New Electrodes for Efficient Electrochemical Advanced Oxidation Processes

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Electrochemical advanced oxidation processes (EAOPs) are well-established technologies characterized by the production of highly active hydroxyl radicals (•OH) that is promising in removal of biorefractory pollutants [1-2]. Importantly, cathode and anode materials have an essential influence on the pollutants removal to improve intrinsic drawbacks of low H_2O_2 yield, narrow pH range and high oxygen evolution potential [3-4]. Therefore, our group aims to modified the anode and cathode to overcome these disadvantages.

For cathode reaction, the production of H_2O_2 is key factor for electro-Fenton (EF). It is well acknowledged that carbon materials are widely used as cathode due to the advantages with good stability, non-toxicity, and high conductivity. Graphite felt (GF) was firstly modified by hydrazine hydrate and carbon back (CB) and polytetrafluoroethylene, improving the in situ production of H_2O_2 by about 2.6 times and 10.7 times, respectively [5-6]. And a novel GF cathode modified with electrochemically exfoliated graphene and CB was developed with very high H_2O_2 generation and with a relatively low energy consumption [7]. In addition, compared with other carbon materials, carbon nanotubes as cathode have higher H_2O_2 production after doping with tert-butyl-anthraquinone that could shift oxygen reduction to $2e^-$ process.

In order to promote application of EAOPs for organic pollutants degradation, powerful free radicals generated by cathode and anode oxide reaction is plays an important role on treatment efficiency and selectivity. For cathode reaction, the technology of in-situ metal-free EAOPs that the generated active sites by the introduced heteroatoms replacing the iron ions in EF was developed, solving the two major shortcomings of EF [8]. And the oxidative degradation and mineralization of imatinib, an antineoplastic drug for cancer treatment, were investigated using a graphene modified GF cathode comparatively with raw graphite felt cathode. The first time that the removal of IMA was investigated by EF, same for the determination of absolute rate constant (4.56×10^9 M^{-1} s^{-1}) for IMA oxidation by •OH. For anode reaction, Blue-TiO_2 nanotubes was modified electrochemical reduction that was promising anode material for wastewater treatment. And compared to the most potential anode material BDD, Blue-TiO_2 nanotubes had a higher •OH production, TOC and COD removal with a low energy consumption.

The superior performance of cathode and anode electrode in EAOPs for in situ H_2O_2 generation and emerging organic pollutant mineralization has a good application prospect. This study shed light on the cathode and anode improvement in EAOPs are promising and green technologies for environmental remediation.

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Material concepts for vanadium redox flow batteries

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The continuous increase of our global energy demand combined with the negative impact of greenhouse gas emissions from fossil fuel combustion on our climate have become major sources of concern. Using energy from renewable sources, such as wind and solar, is one way to reduce air pollution and environmental damage affiliated with the extraction and combustion of fossil resources. However, since wind and solar energy are only intermittently available, novel and more efficient energy storage solutions will be one important key to a sustainable energy supply.

Redox flow batteries appear to be a promising concept for the large-scale storage of excess energy from renewable sources, and are often discussed in the context of the stability of the electrical grid. Lately, the all-vanadium system has sparked considerable interest, utilizing the four aqueous oxidation states of V; $V^{2+/3+}$ at the negative, and $V^{4+/5+}$ at the positive side. State-of-the-art electrodes in these flow batteries are porous carbon felts, which offer a good stability and high electron conductivity at comparatively low cost in the highly acidic electrolytes. One disadvantage, however, is their low electrocatalytic activity.

Various treatments have been proposed in the literature to enhance the felts' activity for the respective reactions. Most common is a thermal activation procedure in air atmosphere at 400 °C for 30 h, which not only increases the wettability of the porous structures with the V-containing electrolyte, but also provides oxygen-containing functional groups for catalysis. It is not clear, however, how long this enhancement effect will last or whether it wears off with time and how it is dependent on storage conditions. Manufacturers would prefer felts with modified fiber surfaces, which would make the activation process obsolete in the future.

Herein, we present alternative strategies for the design of highly active electrodes producing carbon-carbon composites by templating [1] and electrospinning [2]. Two different carbon materials were combined in a porous electrode, where the one component works as the electron conducting network, while the more amorphous second constituent offers high catalytic functionality. The materials were characterized by a combination of methods, such as scanning electron microscopy (SEM), pore analysis (BET and tomography coupled with pore network modeling) and X-ray photoelectron spectroscopy (XPS) as well as electrochemical testing in 3-electrode configuration and real battery measurements. Electrochemical impedance spectroscopy (EIS) was applied to determine degradation phenomena with respect to the commercial felts and modified electrode materials.

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Scaling up and down heterogeneity in Electrocatalyisis

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Understanding electrocatalytic reactivity requires *in-situ* control of the surface properties of the relevant material. This includes surface site distribution as the size of the surface domains change in the nanometric scale. It is well-accepted that use of model surfaces, in which every surface atom site in a well-defined position, supplies useful information for this purpose. In this respect, polycrystalline electrode's reactivity can be easily rationalised from the behaviour of probe reactions on single crystal electrodes [1]. When the size and dispersion of electrocatalytic nanoparticles is required, a careful set of experiments is necessary to understand size effects, starting with surface cleaning. Several techniques may be used in the case of platinum, gold and palladium nanoparticles. Then, surface site characterization and distribution should be attempted, in order to rationalise the different contributions coming from different surface assemblies. In this sense, it is important to perform experiments with nanoparticles with the same shape and different size [2] or the same size and slightly different shape [3], trying always to modify a single relevant parameter (Figure 1). In this communication recent examples will be given, trying to illustrate the surface control of reactive nanosized materials used in practical applications.

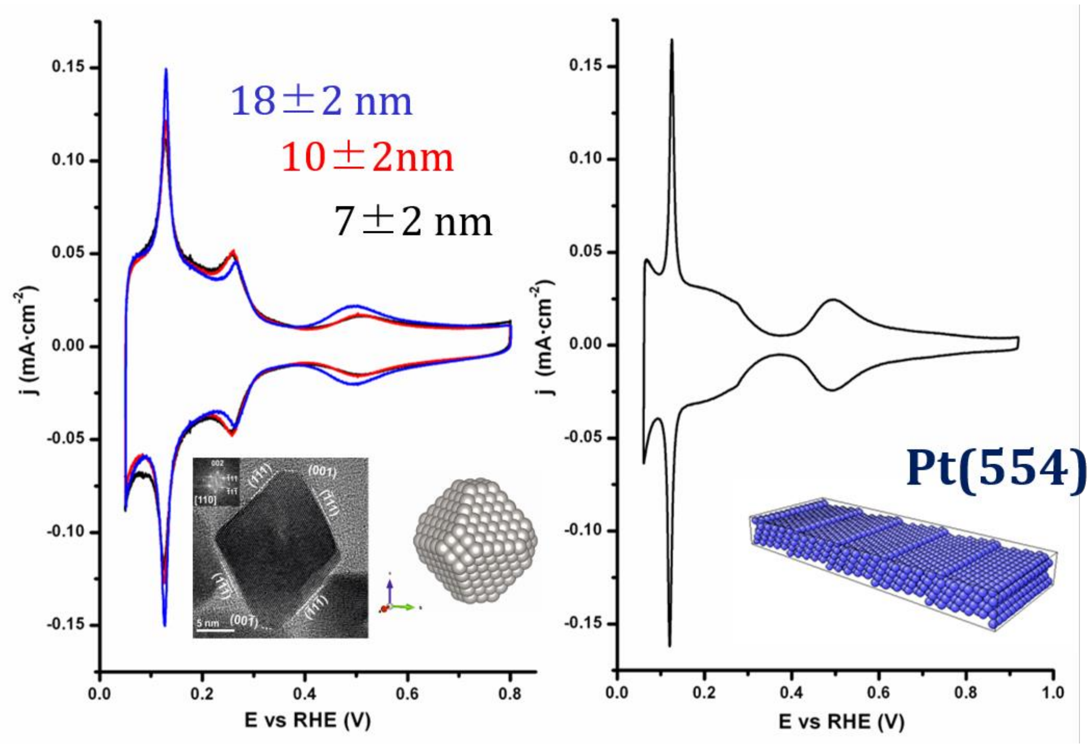

Figure 1. Voltammetric characterization of different size octahedral platinum nanocrystals (left), which exhibit different reactivity for formic acid oxidation. The figure on the right depicts the characteristic voltammogram of a Pt(554) single crystal model surface [2].

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Tuning CO_2 electroreduction selectivity by rational catalyst and electrolyte design

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The utilization of fossil fuels as the main energy source gives rise to serious environmental issues, including global warming caused by the continuously increasing level of atmospheric CO_2. Recently, the electrochemical conversion of CO_2 (CO_2RR) to chemicals and fuels driven by electricity derived from renewable energy has been recognized as a promising strategy towards sustainable energy.

I will provide examples of recent advances in the development of highly active nanostructured single crystal, thin film and nanoparticle (NP) electrocatalysts (Cu, Ag, Zn, and Cu-M with M = Co, Zn, Ag) and how their structure (crystal orientation, atomic arrangement, size, shape, defects,…), oxidation state and composition influence their selectivity in CO_2RR. Additionally, the determining role of the electrolyte in the reaction activity and selectivity will be illustrated by adding cations and anions (Cs^+, Li^+, Na^+, K^+, I^-, Br^-, Cl^-) to aqueous electrolytes. Finally, the importance of *in situ* and *operando* characterization methods (e.g. EC-AFM, XAS, XPS) to gain in depth understanding on the structure- and electrolyte-sensitivity of real CO_2RR catalysts under working conditions will be demonstrated. Our results are expected to open up new routes for the reutilization of CO_2 through its direct selective conversion into higher value products.

Electrochemical Removal of Cyanide from Mining Waters

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Electrochemical treatment is a promising technology for the removal of various contaminants, such as, anions, toxic metals, pharmaceuticals, chromium, arsenic and/or TDS. Currently, treatment of municipal and industrial waters is aiming in bringing the concentration of harmful contaminants to acceptable discharge levels. In this way, mining waters are known to be one of the main producers of sulfate, metal, nitrate and cyanide rich streams. Among others, cyanide is considered as the most toxic contaminant causing serious health and environmental problems. For these reason, it is mandatory to completely remove cyanide from mining waters before the disposal into the aquatic environmental.

This research is focused on the removal of 100 mg dm^{-3} of cyanide from synthetic mining waters using chemical coagulation, electrocoagulation and electrochemical oxidation. Electrocoagulation was performed using iron and aluminum electrodes and likewise, performance comparison was provided for chemical coagulation. In addition, DSA, BDD and carbon anodes were compared for the removal of cyanide by electrochemical oxidation. Tested current densities were 0.1, 1.0 and 10 mA cm^{-2} for electrocoagulation and 1, 10 and 100 mA cm^{-2} for electrochemical oxidation.

Results shown that cyanide was almost completely removed after 3 hours of treatment at 10 mA cm^{-2} using iron electrodes during electrocoagulation. However, using aluminum electrodes resulted in 95% removal of cyanide only after 10 h of treatment applying the same current density. Chemical coagulation tests using $FeCl_3$ and $AlCl_3$ did not result at any cyanide removal. Otherwise, complete removal of cyanide has been observed during electrochemical oxidation when operating with BDD and DSA anodes already after 2 h treatment time at 10 mA cm^{-2}. Removal efficiency and treatment times improved when the current density was set at 100 mA cm^{-2}. Carbon was found to be unsuitable material in terms of cyanide treatment due to the solution pH decrease till 6. The conducted research on the electrochemical removal of anions from mining waters has provided an understanding of the phenomenon occurring during the process. The knowledge about the removal mechanisms of cyanide from mining waters favors the possible development of electrochemical treatment technologies and scale-up of the existing units.

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Use of electrochemical processes for sludge conditioning: Importance in the properties and solubilization of organic matter.

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The world's overpopulation has led to an increase in the demand of water to cover their basic needs as well as to improve their quality of life (FAO, 2014). With this, a serious problem will be the increment in the volume of wastewater treated for reuse, as well as the generation of sludge. In this sense, currently in Mexico, treatment plants generate about 2,000 tons of dry sludge per day, which must be treated to comply with current regulations for reuse or final disposal. In this regard, treated sludge (called biosolids) can be used as fertilizers or soil improvers and in some countries the percentage of reuse is considerable because it represents an economic alternative and sustainable management for water operators. Additionally, sewage sludge can be treated in an anaerobic digestion process, which in addition to making it suitable for agricultural reuse, produces biogas that can be used for cogeneration of energy. In addition, this topic has gained particular importance with the increase in the demand of energy from renewable sources. Despite the potential for biogas formation from sludge, multiple investigations have been carried out to increase methane production through different pre-treatment processes or through new operating strategies in the sludge digestion itself. The aim is to recover the largest amount of energy stored in them and contribute to reducing the cost of operation and maintenance of wastewater treatment plants. These pre-treatments involve physical, chemical, mechanical, biological and thermal processes, which increase biogas production (Dogan and Sanin, 2009; Zhou et al., 2015).

Recently, the use of electrochemical technologies as a pre-treatment alternative for anaerobic digestion has been studied (Barrios et al., 2017; Yuan et al., 2016). These studies report that sludge pretreatment increases biogas production between 63 and 182% compared to control tests.

Consequently, different operating conditions were evaluated for electrooxidation and electrocoagulation of sludge, in terms of current density and time, where for electroxidation different degrees of solubilization of organic matter are obtained. The maximum degree of solubilization obtained was 1.78%, however, for the electrocoagulation process no significant changes were observed in the degree of solubility but an increase of 30% in the release of extracellular polymeric material.

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Degradation of levofloxacin by H_2O_2 generation in electrochemical reactor in plug-flow operation mode

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Currently, different types of compounds generated by anthropic activities reach the environment and promote some type of contamination, such as drugs, especially antibiotics. The present work aims to evaluate the degradation of levofloxacin using H_2O_2 generated in an electrochemical reactor operating in the "plug-flow" mode (cathode: gas diffusion electrode - GDE and anode: DSA®, both with 20 cm^{-2}) where the effluent passes only once inside the reactor. The degradation experiments (150 mA cm^{-2}) were performed in the absence and presence of 2 mmol L^{-1} of $FeSO_4$ on the electrolyte (K_2SO_4 0.05 mol L^{-1} pH 2) and the samples were taken after 15 minutes in each experiment. For the study of the degradation of levofloxacin, the concentration of antibiotic (High Performance Liquid Chromatography-HPLC) and organic load (Total Organic Carbon Analyzer-TOC) were evaluated. Figure 1A shows the variation of the concentration of levofloxacin in different degradation experiments monitored by HPLC. It was observed that the removal of the drug reached values greater than 80% in all experiments in the three flowrates studied. Such high removal may be associated with the type of technique used to monitor antibiotic concentrations, in liquid chromatography, minor modifications in the structure of the molecule under study may promote a decrease in its detection, however, such decrease does not necessarily represent complete degradation of the compound, thus the concentrations of TOC were evaluated in the same experiments and the results are presented in Figure 1B.

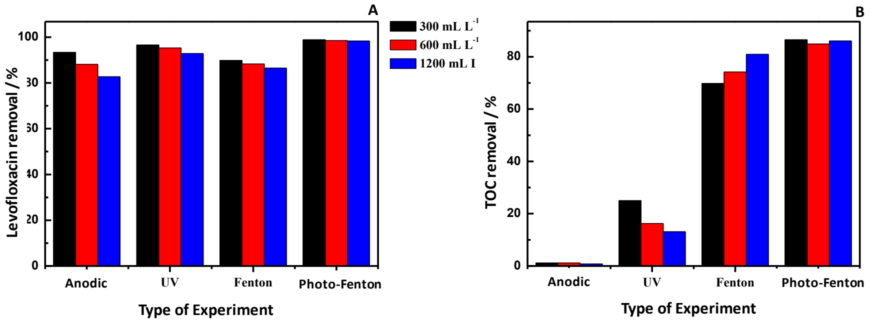

Figure 1 - (A) removal of levofloxacin (%) and (B) removal of the organic load (%) in the degradation experiments in a plug-flow electrochemical reactor.

It can be observed from the data presented in Figure 1B that in the experiments without H_2O_2 generation, the removals were less than 2% (anodic degradation) and less than 27% (UV degradation), but with the in-situ generation of H_2O_2, (75%) for H_2O_2/Fe_{2+} (Fenton) and removal of more than 85% for the $H_2O_2/Fe^{2+}/UV$ (Photo-Fenton) experiment. These results show that in experiments with higher availability of hydroxyl radicals (Fenton and photo-Fenton) they present greater removal of levofloxacin and greater removal of the organic load. Another point to be observed is the influence of the flow, in the absence of H_2O_2, the degradation of the organic matter occurs in the surface of the anode (anodic degradation) and in the vicinity in the UV lamp (UV degradation), thus, lower flows promote a longer time (Fenton and Photo-Fenton) and greater removal of the organic load. However, in the experiments with H_2O_2 generation, the higher flow promoted a higher generation of H_2O_2 on GDE [1], higher generation of hydroxyl radicals (Fenton and Photo-Fenton). With the results presented, the electrochemical reactor operating in the plug-flow mode achieves removals of up to 99% of levofloxacin and 86% of the organic load in the Photo-Fenton experiment at the flow rate of 1200 mL h^{-1}.

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Water treatment and energy conversion with electrochemical cells

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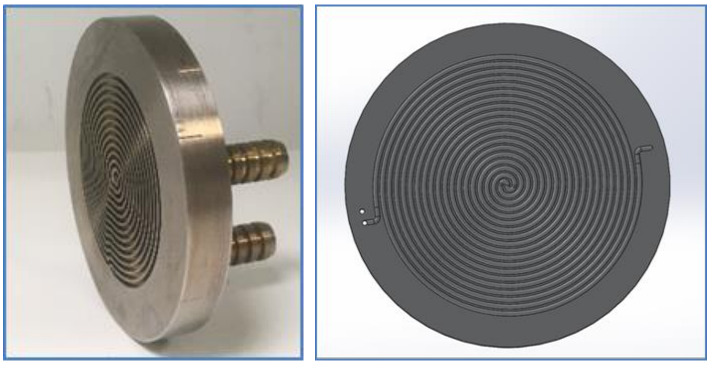
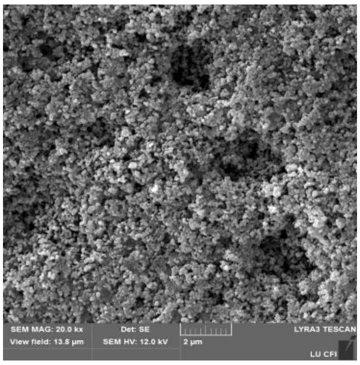
The increasing disposal of pharmaceutical products and organic material in the waste water streams represents an environmental problem. Another large environmental problem is the use of fossil fuels which has resulted in the highest concentration of carbon dioxide in the earth atmosphere, nowadays at 410 ppm. Electrochemical technologies can be used to prevent or diminishing some of these worrying effects of industrialization. As one of the most effective environmentally friendly methods to eliminate organic material from waste water, hydrogen peroxide can be used through the generation of the Fenton reagent that has high oxidation power. An interesting aspect of hydrogen peroxide is that it can be produced at the cathode at high current efficiencies via the reduction of oxygen but also at the anode through the oxidation of water, although the efficiencies are low. This talk will present some experiments to electrochemical produce hydrogen peroxide at the anode. Similarly, the talk will present some electrochemical strategies used to convert carbon dioxide into a useful sustainable fuel such as ethylene. Such conversion has been demonstrated on copper electrodes and the talk will present some novel electrochemical cell designs used and the results with different types of copper electrode structures.



Flow field for gas diffusion electrodes.



Copper (100 nm) on carbon electrode

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Fe-MOF-Derived FeS_2/C Nanocomposite as an Efficient Catalyst for Electro-Fenton Treatment in Urban Wastewater

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Electro-Fenton (EF), one of the most attractive electrochemical advanced oxidation processes (EAOPs), has been proven an efficient technology for the treatment of wastewater contaminated with recalcitrant, toxic, non-biodegradable organic pollutants. The traditional homogeneous EF process is based on the in-situ production of H_2O_2 by the two-electron reduction of oxygen on a suitable cathode. Its catalyzed decomposition by added Fe^{2+} allows forming powerful oxidizing hydroxyl radicals (•OH). Moreover, the continuous regeneration of Fe^{2+} at the cathode is feasible. However, its practical utilization is limited by several drawbacks: (i) the requirement of pH adjustment to 2.5-3.5; (ii) the high amount of iron required; (iii) the deactivation of iron ions; and (iv) the production of iron sludge [1]. Heterogeneous EF process was developed in recent years to overcome these disadvantages, since low iron dissolution can minimize the sludge formation and promote the life span of catalysts, also enlarging the working pH range.

The iron-containing catalysts like zero-valent ion and minerals like iron oxides or pyrite (FeS_2) have been proven successful in Fenton or EF processes. In particular, pyrite was reported as a good candidate, since its dissolution in water leads to the formation of Fe^{2+} as well as H^+, giving rise to a co-existing degradation mechanism comprising homogeneous and heterogeneous catalysis [2]. Although the pyrite-catalyzed EF showed better performance than traditional heterogeneous EF, it still suffered from a too large iron sludge production. Recently, metal organic frameworks (MOFs) have attracted great attention for gas storage, separation, fuel cells, supercapacitors, and catalysis. They may also be promising precursors to synthesize porous metal oxides or carbon nanostructures. In this study, FeS_2/C nanoparticles, fabricated via sulfidation of room temperature from an Fe-MOF precursor, were introduced as heterogeneous EF catalyst for the first time to treat fluoxetine-contaminated wastewater. Fluoxetine, a fluorinated antidepressant, was completely removed after 1 h, with Fe leaching as lows as 1.5 mg L^{-1}. This amount is much lower than that reported for pyrite-catalyzed EF process [2].

Fluoxetine exerts potentially noxious effects on living beings [3]. The treatment of fluoxetine spiked into wastewater was comparatively studied by different systems. FeS_2/C-catalyzed EF process clearly outperformed electro-oxidation (EO), Fe^{2+}-catalyzed homogeneous EF, and natural pyrite-catalyzed EF processes. The effect of operation parameters such as catalyst dosage, current density, and initial pH was investigated. •OH was identified as the dominant radical responsible for the degradation of fluoxetine. The unique mesoporous structure derived from MOF led to such a good catalytic performance. Furthermore, the catalyst retained good activity after five cycles, indicating the long-term catalytic endurance. In addition, the total organic carbon (TOC) abatement and toxicity evolution were investigated with a BDD anode. The PARAFAC analysis of excitation emission matrix (EEM) fluorescence spectroscopy for the treated samples revealed that fluoxetine and other organic pollutants contained in the water matrix were efficiently transformed into smaller molecular species or inorganic compounds.

Acknowledgements

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Electrochemical Removal of Organic Contaminants from Water: Old Limitations and New Opportunities

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The work carried out by our group during the last decade has aimed, primordially, at enhancing the performance of electrochemical water treatment. Among the various potential hazards, we have devoted special attention to organic micropollutants, also demonstrating the feasibility of electrochemical disinfection. With this purpose, we have addressed the improvement of processes, reactors, electrodes, and catalysts. In addition, we expect to extend the applications of the new setups to the treatment of contaminated natural water resources, which is a very challenging topic due to their great complexity. Regarding the development of new technologies, considerable advances have made in the field of the so-called electrochemical advanced oxidation processes (EAOPs) [1]. Among them, the most positive results have been achieved via electrooxidation (EO), photoelectrocatalysis (PEC), and Fenton-based EAOPs like electro-Fenton (EF), photoelectro-Fenton with UVA light (PEF), and solar PEF (i.e., SPEF) [2].

