry of the Interior of the Czech Republic within the framework of the Project No. VI20152019018.

Electrochemical Behavior of the Cotinine at a Boron-Doped Diamond Electrode and its Determination in Saliva by Multiple-pulse Amperometry in an FIA System

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Abstract: Cotinine (CO) is the principal metabolite of nicotine, and it is used as a biomarker to monitor the exposure of an individual to tobacco. The CO determination in biological samples has been widely based on chromatographic techniques, followed by immunological and colorimetric methods. Nevertheless, electrochemical methods have shown promise in determining electroactive compounds in several areas, because they are highly selective and generate little waste. However, saliva is a complex biological matrix that, in addition to CO and other tobacco biomarkers such as heavy metals, may possess a myriad of chemicals, some of them being electroactive compounds and potentially interfering agents. An alternative to surpass this drawback is the detection by multiple-pulse amperometry (MPA), which permits the application of various potential pulses at the surface of the working electrode and simultaneous acquisition of all amperograms, thereby increasing the selectivity of the electrochemical method. Moreover, when the MPA detection is associated with flow injection analysis (FIA), some advantages over stationary electrochemical techniques, such as higher analytical frequency and greater reproducibility of the electrochemical response, can be obtained. In this context, this work sought to present the use of a boron-doped diamond (BDD) electrode for the electrochemical characterization of CO by voltammetric techniques and its quantification in saliva samples by FIA-MPA. In phosphate buffer solution 0.1 mol L^{-1} (pH 7), the CO presented two electrochemical processes, one anodic at +1.8V and one cathodic at -1.2V (vs. Ag/AgCl). The second process was dependent on the first and both processes were irreversible. It was found that CO electrochemical processes are controlled by diffusion and that two-protons and two-electrons are involved in the oxidation reaction. In determination of CO in saliva samples, the MPA detection was used as presented in the Figure 1, applying four potential pulses: (1) at +1.8V/500 ms, generator potential pulse for oxidation of CO; (2) at -1.0V/600 ms, potential pulse for remove possible interferents; (3) at -1.2V/500 ms, collector potential pulse for reduction of the product generated and CO quantification; (4) 1.45V/300 ms, potential pulse for cleaning BDD electrode.

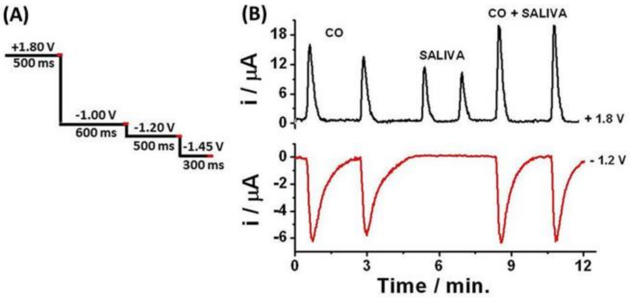

Figure 1. ***(A)*** *Potential pulse scheme applied. The current acquisition was performed in the last 5.0 ms of each potential pulse applied (red highlight in line).* ***(B)*** *Amperograms obtained by FIA-MPA detection in supporting electrolyte with duplicate injections of solutions containing 100 µmol L^{-1} of only CO, only saliva sample, 100 µmol L^{-1} CO added to the same saliva sample. Flow rate: 3.0 mL min^{-1}; Injection volume: 300µL. Potential pulses on BDD electrode: 1.80V/500 ms, -1.00/600 (not shown), -1.20V/500 ms and -1.45 V/300 ms (not shown).*

The proposed method attained an analytical frequency of 36 determinations per hour with a relative standard deviation of 1.46% for 10 measurements of 1.0 x 10^{-5} mol L^{-1} CO. A good linear range from 0.5 to 100 µmol L^{-1} was obtained with a detection limit for CO estimated at 0.06 µmol L^{-1}. Approximately 100% of the CO added to saliva samples was recovered. Therefore, this work presents the electrochemical behavior of the CO at BDD electrode as well as a simple, fast and low-cost method for monitoring the degree of exposure to tobacco by CO determination in saliva samples using the FIA-MPA technique.

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Activity Enhancement of Platinum Nanoparticle Catalysts by Ion-Beam-Induced Defects

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1. Introduction

Pt nanoparticles with a high oxygen reduction reaction (ORR) activity are pursued as cathode catalysts in polymer electrolyte fuel cells. Recently, Pt nanoparticles on the glassy carbon (GC) substrate pre-irradiated with energetic Ar ions were found to have a strong Pt-C interfacial interaction and to show a higher ORR activity than those on the non-irradiated one [1,2]. This suggests that Pt nanoparticles would be electronically influenced by ion-beam-induced lattice defects in the GC substrate. In order to explore the mechanism of the activity improvement, we analyzed the electronic structure of the Pt/GC interface by density functional theory (DFT) calculations.