EO is certainly appealing due to its inherent simplicity and the availability of high oxidation power anodes like boron-doped diamond (BDD). As a classical limitation of EO, the treatment of natural water is difficult due to its low conductivity, high hardness and natural organic matter content. However, there exist opportunities like the use of a solid electrolyte polymer (SPE) cell or microreactors [1]. Another limitation arises from the confinement of $^{\bullet}OH$ within a very localized volume at the anode vicinity, but the application of paired electrolysis involving cathodic H_2O_2 production constitutes an opportunity. Further enhancement is clearly achieved through homogeneous catalysis with iron salts, giving rise to Fenton-based EAOPs [2]. These processes generally outperform EO, thanks to the production of a large amount of free $^{\bullet}OH$ from Fenton's reaction, well distributed in the bulk solution. Furthermore, in photoirradiated systems, the contribution of UV photons is crucial to promote the photoregeneration of Fe(II) catalyst and the photodecomposition of refractory metal-organic complexes. There appear limitations like the need of acid pH and the production of iron sludge. But we are now investigating the use of chelated iron to work at natural pH, as well as the synthesis of MOFs-derived heterogeneous catalysts showing low iron release and small pH variation. Good results have also been obtained upon modification of air-diffusion cathodes with Co-based nanoparticles on MWCNTs. These electrocatalysts show enhanced ability to electrogenerate H_2O_2, and improved stability and durability, as deduced from tests run at pre-pilot scale [3]. At present, we are also performing pilot tests on a 120-L plant at the Plataforma Solar de Almeria (Spain) [4], and collaborating in the modeling of SPEF process. Limitations related to long treatment time, which causes an increase in energy consumption, have been addressed by coupling electrocoagulation with EAOPs. This combination has been proven effective for the treatment of wastewater (olive oil mill, cheese whey, and urban effluents). Other improvements include the use of a continuous PEF reactor, and the application of low input current, which yields very high mineralization current efficiencies in SPEF. Finally, PEC with active photoanodes under sunlight, based on Ag- and Au-doped TiO_2 films, has also allowed overcoming the limitation associated to the use of UV lamps.

Acknowledgements

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Elimination of pharmaceutical pollutants of emerging concerns by solar photoelectro-Fenton

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Pharmaceutical products (PPs) have been found in wastewater worldwide. The problem of water contamination and global water scarcity could be mitigated by the treated wastewater reuse. In order to reduce emissions of PPs, the development of new tertiary treatment is necessary because the level of removal of pollutants in water vary widely depending on the chemical characteristics and concentration of pollutants, the operating conditions, and the treatment technologies [1].

Solar photo-electro-Fenton (SPEF) method is an electrochemical advanced oxidation process (EAOPs) that reach high removal of pollutants. EAOPs, are presented as a clean technology, in terms of the efficiency of emission control, operating costs, minimum requirements of chemical reagents, short residence times and versatility when working under a wide range of pollutant concentration [2]. These processes are based on the in-situ electrochemical generation of hydroxyl radical (•OH) which have a high standar potential of 2.8 V/vs. SHE. •OH reacts non-selectively with most organics up to their mineralization to CO_2, water and inorganic ions.
SPEF process belongs to this group of advances processes and it is based on Fenton's reaction, where Fe^{2+} reacts with H2O2 to produces •OH at pH 2.8, as shown by Eq. (1).

$$Fe2+ + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad (1)$$

H_2O_2 is electrogenerated *in situ* on the cathode surface by the reduction of oxygen (Eq. (2)). For example, at a carbon-PTFE gas (O_2 or air) diffusion cathode

$$O_2 + 2H+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$

Eq. (1) is catalytic and can be mainly propagated from Fe^{3+} reduction to Fe^{2+} at the cathode.

In this work, the removal of 5 pharmaceutical compounds (5 mg L-1 of each compound: Salicylic acid, sodium Sulfamethazine, Tetracycline, sodium Diclofenac and sodium Ampicillin) was studied. 10 L of solutions containing 12 mg L^{-1} of Total Organic Carbon (TOC) with 0.5 mM de Fe^{2+} and 0.05 M Na_2SO_4 at pH 3.0, applying a current density of 10, 25 and 50 mA cm^{-2} were treated in a pilot plant constructed in our laboratory. The pilot plant contained an electrochemical filter press cell with a DSA anode and an Air-diffusion cathode (50 cm^2 of exposed area) coupled to solar photo-reactor.

A complete mineralization of the mixture of compounds was obtained by SPEF process at the end of electrolysis applying current densities over 25 mA cm^{-2} and a complete elimination of all drugs is obtained at short times. Intermediates of reaction such as aromatic, carboxylic acids and inorganic ions were found during the oxidation process. Solar radiation favors the mineralization of the organics in cost and efficiency in comparison with other electrochemical methods.

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Challenges and Hurdles in the Operation of a Capacitive Deionization Pilot Plant

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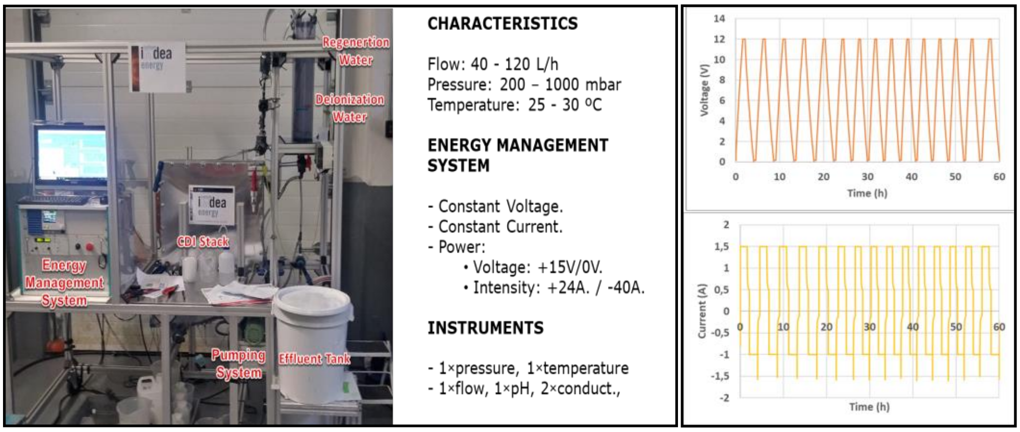
Capacitive Deionization (CDI) is a promising electrochemical water treatment technology that has attracted the attention of the scientific community since the beginning of the XXI century [1]. CDI mechanism is based on the adsorption of charged particles (ions) in the electrical double layer of an electrode upon polarization by a direct current power source. This is essentially the same work principle as charging a supercapacitor [2]. Therefore, water production while storing energy is possible when operating a CDI system. Despite the many benefits the technology has to offer; energy-efficient [3], does not require high pressures or temperatures, no need of using additional chemicals, the scalability of the technology and the long-term operation still remains as a scientific challenge.

In this work a CDI pilot plant has been operated using different operational parameters (mainly, current, cell voltage and operational time) and electrolyte concentrations. Salt Adsorption Capacity (SAC, mg g^{-1}), Average Salt Adsorption Rate (ASAR, g h^{-1} m^{-2}) and water production (L m^{-2} h^{-1}) were evaluated. Additionally, energy consumption parameters such as specific energy consumption (Wh g_{salt}^{-1} and kWh m^{-3}), energy efficiency and energy recovery.



CHARACTERISTICS

Flow: 40 - 120 L/h
Pressure: 200 – 1000 mbar
Temperature: 25 - 30 ºC

ENERGY MANAGEMENT SYSTEM

- Constant Voltage.
- Constant Current.
- Power:
  - Voltage: +15V/0V.
  - Intensity: +24A. / -40A.

INSTRUMENTS

- 1×pressure, 1×temperature
- 1×flow, 1×pH, 2×conduct.,

Fig. 1. CDI System and operational characteristics (Left). CDI system response in terms of current and voltage.

Experiments demonstrated the importance of maintaining both current density and volumetric flow rate well correlated, which might limit the water production. Electrochemical analysis indicated that 60-70% of the energy consumed in the ion removal step could be recovered. Long-term operation of the CDI system showed a robust operation for 60h. Energy consumption and water production analysis revealed a stable performance and the promising potential of the CDI technology.

We acknowledge the collaboration of GS-Inima and Proingesa on developing the CDI system. We also thank the Network of Excellence "Environmental and Energy Applications of the Electrochemical Technology" (CTQ2017-90659-REDT).

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Cathodic hydrogen production by simultaneous oxidation of methyl red and 2,4-DNa aqueous solutions using Pb/PbO$_2$, Ti/Sb-doped SnO$_2$ and Ti/Si/ BDD anodes

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In this work, the electrochemical oxidation of the Methyl Red (MR) dye and the Sodium 2,4-Dichlorophenoxiacetate (2,4DNa) herbicide was investigated on Ti/Si/BDD, Pb/PbO$_2$ and Ti/Sb-doped SnO$_2$ anodes in aqueous acidic media by applying 30 mA cm^{-2} at 298 K. The electrochemical experiments were carried out in a two-compartment electrochemical cell separated through a Nafion® membrane 417 type in order to use two type of supporting electrolytes in order to measure the consumption of the organic compound, the hydrogen production as well as the amount of the oxygen produced in parallel with the oxidation of the model organic pollutants. Although the main goal of this study is to understand the relationship between these processes, in this first work, the oxidative capacity of the aforementioned anodes to degrade the proposed pollutants, was analyzed in order to evaluate their current efficiencies (η) for an electrolysis time relatively short. The results clearly showed that MR and 2,4DNa can be oxidized on such anodes, but both the oxidation level and the η varied significantly between them. Thus, although the MR solutions were completely discolored in all cases only on Ti/Si/BDD anodes MR was oxidized until carboxylic acids in less than 15 min of electrolysis time. On Pb/PbO$_2$ and Ti/Sb-doped SnO$_2$ anodes the discoloration was slower and the oxidation less complete, leaving still in solution some organic by-product, such as 2-aminobenzoic acid and/or N,N'-dimethyl-*p*-phenylenediamine, in the fixed electrolysis time, however, the oxidation trends suggests a complete oxidation to a longer electrolysis time. The situation changes with 2,4DNa because this organic pollutant is more difficult to degrade due the presence of chlorine groups in the aromatic ring which makes to the 2,4DNa a more stable molecule. The fist oxidation stage produces 2,4DP in all cases, but on Ti/Si/BDD anodes this intermediate is quickly consumed which was not so on Pb/PbO$_2$ and Ti/Sb-doped SnO$_2$ anodes were their consumption requires longer electrolysis time to that fixed for this case. From the polarization results and the corresponding Tafel analysis, a reaction scheme for the formation and consumption of 2,4DP was proposed.

Electrokinetic-Fenton remediation for the remediation of petroleum from contaminated kaolinite

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Recently, an increasing interest in the remediation of soil and water polluted with petroleum has been attained. In this case, the contamination is often associated with fuel, oils, jet fuel, etc., consequently, the impact on the environment is due to their hydrophobic characteristics. Petroleum can be represented as total petroleum hydrocarbon (TPH). TPH is a broad family of organic compounds, for this reason, is represented as the function of equivalent carbon number. These are sometimes referred to as gasoline and diesel range organics due to the boiling point ranges of the hydrocarbon in each roughly correspond to those of gasoline (C_6 to C_{10}-$_{12}$) and diesel fuel (C_8-$_{12}$ to C_{24}-$_{26}$), respectively. Nowadays, electrokinetic remediation (ER) is a technique has been used in the treatment of polluted soil by which contaminants can be moved to controlled extractions points. In this context, Electrokinetic Remediation-Fenton (ER-Fenton) technology have been developed for soil remediation. In this context, this work aims to investigate, for the first time, the coupling of ER-Fenton process to eliminate total petroleum hydrocarbon (TPH), from kaolin soil. Bench-scale ER-Fenton experiments were conducted using a kaolin, a low permeability clayey soil, spiked with petroleum. In ER-Fenton experiments, 0–10% H_2O_2 solution was delivered from the anode and citric acid solution from the cathode. An electric potential of 1 V / cm was applied in all tests to induce electroosmotic flow for 14 days. The information about the experiments is described in Table 1. Maximum TPH oxidation was observed by $Exp_{H2O2+citric\ acid/citric\ acid,}$ this result reveal that an optimized in situ combined technology of EK and Fenton-like process has the potential to oxidize PAHs in low permeability and/or high buffering soils.

Table 1. Electrokinetic Remediation-Fenton parameters used in this study.

Treatment	Supporting electrolyte		Electric field (V/cm)	Time (days)
	Anode	Cathode		
$Exp_{water/water}$	Water	Water	1	14
$Exp_{H2O2/water}$	10% H_2O_2	Water	1	14
$Exp_{H2O2/citric\ acid}$	10 % H_2O_2	0.1 M Citric acid	1	14
$Exp_{H2O2+\ citric\ acid/citric\ acid}$	10 % H_2O_2 + 0.1 M Citric acid	0.1 M Citric acid	1	14

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Synergist and antagonist effects during the integral treatment of Isoniazid contaminated water based on electrochemical and photochemical processes

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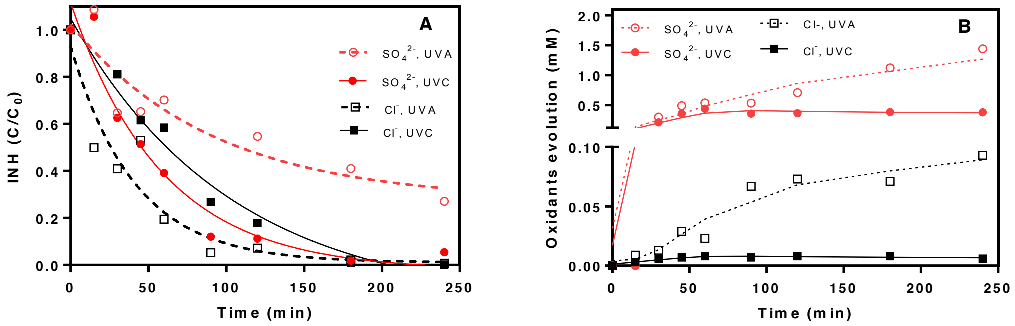
Reports of the presence of pharmaceutics in different water bodies have been increasing and deeply described during the last decade. Special attention has been increased for antibiotics case given their evidenced relationship with bacterial resistance. Previous investigations evidence the problematic of antibiotics in the environment to diverse facts, in which the absence and/or the inefficient wastewater treatments could be highlighted. As consequence, new and un-conventional processes have emerged as alternative treatments known as advanced oxidation processes (AOPs); efficiently applied for emergent contaminants eliminations such as antibiotics. Isoniazid (INH), a powerful first-line anti-tuberculosis drug, had a high consumption during the last decade due tuberculosis has been widespread with mayor impact in undeveloped countries. A few investigations have been developed regarding the elimination of INH related to photochemical processes. Although the reported investigations showed favorable results against the INH elimination, no total removal was reached in most cases. Under this outlook and considering the complexity of the contaminated waters were INH is found, the application of a single process does not represent a promising solution of this problematic. For that reason, the strategy of coupling or integrating different systems becomes an interesting alternative due increasing the efficiency of the water treatment and reducing the treatment global cost. During this work, the degradation of INH was performed by the integration of electro-oxidation (EO) and photolysis (UV) in the presence of sulfate and chloride ions, as supporting electrolytes. Both processes were initially individually tested. A dependence of the applied current density was observed for the EO treatment in the presence of sulfate in which the degradation was mediated by both hydroxyl radicals and sulfate-based oxidants. On the contrary, in the presence of chloride, INH degradation was highly promoted by chlorine active species and not influenced by the current density. The photo-degradation of the pollutant was promoted only UVC radiation but not UVA. Enhanced and inhibition effects were obtained, regarding the direct photolysis, by the presence of Cl^- and SO_4^{2-}, respectively. The integration of the both processes lead to the contribution of different oxidants ending up into synergistic and antagonist effects. Promising results were obtained the EO/UV system using UVA-chloride and UVC-sulfate, showing the highest INH degradation and low energy consumption regarding the organic matter oxidation. Hence, results evidenced the dependence of the integration system EO/UV as dependent on the electrolyte nature and the UV radiation energy.



Evaluation of the integrated system under UVA and UVC irradiations by using different supporting electrolytes: **A)** INH degradation; **B)** oxidants evolution. [INH]=20 ppm; [NaCl]=[Na_2SO_4]=0.05 M; 6 W.

Testing a new concept of heterogeneous electroFenton reactor for wastewater treatment

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The electrochemical advanced oxidation technologies (EAOPs) have been extensively studied on laboratory scale for the efficient abatement of recalcitrant organic pollutants in wastewater. The objective of the present work is the combination of two EAOPs, namely anodic oxidation and electroFenton, on a bench-scale reactor with potential to be scaled up for industrial applications.

In particular, the main features of the system are *i)* a pressurized-jet aeration system, a powerful and synergistic combination of a jet aerator and a pressurized circuit *ii)* a microfluidic flow-through electrochemical cell, which combines a low ohmic resistance, a high mass transfer and *iii)* state-of-the-art 3D electrodes, to maximize the mass transfer rate and *iv)* a fluidized bed of iron particles, to promote the Fenton reaction avoiding the issues related to the use of an homogeneous catalyst .

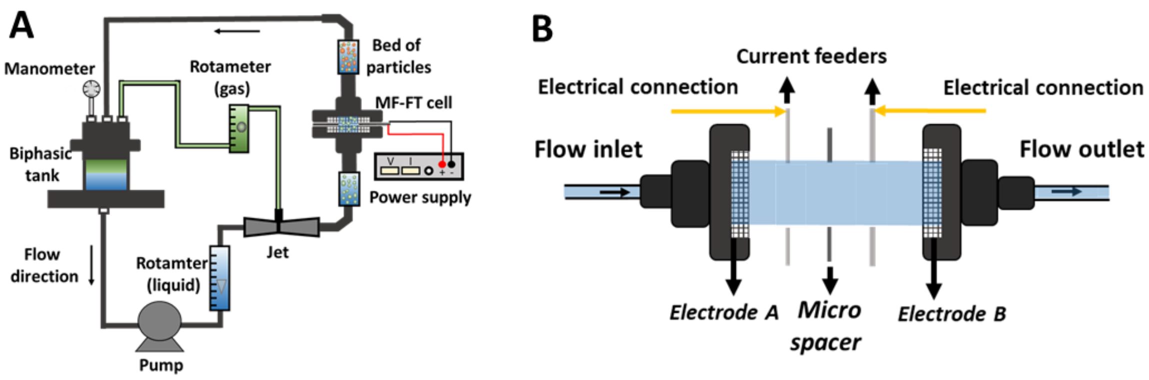

Figure 1. A) Schematic setup of the system; B) A micro-fluidic flow-through cell

Preliminary results show an outstanding performance of the microfluidic flow-through cell in comparison to a commercial flow-by [1], a synergistic combination of anodic oxidation and electroFenton in this reactor most likely due to the membrane-like effect [2] or the lowest specific energy consumption reported (3.65 kWh / kg H_2O_2 @ j = 10 mA cm^{-3} and 0.05 M Na_2SO_4 as electrolyte) for the production of hydrogen peroxide [3]. The present communication summarizes the latest results obtained in the use of this reactor for the selective abatement of complex organics contained in different types of wastewater.

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Application of electrochemically synthesized nitrogen doped graphene for treatment of produced water by electro-Fenton process

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Electro-Fenton is widely used as a method for wastewater treatment based on the in-situ generation of H_2O_2 by oxygen reduction reaction (ORR). Nitrogen-doped graphene has recently drawn a great deal of attention due to its good electrical conductivity, the stability of graphene as well as good activity towards ORR. Nitrogen-doped graphene was synthesized using electrochemical exfoliation of graphite foil in the presence of an inorganic salt. Raman spectroscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy were employed to characterize the prepared materials. In-situ generation of H_2O_2 for different materials was investigated by applying a constant potential in a divided cell. The efficiency of synthesized material for the electro-Fenton process was evaluated in the treatment of produced water. The removal of organics as well as the effect of different operating parameters such as pH, current density, organics concentration and retention time were explored. Organics concentration and by-products were determined using total organic carbon analysis and ultrahigh-resolution mass spectrometry. The results demonstrate that the synthesized materials can efficiently reduce the concentrations of organic contaminants. These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Hydrated silica removal from five different groundwater sources by electrocoagulation process

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The exposure to hydrated silica in drinking water mainly affects the lungs, increasing the risk of suffering tuberculosis, silicosis, lung cancer, among others. In addition, high concentrations of silica generate problems in industrial pipes and in several unit operations such as heat exchangers, where silica salts are impregnated in the walls of the equipment. In groundwater, in Central Mexico, hydrated silica is present with other coexisting ions such as arsenic and fluoride [1-2]. These two latter pollutants lead to the appearance of different types of chronic diseases. The hydrated silica is not regulated in México, however, there is a recommendation that suggest a limit < 12 mg L^{-1} (NMX-AA-075-1982). The WHO guidelines for As and fluoride are 10 μg L^{-1} and 1.5 mg L^{-1}, respectively. There are several techniques that have been implemented for the removal of hydrated silica, however, our research group have evidenced that the EC allow to the abatement of hydrated silica from groundwater and other coexisting ions as arsenate and fluoride [1]. This work deals with the hydrated silica removal with other coexisting ions such as arsenate and fluoride from five different groundwater samples (collected in Central Mexico) by electrocoagulation using an electrocoagulation reactor with a six-cell stack, in serpentine array. The cell is open to the atmosphere at the top for the gas release. Aluminum plates were employed as sacrificial anodes. The EC tests were carried out at mean linear flow velocities between $1.2 \leq u \leq 4.8$ cm s^{-1} and current densities between $4 \leq j \leq 10$ mA cm^{-2}. When the solution leaves the electrocoagulation reactor, the mixture water-flocks is sent to the jar test for the aggregate growth and sedimentation of the aggregates. Then, the clarified solution is analyzed. The best hydrated silica removal was obtained at current densities between 7-10 mA cm^{-2} and flow rate of 1.2 cm s^{-1}, Fig. 1. The concentration of arsenic and fluoride after the EC, for the same electrolyzes trials were $0 < [As] < 9.9$ μg L^{-1} and $0.7 < [F^-] < 2.64$ mg L^{-1}. SEM-EDS, XRD, and FTIR analyses shown that the flocs are composed of aluminum silicates, indicating that silica reacts with aluminum salts, while arsenates are adsorbed on the aggregates, and fluoride replace a hydroxyl group of aluminum flocs.

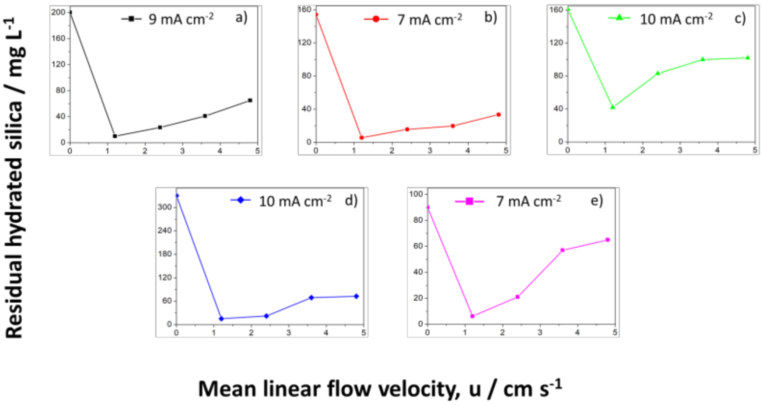

Fig 1. Removal of hydrated silica by electrocoagulation from five different groundwater samples collected from Central Mexico: a) Cabañas, b) Campuzano, c) El Carmen, d) Ex hacienda, e) Mojoneras.

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Pesticide Removal from Groundwater Using a Solid Polymer Electrolyte Cell with a Mesh BDD Anode

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The use of synthetic pesticides in intensive agriculture allows increasing the production by counteracting pests of all varieties. However, once put into practice, this activity automatically becomes detrimental for both, soil and water. The massive centralization and industrialization in crop production during the last decades has spread these toxic xenobiotics in the environment, particularly in the most important agricultural areas. As a result, persistent organic pollutants (POPs) are becoming accumulated in underground water masses. In fact, contamination by pesticides constitutes one of the major environmental impacts on groundwater coming from agricultural lands.

Lately, a great improvement has been made on technologies for the removal of organic pollutants, either from urban or industrial wastewater, as is the case of the so-called electrochemical advanced oxidation processes (EAOPs). These are environmentally friendly processes based on the in situ generation of hydroxyl radicals ($^{\bullet}$OH) and, among them, electrooxidation (EO) stands out as the simplest and most versatile one. The main reason to explain the scarce expansion of EO as a viable technology for the decontamination of natural and urban water and many industrial and hospital effluents is their typically low conductivity. The most common approach to overcome this limitation is the addition of a supporting electrolyte. Groundwater presents other less evident difficulties to be electrochemically treated, such as the presence of refractory organic matter and the high amount of carbonate and hydrogencarbonate that can cause the precipitation of Ca and Mg ions. This results in the cathode fouling. An innovative approach relies on the use a solid polymer electrolyte cell (SPE), composed of a membrane packed between two electrodes. This configuration allows working at a low cell voltage even at low conductivity.

This communication reports the high performance of an SPE cell for the removal of imidacloprid from natural groundwater with low conductivity. The cell was equipped with a Nafion® N117 membrane packed between two mesh electrodes, Nb/BDD anode and Ti/RuO_2 cathode. The natural water matrix was first softened using valorized industrial waste in the form of zeolite (NaP1-NA) as reactive sorbent. Total removal of pesticide was achieved, always obeying a pseudo-first-order kinetics, and getting maximum mineralization degrees of 70-87%. The main oxidative contribution can be attributed to active chlorine in the bulk and $^{\bullet}$OH at the BDD surface. Studies using simulated water revealed that the natural organic matter interfered in the groundwater treatment. The initial N and Cl atoms of imidacloprid were primarily transformed into NO_3^- and Cl^- ions, being the latter anion converted to ClO_3^- and ClO_4^- ions. 6-Chloronicotinonitrile, 6-chloro-pyridine-3-carbaldehyde, and tartaric acid were identified as oxidation products.

Acknowledgements
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Successful Removal of Micropollutants by the Nyex^{TM} Advanced Oxidation Process

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Improvements in analytical techniques coupled with increasing research in the field of organic freshwater pollution mean that increasing focus is being directed at ways to cleanse waters of organic contaminants. While individual organic compounds may not present particularly high toxicity alone, mixtures of contaminated waters may pose cumulative effects greater than the sum of risks posed by individual contaminants due to inherent difficulty in ecotoxicological quantification of mixtures of chemicals. Worries about ecosystem damage, carcinogenicity and endocrine disruption are among key concerns and these factors have led to increasing resources directed at improving efficacy of water treatment practices overall.

However, cost effective removal of organic micro-pollutants has proven to be one of the most significant challenges facing the water industry. We present here a different approach to removal and destruction of these micro-pollutants using a continuous process of adsorption coupled with simultaneous electrochemical regeneration, in Arvia's patented Nyex™ treatment units.

The Arvia^{TM} Process combines the advantages of an adsorption process which concentrates organic compounds in low concentration, and electrochemical oxidation, which allows regeneration of the adsorbent by oxidising the organic compounds once adsorbed. This process enables what are currently contaminated effluents into useful sources of low-grade water which can then be safely reused in an industrial or process environment, or discharged to the environment while protecting fragile ecosystems.

A Wastewater Treatment Plant (WWTP) in Switzerland indicated that they were having problems with several micropollutants in the water they were discharging. A trial was planned based on initial results showing up to ~15 µg/L total contamination primarily by a range of anthropogenic micropollutants.

All determinant micropollutants were shown to have been removed by the Nyex™ technology to below the Limits of detection (LOD) of the analysing laboratory, in all cases.

Table 1. Mean experimental results obtained from wastewater treatment trial run on-site at a Wastewater Treatment Plant in Switzerland.

Determinant	Inlet (µg/L)	Treated Outlet (µg/L)	Removal (%)
Amisulpride	0.29	<0.01	**97**
Benzotriazole	5.92	<0.25	**96**
Candesartan	1.17	<0.01	**99**
Carbamazepine	0.69	<0.01	**99**
Citalopram	0.28	<0.01	**96**
Clarithromycin	0.27	<0.01	**96**
Diclofenac	1.57	0.01	**99**
Hydrochlorothiazide	0.46	<0.02	**96**
Irbesartan	0.17	<0.01	**94**
Methylbenzotriazole	1.26	<0.05	**96**
Metoprolol	0.35	<0.02	**94**
Sulfamethoxazole	1	<0.01	**99**

Investigation towards clean water: heterogeneous electro-Fenton and voltammetry coupled for ionic liquids elimination

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In recent times, a new type of 'green' solvents, called ionic liquids (ILs), has gained a wide interest owing to their remarkable number of applications. ILs present unique properties such as high chemical and thermal stability, non-flammability and negligible vapour pressures that makes them an alternative reaction media to traditional volatile organic solvents. Moreover, ILs have caught considerable attention in the analytical chemistry field due to their excellent extractant properties, which can be tailored to specific values of viscosity or miscibility [1]. Nevertheless, several studies have shown that ILs are, in some cases, even more ecotoxic than commonly used solvents. Therefore, these compounds are considered to be "Contaminants on the Horizon" and their entrance in the environment poses a potential threat. Conventional water treatment plants were not originally designed for the elimination of this types of pollutants. Thus, it is necessary to find processes able to deal with the elimination of ILs [2].

In this context, the objective of the present study was to investigate the effectiveness of the electro-Fenton (EF) process towards the degradation of the 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride IL present in a water matrix. Heterogeneous EF was selected, using iron alginate beads as the solid catalyst. Furthermore, differential pulse voltammetry analysis was performed on screen-printed electrodes in order to follow the evolution of the IL degradation in 'real time'. During the reaction time, several intermediates (such as 2,4,6-Trimethyphenol, 2,4,6-Trimethylaniline and various carboxylic acids) were detected (Fig. 1). Additionally, the results were corroborated by carrying out HPLC and IC analysis. Based on the results obtained, it can be concluded that the combination of EF process with the DPV technique provides useful information on the degradation pathway followed by the contaminant.

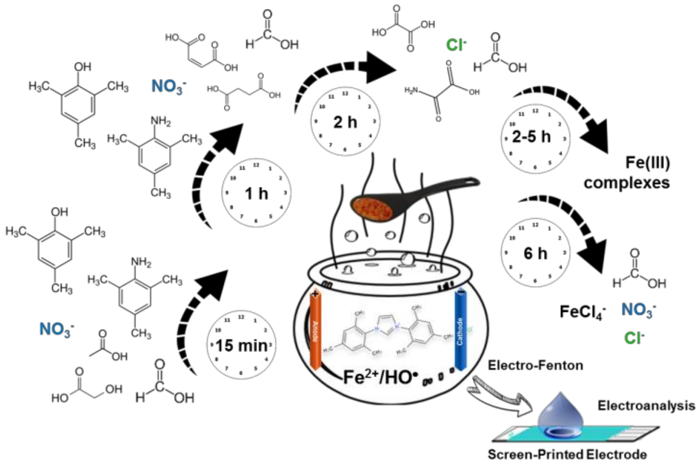

Fig. 1. Representation of the degradation pathway followed by the IL with time

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ANSWER solution: Validation of bioelectrochemical and electrochemical technologies for agri-food wastewater treatment

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Nowadays, brewing process is accompanied by the production of high flow rates of wastewater characterized by high concentrations of easily biodegradable organic matter, but also high concentrations of suspended solids and nutrients (specially nitrogen and phosphorous) being necessary the implementation of suitable wastewater treatments to accomplish with the European and National effluent discharge limits. In this context, the ANSWER project (LIFE15 ENV/ES/000591) aims to demonstrate the technical and economic feasibility of the integration of electrocoagulation (EC) and bioelectrochemical technologies (a fluidized bed bio-electrochemical reactor, FBBR), at pilot scale for the treatment of wastewater.

Firstly, an electrocoagulation reactor, with a treatment capacity of 10 m^3/h, is fed with raw brewing wastewater. During the electrochemical treatment, nitrogen and phosphorous concentration decrease under the discharge limits using recycled aluminum as anode material in order to decrease the capital cost of the operation and accomplishing with the Circular Economy principles. Before the pilot EC operation, Lab-scale experiments have been performed in EC cells of 2 L in order to optimize the pilot EC unit evaluating key operational parameters as electrode separation or applied current.

A bioelectrochemical treats the electrocoagulation effluent. The FBBR unit ($V = 0{,}5\ m^3$) works as a microbial electrolysis cell (MEC), where anode material, conductive activated carbon, is polarized by a potentiostat. Electroactive bacteria is inoculated, favoring the biofilm growth on the surface of the carbon particles rapidily decreasing the COD concentration of the wastewater and generating a valuable electric current. In addition, it has been observed the presence of high concentration of hydrogen in the generated biogas increasing the energy content of this product that could be further valorized. The FBBR unit is actually working in continuous mode achieving up to 90% of COD removal and an enriched biogas with a high fraction of methane (70%) and hydrogen (2%). As studied in EC unit, deep experimental research at lab-scale and pre-pilot scale has been developed during the last years in order to optimize the process and to enhance the technical knowledge of this unit. The continuous long-operation of the FBBR and the obtained experimental results technically and economically validates the bioelectrochemical technology as an innovative technology for the industrial wastewater treatment.

Finally, after the electrochemical technologies, the FBBR effluent is treated by a UF unit and UV radiation obtaining a high-quality treated water that properly accomplish the national Royal Decree 1620/2007 for water reuse.

Fig.1. Raw brewery wastewater vs ANSWER treated water.

Study of the Effect of Some Operational Variables on the Electro-Fenton Degradation of Triclosan

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There are several recalcitrant compounds that after being employed in the chemical industry, are discharged to the environment in aqueous effluents, thus creating a serious contamination problem in water ponds, rivers and lakes. In this regard, several research groups around the world are developing technologies to efficiently oxidize these chemicals and clean up water sources. Among the technologies that have been explored, the electro-Fenton approach is one of the most promising. In this way, by combining Fe(II) species with electrochemically generated H_2O_2 on carbonaceous surfaces, it is possible to produce the $^{\bullet}OH$ radical species, which is a powerful oxidant capable of mineralizing a large variety of recalcitrant pollutants.

Recently our group developed an electrochemical reactor in which the cathode is an activated carbon packed bed that is also used as an adsorbent. The arrangement of this reactor contains two Fe loaded resin compartments and a switching cycling mode that eliminates the need to use low pH conditions at the inlet and neutralization and cation removing stages for the treated water effluent. Triclosan on the other hand, is anti-bacterial compound commonly used in health care products. It is recalcitrant, i.e. resistant to biological treatment, and usually found in contaminated waste water. In this work, the electro-Fenton reactor developed in our group was employed to test and later optimize the degradation of a triclosan contaminated effluent.

In this way, four factors were studied using a design of experiments approach in terms of their effect on the electro-Fenton degradation of triclosan solutions. The four factors had two levels each and consisted on i) treatment time, ii) amount of Fe loaded resin, iii) supporting electrolyte composition and iv) operation mode (batch and continuous flow). The 2^4 experimental design revealed the most significant factors, the interaction parameters for the process as well as the empirical equation that describes the performance of the electrochemical reactor. The best operational conditions within the frame of the parameter window under study showed a 97% triclosan degradation in 85 min, using 0.5 of Fe loaded resin operating in a batch mode.

It is also important to note that although the electro-Fenton approach employed resulted in most cases in high triclosan degradation percentages, the byproducts obtained could be newly formed pollutants that also require identification and perhaps further oxidation processes. In this regard, the electro-Fenton degradation experiments were carried out using a high-resolution mass spectrometer coupled to gas chromatography. The results of the analysis showed the identity of some byproducts of the Fenton promoted oxidation process, and allowed a degradation mechanism to be proposed.

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Rapid and selective (electro)catalytic removal and recovery of sulfide from wastewater

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Removal of hydrogen sulfide from wastewater is a major concern because of its toxicity to humans and the ecosystem in general. In addition to this, solutions containing sulfides are highly corrosive, which leads to fouling of metal pipes through sulfidic scaling. Electrochemical treatment has been suggested as a versatile and robust method for *in situ* removal of hydrogen sulfide, thus avoiding the risks related to dosing and transportation of chemicals and stream pretreatment.

Here we propose a low-cost *in situ* method for sulfide removal using electrochemical cell equipped with novel MnOx-coated graphite felt (GF) electrodes. The procedure of the material synthesis was tailored towards increasing the catalytic activity of MnOx coating in selective oxidation of sulfide to sulfur. Catalytical activity was estimated in the OC experiments (i.e., without the applied potential). The observed sulfide removal rates were enhanced 25 times compared to pristine GF (Figure 2). However, when this material was applied again for sulfide removal, the rates were lower compared to the first application, which can be explained by gradual depletion of manganese available for catalytical reaction. Moreover, as was indicated by XRD analyses, the manganese oxidation state in samples subjected to sulfide solution was generally decreased.

Application of low anode potentials (i.e, 0.2-0.4 V vs Ag/AgCl) had a limited impact on the sulfide oxidation rate, yielding only a slight improvement in the rate constants. However, anodic polarization of MnOx-coated electrode enabled the recovery of manganese that was reduced in the reaction with sulfide ion. Final product of the oxidation was elemental sulfur, which was physically separated from the stream thus avoiding further reformation of sulfide. Since elemental sulfur is characterized by high electrical resistance, its deposition leads to electrode passivation and eventually halts the process. To overcome this limitation, we have successfully recovered the deposited sulfur in the form of sulfide with cathodic polarization. While MnOx-coating is also reduced by the application of the negative potential, it could be easily recovered to the initial oxidation states by switching the applied potential back to positive values.

This study demonstrates for the first time an exceptional potential of the MnOx-coated electrodes for sulfide removal, and more importantly sulfur recovery from wastewater due to their excellent (electro)catalytic activity, electrochemical stability and selectivity towards sulfur as the final oxidation product.

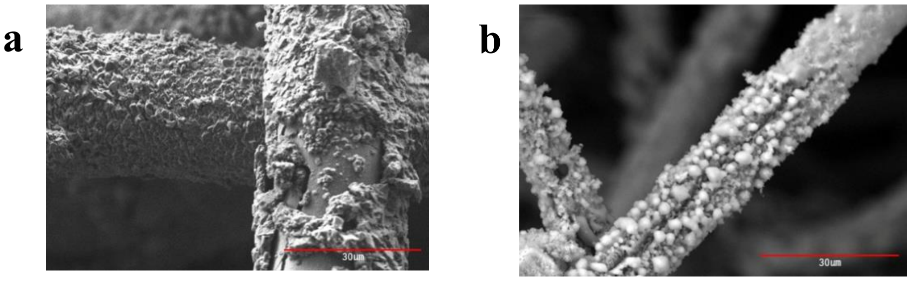

Figure 1. GF fibers a) with deposited MnOx nanoplates b) after application for sulfide removal with electrodeposited sulfur

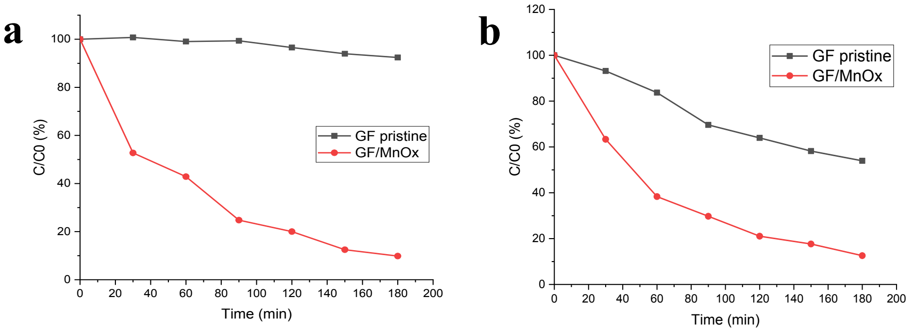

Figure 2. Sulfide removal a) during the OC experiment using pristine GF or GF/MnOx b) at 0.4V applied using pristine GF or GF/MnOx electrodes

Coupled Processes for Wastewater Treatment: Considerations on Electrochemical Configurations

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The traditional water and effluent treatments have proven to have limitations and consequently, alternative treatments have been studied. Among these are those that make use of electrochemical processes alone or associated processes such as photolysis and sonolysis. Each aqueous medium presents peculiarities that need to be considered to establish the process or set of processes to be used in its treatment. Moreover, the association of the processes has a fundamental aspect and depends on factors such as the presence of ionic and non-ionic species and electrode composition. In this lecture will be compared electrolyses using anodes of mixed metal oxide (MMO) and boron doped diamond (BDD), without and in association with photolysis and sonolysis processes. Considering the characteristics of the oxidants formed by both types of electrodes, the mixed treatment processes will be presented and both the synergistic effects and the limitations of use will be discussed. For instance, the effect of cavitation on the different possibilities of association of sonolysis and electrooxidation using BDD anodes will be considered. In addition, the performance of recently developed MMO anodes by synthesis using ionic liquids will be discussed in comparison with that of commercial electrodes, taking into account the conditions of preparation of the titanium substrate and the oxide layer itself.

Keywords: Electrooxidation; Hybrid processes; Sonolysis; Photolysis; Wastewater.

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Electrochemical regeneration of activated carbon from wastewater and drinking water treatment plants: Effect of the source and optimization.

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The enhancement of wastewater and drinking water treatment industrial processes towards more environmentally-oriented alternatives are a main topic considering the promotion of more restrictive environmental protection legislations. Although the use of activated carbons (AC) as a high-performance adsorption material for the removal of pollutants in water is a well-established technology, the management of spent AC after saturation is environmentally harmful itself. Currently, the partial regeneration of textural properties of the spent AC is carried out in the industry mainly by thermal processes, involving high costs in logistics and energy, as well as high levels of CO_2 emissions [1]. Electrochemical processes have been used as an eco-friendly alternative, obtaining better performance results at lab-scale and pilot plant-scale and showing the potentialities of *in situ* applications [2]. However, most of previous works of electrochemical regeneration of AC have been done using self-prepared samples, by saturation of a commercial AC with organic compounds, or using real samples from a single source, thus obtaining a wide range of results that hamper the scaling up of the electrochemical regeneration to industrial-scale. Since the source of the samples is shown as an important factor, here we present the study of the electrochemical recovery of the textural properties of spent activated carbons, using real samples from several sources, specifically from wastewater and drinking water treatment plants, geographically spaced within Spain and Portugal, gathering several sample starting parameters as: disparity of adsorbed molecules and activated carbon properties such as pore size distribution, particle size (granular, powder, compact powder or pellet) and surface area. The samples were submitted to the electrochemical regeneration treatment at lab-scale using an electrochemical filter-press cell designed and developed in previous works [3]. A stainless-steel plate was used as a cathode, and a platinized titanium mesh as an anode, separated by a cationic membrane. 10g of sample were placed in the cathodic compartment of the cell and electrochemically treated using different electrolyte solutions (sulfuric acid, sodium sulfate and sodium hydroxide). All experiments were duplicated by adding an acid pretreatment to the samples during 1 hour without current. In all cases, the current density during the electrochemical regeneration treatment was set at $0.025 A/cm^2$, applied during 3 hours.

The AC samples were characterized by physical adsorption of gases to analyze the surface area and the pore size distribution. The efficiency of the regeneration process was measured by comparison of the textural properties of the spent, regenerated and pristine AC samples. The content of desorbed species in the electrolyte solution was characterized by ICP, UV-VIS and TOC. The effect of the electrolyte and the acid pretreatment has been analyzed in order to explore the most suitable conditions for the recovery of the porosity of the spent AC in each case. As expected, the sample source plays an important role in the optimization of operating parameters for the electrochemical regeneration of the AC from wastewater and drinking water treatment plants, principally due to the disparity of adsorbed molecules, directly related to the quality of water in every region. Furthermore, even though the electrochemical treatment shows a better performance than thermal regeneration and the optimization of operating parameters for every source is presented, we conclude that further studies are necessary to create operating profiles for different types of sources, in order to lead an easier scaling-up and implementation in industry.

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High performance ELOX in zero-discharge regeneration of RAS water

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Nowadays, aquaculture provides almost half of all fish for human food. In economic terms, the value of world trade in fish and its production has grown, with exports rising from USD 8 billion in 1976 to USD 143 billion in 2016 (FAO, 2018). The relevance of the sector and the acute water shortages makes necessary to optimize the use of water at all levels. Aquaculture water remediation has been the subject of several works using different technologies, such as selective ion exchange, flocculation, reverse osmosis, biofiltration and membrane bioreactors, among others. In the growing practice of Recirculating Aquaculture Systems (RAS) (Science for Environment Policy, 2015) biological filters are the most extended technology for removal of nitrogenous waste products excreted by the aquatic organisms being cultured. However, biofiltration suffers of several limitations including the large space needed, biofouling, biological upsets, and wide fluctuations in performance as consequence of the dynamic properties of RAS and fish metabolism.

Recently, electrochemical oxidation has been considered a promising alternative for the treatment of water with nitrogen compounds, due to a number of advantages: minimal generation of byproducts, easy operation, and adaptable technology in dynamic systems. Also, this technology can cope with high salinity or variations in the contaminants concentration, both factors being severe disturbances for biofiltration. Through an indirect electrooxidation process, nitrogenous substances in the treated water are reduced to N_2 by strong electrogenerated oxidants such a hypochlorite. Previous studies demonstrated the feasibility of electrooxidation for the treatment and reuse of seawater in intensive RAS, eliminating the pollutants and byproducts generated by this activity (Díaz *et al.*, 2011).

This study aims to get further insight on the electrochemical regeneration of aquaculture waters by defining and analyzing different process configurations. Thus, in this work we compare the direct electrochemical remediation of RAS waters using Ti/RuO_2 anodes with the electro-generation breakpoint chlorination of nitrogen species. The effectiveness of both alternatives is determined in terms of total aqueous nitrogen (TAN) removal as well as on the formation of undesirable trihalomethanes (THMs) and high oxidation byproducts. Besides, the comparison of both process configurations is also made in terms of energy consumption. The results of this work provide the guidelines for the design of the optimum electrochemical RAS water remediation with minimum energy consumption and minimum generation of harmful by-products.

Acknowledgments

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Alternatives for the Efficient Electrochemical Degradation of Non-Polar Organochlorine Compounds

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Agriculture is considered the greatest contributor to pesticides contamination in European surface and groundwater (Köck-Schulmeyer et al., 2013). Various countries in Europe report that the contamination with pesticides in groundwater surpass the quality standards. According to data reported by the European Environment Agency, about 7 % of the groundwater stations recorded excessive levels for one or more pesticides. This contamination damages the water quality and restricts its use as drinking water.

The electrochemical degradation technologies gained a special attention within the last years and many researchers focus their attention to develop and integrate this technique. Among the main advantages of these group of techniques, it is worth mentioning that the addition of chemicals or other products is not necessarily required and that the main external requirement is the electricity, thus being easily coupled with renewable energy sources.

On the other hand, one of the main drawbacks of electrochemical technologies is the loss of efficiency when treating diluted solutions, due to the occurrence of mass transfer restrictions. In order to minimize these limitations a novel alternative consists in the development of concentration strategies, which can be integrated into the main degradation process or coupled as a pre-treatment step. The concentration strategy to be used dramatically depends on the nature of the pollutant to be treated, being specially relevant if the pollutant is polar (high water solubility) or non-polar (low water solubility). In this field, our group recently presented works that used electrodialysis for the concentration of ionic soluble pesticides (Raschitor et al., 2017) and electrocoagulation for the concentration of insoluble organochlorine compounds (Muñoz et al., 2017).

In the present work, we present and compare different alternatives for the degradation of oxyfluorfen, a model non-polar organochlorine herbicide. In all cases, the degradation process consists of two steps. First, the pollutant is concentrated by electrocoagulation with iron anodes, generating a concentrated stream containing iron and a high concentration of the target pollutant. Next, the degradation of the pollutant was confronted by electro-oxidation and electro-fenton processes. In both cases, the efficiency of the combined concentration-degradation system overcomes the performance of the direct electrochemical degradation of the raw stream. Moreover, it was observed that the most efficient process was the combination of electrocoagulation and electro-fenton for the degradation of oxyfluorfen.