2. Calculation models and methods

The interface was modeled as an icosahedral Pt_{13} cluster and three layers of graphene with (b) a single-vacancy or (c, d, e) multiple-vacancy (Fig. 1). DFT calculations were performed with VASP using the projector-augmented wave method. The revised Perdew–Burke–Ernzerhof edition of the generalized gradient approximation (GGA-RPBE) was employed to describe electron exchange-correlation functional, and a plane wave basis set with an energy cutoff of 400 eV was used. The energy converge criterion was set to be 10^{-4} eV for self-consistent calculations with a gamma-center 9×9×1 k-mesh.

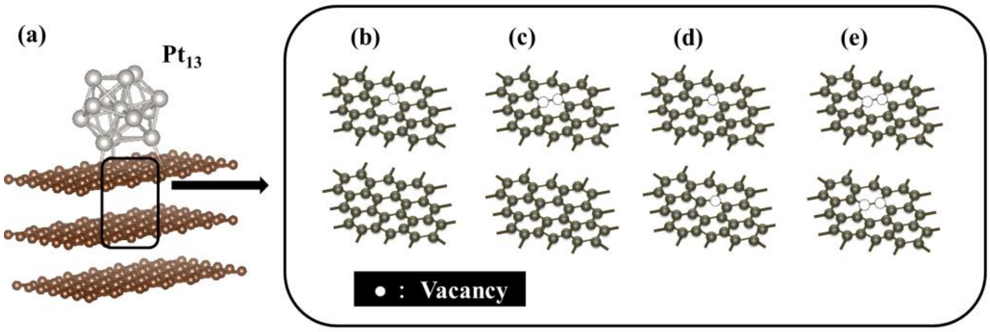

Fig. 1 (a) The model of the irradiated GC and Pt nanoparticles ((b) SV, (c) DV, (d) 2SV, (e) 2DV)

3. Results and Discussion

While the average Pt-C bond length in the pristine model and SV is 2.17 Å, the length is shorten in the case of the multiple-vacancy models (DV: 2.10 Å, 2SV: 2.08 Å, 2DV: 2.11 Å). This result suggests that multiple-vacancy of the carbon supports probably contributes to a strong Pt-C interaction. We also find that the multiple-vacancy reduces the average energy of d states (d band center) of the supported Pt cluster by about 0.05 eV compared to that of the pristine model. This reduction would weaken the binding of O and OH species on the Pt surface and promotes the rate-limiting step of ORR (removal of adsorbed species from the Pt surface) [3]. Thus ion-beam induced multiple-vacancy defects lead to the enhancement of the ORR activity of Pt nanoparticle catalysts.

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Hydrogel fabrication based on electrodeposition using electrochemical devices

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We previously reported 3D hydrogel fabrication based electrodeposition [1-3]. In the previous reports, tubular hydrogels were formed around a wire electrode for vascular-like constructions [1], and electrodeposited microwell hydrogels were used for fabrication of cell aggregates [2]. Furthermore, hydrogel lithography was conducted by scanning electrodes [3]. These methods is useful for tissue engineering and biosensors. In the present method, 3D complex hydrogels were fabricated using a large-scale integration (LSI) amperometric device.

We previously reported an LSI-based device for electrochemical imaging [4,5]. The device consists of 400 Au disk electrodes on the bottom of SU-8 microwell in 40-µm diameter and 5 µm deep. The electrodes work independently to induce addressable electrochemical reaction. The sensor electrodes are arranged in 250-µm pitch. The device was previously applied for electrochemical imaging for cell analysis. Since the desired potentials can be applied at desired sensors, hydrogels can be electrodeposited on only desired sensors. When the electrodeposition is sequentially conducted, 3D complex hydrogels are fabricated as shown in Fig. 1.

For hydrogel electrodeposition, we utilized an anodic method to deposit hydrogel films of the aminopolysaccharide chitosan that the group in University of Maryland reported [6]. In the method, reactive chlorine species (e.g., HOCl) is generated via the electrolysis of chloride, so that chitosan is oxidized to form chitosan hydrogels on the electrode through Schiff base linkages (Fig. 2). By using the scheme, 3D complex hydrogels were successfully fabricated on the LSI-based device. The hydrogels are useful for 3D organs in tissue engineering and biosensors using hydrogels.