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Acknowledgements

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Electroflex network of infrastructure: Connecting Europe's infrastructure and expertise on (bio)electrochemical metal recovery

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Europe is highly dependent on the import of raw materials to supply its core industrial activities. Over the years, several initiatives have been launched to increase resource efficiency and convert the current linear economic model into a circular approach. This requires a range of innovative technologies and infrastructures that are adaptable to different resource types, availabilities and product compositions. One of the biggest hurdles for this innovation is, however, that it requires extensive and capital-intensive infrastructure. The European Institute of Technology (EIT) has created the knowledge and innovation community EIT RawMaterials to tackle these challenges in the field of raw materials. EIT RawMaterials formed virtual pools of state-of-the-art infrastructure within a certain domain of the raw materials value chain, *i.e.* networks of infrastructure (NoIs). The ZeroWaste cluster comprises a group of nine NoIs that aims at providing and promoting services for unit processes in the ZeroWaste metallurgical toolbox (Figure 1). Electroflex is one of these nine NoIs, targeting innovation enhancements for the valorization of complex, low-grade ores and residues by bringing together infrastructure on electrochemical metal recovery in Europe, and offer it to potential customers in a comprehensive way. The ElectroFlex network provides easy access to equipment and expertise via a web-based tool and a central point-of-contact, matching demand with availability. Infrastructure within the network includes equipment at lab and pilot scales, production of electrochemical components, equipment for material and electrochemical characterization as well as modelling software (Figure 2). The Electroflex service platform was launched recently (October 2018) in the form of a publicly available webtool - https://electroflex.zerowastecluster.eu/.

In this presentation, detailed information about the ZeroWaste cluster will be provided, with special emphasis on the services available through the Electroflex NOI and its potential application for researchers, SMEs and industries.

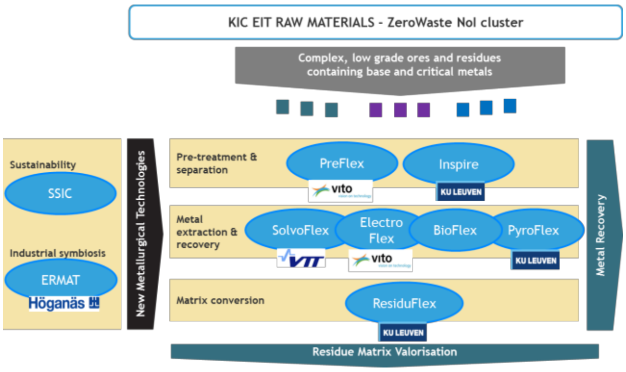

Figure 1: Structure of the ZeroWaste cluster

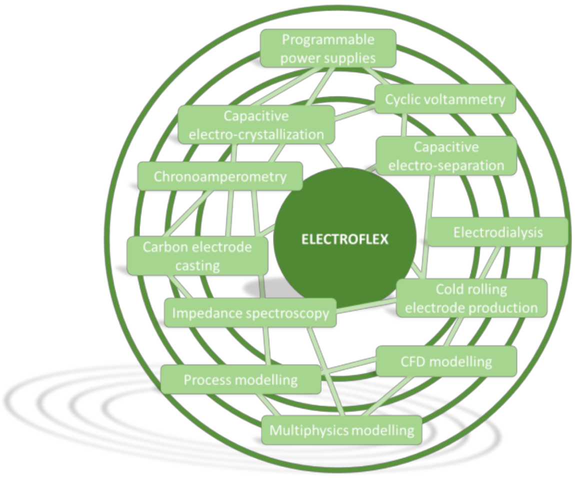

Figure 2: An overview of the Electroflex network

Fabrication of Silver Current Collectors and Photo-Electrode Supports by 3D Printing

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We are developing 3D inkjet printing of silver 'inks' to fabricate micro-current collectors for solid oxide fuel cells (SOFCs) and electrolysers (SOEs) [1,2] and to form perforated electronically-conducting mechanical supports for photo-bipole electrodes for solar energy conversion and fuel production [3,4]. The exceptionally high conductivity of Ag (6.3×10^7 S m^{-1} at 293 K [5]) has to be normalized by its price (ca. 500 \$ kg^{-1}), but its other properties are important for such applications. Perforated photo-bipolar electrodes would expose silver substrates to a wide range of potentials, but at pH ca. 14, Ag_2O [6,7] is predicted (Figure 1) to passivate and so protect the underlying Ag exposed to oxidising conditions at photo-anodes. As $T_m(Ag) = 1234.93$ K, Ag can be used for SOFC / SOE current collectors, as Ag_2O is not stable at high temperature. Additive manufacturing enables amounts of Ag to be minimised and optimised for the fabrication of micro-structures, while achieving the required physical properties.

Aqueous dispersions of (ca. 13 wt.%) silver particles (ca. 130 nm) were synthesized by reduction of Ag^+ ions (Figure 1) with ascorbate ions at neutral pH; adsorption of polynaphthalene sulfonate (Daxad 19, www.geosc.com) both limited their growth and charged them electrostatically (Figure 2), stabilising the dispersions against aggregation [8]. However, to achieve printability of the dispersions with the Ceradrop Serie X printer, water-soluble polymers (polyethylene glycol and cellulose-based materials) had to be added to increase their viscosities, potentially decreasing colloidal stability.

Results will be presented of inkjet-printed Ag films used as electronically-conductive substrates for photoelectrochemical reactors and as optimally-spaced current collectors for solid oxide electrochemical reactor electrodes.

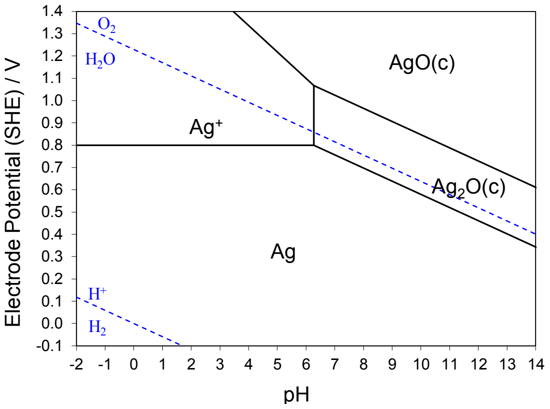

Figure 1. Potential-pH diagram for Ag-H_2O at 298.15 K, 0.1 MPa and unit dissolved Ag^+ activity.

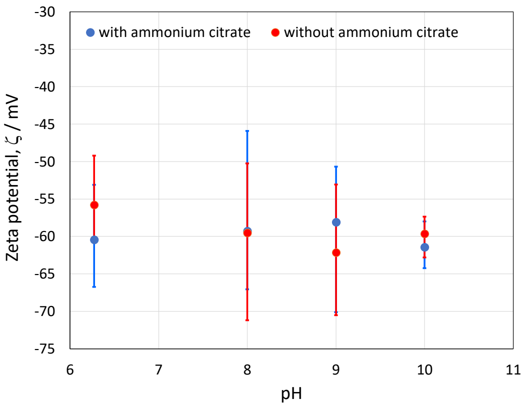

Figure 2. Effect of pH on zeta potentials of aqueous dispersions of ca. 130 nm Ag particles.

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Visible-light driven photoelectrocatalysis on a FTO/$BiVO_4$/BiOI anode for water treatment involving emerging pharmaceutical pollutants

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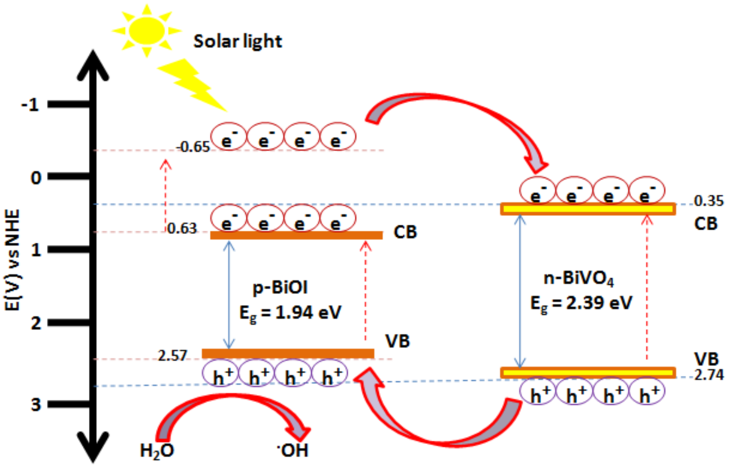
Contamination of water bodies by harmful and recalcitrant organic substances is a global challenge. A promising technique for removing these organics from water/wastewater is photoelectrocatalytic oxidation (a subset of electrochemical advanced oxidation process) which combines electrolytic and photocatalytic processes. Furthermore, there is need to improve this technique by designing novel electrodes that can harvest solar light and have low recombination rate. Herein, we report the degradation of emerging pharmaceutical pollutants – acetaminophen and ciprofloxacin - at a $BiVO_4$/BiOI heterojunction photoanode under visible irradiation via photoelectrocatalytic (PEC) process. The $BiVO_4$/BiOI was electrodeposited on a FTO glass and characterised with XRD, SEM, EDS and diffusive reflectance UV-Vis. The results confirmed the successful electrodeposition of $BiVO_4$/BiOI on the glass substrate. Mott-Schotty plots confirmed the formation of p-n heterojunction between the two electrodeposited semiconductors. The calculated charge carrier density of $BiVO_4$/BiOI was higher than those of pristine $BiVO_4$ and BiOI. The binary electrode also gave improved photocurrent response compared with unitary electrodes in the presence of light in the visible region. Degradation efficiencies of 68% and 62% were achieved upon application of the prepared photoanode (FTO/$BiVO_4$/BiOI) in PEC degradation of acetaminophen and ciprofloxacin respectively using a bias potential of 1.5 V within 2 h. A synthetic pharmaceutical wastewater containing a mixture acetaminophen and ciprofloxacin was also treated with the photoanode. The findings of this study suggest the suitability of the prepared photoanode for the photoelectrocatalytic degradation of organic pharmaceutical pollutants in wastewater.



Schematic diagram of band edge alignments of BiOI and $BiVO_4$ forming p-n heterojunction.

Electrochemical Sulfide Removal And Caustic Recovery From Real Spent Caustic Streams

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Spent caustic streams (SCS) are produced in petrochemical refineries and contain elevated concentrations of caustic and toxic sulfide, as well as phenolic and hydrocarbon compounds. The high alkalinity (5 – 12 wt.% NaOH) and sulfidic content (0.1 – 4 wt.% sulfide-S) of SCS limit the feasibility of biological treatment (Ben Hariz et al., 2013). Common treatment methods entail environmental hazards and high operational costs, while the possibility for resource recovery is limited. An alternative to conventional treatment is electrochemical treatment, which has been proven efficient in sulfide oxidation and caustic regeneration in synthetic streams. Previously, we reported excellent performance on synthetic SCS (Vaiopoulou et al., 2016), enabling a 5.1 ± 0.9 wt.% NaOH stream recovery combined with a sulfide removal efficiency of 67 ± 5%. The overall treatment was evaluated as effective and in terms of costs acceptable.

Here, as a next step, we treated real SCS with an electrochemical setup aiming at sulfide removal and NaOH recovery. We compared as anodes two commercially available titanium (Ti) based anodes, an Iridium (setup 1, S1) and a Ruthenium mixed metal oxide (MMO) (setup 2, S2). All electrochemical experiments were conducted with a 200 x 50 mm two-compartment electrochemical cell, separated by a cation exchange membrane (CEM). Continuous galvanostatic experiments at 300 A m^{-2} were performed with real SCS consisting of 1.8 ± 0.4 M Na_2S, 3.9 ± 0.2 M NaOH (~16 wt.%) and 0.5 ± 0.1 M ethanol, for a period of 20 days. A 3 M (~ 12 wt.%) NaOH solution was used initially as catholyte, recirculated in batch mode. The operational performance was monitored based on sulfide removal rate (RE_{HS^-}), Coulombic efficiency (CE_{HS^-}) calculated based on the $2e^-$ process (Ntagia et al., 2019), anode potential (E_{WE}), cathode potential (E_{CE}) and cell voltage (E_{cell}).

Both S1 and S2 were operated in parallel for 20 successive days, maintaining a constant removal rate of sulfide combined with a constant E_{cell}. The sulfide removal rate achieved in S1 was 1.1 ± 0.4 mol S d^{-1}, combined with a CE_{HS^-} of 80 ± 31% and a E_{cell} of 1.75 ± 0.12 V. The S2 reached a E_{cell} of 2.34 ± 0.15 V and in this case the sulfide removal rate was 1.3 ± 0.4 mol S d^{-1}, achieved at a CE_{HS^-} of 93 ± 27 %. Both of the setups demonstrated high energy efficiency with an average power input of 75 and 101 kWh m^{-3} SCS treated and 0.12 and 0.10 kWh mol^{-1} S removed, for S1 and S2, respectively. The high CE_{HS^-} was accompanied in both cases with elemental sulfur as the main product of sulfide oxidation. Both systems allowed for a higher than 10 wt.% NaOH stream recovery, at the cathodic side. The organics content of the incoming SCS remained unchanged though the course of the experiments.

This work demonstrated that real SCS can be treated continuously and efficiently in an electrochemical system with limited energy input. Both Ir MMO and Ru MMO anodes were proven efficient in removing sulfide and maintaining a constant potential under the applied harsh conditions of a solution containing ~16 wt.% NaOH combined with ~2 M sulfide and a current density as high as 300 A m^{-2}. The limited energy input combined with high sulfide removal efficiencies and possibilities for resource recovery, show the advantage of the electrochemical SCS treatment over conventional treatment methods, leading to up-scaling possibilities for treatment of complex industrial waste streams.

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Electrochemically-assisted ozonation of textile effluents

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To treat the effluents deriving from the textile industries, a wide range of advanced oxidation processes, based on the powerful action of $^\bullet$OH radicals, have been tested. Major critical issues for their application have been: high initial pH, high chloride content, with possible formation of undesired by-products, and high content of carbonates which, as known, act as scavengers for the radical species produced. For this reason, many of the tested tests have shown little feasibility.

In this study we propose the use of a new advanced treatment in which the conventional ozonation process is enhanced through combination with ozone reduction on cheap steel cathodes. In fact, it has been verified that under acidic pH, due to the ozone reduction, the electrogeneration of hydroxyl radicals occurs.

The proposed treatment has been tested for the degradation of a complex solution simulating a real wastewater deriving from a dye bath, which contained a reactive azo dye (Reactive Red 120), salts, surfactants and carbonates. The initial concentration of total organic carbon (TOC) was equal to 175 mg/L while initial pH was 10. The effect of some parameters on the treatment such as pH, ozone diffusion modalities and current intensity has been evaluated,

To maximize the degradation efficiencies, different combinations of the two processes (ozonation and electrolysis) have been adopted and discussed based on the oxidizing species involved. The best performance of the combined process results from a short ozonation at the original alkaline pH of the untreated effluent, followed by acidification and electrochemically-assisted ozonation. In these conditions, a few minutes of treatment were sufficient discolor the solution, while after 90 minutes approximately 76% and 83% TOC removal was achieved, at 100 mA and 200 mA, respectively.

To lower the costs associated to reach the acidic pH values suitable for treatment and also to maximize the current supplied, the possibility of adopting a divided reactor was finally evaluated. In this last case, the required acidification was provided in the anodic compartment due to the water discharge, while the degradation via hydroxyl radicals electrogenerated by the ozone reduction occurred at the cathode, upon transfer or alternating cycles applications.

Continuous Electro-Osmotic Dewatering of Phosphatic Clay Suspensions

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A dilute 2-3 wt.% suspension of phosphatic clay is produced as a waste stream in the beneficiation of phosphate ore. A typical Florida phosphate mining operation produces more than 6,300 L/s of phosphatic clay. The clay-water suspension is pumped into large impoundments called clay settling areas in which separation is achieved by hindered settling and self-consolidation. As it settles, the supernatant water is recycled for use in the beneficiation plant. A top crust is formed after a few years, but the clay beneath the crust has a large water content and a pseudo-plastic character that limits the amount of weight the settling area can support. Clay settling areas cover about 30-40% of the land mined for phosphate in Florida, occupying roughly 390 square kilometers of land. Uses for the land are limited by the properties of the clay that leave the settling areas unstable, even after 50 years of elapsed time. The objective of this research was to develop an effective electrokinetic separation process applied to phosphatic clay suspensions, generated during the beneficiation of phosphate ore, a major component of fertilizer. The use of an electric field to separate the water from the solids is attractive because the inherent stability of the clay suspension is due, in part, to the surface charges residing on the platelets.

A single-stage design was developed for continuous electro-osmotic dewatering of phosphatic clay suspensions that demonstrated efficient production of a dewatered cake with a solids content of 35 wt.% at a dry-clay production rate of 4.5 kg/h m^2 from a feed clay of 10 wt.% [1,2]. As rheological measurements showed that the clay suspensions exhibited a yield strength for solids contents greater than 7.5 wt.%, separation based on electro-osmotic principles was found to be appropriate for the operating range of solids content. An economic analysis for the single-stage design yielded an estimated total cost of $11-12/metric ton of dry clay produced.

A mathematical model, accounting for compressibility of the cake and for both electro-osmotic and hydraulic permeability, was shown to adequately represent experimental data collected for the operation of the lab-scale continuous electrokinetic dewatering prototype [3]. An optimization strategy for an industrial-process was developed that yielded a minimum of the total cost. The optimization strategy consisted of a constrained maximum electric field and final solids content of 35 wt.% for a continuous electrokinetic dewatering process starting with a feed clay with a solids content of 10 wt.%. Optimal operating parameters were identified for an industrial-scale continuous electrokinetic dewatering process capable of processing the effluent produced by the Mosaic Co. Four Corners Mine. The simulation results suggest that lower total costs may be achieved with small electrode gaps. The cost-optimized process parameters were a feed-side gap of 8.5 cm, a residence time of 1.3 hours, and a dry-clay production rate of 7.6 kg/h m^2. An total electrode area was estimated to be 0.17 km^2. The estimated total cost of an optimized industrial-scale continuous electrokinetic dewatering process was $9 per metric ton of dry clay.

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Electrochemical Oxidation and mineralization of cooling tower blowdown water organic compounds

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Abstract: Process industries discharge a large amount of water as cooling tower blowdown (CTBD) which mainly contains salts and organic compounds (OC) [1]. Membrane-based desalination techniques have been used for salts removal from CTBD water. However, these technologies failed due to membrane fouling by the OC added in the cooling tower (CT) as corrosion inhibitor, antiscalant and biocides[2]. Therefore, in this study, electrochemical oxidation (EO) of OC in CTBD has been investigated. Electrochemical experiments were carried out at boron-doped diamond (BDD) and Ti/ RuO_2 (MMO) anodes in an undivided flat cell in a batch recirculation reaction system. The role of operational parameters such as applied current density (2.3-8.7mA/cm^2 for BDD and 5.5-8.7 mA/cm^2 for MMO), pH (3-11.5), recirculation flow rate (17 L/h-46L/h), and Na_2SO_4 addition (28mM) to the CTBD- were studied. The EO performance was express as chemical oxygen demand (COD) removal, total organic carbon (TOC) removal, and energy consumption (EC). The tests results indicate that the BDD anode had an almost twofold better removal performance than the MMO anode. For instance, the COD and TOC removal efficiency of the BDD anode was 85% and 50.5% respectively under 8.7 mA/cm^2, 6.95 pH, 30L/h flow rate, and 3 hours of treatment, whereas, it was 50% and 16% at the same conditions on the MMO anode. In addition, with the increase of current density from 2.3 to 8.7 mA/cm^2 on the BDD anode COD and TOC removal increased from 47% to 85% and 45% to 52% respectively. A similar trend was found on MMO anode. Due to partial oxidation of the OC TOC removal was low. Other parameters such as pH, flow rate and Na_2SO_4 addition had a slight influence in COD and TOC removal performance in both anodes. However, the addition of Na_2SO_4 salt reduced 25% energy consumptions by lowering the internal resistance. Microtox toxicity analysis indicated that the treated water was more toxic to Vibrio fischeri bacteria than untreated CTBD water. Active chlorinated species generated during the treatment was the key cause of toxicity rather than the organic by-products. However, from application perspective the production of hypochlorite (ClO^-) is rather beneficial since it can act as a biocide in the CT system Therefore, EO using a BDD anode is a potential CTBD treatment step since half of the OC is removed and almost other half was partly converted into small organic compounds.

Table 1 Performance of the EO process for the CTBD water treatment in terms of COD and TOC removal, Instantaneous current efficiency (ICE) and energy consumption (EC)

Anode	Applied current (mA/cm^2)	% COD removal	% TOC removal	%ICE	EC(kWh/m^3)	EC(kWh/kg COD)
BDD	2.3	46.67	35.58	41.59	1.76	13.62
	5.5	78.10	44.81	29.00	5.57	25.81
	8.7	85.32	50.46	20.77	10.95	44.74
	8.7 (mA/cm^2)+ 28mM Na_2SO_4	90.25	50.19	22.33	8.18	31.07
MMO	5.5	16.86	8.07	7.07	4.22	81.90
	8.7	49.67	15.96	13.49	10.43	65.59
	14.5	56.68	18.37	8.33	22.76	137.73
	14.5 (mA/cm^2)+ 28mM Na_2SO_4	53.94	20.29	8.78	18.95	108.76

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Electrokinetic – Enhanced Ryegrass Cultures in Soils Polluted with Organic and Inorganic Compounds

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Soil is the habitat for plants, microorganisms and animals and its quality is essential for a good production of crops, which is the base for human feeding. The rapid industrialization and the bad management of wastes had led to a serious contamination of soil and the main contaminants in this media are toxic heavy metals (such as chromium, cadmium, mercury, lead,…) and a series of hydrophobic organics (hydrocarbons, PAHs, PCBs, solvents, pesticides,…). Several remediation technologies have been proposed to palliate the contamination in soil. Among them, phytoremediation has been proposed as a benign technology that is able to deal with organic and inorganic contaminants in soil and groundwater (Batty and Dolan, 2013). The coupled technology electrokinetics-phytoremediation have been proposed as an alternative to deal with the limitations of phytoremediation (the concentration of contaminants and the remediation depth limited by the rhizosphere) (Sarwar *et al*., 2017; Cameselle *et al*., 2013). Electrokinetics-phytoremediation is based on the application of an electric field near a growing plant that may enhance the remediation capacity of the plant by mobilization of nutrients and contaminants that will be more available for plant uptake. In this study, the effect of electric fields on seed germination and development of ryegrass (*Lolium perenne* L.) was studied in clean and contaminated soil with heavy metals and/or PAHs (Figure 1). The application of 0.2 DCV/cm in clean soil near ryegrass seeds enhanced the germination by 75%. The presence of contaminants in soil hindered the germination and growing of ryegrass. However, the application of DC electric field favored the germination and growing of plants compensating the negative effects of the contaminants. The electrode material in anodes has a decisive influence in the germination and growing of ryegrass. Stable anode materials have to be used to avoid the release of toxic ions in the soil that affect the development of the plant. Graphite anodes are very appropriate because they are inexpensive and does not generate toxic effects on plants. The electro-phytoremediation of mixed contaminated soil with ryegrass showed very promising results, especially AC electric fields. The tests with AC current showed the highest biomass production in a treatment of 1 month (250%). The more biomass production the more removal of heavy metals and PAHs from soil (removal efficiencies: 42% phenanthrene, 25% anthracene, 10% Pb, 11% Cr and 15% Cd).

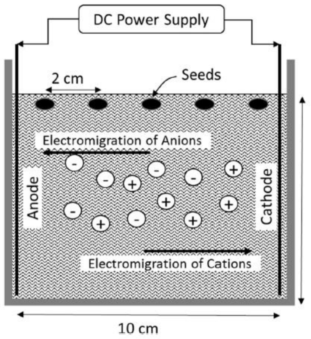

Figure 1. Experimental setup for the growth of *Lolium perenne* L. in contaminated and uncontaminated soil under the effect of electric fields.

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Effect of the air pressure on electro-Fenton process

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Electro-Fenton process is considered a very promising tool for the treatment of waste waters contaminated by organic pollutants refractant or toxic for microorganisms used in biological processes [1-6]. In these processes H_2O_2 is continuously supplied to an acidic aqueous solution contained in an electrolytic cell from the two-electron reduction of oxygen gas, directly injected as pure gas or bubbled air. Due to the poor solubility of O2 in aqueous solutions, two dimensional cheap graphite or carbon felt electrodes give quite slow generation of H_2O_2, thus resulting in a slow abatement of organics.

In this context, we report here a series of studies [7-9] on the effect of air pressure on the electro-generation of H_2O_2 and the abatement of organic pollutants in water by electro-Fenton process. The effect of air pressure, current density, mixing and nature of the organic pollutant was evaluated.

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Electrochemical Oxidation of Poly- and Perfluoroalkyl Substances (PFASs) with Novel TiO_2-NT/doped-SnO_2 Anode Materials

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Nowadays, there is great concern about the presence of poly- and perfluoroalkyl substances (PFASs) in the environment due to their persistent, toxic character. As conventional wastewater treatment plants cannot degrade PFASs, new advanced technologies are necessary. Electrochemical oxidation has been proven to be an effective method for PFASs abatement. Among different electrodes, boron-doped diamond (BDD) has been widely studied due to its extreme stability under anodic polarization and high overpotential for oxygen evolution reaction (OER). However, the cumbersome fabrication method by chemical vapor deposition (CVD) and high cost of conductive diamond have limited its large-scale application. Doped-SnO_2 electrodes have attracted interest in recent years as an alternative material to BDD due to their low cost, high conductivity and high overpotential for OER. While doped-SnO_2 electrodes have been employed for PFASs degradation in laboratory settings, their short service life-time remains one of their main limitations [1]. In this work, novel doped-SnO_2 electrodes were synthesized by electrodeposition on TiO_2 nanotubes (TiO_2-NT) substrates of high surface area with the aim of increasing the service life-time and electrochemical activity. Two different dopants were tested, the more common, but toxic Sb, and the more environmentally friendly Bi. The synthesized materials (herein, TiO_2-NT/SnO_2-Sb and TiO_2-NT/SnO_2-Bi) were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (IES), scanning electron microscopy (SEM) and X-Ray diffraction (XRD). Then, TiO_2-NT/SnO_2-Sb and TiO_2-NT/SnO_2-Bi were employed as anodes for degradation of six model PFASs and their performance was compared to that of commercial BDD mesh. Solutions containing 100 µg/L of perfluorobutanoic acid (PFBA), perfluorobutane sulfonic acid (PFBS), perfluorohexanoic acid (PFHxA), perfluorohexane sulfonic acid (PFHxS), perfluorooctanoic acid (PFOA) and perfluoroctane sulfonic acid (PFOS) were treated in an undivided flowthrough cell. Samples were withdrawn periodically for analysis by LC-MS/MS and Adsorbable Organic Fluoride (AOF). Results showed TiO_2-NT substrates provided a two-fold increase on the service life-time of doped-SnO_2 when compared to pure Ti substrates. TiO_2-NT/SnO_2-Sb and TiO_2-NT/SnO_2-Bi displayed a higher overpotential for OER than BDD (1.9, 1.8 and 1.7 V vs Ag/AgCl, respectively). As can be observed in Figure 1, BDD, TiO_2-NT/SnO_2-Bi and TiO_2-NT/SnO_2-Sb showed promising catalytic activity towards degradation of the longest-chained PFASs in this study (i.e. PFOA and PFOS). The most effective material was TiO_2-NT/SnO_2-Sb, with 40% PFOA and 100% PFOS removal at 3h.

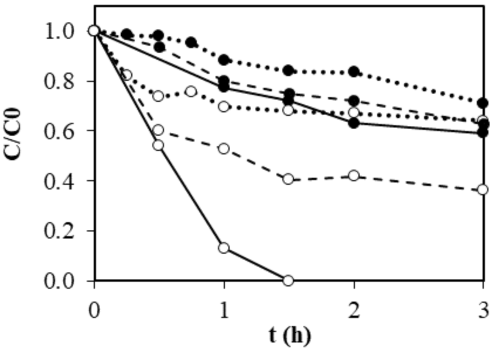

Figure 1. Electrochemical oxidation of (●) PFOA and (○) PFOS with TiO_2-NT/SnO_2-Bi (dotted line), BDD (dashed line) and TiO_2-NT/SnO_2-Sb (solid line). (j = 10 mA/cm^2, supporting electrolyte: $NaClO_4$ 30 mM)

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Treatment of landfill leachates by combined heterogeneous electro-Fenton / anodic oxidation process using TiO_x anode and Fe(II)Fe(III) layered double hydroxide modified carbon felt cathode

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Introduction: The implementation of membrane bioreactor (MBR) followed by nanofiltration (NF) is one of the treatment strategy currently used for managing landfill leachates. However, biorefractory organic pollutants are accumulated and concentrated during NF. The objective of this study was to implement EAOPs for mineralization and biodegradability enhancement of such NF concentrate. For the first time, TiO_x anode and Fe(II)Fe(III) layered double hydroxide modified carbon felt (LDH-CF) cathode were used for the treatment of a real effluent. A particular attention was also given for understanding mineralization mechanisms by using various analytical tools.

Material and methods: TiO_x anode was provided by St-Gobain Coating Solutions and LDH-CF cathode was synthesized as reported by our research team [1]. Experiments were performed in open cylindrical batch reactor. Effluent biodegradability was assessed by respirometric measurements using similar operating conditions than in the real industrial MBR. Other analyses included dissolved organic carbon (DOC), Microtox®, 3D fluorescence spectroscopy, inorganic ions and short-chain carboxylic acids.

Main results: Combined electro-Fenton/anodic oxidation process using TiO_x anode and LDH-CF cathode was the most suitable process for mineralization of organic pollutants. At 4.2 mA cm^{-2}, 45% removal of DOC was achieved after 4 h (Figure 1) with limited energy consumption (0.11 kWh g^{-1} of DOC removed, *i.e.* 49.5 kWh m^{-3}). Up to 96% removal of DOC was also obtained by using higher current density and treatment time. The use of TiO_x anode was a key parameter for improving the degradation and mineralization of organic nitrogen. From 3D fluorescence spectroscopy analysis, colloidal proteins were observed to be the most refractory organic compounds to electro-oxidation. Therefore, improving the retention of such compounds in the MBR could improve the global process efficiency. Besides, significant biodegradability enhancement was observed after 4 h of treatment by heterogeneous EF/AO, thus making possible the recirculation of the effluent towards the MBR in order to improve the cost-effectiveness of the process. This result was consistent with the generation of more biodegradable and less toxic by-products such as carboxylic acids. As regards to the fate of inorganic species, the formation of ClO_3^- could be limited by stopping electro-oxidation at 4 h, but enhanced nitrification would be required in the MBR because of the release of NH_4^+ from mineralization of organic nitrogen.

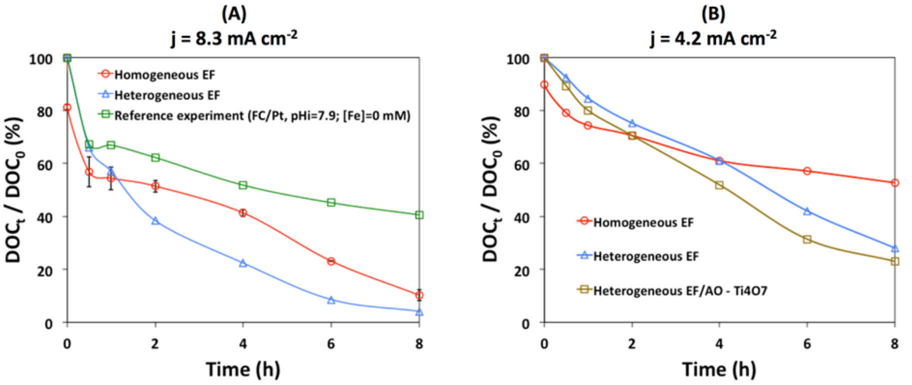

Figure 1. Dissolved organic carbon (DOC) removal efficiency vs time during the mineralization of NF concentrate. Comparison of different configurations and operating conditions.

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Modular stand-alone photoelectrochemical reactor for wastewater treatment

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Fig. 1 Modular stand-alone reactor

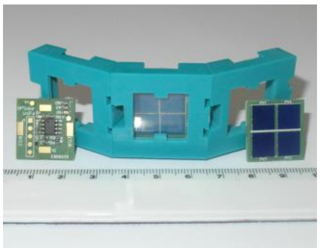

Fig. 2 Complete reactor element

In the last few decades, advanced oxidation processes (AOPs) have been developed as an emerging decontamination technology resulting in the mineralization of most organic contaminants. Among these processes, the photocatalysis is in particular the most promising [1]. Photocatalytic degradation of organic waste can be performed by using a photo-electrochemical (PEC) cell, thanks to which the solar radiation can be converted also into useful forms of energy or fuels, such as electricity and hydrogen, obtaining a double environmental benefit [2]. We developed a modular and completely stand-alone reactor (Fig. 1) for the photo-degradation of organic compounds with the simultaneous production of hydrogen as added value to the process of decontamination. The reactor is based on modules integrated in PVC frames with size 30x30 mm^2. The frames can be connected together to form a cylindrical structure embedded between two tubes. The gap between the two tubes is used to pump water in the reactor, while the internal tube acts as a sink for the treated water. Each element (Fig. 2) is composed by a photoanode in a tandem cell (TC) configuration with four Si solar cells connected in series, electronic components and a metallic cathode (Ni, Au, Pt), encapsulated into the PVC frame, which makes each element completely independent and waterproof. The photoanode consists of 1μm-thick film of colloidal tungsten trioxide (WO_3) deposited on a transparent and conductive FTO (Fluorine-doped Tin Oxide) layer over a glass substrate. WO_3 was chosen instead of the more common used titanium dioxide (TiO_2) thanks to its lower activation energy (~2.7eV) that allows to exploit also part of the visible solar spectrum. WO_3 is photo-activated by light with wavelength below 470 nm (15% of AM 1.5 solar spectrum) generating OH• radicals for pollutants oxidation [3] and the photocatalytic effect is increased by biasing the photoanode with the Si cells in order to generate solar hydrogen at the cathode. On the other hand, polarization effects occur and the catalytic efficiency drops down to a minimum after a few minutes. This limiting effect can be overcome by periodically applying a small reverse potential using the electronic components. In particular, a microcontroller, directly powered by the solar cells, provides the required voltages (+2.0↔+2.5 V, -0↔-0.3 V) and timings to reduce the polarization effects.

The reactor was developed within the HP Solar project, part of the POR-FESR 2014-2020 program funded by Emilia-Romagna Region and the European Union through the European Regional Development Fund. The results show an effective reduction of COD (Chemical Oxygen Demand) in wastewater samples provided by the local water treatment and management authority HERA S.p.A. Moreover, tests performed on emerging micro pollutants, like atenolol and carbamazepine, barely eliminated by current wastewater treatment (WWT) plants, display a photo-degradation of 60-70 % in 7 hours, suggesting the tertiary use of the reactor in WWT plants.

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H_2 Electrochemical Generation: On the Opportunities and Knowledge Gaps of SO_2 Catalytic Oxidation

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SO_2 is a poisonous pollutant that is often found in the atmosphere due to the use of fossil fuels; so that, the reduction of its emissions is in discussion in almost every energy agreement. However, the world atmosphere is already full of this gas that can injure the human health at very low concentrations, such as 5 ppm. With this in mind, a mitigation pathway for working out this problem and possibly transform SO_2 in a useful chemical, such as H_2SO_4 is desirable. By aqueous electrochemical SO_2 oxidation, the H_2 evolution, a highly desirable solar fuel, is possible to be observed as the counterpart reaction.

In this work, SO_2 oxidation was investigated by IRRA spectroelectrochemical measurements and the differences between Pt and Au electrodes could be observed. The mechanism proposed for Pt electrodes involves species that are not commonly cited in the literature as intermediates, like dithionate, $S_2O_6^{2-}$. The formation of PtOH and PtO were confirmed as oxidized species for this surface. The situation observed for Au electrodes was completely different. The electrolyte chaotropicity influences on the nature of the adsorption bond Au-SO_2. In more chaotropic media, it takes place by the S atom, leading to the formation of $S_2O_5^{2-}$, pyrosulfite as well as Au-SO_3 complex in solution. The higher the Au-S surface bond, the higher amount of $S_2O_5^{2-}$ and Au-SO_3 are observed. Different mechanisms for different electrolytes are proposed for Au electrodes.

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Outstanding electrolysis of poly- and perfluoroalkyl substances (PFASs). Evaluation of energy needs

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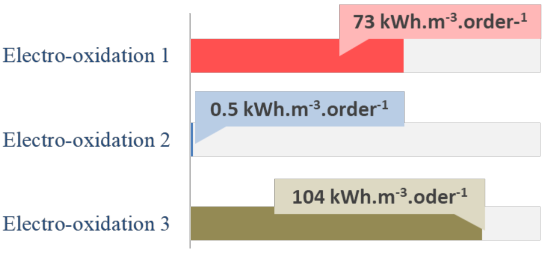
Among emerging water pollutants, poly- and per-fluoroalkyl substances (PFASs) have gained increasing attention because of their extreme persistence and mobility in the environment, and high resistance to conventional water treatment technologies. Remarkably, those limitations have been overcome by the electrochemical oxidation on BDD anodes, that has demonstrated its capability to completely degrade and defluorinate PFASs [1]. However, previous studies on BDD anodic oxidation dealt mostly with model solution of single fluorinated compounds at unusually elevated concentrations, much higher than those found in real environmental matrices. Moreover, the reported PFASs removal rates were very diverse [2]. Taking into account this background, the present work aims to investigate the removal of PFASs, at low concentrations, relevant in industrial emissions. The effect of using BDD anodes manufactured by different providers will be studied. Moreover, treatment costs will be estimated based on energy consumption.

The effect of the chemical composition and morphology of the BDD anodes was assessed using model solutions of perfluorooctanoic acid (PFOA, 100 mg.L^{-1}) and two types of materials: (a) a microcrystalline diamond (MCD) coating on silicon, and (b) an ultrananocrystalline (UNCD) coating on niobium. Next, the best anode was tested for the removal of PFASs contained in real industrial wastewater (ΣPFASs concentration, 1.65 mg.L^{-1}), although the load of organic contaminants was much higher as denoted by its total organic carbon content (TOC, ~100 mg.L^{-1}). Figure 1 shows the different electrochemical responses offered by the MCD and UNCD anodes. Whereas the MCD anode achieved the complete degradation of PFOA in 4h at 5 mA.cm^{-2}, only 21% PFOA removal was obtained when using the UNCD anode. The higher content of sp^3 carbon, the lower B content, and the lower amount of H-terminated carbon in the MCD anode favored the more efficient PFOA removal. Furthermore, the practical feasibility of MCD anode was evidenced by the 99.7% PFASs reduction in the industrial wastewater, after 10 h, at current density of 50 mA.cm^{-2}, while the TOC removal was 91%.

Finally, Electrical Energy per Order (E_{EO}) was calculated to compare the treatments on the basis of energy consumption. As a result of the optimal response of the MCD anode, the energy needed for PFOA elimination was only 0.5 kWh.m^{-3}order^{-1}, two orders of magnitud lower than for the UNCD anode (73 kWh.m^{-3}.order^{-1}). However, the energy demand of the industrial wastewater treatment was increased to 104 kWh.m^{-3}, due to the use of the applied current for the simultaneous degradation of unknown organic compounds contained in the TOC. The results were compared to the treatment of the same model solution by means of heterogenous photocatalysis using an advanced TiO_2-rGO composite catalyst, that resulted in 2650 kWh.m^{-3}order^{-1} [3]. Therefore, electrochemical oxidation by means of MCD anodes offers the most efficient technological alternative for PFASs removal, even at the low concentration range of interest.

Figure 1. PFASs removal kinetics in model and industrial wastewater, and energy consumption in each case of study

Water treatment	**[PFASs]$_0$** mg.L^{-1}	**k_{PFAS}** (h^{-1})
ELOX 1 *UNCD anode*	$[PFOA]_0=100$	0.06
ELOX 2 *MCD anode*	$[PFOA]_0=100$	1.82
ELOX 3 *MCD anode*	$[PFASs]_0=1.65$	0.58



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Physicochemical Characterization of RuO_2-Ta_2O_5|Ti and IrO_2-Ta_2O_5 | Ti for the Removal of Phenolic Compounds from Wastewater

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Titanium electrodes coated with transition metal oxides have a large number of applications and they have been the subject of constant research and improvement. One of the most important applications for this type of electrodes is the electro-generation of hydroxyl radicals (•OH) via water splitting. RuO_2-Ta_2O_5|Ti and IrO_2-Ta_2O_5|Ti electrodes are characterized by their shape and structural integrity and included a catalytic coating with corrosion resistance properties. These materials are very appealing for many applications because of their high chemical and electrochemical stability, low cost and exceptional ability to catalyze electrochemical reactions. These electrodes are able to produce hydroxyl radicals (•OH) at the interface level, which may have a large number of applications by their catalytic properties and stability against corrosion. In this research, RuO_2-Ta_2O_5|Ti and IrO_2-Ta_2O_5|Ti were characterized by scanning electron microscopy (SEM, Figure 1A), energy disperse X-ray spectroscopy (EDX, Figure 1B), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to understand their high removal efficiency of phenol, o-, m- and p-chlorophenol from wastewater.

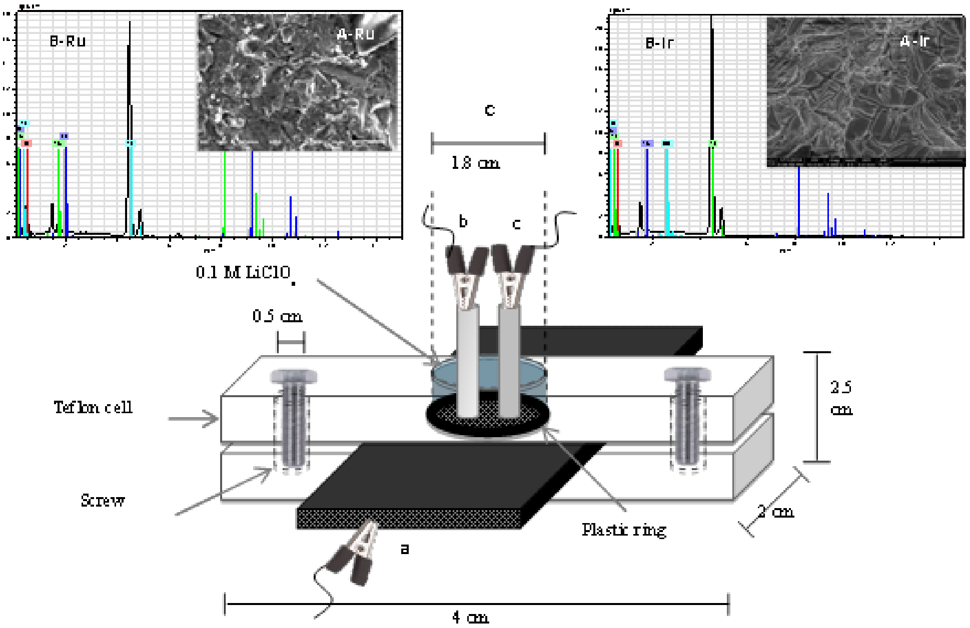

Figure 1. Micrographs obtained by SEM at 2 000x (A) and microanalysis EDX (B) for RuO_2-Ta_2O_5|Ti and IrO_2-Ta_2O_5|Ti. Representation of the electrochemical cell (C) used to obtained CV and EIS, where: (a) RuO_2-Ta_2O_5|Ti or IrO_2-Ta_2O_5 |Ti as working electrode, (b) pseudo-reference of Ag electrode and (c) wire of platinum electrode as counter-electrode.

Metal Coated Graphite Felts Modified by Ag Nanoparticles for Reductive Dechlorination of Chloroacetamide Herbicides

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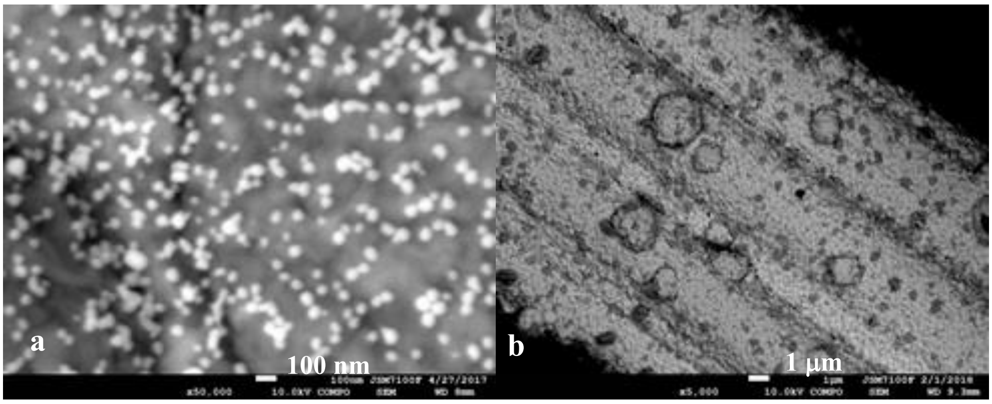
Chloroacetamide herbicides such as alachlor have been widely used to remove annual grasses and broadleaf weeds and promote crops yield, leading to contaminations in surface water and farming soil. This is particularly worrying since chloroacetanilides toxicity has already been reported as well as their probable carcinogenicity. Electroreduction processes have been proposed as one alternative for the removal of hazardous organic halides since they are selective and well-controlled processes and are likely to increase chloroacetamides biodegradability since chloro-groups are often responsible of the biorecalcitrance of substrates. It has been proved that Ag possesses good electrocatalytic ability regarding the cleavage of the C-Cl bond at low cathodic potential with a high removal yield.[1] Nanoscale Ag can decrease the manufactural cost of the cathode, when dealing with a large volume of water, and can enhance the electrocatalytic performance by high surface/volume ratio, compared to the polycrystalline bulk counterpart.

Recently, we have selected nickel covered graphite felt as electrode supports for Ag nanoparticles owing to its very good electronic conductivity, good mechanical resistance, and large void volume fraction to improve mass transfer.[2] In this work, nano-Ag modified 3D electrodes, Ag-PVP-Ni@GF, were prepared by spontaneous deposition of silver. The modified electrode exhibited a high catalytic efficiency (98% conversion yield) for dechlorination of Alachlor in aqueous solution. To improve the current efficiency, we also envisaged to use bismuth as support owing to its high hydrogen evolution overpotential. We report here the preparation and the high catalytic activity of Ni and Bi-coated graphite felt electrodes modified by silver nanoparticles for the reductive dechlorination of chloroacetamide herbicides.



SEM images of (a) Ag-PVP-Ni@GF and (b) Ag-PVP-Bi@GF

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Solid Oxide Co-Electrolysis process – Modeling and Experimental Kinetic Study

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High temperature solid oxide steam electrolysis (SOE) represents, besides the alkaline and PEM water electrolysis, promising alternative process of hydrogen production and power-to-X process. There are several advantages of the SOE compared to conventional alkaline water electrolysis. First, the SOE operates in high temperature range between 700 °C and 900 °C in favor of reduced reversible cell voltage and accelerated electrode reaction kinetics. This allows omitting platinum-based electro-catalyst in the electrode construction. A promising branch of the SOE represents co-electrolysis of mixture of steam and carbon dioxide (solid oxide co-electrolysis - SOcoE). It can reinstate captured carbon dioxide together with excess electric and heat energy into the energy consumption chain in a form of a syngas (mixture of hydrogen and carbon monoxide). The resulting gaseous mixture represents an attractive raw material for subsequent organic synthesis targeting various hydrocarbon compounds. This is feasible also due to high operating temperature at which the catalyst maintains high catalytic activity even at the presence of catalyst poisons (e.g. carbon monoxide). It is therefore of great importance to fully understand the mechanism of reactions taking place inside the co-electrolysis cell cathode, involvement of different regions of the SOcoE cell, the impact of electrode materials and operating conditions used etc..