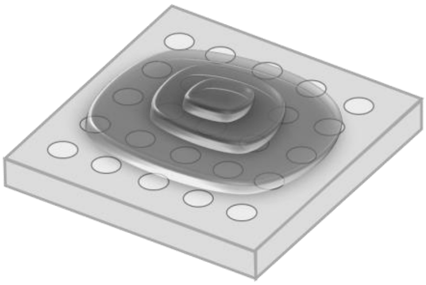
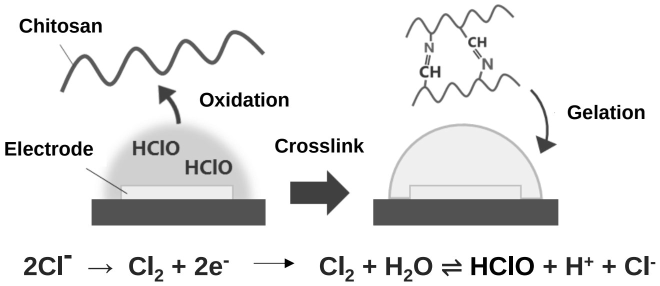


Fig. 1 General outline.



$$2Cl^- \rightarrow Cl_2 + 2e^- \longrightarrow Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-$$

Fig. 2 Scheme for hydrogel fabrication [6].

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Pd nanoparticles support on rGO-C@TiC coaxial nanowires as a novel 3D electrode for NaBH4 electrooxidation

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Recently, direct borohydride fuel cell (DBFC) is one kind of direct liquid feeding fuel cells, has been considering as a promising energy conversion devices. However, there are still some main issues retaining in DBFC. In practically, the competitive relation between the borohydride oxidation reaction and borohydride hydrolysis reaction will resulted in the actual number of electrons exchanged less than eight electrons and further leaded to the lower utilization of $NaBH_4$ and thus decrease the cell performance. Furthermore, the produced hydrogen bubble will be adsorbed on the electrode surface and further hindered the ion transport to the actively catalyst sites, thereby reducing the electrode activity. Compare with transition metals[1] and their borides[2] and AB_2 and AB_5 types hydrogen storage alloys[3], noble metals (platinum, palladium, gold and etc.) and their alloy [4] exhibit a better integral property with high catalytic and superior stability performance for borohydride oxidation reaction. However, the high prices increase the cost of DBFC system and thus restrict their extensive utilization. Therefore, designing and developing of anode catalysts along with high performance, low-cost, and stable for borohydride oxidation becomes the hot research areas at present.

Here, a novel 3D electrode for $NaBH_4$ electro-oxidation with rGO nanosheet deposited on C@TiC coreeshell nanoarray as a bind-free current collector substrate to support Pd nanoparticles is prepared (Figure 1). Coaxial nanowire arrays consisting of carbon shell and TiC core (denote as C@TiC) have been chosen as a 3D current collector due to its high electron conductive of both carbon and TiC. Reduced graphene oxide nanosheets are electrodeposited on this C@TiC substrate to provide more sites for the following electrodeposition of noble metal nanoparticles. Pd is selected as the borohydride oxidation catalyst in this work attributed to its high activity and fast electrode kinetics similar to that of Pt but the price is cheaper than Pt. The resulting electrode exhibited high catalytic performance and good stability for $NaBH_4$ electro-oxidation. The oxidation current density of 1.35 A cm^{-2} mg^{-1} Pd was achieved at 0.6 V and a DBHPFC employing with the as-prepared Pd-rGO-C@TiC electrode as anode catalyst and a Pd/CFC electrode as cathode catalyst is assembled and a maximum power density of 68.5 mW cm^{-2} is obtained. This study also provides a facile strategy for fabricating a 3D hetero-nanostructured electrode for other fuel cell, such as ethanol, methanol and N_2H_4 etc.

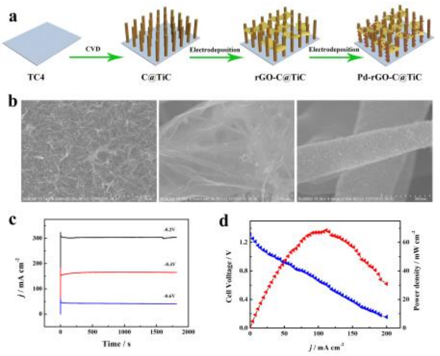

Figure 1 (a) Schematic illustration of the Pd-rGO-C@TiC electrode fabrication. (b) SEM images of Pd-rGO-C@TiC. (c) Chronoamperometric curves at different potential in 2.0 mol L^{-1} NaOH + 0.16 mol L^{-1} $NaBH_4$. (d) Cell voltage and power density versus current density for an DBHPFC single fuel cell with Pd-rGO-C@TiC as anode catalyst and Pd/CFC as cathode catalyst at 20℃

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Facile synthesis of morphology-controlled Co_3O_4 nanostructures and its application for H_2O_2 electroreducion