Within the framework of the SElySOs project, a two-dimensional macroscopic (macro-homogeneous) phenomenological mathematical model of the SOcoE cell was developed. This model considers complex system of electrochemical and heterogeneous chemical reactions described by a micro-kinetic model. Moreover, different macro-kinetic equations based on variety of simplifying assumption were employed. The models proposed were used for an analysis of relevant experimental data obtained both at open circuit (OCV) and under current load conditions. It enabled verification of the reaction mechanism described by micro-kinetic model, evaluation of the kinetic parameters and rate determining steps (RDS). An effect of the cathode properties, operating conditions, gas residence time in the cathode and catalyst activity were investigated. It was observed, for example, that the surface reactions between the constituents adsorbed on the catalyst surface are the RDS under the OCV conditions. The resulting validated model is intended to be employed in the process optimization or scale-up, and in consideration of an effect of variety of degradation phenomena. The models were implemented in COMSOL Multiphysics^{TM} and solved by finite element method.

The corresponding experimental measurements were performed using small single button-cell in a temperature range from 800 °C to 900 °C, for various H_2/CO_2 ratio in feed gas mixture and several different catalyst and cathode composition. A composition of the output gas mixture was determined by means of online gas chromatography.

This project (acronym: SElySOs) has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No (671481). This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation program, Hydrogen Europe and Hydrogen Europe research.

Photoelectrocatalytic Treatment of an Azo Dye with Electrosynthesized Films of Nanostructured Mixed Oxides of Bi_2O_3/WO_3

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Photoelectrocatalytic technologies are emerging technologies that exploit the synergistic effect of light-driven and electrochemically driven advanced oxidation processes. The principal technology barrier for implementation in developing countries of photoelectrocatalysis is the need of UV irradiation to photogenerate the charge carriers. This limitation is defined by the high energy band-gap of TiO_2, the most studied photocatalyst. The development of alternative photoelectrocatalysts to overcome this challenge is required to stimulate market opportunities.

In this research, the electrosynthesis of alternative nanostructured films of mixed oxides of Bi_2O_3/WO_3 was explored. The optimized electrodeposition method allows obtaining highly homogeneous and stable thin film coatings supported on FTO. The characterization of the photoelectrocatalytic films by XRD, FTIR and EDX allowed identifying nanostructured films with mixed Bi_2O_3/WO_3 nanoparticles with average size of 75 nm. The mixed films presented a 4-fold increase on their photocurrent response in comparison to the pristine semiconductors. This increased performance is associated to the stabilization of the charge carriers due to the semiconductor/semiconductor interface.

The nanostructured photoelectrocatalytic films were applied to the treatment of Methyl Orange solutions. Under potentiostatic conditions solutions of high concentration of dye (50 mg L^{-1}) were completely decolorized after 30 min of photoelectrocatalytic treatment under LED irradiation. The thin film photo-electrodes were reused in more than 20 consecutive cycles with high reproducibility. These results suggest the higher stability and adherence of mixed oxide films on FTO in comparison to pristine WO_3 that wears off after three cycles. These promising results suggest the potential application of electrosynthesized Bi_2O_3/WO_3 thin films in environmental remediation.

Acknowledgements: This research has been conducted under the financial support of FONDECYT of Peru under contract 105 2015.

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Electrodeposited $Ni_xFe_{1-x}O_y$ Electrocatalysts for Energy and Environmental Applications

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The broad efforts on electrochemical systems for energy and environmental applications seek toward a practically deployable electrocatalyst for water splitting as well as direct/indirect electron transfer from aqueous organic compounds (pollutants) among others. The main drawbacks on Ir and Ru oxides, currently used in commercial electrochemical systems, would be the substantial material costs which can be fully alleviated by mixed $Ni_xFe_{1-x}O_y$. This study investigated $NiFeO_x$ electocatalysts immobilized on Ti substrate by cathodic electrodeposition with thermal treatment, for potential application in water splitting and fuel cell devices. The activity of oxygen evolution reaction (OER) was found to depend on the electrodeposition current density, duration, and the molar ratio of Ni to Fe in precursor, while a series of surface interrogation indicated a preferential deposition of Fe oxides. The lowest OER overpotential (0.4 V) was observed in 1 M KOH solutions, at 50 μA/cm^2 of current density and 30 minutes of duration in Ni:Fe of 9:1 precursor solutions. These observations corroborated the reported partial-charge-transfer activation effect of the Fe component, even after the annealing process. On the other hand, the NiO_x electocatalysts showed a direct electron transfer activity from a model organic pollutant (urea) at the applied anodic potential near 0.7 V NHE. A parametric study revealed that Ni component rather than Fe analogous accounted for the observed activity for potential application in wastewater fuel cells. Utilizing a Ni foam substrate brought about an enhanced power density in correlation with the surface area, especially in the absence of the annealing process due to the pronounced role of Ni oxyhydroxide. The outcomes of this study should broaden the usage of earth-abundant electrocatalysts for water treatment and energy conversion.

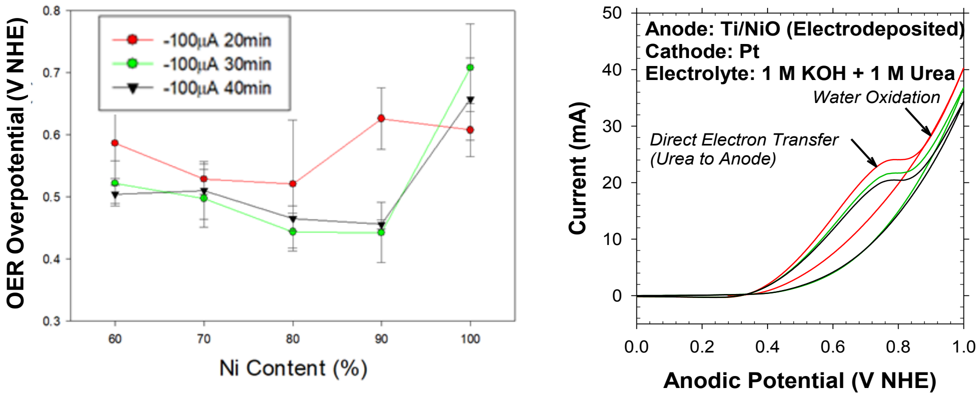

Figure. (left) OER overpotential of $NiFeO_x$ electocatalysts 1 M KOH solutions and (right) current generation of NiO electrocatalysts in linear sweep voltammetry.

Acknowledgement

This work was financially supported by the Basic Research Laboratory (NRF-2018R1A4A1022194) and Nano Material Technology Development Program (NRF-2016M3A7B4908161) through the National Research Foundation (NRF) of Korea.

Assessment of the air humidity impact on the operation of the PEM fuel cell with the use Dynamic Electrochemical Impedance Spectroscopy

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The amount of water present in the fuel cell has a crucial effect on its performance. The currently used PEMFC monitoring methods provide limited information without indicating the processes or components on which the relative humidity has a significant impact. The authors propose the use of novel approach of impedance measurement with the use of multisinusoidal perturbation, which enables impedance measurements under dynamic operating conditions. In this work Dynamic Electrochemical Impedance Spectroscopy (DEIS) was used to obtain impedance spectra for cell during linear change of load at different humidity of the supplied air and linear change of relative humidity at different load levels. This method has been successfully used to identify a faulty cell [1,2], as well as the tool for the selection of optimal working conditions of direct methanol fuel cell [3,4]

The analysis of changes in the value of the equivalent circuit elements was carried out. On this basis, it was determined which process is the determining of the fuel cell operating efficiency depending on the current range and air relative humidity. It allowed to determine the optimal value of oxidant relative humidity depending on the amount of energy generated.

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Harnessing iron ore as an efficient bifunctional electrocatalyst for water splitting reaction

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The choice of catalyst materials to split water into hydrogen and oxygen in water electrolysers is now a great concern. Currently, catalyst materials are mostly based on expensive platinum, iridium and ruthenium based alloy which is not viable for commercial applications. There are extensive research progressing to use the earth abundant transition metals, catalysing the water splitting reaction effectively using electricity generated from intermittent renewable energy sources. However, the applicability of raw ore directly mined from earth's surface has not explored yet in such energy production applications. Herein, we demonstrate a novel approach of using raw ore directly as an effective electrocatalyst both for hydrogen and oxygen evolution simultaneously in water splitting reaction. As a result of the synergy between iron, nickel and sulphur species within the as received iron ore showing higher performance as a bifunctional electrocatalyst in an alkaline environment. The excellent bifunctional activity showed the current density of 10 mA cm^{-2} for oxygen evolution at a potential of 1.60 V and for hydrogen evolution at -0.3 V in 1 M NaOH with a turnover frequency of 1.07 s^{-1}. Further, this robust catalyst showed excellent stability in extensive chronopotentiometric stability test without any degradation in performance. This straightway method of using cheap raw ore in producing oxygen and hydrogen could further be utilized in commercial electrolysers directly.

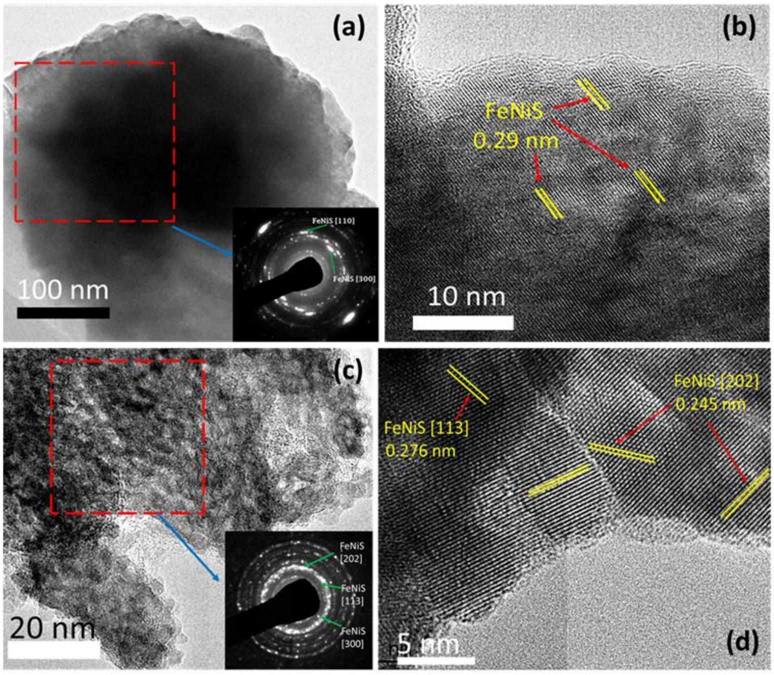

Figure 1. HR-TEM images of raw material (a-b) and activated within the water splitting region (c-d).

Durability of Chemically Crosslinked SPPSU Membrane for PEM Fuel Cells

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Polymer electrolyte membrane fuel cells (PEMFCs) would be expected to give a high power and clean energy system as a power generating device for future energy sustainable society. One of the important factors builds infrastructure facilities such as hydrogen station, storage, and production. At the same time, in research and development of fuel cells, it is aiming for further higher performance while carrying out basic research in each component field. Proton electrolyte membranes are required to have both high proton conductivity and high durability under low/high humidification, and also to develop low-cost materials than fluoropolymers.

We are developing hydrocarbon polymer electrolyte membranes [1 – 4]. As a hydrocarbon polymer electrolyte, polyphenylsulfone (PPSU) polymer (Fig. 1a) was directly sulfonated in the ion exchange capacity of about 3.5 meq/g (DS = 2) (Fig. 1b). The SPPSU electrolyte membranes (Fig. 1c) were prepared by thermal crosslinking method using a solvent cast processing. The chemically crosslinked SPPSU membranes (Fig. 1d) were obtained by a sulfone bridge between sulfonyl group and sulfonyl group (Fig. 1e). An activation process was used to remove the sulfur dioxide as a byproduct during crosslinking reaction. As a result, the membrane showed high mechanical stability and proton conductivity. Using the membrane, a cell performance and durability test was done. A durability test will be reported in the conference.

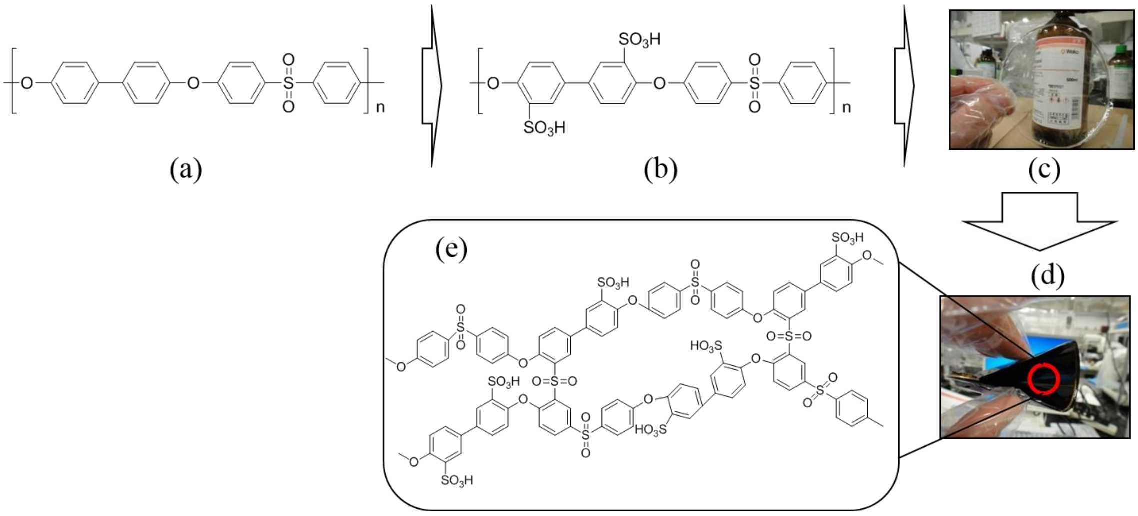

Figure. 1 Chemically crosslinked SPPSU; (a) polyphenylsulfone (PPSU), (b) sulfonated PPSU (DS = 2), (c) SPPSU membrane, (d) chemically crosslinked SPPSU membrane, (e) chemical structure.

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Analyzing oxygen transport resistance and effect of Pt particle growth in the cathode catalyst layer of polymer electrolyte fuel cells

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The oxygen transport resistance in the cathode catalyst layer(CL) of polymer electrolyte fuel cells (PEFCs) has been reported to be considerably higher than expected, especially when the platinum(Pt) loading is low and/or the degree of CL degradation is severe. We numerically analyzed the oxygen transport resistance behavior in the cathode CL under various CL design and operating conditions. Particular emphasis is placed on the aged CL wherein Pt particle growth and active Pt surface area loss are observed. For this study, previously developed micro-scale catalyst model has been improved to account for a Pt particle size for calculations of catalyst activity and electrochemically active surface areas as well as various transport resistances through the ionomer and liquid films. After coupling the catalyst model into a three-dimensional PEFC model, multi-scale simulations are carried out under various PEFC catalyst designs and operating conditions (drying or flooding of electrode, high or lower current density). Provided with extensive multi-dimensional contours of species concentration, temperature, and current density inside PEFC, for comprehensive understanding of oxygen transport resistance in the cathode CL in different PEFC situations.

Three-Way Interactions of Two-Dimensional Crystals

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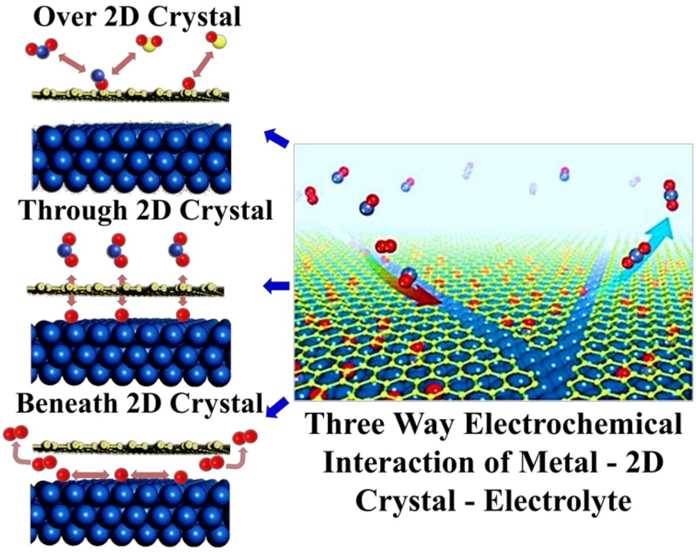
Graphene and related two-dimensional (2D) crystals, a new class of advanced materials, not only improves the performance of the current technological devices but also create new disruptive technologies[1]. From the interfacial electrochemistry's perspective, 2D crystals possess a porous double-sided surface and its integration into a device can lead to multiple interactions namely: i) an electrochemical interaction between the 2D crystal and the electrolyte[2]. ii) The protons (in the case of pristine 2D crystal[3]) or ions (in the case of defect-engineered 2D crystal[4]) permeation through the lattice of 2D crystals. iii) A confined electrochemical interaction in-between the region of 2D crystal and the conducting metal substrate[5]. The three-way electrochemical interaction of 2D crystals makes it a unique material and performance tuning of these interactions can radically transform electrochemistry-based technologies.



Therefore, the primary goal of the talk is to present a detailed analysis of a model metal – 2D material – solution interface, i.e. Pt(111) – graphene – electrolyte interface[6], with an objective to emphasize and define the fundamental aspects behind the three-way electrochemical interactions. The strategy to examine the three-way electrochemical interactions of Pt(111) – graphene- electrolyte interface is to isolate the region for individual interaction and investigate them. The first part of the talk focuses on understanding electrochemical interaction between the graphene and the electrolyte (reaction over 2D crystals): A detailed electrochemical analysis of graphene oxidation kinetics and graphene oxide reduction kinetics will be presented. The second part of the talk will focus on electrochemical permeation of protons through graphene: A comprehensive analysis of temperature dependence of electrosorption of proton on to Pt(111) via graphene permeation in the aqueous electrolyte will be presented. Finally, the talk will focus on understanding the electrochemical reaction below graphene. A comprehensive electrochemical study of hydrogen evolution reaction (HER) on graphene – Pt (111) electrode in the aqueous electrolyte will be presented. These fundamental-level analyses of the three-way electrochemical interaction of 2D materials would be of crucial importance for both the scientific and commercial success of 2D material.

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Molecular Stop-Motions: Unravelling Transient Electrochemical Phenomena at the Millisecond Timescale using EC-MS

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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, while contributing to the abatement of CO_2. Copper is the only pure metal able to perform CO_2RR with appreciable activity and selectivity towards multi-carbon products, especially when the electrode is nanostructured and derived from an oxide. Interestingly, when the Cu catalyst undergoes sudden potential changes, transient phenomena arise showing that the long-term activity and selectivity of the catalyst is not always reflected on the sub-second timescale. The lack of techniques that can probe the electrochemical performance in a time-resolved fashion prevents the detection of phenomena that can give a remarkably different picture of working catalysts. Here, we study Cu electrocatalysts using ultra-sensitive time-resolved electrochemistry and mass spectrometry (EC-MS) to reveal hidden transient phenomena during CO_2RR and HER.

Oxide-derived copper (OD-Cu) electrodes exhibit activity and ethylene selectivity higher than pristine copper during the carbon dioxide reduction reaction (CO_2RR), whereas methane production is suppressed.[1] However, by exposing pristine Cu nanoparticles to gaseous dioxygen (O_2), while resting the working electrode at 0.0 V vs RHE, a reproducible, high transient production of CH_4 is seen at the onset of constant-potential CO electroreduction (Fig. 1).[2] Interestingly, this transient behavior is not observed on H_2 or C_2H_4, which indicates that only the reaction pathway towards single-carbon reaction products is affected. With DFT we show that O weakens the binding for *CO on both kink and step sites, whereas *CHO is stabilized on step sites and destabilized on kink sites. Thereby the kink sites, which were previously inaccessible to CH_4 production, get activated.

In a second experiment, when cycling the potential of a Cu electrode between -0.3 to 0.45 V vs RHE, a surprising double feature appears in the H_2 formation on the electrode. At cathodic potential, H_2 evolves as expected due to HER, while scanning the potentials anodic of the reversible hydrogen potential, a second desorption of gaseous H_2 is observed.[2] This is surprising as the reduction of water to H_2 is thermodynamically prohibited at such anodic potentials. We propose that H_2 may be released through a surface replacement reaction, where adsorbed hydrogen species are replaced with surface adsorbed OH, once the latter becomes more energetically favorable.

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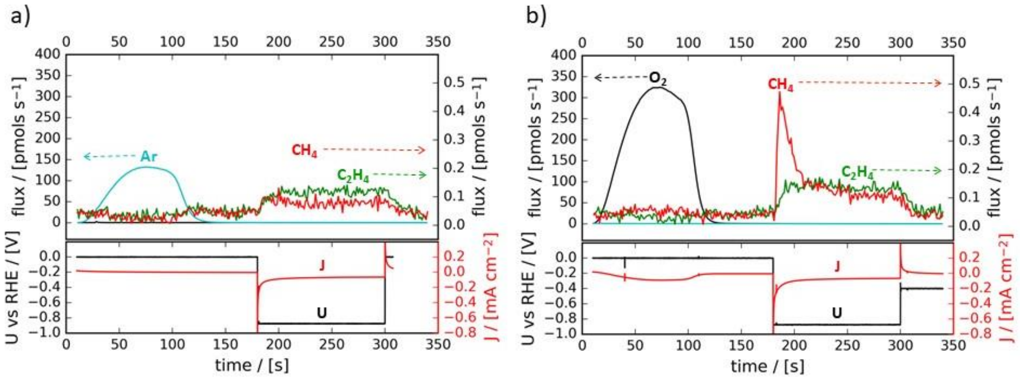

Figure 1. The effect of oxygen demonstrated by two consecutive constant-potential CO electroreduction experiments performed at -0.9 V vs RHE.

Enabling Real-Time Detection of Electrochemical Desorption Phenomena with Sub-Monolayer Sensitivity

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Across many scientific and industrial fields, it is a challenge to analyze chemical reaction products with high sensitivity and fast time-response. This is especially true in systems related to electrochemical energy conversion and storage, such as batteries and fuel cells, where accurate monitoring of fast and transient reaction phenomena often reveals key insights.

Here, we present a unique analysis instrument using a microchip-based inlet system to couple a mass spectrometer directly to any liquid test environment, aqueous or non-aqueous, and exhibits a sensitivity 3-4 orders of magnitude than conventional differential electrochemical mass spectrometry (DEMS).[1–4] The instrument allows to measure the evolution of volatile products and consumption of reactants at electrode surfaces. Due to its extraordinary sensitivity, the system can measure all the individual volatile molecules desorbing from an electrode surface during a single electrochemical turnover. Product formation can be measured from total Faradaic currents of 1 mA all the way down to 1 nA, corresponding to approximately 10 ppm of a monolayer desorbing from the electrode surface in 1s. These features enable time-resolved, fully quantitative measurements of transient phenomena during electrochemistry, providing fundamental insight in the electrochemical reaction mechanisms. Furthermore, an accurately calibrated on-chip gas system allows rapid gas switching between different gases, both inert and reactive. Due to the near-instantaneous equilibration between gas and electrolyte, the transient response of electrodes to rapid gas exposure changes can be measured.

The capabilities of this analysis system are showcased by various examples, including electrochemical water-splitting at low overpotential and low-surface area CO-stripping. *In situ* quantification of hydrogen and oxygen evolution is shown at Faradaic currents on the order of 1 nA. In comparison, conventional techniques can only detect down to about 10 µA of continuous product formation. Finally, the electrochemical stripping of < 1 % of a CO monolayer at standard potential scan-rates of 50 mV/s is shown (Fig. 1).

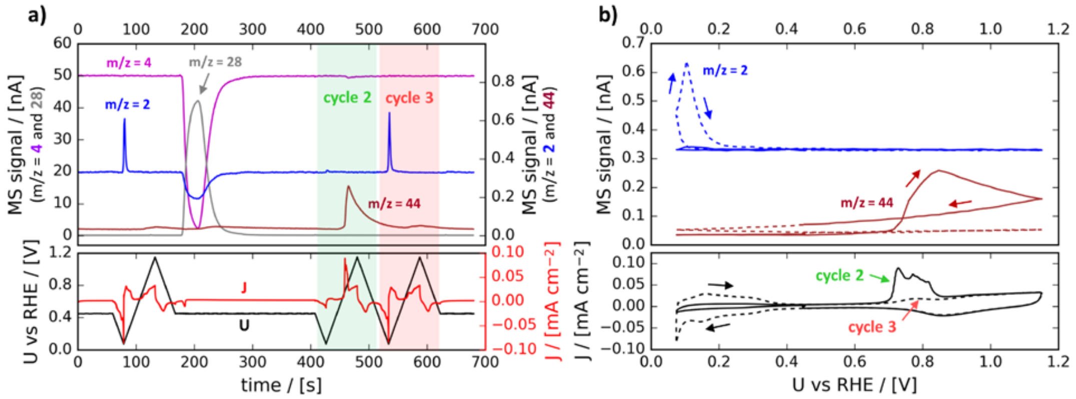

Figure 1. H_2 evolution and CO stripping experiments using a polycrystalline Pt electrode in 1M $HClO_4$.

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Atomistic Picture of Platinum Structural Changes During Electrocatalysis and Mitigation Strategies for Long Term Stability.

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The durability of an electro-active material (e.g. Pt catalyst in proton exchange membrane fuel cells (PEMFC)) is a major barrier, preventing faster commercialization of energy conversion and storage devices for stationary and transportation applications. In the case of PEMFC, the decrease in performance is partially due to irreversible processes in the catalyst layers, such as dissolution and morphology changes of Pt nanostructures. Even though these processes have been extensively studied in the past, there are still many important questions unanswered related to the actual degradation mechanisms [1 and references there-in]. Therefore further fundamental understanding of the Pt oxidation, reduction, dissolution, and restructuring mechanisms, togehter with their atomistic picture, is clearly needed in order to incorporate the state-of-the-art catalysts into the PEMFC device and make the technology more commercially competitive.

I will discuss the results of in-situ and operando structural X-ray studies performed on various Pt single crystal surfaces (Pt(111), Pt(100)) and on nanoparticle catalysts (NP) during the electrochemical oxide formation and its reduction [2-8]. We use advanced synchrotron based diffraction techniques to gain a detailed atomistic picture of the place-exchange (PE), dissolution and restructuring taking place in idealized conditions of the half cells and in PEMFC during operation.

Severe surface reorganization due to the PE process occurs in the potential range relevant to the ORR. Interestingly, the exact position of the PE atom on the surface is the decisive factor which determines the extent of surface restructuring and dissolution. If the PE atom is positioned exactly above its vacancy (e.g. on Pt(111) at low potentials), the PE process is reversible. However, if the PE atom moves laterally from its vacancy, the diffusion barrier prevents the diffusion back to the vacancy and the surface restructures and dissolves in the reduction step. The surface orientation, potential, and time play a decisive role in this process. The PE and surface restructuring have severe consequences as they cause activity loss of the state-of-the-art shaped NP catalysts (octahedra, cubes) in accelerated stress tests and they are also responsible for the poor stability of core-shell nanostructures. It is also one of the main reasons why the incorporation of advanced Pt based catalysts into the next generation PEMFCs remains a challenging task.

Yet nothing is lost and possible knowledge based mitigation strategies, involving additives, particular core-shell structures and defects engineering, can be developed. For example, a new class of defectous Pt catalysts show extraordinary stability, as the reorganization does not significantly alter the morphology which is solely responsible for the high activity [9]. In these materials the defects are used to tune the electronic structure, instead of more traditional approaches such as alloying or shape engineering.

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TiO_2 Films with Enhanced Photoelectrochemical Activity Obtained by Plasma Electrolytic Oxidation

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Titanium dioxide is the most practical photocatalytic material for applications in environmental remediation, self-cleaning of surfaces and light-assisted hydrogen generation [1]. Several techniques have been proposed to synthesise TiO_2 films and powders and, among them, Plasma Electrolytic Oxidation (PEO) has attracted attention, due to the crystallinity, excellent interfacial bonding and electrical contact of TiO_2 films with titanium substrate [2,3]. This work aims at demonstrating that PEO is a suitable technique to easily synthesize TiO_2 films having excellent photocatalytic activity tuned by controlling the PEO processing parameters. In particular, the effects of oxidation cell voltage (100, 150 and 200 V), and processing time (0.5 - 15 min) on morphology, crystallographic structure, Incident Photon-to-Current Efficiency (IPCE) and electrochemical surface area (ECSA) of TiO_2 catalysis were investigated [4]. According to SEM analysis the oxide layers are porous and homogenous at low voltages, and with sponge-like morphology when anodization voltage is increased at 200 V. The XRD patterns evidences that films were crystalline and consisted in a mixture of anatase and rutile. Based on the XRD patterns (Fig.1-a) the predominant crystalline phase shifts from pure anatase to a mixture of anatase and rutile and then pure rutile when cell voltage changes increases from 100 to 200 V and correspondingly, the band gap was 3.29, 3.18 and 3.02 eV, according to the UV-Vis spectra. The photocurrent and the corresponding IPCE of TiO_2 films obtained at 100 and 200 V exhibit a Gaussian-like shape (Fig. 1-b), and a double-peaked curve at 150 V which might be attributed to the activity of both anatase and rutile phases. At processing voltage of 100 V the maximum IPCE is 60% at 300 nm, while by increasing the voltage to 200 V, the IPCE changes to 1% and peaks at 400 nm. On the other hand, specimens obtained at 150 V exhibit a double-peaked IPCE curve reaching 93% at 310 nm and 65% at 380 nm, with photoactivity extending up to 410 nm, *i.e.* into visible region. The ECSA of TiO_2 samples obtained at 150 V is more than 4 times higher than that of samples processed at 100 V, suggesting a possible explanation for the higher IPCE values.

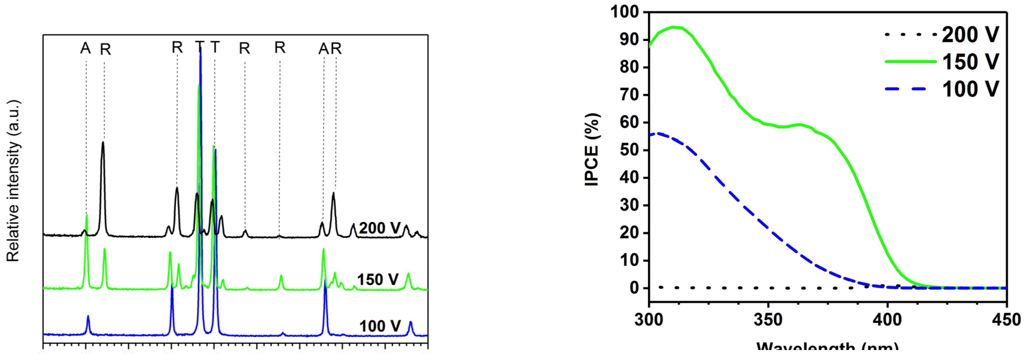

Fig. 1: (a) XRD pattern of TiO_2 films obtained by PEO at different processing voltages; (b) IPCE as a function of wavelength.

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Evaluation of Metal-Organic Frameworks with Incorporated Ruthenium(0) Nanoparticles as Efficient Electrocatalysts for Borohydride Oxidation Reaction

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As the human exigency for energy is constantly increasing, the world is facing excessive use of fossil fuels as energy sources known to have undesirable impact on human lives and environment. Hence, with the development of modern society, the need for clean energy and shift to low carbon economy has also been growing. In order to deal with those issues, researchers have introduced different fuel cell designs as a promising class of sustainable power sources. Thus, direct borohydride fuel cells, DBFCs, have been receiving great attention of the science community [1]. Despite many advantages, practical application of those devices has been hampered due to their high investment cost, mainly related to high price of anodic catalyst used (usually, a precious metal). To overcome this issue, development of efficient, low cost and durable electrocatalysts is required. That can be achieved by alloying noble metals with other metals of lower price or by using a support with high surface area and capacity to stabilize metal particles [2].

Metal-organic frameworks (MOFs) have emerged as novel materials showing immense potential for energy conversion application due to their unique attributes such as ultrahigh porosity and internal surface area, good thermal stability and versatile framework, as well as their cheap and high-yield synthesis methods. Herein, MIL-101 and sulfonic acid functionalized MIL-101 MOFs were synthesized and used as host materials to stabilize guest ruthenium(0) nanoparticles (Ru@MIL-101 and Ru@S-MIL-101), which were fabricated by following our previously reported synthesis protocols [3,4]. The present work aims at evaluating the performance of the prepared materials as electrocatalysts for borohydride oxidation reaction (BOR), since Ru alloyed with non-precious metals (e.g., Ni) or dispersed on high surface area carbon, has already been proven to have good electrocatalytic activity towards BOR [5,6].

The electrocatalysts (Ru@MIL-101 and Ru@S-MIL-101) were characterized by using multi-pronged techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES), Fourier-transform infrared spectroscopy (FTIR), powder X-ray diffraction analysis (P-XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and N_2-ads.-des. technique. Cyclic and linear scan voltammetry techniques were used to examine the catalytic activity of the materials for BOR at different temperatures (25 – 65 ºC) and concentrations (0.01 – 0.12 M $NaBH_4$). For all experiments 2 M NaOH was used as supporting electrolyte to guarantee the alkalinity of the media. BOR kinetic parameters, such as charge transfer coefficient, number of exchanged electrons, activation energy and order of reaction were calculated and compared with those reported in the literature. A small-scale DBFC (using hydrogen peroxide as a liquid oxidant) was assembled using the Ru nanoparticles immobilized on MOFs as an anodic catalyst and the fuel cell performance was assessed at different temperatures.

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Newly developed electrochemical synthesis of Co-based Layered Double Hydroxides: application to 5-(hydroxymethyl)furfural electro-oxidation

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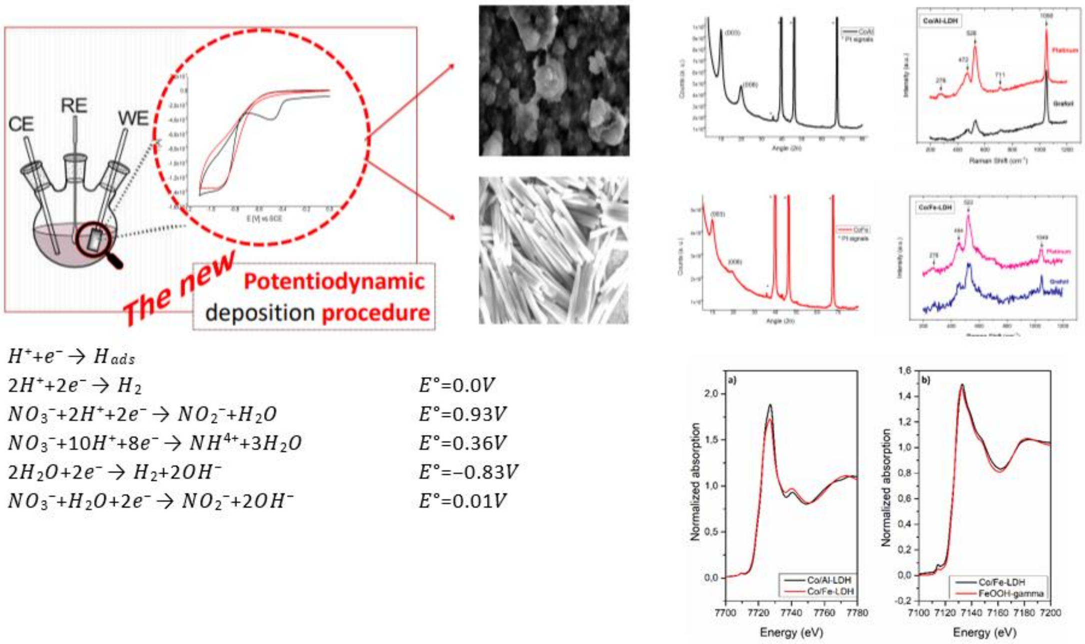
A newly developed electrochemical synthesis protocol[1] that allows for the deposition of thin films of Co/Al and Co/Fe layered double hydroxides (LDHs) on different supports is hereby proposed. The approach is based on a potentiodynamic cathodic reduction. All the films have been characterized by cyclic voltammetry, powder X-ray diffraction, scanning electron microscopy, and Raman and atomic emission spectroscopies. Moreover, the LDHs electrosynthesized on graphite-sheets have been also investigated by X-ray absorption spectroscopy to analyze their local metal structure (Fig. 1). These conductive supports are particularly interesting for the plethora of LDHs applications ranging from energy storage, sensing, electrocatalysis, also of industrial importance, due to their low cost, ecocompatibility, and easy handling. Among the possible applications, the LDHs modified electrodes were successfully tested for the 5-(hydroxymethyl)furfural (HMF) electro-oxidation. Nowadays, HMF molecule is considered a fundamental platform chemical, i.e., it is a key precursor for a great number of chemicals which find application in fuel and polymer industry.[2]



$H^{+}+e^{-} \rightarrow H_{ads}$

$2H^{+}+2e^{-} \rightarrow H_2$ $E°=0.0V$

$NO_3^{-}+2H^{+}+2e^{-} \rightarrow NO_2^{-}+H_2O$ $E°=0.93V$

$NO_3^{-}+10H^{+}+8e^{-} \rightarrow NH^{4+}+3H_2O$ $E°=0.36V$

$2H_2O+2e^{-} \rightarrow H_2+2OH^{-}$ $E°=-0.83V$

$NO_3^{-}+H_2O+2e^{-} \rightarrow NO_2^{-}+2OH^{-}$ $E°=0.01V$

Figure 1: Electrosynthesis and characterizations of Co-based LDHs

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Membranes of polybenzimidazole crosslinked with PVBC for high performance energy applications

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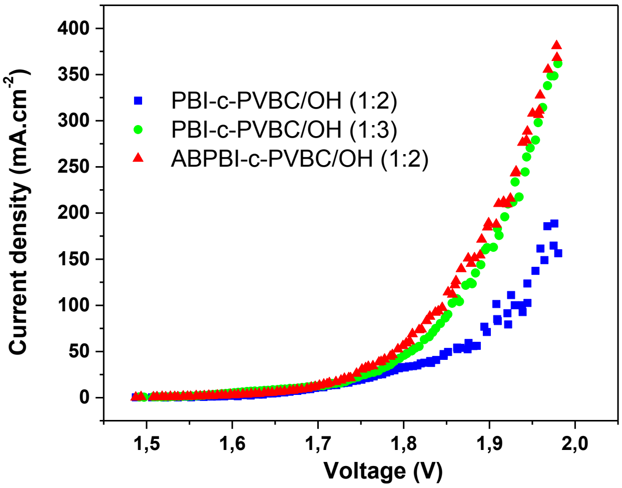
New technologies are needed to overcome the petroleum end and reduce the climate change so a sustainable energy system can be made real. Electrolizers and fuel cells are technologies more developed each day due to the interest they have attracted thanks to their high potential. In the case of electrolizers the have the ability to transform electrochemically using electrical power water to hydrogen (a near-zero emission energy carrier applicable to all energy sectors) and oxygen, while fuel cells do the opposite, they use a fuel (H_2 for instance) and an oxidant to produce electrical power. The coupling of both technologies allows to accumulate energy in excess in the form of H_2 and transform it to electrical power with a fuel cell when needed. Both are also highly interesting for the transition stage from a petroleum based energy system since the electrical power (for electrolizers) or the H_2 (for fuel cells) can be produced from petroleum. Anion exchange membranes (AEMs) are key components of some electrolizers and fuel cells, concretely the zero-gap liquid alkaline water electrolyzers (LAWEs) and anion exchange membrane fuel cells (AEMFCs). Important improvement is needed so the membranes have better conductivity of ions and better chemical and mechanical stability in order to make these devices more economically viable. [1] Different approaches have been tried; the one we use in this work has demonstrated outstanding results and is based in the idea of synthesizing a homogenous membrane with positively charged quaternary ammonium groups in the structure.[2] We describe in this work the synthesis of membranes composed of PBI/ABPBI crosslinked with PVBC at different ratios and quaternized with DABCO. We also investigate the structure characterization by FTIR and SEM and the evaluation of the swelling ratio, KOH and water uptake, ionic conductivity, thermal and chemical stability and finally the good performance results obtained in a zero gap water electrolyzer with KOH 1M at 50°C and in a anion exchange membrane fuel cell with EtOH (2M)/KOH (2M). We consider the results are promising and demonstrate the great applicability of the membranes.



Performance of the zero gap water electrolizer using different ratios and chemistries of polybenzimidazole crosslinked with PVBC. The conditions were 1M KOH at 50ºC with Ni foam electrodes.

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Metal Organic Frameworks based on iron applied in photoelectrocatalysis.

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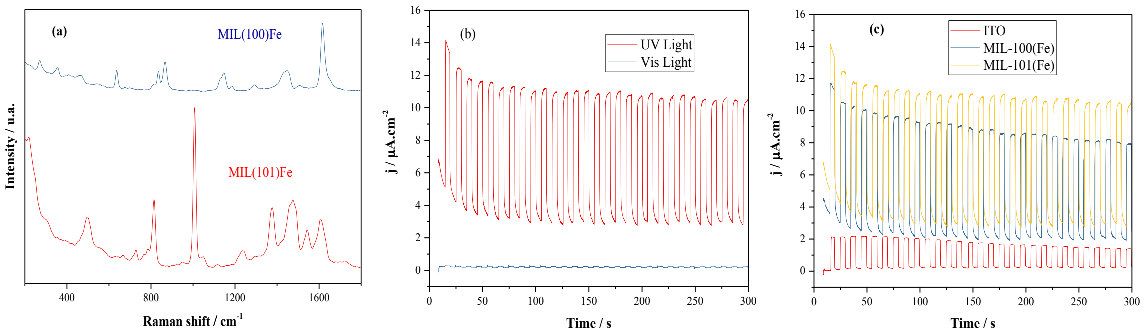
The photoelectrocatalysis has been widely studied its efficiency in the removal of organic contaminants in the until reaching the mineralization of these pollutants. Also, the development of a new type of photocatalyst with superior performance for removal organics pollutes is important yet challenging. Herein, we reported the synthesis of two Fe-based metal-organic frameworks [MIL-100(Fe) and MIL-101(Fe)] and the deposition of these materials on ITO to apply as a photoanode in the photoelectrocatalysis of the methylene blue (MB) dye under visible and UV light. The materials were characterized by different techniques, such as DRX, TGA/DTA, MEV, Raman (Figure 1(a)), among others. The films were deposited on glass plates coated with conductive layer (ITO) by the Layer by Layer (LbL) technique with 1, 3, and 5 layers. Besides, the films were characterized by electrochemical techniques, such as cyclic voltammetry and chronoamperometry. The photoelectrochemical profiles electrodes showed an augmentation in photocurrent with layer increasing, during the anodic scan. So, the electrodes containing 5 layers of MIL-100(Fe) and MIL-101(Fe) shown the higher photocurrent density. Therefore, the photocurrent density was higher for all electrodes irradiated with UV light when compared with visible light irradiation or electrochemical process at dark, Figure 1(b). The film composed by MIL-100(Fe) with 5 layers presented the highest photocurrent with an approximate value of 7.89 μA cm^{-2}, and the MIL-101(Fe) film composed by 5 layers with 10.32 μA cm^{-2}. The photocatalytic activity of these synthesized materials was tested in photooxidation of MB, following the pseudo-first order kinetics. All electrodes synthesized presents better which greater the number of layers, increased the photocalytic efficiency. The electrodes that presented the best catalytic activity in the decolorization under UV light were of containing 5 layers of MIL-100(Fe) and MIL(101)-Fe with a observed kinetic constant (k_{obs}) approximately 3.5×10^{-3} and 4.1×10^{-3} min^{-1} and decolorization of 34 and 40 %, respectively, in 120 min. Besides, photocatalysis was held to be proven its inefficiency against photoelectrocatalysis. The decolorization in photocatalysis was 11 and 14 % for MIL-100(Fe) and MIL(101)-Fe, respectively. This shows that the junction of electrochemical and photochemical techniques improves the efficiency of a catalytic material. This is due to the motion of the excited electron from the semiconductor to be transported to the counter electrode while the hole generated form radicals OH• to oxidize organic molecules.

Figure 1. (a) Raman spectra of MIL-100(Fe) and MIL(101)-Fe. (b) Chopper of MIL-101(Fe) under visible and UV light with 5 layers. (c) Comparison of the photocurrent generated of pure ITO, MIL-100(Fe) and MIL(101)-Fe with 5 layers under UV light.



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Probing Ionic Liquid Interfacial Structures Towards the Enhancement of Charge Efficiency for Advanced Energy Storage Applications

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Energy storage devices are core elements for increasing the energy efficiency generated from environmentally-friendly and reliable resources and for an appropriate response to the increasingly high energy society's demand [1]. Electrolytes are considered to be one of the most influential components in the performance of electrochemical energy storage devices. Higher ionic concentration in the electrolyte is required for the improvement of the energy stored and ionic liquids present interesting properties that make them suitable candidates for the replacement of the conventional electrolytes. Actually, it is very challenging for an ionic liquid to meet all the requirements of an ideal electrolyte, since each electrolyte may present its own advantages and shortcomings. In order to overcome some of these shortcomings, ionic liquids mixtures become an interesting strategy to fine-tune the composition-dependence of the electrolyte properties, opening up new advances for particular practical applications.

In this work, we present our recent advances obtained from the electrochemical studies using pure ionic liquids and its mixtures as promising electrolyte candidates on energy storage systems. Recent results showed that the use of ionic liquids with ions of different sizes could lead to an increase in the charge accumulation at a specific potential (optimal composition range for the ILs mixtures that maximizes the differential capacitance). Formulation of ionic liquids mixtures at charged surfaces with a common cation and varying the molar fraction of anions different in size and geometry seems to favor the accumulation of smaller counterions on the electrode adjacent layer with simultaneous displacement of the bigger counterparts. The charge accumulation mechanism proposed may also lead to the co-ions exclusion from the electrode surface [2].

Nonlinear optics studies were performed by using the Second Harmonic Generation (SHG) technique to probe the air/liquid and solid/liquid interface to deeper understand the microscopic structure of pure ILs and ILs mixtures based interfaces. Polarization analysis of the nonlinear optical intensity was obtained as a function of the alkyl chain length of pure/mixtures of ILs and the results are interpreted in terms of the structural organization of the interface.

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Investigation of Physical and Electrochemical Properties of PILs in HT-PEFCs

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There is an increasing requirement in the field of polymer membrane fuel cell (PEFCs) for new proton conducting membrane electrolytes that can be operated at the temperature of around 100 °C and with low water activity. The proton conductivity of perfluorinated polymers with sulfonic acid groups relies on sufficient water swelling. Thus, traditional low temperature PEFCs based on Nafion® membranes are faced with a drying problem that requires feed gas humidification or increased feed gas pressure. Operation above 80 °C is hardly possible. High temperature PEFCs (HT-PEFC), based on phosphoric acid (H_3PO_4) doped polybenzimidazole membranes (PBI), allow operation of up to 160 - 180 °C. However, due to poisoning effects by H_3PO_4 species on the redox catalyst and a low solubility of oxygen in H_3PO_4, the ORR kinetics is sluggish, leading to an insufficient power density and to high costs of the cell.