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As one type efficient and clean energy converters, fuel cell has attracted much attention in recent years [1]. However at the current stage of technology, the cost is one of the big obstacles hindering the commercialization of fuel cells. Especially, the high noble metal loading required for the oxygen reduction reaction (ORR) occurred at the cathode region (0.4 mg cm^{-2} Pt for ORR, 0.05 mg cm^{-2} Pt for the anode reaction [2]). In order for the fuel cell to replace the internal combustion engines currently used, significant decrease in the cost is urgently required. Very recently, H_2O_2 replaced O_2 as oxidant has been investigated in several low-temperature fuel cells, particularly in air-free environments (space or underwater) [3, 4]. That is due to its easy handling, storage, faster reduction kinetics than oxygen and higher standard reduction potential than oxygen [5, 6]. Recent study has also shown that H_2O_2 as a powerful oxidant could significantly increase the power density of a fuel cell. Among several types of electrocatalysts for H_2O_2 reduction, Co_3O_4 have been conceived as a promising cost-effective and scalable alternative, in place of precious metals, for H_2O_2 electroreduction.

A facile synthesis of morphology-controlled Co_3O_4 nanostructures through the solvothermal synthesis was successfully demonstrated (Figure 1). With the control of the solvent composition, we have obtained five different nanostructures (nanosheet, nanowire, ultrafine nanowire net, nanobelts, and nano-honeycombs). The ethanol introduced in the synthesis processes plays an important role on the crystal size, morphology, as well as their catalytic performance for H_2O_2 electroreduction. The sample prepared in the 2:1 C_2H_5OH/H_2O solvent displays an ultra-fine nanowire net morphology, which possesses an open, porous nanostructure with a large surface area. These characteristics of Co_3O_4 nanostructures make it facilitate electrons/ions transferring and enhance the catalytic efficiency when used as an electrode. The resulting electrode shows better performance for H_2O_2 electroreduction in an alkaline medium in terms of the catalytic activity than Co_3O_4 nanowire array electrode prepared in the pure water solvent. In the solution of 3.0 mol L^{-1} KOH+0.5 mol L^{-1} H_2O_2, the current density at -0.4 V could maintained at 0.214 A cm^{-2} during the test period. This simple solvothermal method has a great potential for the preparation of morphology-controlled Co_3O_4 nanostructures due to its facile synthesis, low cost, especially high performance for H_2O_2 reduction.

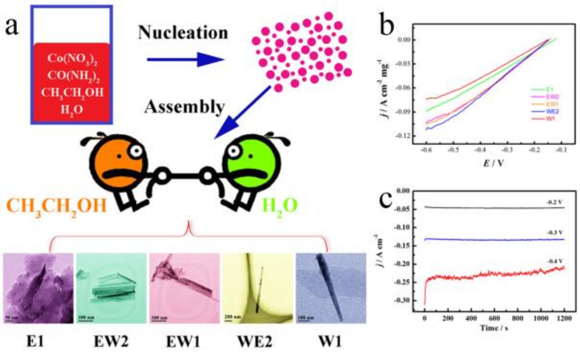

Figure 1 (a) Schematic diagram showing the mechanism for the formation of different nanostructures Co_3O_4. (b) The comparation of the as-prepared Co_3O_4 nanostructures in the growth solution with different C_2H_5OH/H_2O volume ratios. Chronoamperometric curves for H_2O_2 reduction on the as-prepared Co_3O_4 using C_2H_5OH/H_2O volume ratio 1:2 (WE2) at different potentials.

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Anticorrosion Behavior of Bio-drug on Mild Steel Surface: AFM and SEM Characterization

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Corrosion rates are influenced by the formation of inhibitor aggregates at the steel surface. Detail surface characterizations of mild steel have been studied before and after adsorption of different drugs in 1N HCl solution. Scanning electron microscopy (SEM), atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR) were used to examine the effect of drug adsorption on steel surface. SEM analysis suggested that the metal had been protected from aggressive corrosion because of the addition of the inhibitors. AFM visualization confirmed the formation of protective layer on steel surface, resulting the decrease in surface roughness with corrosion rates. The nature of metal surface has been analyzed by FTIR. It was revealed that the drug molecules effectively adsorbed on the surface.

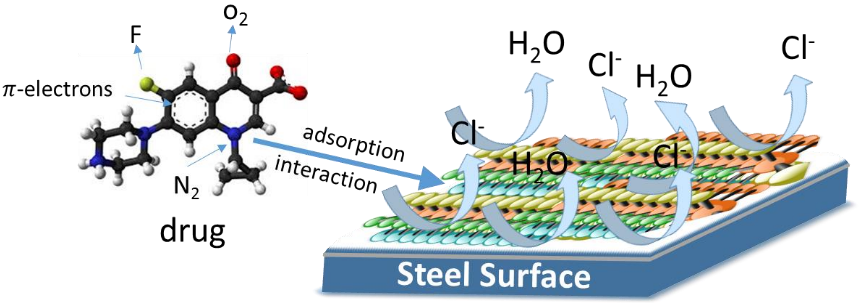

Figure 1: Drug adsorption and corrosion prevention mechanism on mild steel surface