Proton conducting ionic liquids (PILs) are of special interest because they normally exhibit a high ionic conductivity, low volatility and high thermal stability, as well as a high electrochemical stability over a wide temperature range. Thus, PILs are promising substitutes for H_3PO_4 as non-aqueous acidic proton conductors for operating temperatures of up to 120 °C.

This study is focused on acidic PILs based on sulfoalkylammonium cations. Wippermann et al. demonstrated that the 2-sulfoethylammonium triflate shows superior ORR kinetics on Pt catalysts compared to H_3PO_4 at a temperature above 90 °C in the application-relevant potential range [1]. In this study, PILs with a 2-sulfoethylmethylammonium cation in combination with various anions such as hydrogensulfate, triflate and tosylate were considered. The essential physico-chemical properties for fuel cell operation, i.e. current density, oxygen solubility, oxygen diffusivity, electric conductivity, thermal stability and the viscosity of PILs, are measured at different temperatures. Small amounts of water in PILs can change the properties of metal/PILs interfaces and thus ORR kinetics [2] as well as the conductivity of PILs. Therefore the PIL-water system is investigated during fuel cell operation, water will be produced.

The electrochemical measurements of PILs are performed at different temperatures. The influences of the cations or anions on the ORR kinetics (oxygen diffusivity and concentration in PILs) and conductivity are investigated. The results show that with different cation/ anion combinations, significant differences in ORR kinetics, electrochemical stability and electric conductivity are present.

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Differential Impedance Analysis as a Tool for the Real-Time Evaluation of Automotive Fuel Cells

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In automotive applications, fuel cells operate within a wide operational parameter range. Thereby, it is commonly seen that the lifetime of the stack is limited by the lifetime of single cells. Inhomogeneous operational conditions within the stack are a major issue that causes different lifetimes of the cells within a fuel cell stack. Additionally, fuel cells in automotive systems need to operate under highly dynamic conditions. This leads to increased requirements towards quick and precise detection of the operational parameters of single cells. Electrochemical impedance spectroscopy (EIS) is one tool that allows to estimate different parameters of single cells within a stack. In comparison to external sensors, EIS decreases the delay between an event and the measurement and increases the measurement accuracy due to decreased cross influences[1]. The determination of cell humidification using EIS is already commonly reported for automotive applications[2]. In that way, the analysis is based on the impedance measured at a single frequency. EIS also contains information about media supply of the fuel cell. Differential impedance analysis (DIA) in combination with a Randles-like local operating model can thereby be used to determine membrane and activation resistance as well as the faradaic contribution due to the oxygen reduction kinetics[3]. An automotive size single cell and short stack were tested in this work within a wide operational parameter range. Impedance spectra were recorded and analyzed via DIA within a frequency range of 15 to 300 Hz. The analysis shows that media starvation at the cathode side can be detected using DIA and serve as input signal to optimize the operational strategy of automotive fuel cell systems. It can be shown that measuring only 5 frequencies is sufficient to determine humidification and stoichiometry of automotive single cells. The measurement and analysis time is therefore only few seconds. This allows the observation of single cells also during dynamic fuel cell system operation; and the results can serve to reach a more optimal stack operation.

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Reproducible Activation of Glassy Carbon Electrode

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Glassy carbon (GC) is very interesting electrode material frequently used in laboratory practice. It is often material of first choice when investigating behaviour of (novel) compounds on carbon electrodes. Its electrocatalytical properties are largely dependent on the electrode surface functionalisation (presence of surface groups like -C=O, -C-OH or -COOH). The largest electrocatalytic activity is ascribed to the surface -C=O groups moieties which are relatively scarce at the pristine/nonactivated GC surface. Though numerous procedures for GC electrodes activation (based on surface cleaning, polishing, plasma etching, vacuum and/or thermal treatments, chemical modifications and finally also electrochemical modifications) have been described in the literature over the years, there is no widely accepted standard activation procedure.

In the present contribution, detailed systematic investigation of pretreatment of GC electrode performed by electrode potential cycling in strongly alkaline environment is reported. Under such conditions the surface activation should be, according to the literature, limited to the very surface as well as reproducible. We have focused on the thorough optimisation of the upper potential limit applied, which was, so far, lacking. The composition of the surface of tested electrodes was determined by means of X-ray photoelectron spectroscopy. Analysis of the detained spectra allowed identification of overall atomic composition of the surface layer as well as identification of the surface functional group moieties. The electrocatalytic properties of the activated electrodes were assessed using representatives of the three principally different groups of redox couples ($Fe^{3+/2+}$, $Fe(CN)_6^{3-/4-}$ and quinone/hydroquinone) by means of evaluating peak separation in cyclic voltammetry as a measure of electrocatalytical activity. In all cases, the highest electrocatalytic activity was observed for the electrodes activated with upper potential at which the surface concentration of –C=O moiety was found to be highest. In summary, it was shown that combining information from spectroscopical and electrochemical experiments allowed finding correlation between electrode surface layer composition and its electrocatalytic activity and to identity optimal activation conditions resulting in reproducible, highly stable and active electrode surface. We believe that due its simplicity and efficiency, the present activation procedure has the potential to become a standard method for GC electrode activation.

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Performance of the Polymer Electrolyte Alkaline Water Electrolyser Stack utilizing Diluted KOH Solutions

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Increasing share of the renewable sources of electricity increases the necessity of the stabilization of their output. This is due to the strong dependence of the most widely used sources *i.e.* sun and wind energy, both on the seasonal as well as on the actual weather conditions. One of the promising technologies enabling the balancing of the electricity distribution grid with significant amount of connected renewable sources represents water electrolysis. It is based on the decomposing of water molecules into the molecules of oxygen and hydrogen by corresponding amount of an electric work. The hydrogen is considered as an excellent energy vector. It is due to its reactivity, high energy of the chemical bond with oxygen and versatility of its further utilization. Its production by water electrolysis is connected with the electricity consumption while the reaction with oxygen in fuel cell allows the electricity recuperation. Nowadays, three main technologies of water electrolysis are under research and development. These are high temperature water electrolysis, PEM water electrolysis and alkaline water electrolysis. High temperature water electrolysis offers the advantage of the high production capacity and high efficiency, but solves the problems of material's stability. PEM water electrolysis utilizes the proton exchange membrane as separator of the anode and cathode compartment, achieving the high flexibility, good efficiency and reasonable production intensity, however the need of the platinum metals utilizing as electrocatalysts results in high capital cost. Alkaline water electrolysis is well-established in industry due to its reliability and robustness, but it has not been significantly improved for decades. Drawbacks of this technology lay mainly in the limited flexibility. The utilization of the polymer anion selective membrane as a separator of the electrodes compartments similarly to the PEM technology can into the significant degree eliminate both of the mentioned drawbacks. This is mainly connected with reduction of the distance between the electrodes (nowadays typically in the range of tens of millimeters) to the thickness of the polymer membrane and of the concentration of liquid electrolyte (nowadays potassium hydroxide (KOH) 25-30wt.%).

The aim of this work is to evaluate the influence of the liquid electrolyte concentration on the performance of the laboratory scale polymer electrolyte bipolar alkaline water electrolyser (PEAWE) stack consisting of three cells including the evaluation of the current and energy efficiency. The commonly available materials are used for the stack construction. Distribution plates are made of polyvinylchloride (PVC), the electrodes of geometrical area 78 cm^2 are made from Nickel foam and bipolar as well as terminal electrodes from Ni sheets. As the separator of the electrodes compartments the chloromethylated block copolymer of styrene-ethylene-buthylene-styrene (PSEBS-CM) carrying the functional groups of 1,4-diazabicyclo[2.2.2]octane (DABCO) is used. The average thickness of the fully swollen PSEBS-CM-DABCO membrane is approximately 0.18 mm. The Ni foam electrodes are pressed directly to the surface of the membrane. The liquid electrolyte of the 1, 5, 10 and 15 wt.% KOH is used as circulation media to evaluate the influence of the KOH concentration on the current efficiency and performance of the laboratory scale PEAWE stack. The higher concentration of the liquid electrolyte improves the performance of the alkaline water electrolysis due to the improved contact in the bulk of the porous Ni foam electrodes. On the other hand, the higher concentration increases the conductivity of the pathway for the parasitic current decreasing thus the current efficiency. Using the anion selective polymer membrane as the separator of the electrode compartments it was possible to achieve the performance of the industrial technology using even the KOH solutions with reduced concentration and lower temperature.

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Asymptotic Analysis of Conductivity Relaxation Data for Determining Oxygen Exchange and Diffusion Coefficients for Mixed Ionic Electronic Conducting Oxides

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Conductivity relaxation is a frequently applied technique for determination of chemical surface exchange and bulk diffusion coefficients of oxygen in mixed ionic electronic conducting oxides. The technique is based on the measurement of relative oxygen mass change caused by a step change in the partial pressure of oxygen by monitoring the electronic conductivity of a sample. The purpose of this paper is to demonstrate an improved methodology for the interpretation of conductivity relaxation data, based on the asymptotic solutions to Fick's 2nd law for linear surface exchange condition. The asymptotic cases (a-d) include a) short-time and b) long-time solutions and rate control by c) surface exchange and d) bulk diffusion of oxygen. It is demonstrated that the use of the asymptotic solutions for analysis of experimental data can improve the accuracy of the determined coefficients, which may in some cases be in error by almost an order of magnitude by uncritical fitting of data to the Fourier series solution of Fick's 2nd law.

Pressure-based electrochemical impedance spectroscopy in polymer electrolyte membrane fuel cells: the role of outlet backpressure

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Keywords: PEM fuel cell, EIS, EPIS, mass transport phenomena

The polymer electrolyte membrane fuel cell (PEMFC) is a simple power device but inside it a complex and coupled mass transport phenomena are key factors in governing its performance and durability [1]. Over the period the membrane electrode assembly degrades, the diagnosis is usually done by a popular technique called electrochemical impedance spectroscopy (EIS). It gives out information like source of degradation, but it fails considerably to comment on and distinguish between mass transport processes [2]. The PEMFC offers us a non-electric variable to observe i.e. gas pressure. When combined with current or voltage it gives us additional definitions of impedance and using this technique in harmonic conditions is called electrochemical pressure impedance spectroscopy (EPIS). [3]

In 2006, Amirinejad et al found out that the fuel cell performance has positive effect if the cathode side is set at a higher pressure than the anode side [4]. Zang et al (2009) [5] reported that increasing backpressure in a PEMFC enhances the fuel cell performance by boosting the fuel cell thermodynamics, exchange current densities and improving the mass transport processes. But also, increasing the cathode backpressure beyond a certain level may cause nitrogen to diffuse across the membrane and in turn cause mass transfer losses. At high current density the fuel cell may starve even in case of sufficient supply of reactants due to significant nitrogen accumulation [6]. The experiments were examined with EIS but no very precise comment could be made on transport processes in the cathode side due to insufficient accuracy of the data at low frequency.

In this work, the focus is on applying EPIS to PEMFC and developing it for better understanding the effect of cathode backpressure on the transport process inside PEMFC. A sinusoidal variation in the cathode backpressure is applied using a pressure regulator to record the voltage response of the fuel cell at constant current in a frequency range of 5 to 800 mHz with pressure amplitudes of a few mbar. The experiments conducted at OCV without any humidification have given out some quite fascinating results: a negative phase angle for pressure impedance (P_{out}/P_{in}) whereas the voltage-pressure impedance has visible complex value, depending on the frequency. We are currently working on the possible use of pressure-pressure impedance in terms of phase shift and modulus of impedance in further experiments, which will enable us to comment on the complexity of the transport processes inside PEMFC and effect of cathode backpressure excitation on the PEMFC mass transport and performance.

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Construction of porphyrin-sensitized solar cells containing Toray™/TGP-H-060 carbon – based cathodes

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In this work, we present the construction and photovoltaic response of porphyrin-sensitized solar cells containing Toray^{TM}/TGP-H-060 carbon – modified indium-doped tin oxide (ITO) cathodes (ITO/C), as a viable alternative for substituting platinum oxides – modified ITO cathodes (ITO/PtO$_x$), which are traditionally employed for designing dye-sensitized solar cells. In this case, a binary mixture (75:25) of propylene carbonate (PC) : 3-methoxypropionitrile (MPN), containing 0.015M I_2 plus 0.285M LiI was employed as electrolyte for filling the photo-cells.

On one hand, our experimental results demonstrated that both cathodic systems, ITO/C and ITO/PtO$_x$, had a very comparable electron transfer kinetics when studied the cathodic semi-reaction $I_3^- + 2e^- \rightarrow 3I^-$ at these electrode surfaces.

Table 1. Electron transfer constants ($k°$) and cathodic transfer coefficients (α_c) obtained for the semi-reaction $I_3^- + 2e^- \rightarrow 3I^-$ at ITO/C and ITO/PtO$_x$ cathodes. Electrolyte: 0.015M I_2 plus 0.285M LiI contained in a binary mixture 75:25 of PC:MPN at 25°C. A polycrystalline Pt cathode was also employed for comparison purposes.

cathode	Electron transfer kinetic parameters	
	$k°/10^{-4}$ (cm/s)	α_c
Pt	5.31	0.27
ITO/PtO$_x$	3.35	0.26
ITO/C	2.70	0.23

On the other hand, a detailed revision of Table 2 reveals that the photovoltaic responses of porphyrin-sensitized solar cells containing ITO/C and ITO/PtO$_x$ cathodes were comparable under simulated solar light (AM1.5, 100mW/cm^2). These interestingly results confirmed that Toray^{TM}/TGP-H-060 carbon – modified ITO cathodes are promising to substitute those PtO$_x$ – modified ITO cathodes typically employed for constructing dye-sensitized solar cells.

Table 2. Photovoltaic responses obtained for porphyrin-sensitized solar cells containing ITO/C and ITO/PtO$_x$ cathodes, where: E_{oc}, j_{sc}, *ff* and ξ are open-circuit potential, short-circuit photocurrent, fill-factor and global conversion efficiency, respectively, under simulated solar light (AM1.5, 100mW/cm^2).

cathode	E_{oc} (V)	j_{sc} (mA/cm^2)	*ff*	ξ(%)
ITO/PtO$_x$	-0.30	1.23	0.39	0.17
ITO/C	-0.35	1.18	0.40	0.19

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Study of impact of the hot-press process parameters on the three-phase contact in low temperature PEM fuel cell MEA

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The heart of any PEM fuel cell is the membrane-electrode assembly (MEA). MEA consists of a polymer electrolyte membrane and gas diffusion electrodes containing catalytic layer (GDE). The performance of MEA depends critically on the conductivity of membrane and activity of the catalytic layer. Conductivity of membrane then depends on ionomer used for membrane preparation and on its pretreatment. Ionomers used nowadays in the low temperature PEM type fuel cells are based exclusively on the perfluorinated sulfonated acids. It is formed by perfluorinated backbone chain with functional group carrying side chains attached through etheric bond. Conductivity of ionomer and its mechanical and chemical properties depend on the length of the side chain, equivalent weight and functional group nature. GDE can be based on carbon cloth, or on carbon paper. Both materials have a different level of porosity, electric conductivity and mechanical properties. Selection depends mainly on the membrane properties. Catalytic layer is mechanically stabilized by Nafion binder creating at the same time three-phase contact inside the catalytic layer structure. Prepared electrodes can be assembled with the membrane either directly in the fuel cell, or by pressing them onto each side of proton exchange membrane under high pressure and temperature (hot-pressed MEA). The method of the MEA preparation plays an important role in final performance of the resulting fuel cell. Different properties of electrodes and membrane materials, as well as parameters of MEA fabrication represent a broad field for optimization.

In the present study, the impact of hot-press parameters on membranes of different thickness and ionomer structure was investigated. Membranes commercially available under name Nafion and Fumapem were used for this purpose. Commercially available GDE SLGDE-CT (Fuel cell Etc.) with loading 0.5 mg cm^{-1} of platinum on Vulcan were used. These electrodes are based on carbon cloth gas diffusion layer. Porosity and wettability of electrode material have a crucial influence on their transport properties. These parameters can be influenced by the ionomer used as a binder in catalytic layer. It is at the same time responsible for formation of required three-phase contacts, i.e. point, where reactant, ionic and electronic conductors are in contact. Temperatures of glass transition points of both ionomers have to be close to ensure good connection of ionically conductive phase in the electrode and ionomer of the membrane. Application of elevated temperatures during hot-press process contributes to formation of intimate contact between both phases. Application of too low temperature leads to imperfect connection, whereas exposition of MEA to excessively high temperature leads to filling of free areas in electrodes by melted ionomer and collapse of internal reactants transport pathways. Optimization of applied force is important too. Application of excessive force leads to two problems. First is collapse of electrode structure and losing reactants transport pathways again. Second problem represents risk of mechanical damage of the membrane by the electrodes. Membranes with thickness less than 150 µm, have an insufficient mechanical strength. It is thus easy to perforate them. This problem can be solved by using reinforced membranes. Unfortunately, fibers of reinforcement, e.g. polytetrafluoroethylene, are not distributed homogeneously in the volume of the membrane. They thus cause spontaneous rolling of membranes resulting again in imperfect contact between the electrode and membrane. Second problem represents the fact, that reinforcement fibers are ionically nonconductive and thus decrease active cross section of the membrane. All prepared MEAs were compared with commercially available MEA, HO-5MEA and HO-3CCM (Fuel Cell Etc.). All MEAs were characterized by loading curves, impedance spectroscopy and post mortem by scanning electron microscopy with focused ion beam. The target of this study is to provide more insight into above-mentioned method of MEA preparation for the selected membranes.

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Steam Electrolysis with Solid Oxide Cells: Progress in Long-Term Stability and Operation under Fluctuating Load

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Current long-term testing activities of EIFER with respect to steam electrolysis with solid oxide cells are focused on electrolyte supported cells (ESC) with Ni-GDC H_2 electrodes. That cell type has shown to fulfill to a large extent the requirements for industrial application, including the reversible fuel cell/electrolysis cell (SOFC/SOEC) operation mode [1]. A benchmark operation time of 23000 h was achieved for a current density of -0.9 Acm^{-2} at a maintained low voltage degradation (~7 mV/1000 h) [2]. For the used current density, operation occurs close to the thermal neutral voltage which yields highest possible efficiency. No indications were found for a critical loss of Ni, the catalytically active material in the H_2 electrodes. That Ni loss is, at cells with the classical Ni/YSZ electrodes, responsible for accelerated degradation when operated at higher magnitudes of the current density (e.g., [3]).

A (running) follow-up long term test done at lower temperature (<800°C) with an ESC has in the meantime exceeded the above given benchmark time and will be presented in more detail (compare [4]). Impedance spectroscopy is used in that test under steady state operation conditions as highly sensitive tool for *in-situ* degradation analysis, allowing separation of the ohmic and the different reaction terms.

First performance tests of commercial cells of comparable electrode structure using the classical and robust 3YSZ electrolyte, but with a reduced thickness (down to 40 µm), have reached several thousand hours of operation time (*U-j* data in Figure 1).

The current ON/OFF switching of individual stacks is discussed as means for load following. If done with a cell voltage at the thermal neutral voltage (~1.3 V), switching is not accompanied by changes in the thermal load, which is of advantage for the stack/system operation. Sufficient stability is indicated by a test with 80 000 completed ON/OFF cycles.

A large part of the mentioned work to be treated in the meeting was done in the frame of the research project GrInHy of the European Union on reversible SOFC/SOEC [5].

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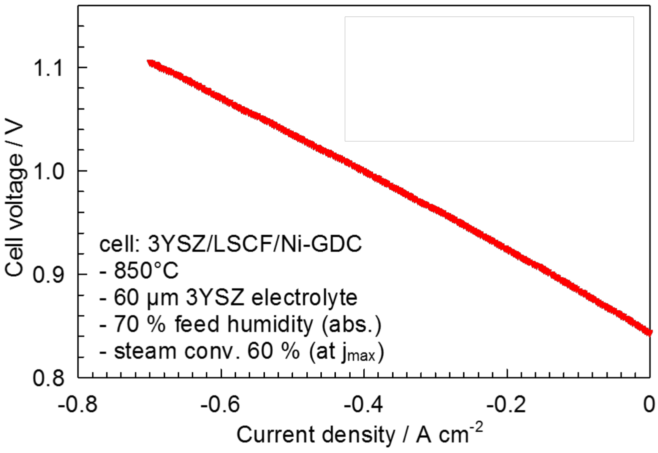

Fig. 1. Voltage-current behavior of an electrolyte supported solid oxide cell with a thin (60 µm) 3YSZ electrolyte operated in the steam electrolysis mode.

Electrochemical Free-Standing Carbon Nanotube Filters: Spectroelectrochemistry Evaluation of the Performance of the Filtration Process

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Electrochemical filtration is a very interesting alternative for oxidation of aqueous organic pollutants. Single-walled carbon nanotubes (SWCNT) can be used as membrane for water treatment. Free-standing SWCNT electrodes can be prepared using very simple and effective methodologies [1]. These SWCNT membranes can be independently functionalized with nanoparticles, polymers, etc. [2] making possible to obtain a Janus film. In this communication, the combination of electrochemical free-standing single-walled carbon nanotube filters and spectroelectrochemical techniques in a new device [3] demonstrates that this route is not only an attractive methodology for the treatment of wastewater but also it is very useful to quantify the removal of different contaminants. The new device has been validated using a typical reference redox system for spectroelectrochemistry (o-tolidine) and it has been used to study systems of diverse nature. Furthermore, the possibility of designing modified carbon nanotube filters with different catalysts opens new gates for future and very attractive applications.

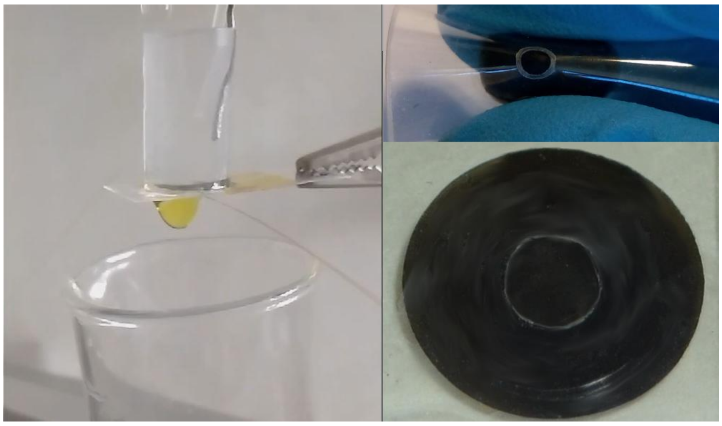

Figure 1. Experimental setup used to follow the electrochemical filtration process and details of the free-standing single walled carbon nanotube filter.

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Combined Electrode Materials and Techniques to Achieve Effective Systems for Production and/or Storage of Energy

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Nanostructured materials are of strategical importance in the field of energy production and storage. No matter what form of energy is used, low-cost nanomaterials are generally adopted for highly efficient energy production and conversion, as well as for the development of efficient and inexpensive energy storage systems. In all these applications, the crucial point is to synthesize the right structures, with controllable sizes and shapes, to match the desired physical – chemical characteristics: however, due to thermodynamic limitations, this task, sometimes, results to be very challenging.

This work presents a discussion on the main characteristics required in nanostructured electrodes, to be effective for the photo-electro-catalytical production of H_2 or in the energy storage process. The behavior of nanostructures based on TiO_2, as single phase or combined with other organic/inorganic compounds, is discussed in different scenarios.

In fact, only a careful analysis of the involved processes, combined with the study of the properties of the materials and their working mechanism, can give useful information to synthesize, characterize, and to model effective nanomaterials with unique properties.

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Electrochemical Promotion of Ethylene Epoxidation over Ag-based composite electrodes

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Electrochemical Promotion of Catalysis (EPOC) is an innovative concept for boosting catalytic processes in a reversible and controlled manner [1]. The EPOC phenomenon takes place in fuel-cell type reactors where the catalytic coating is an electrode supported on a dense ionically conducting ceramic material (solid electrolyte). Ions, such as K^+, contained in these solid oxide electrolytes are electrochemically supplied to the catalyst surface, changing its local electronic density. This way, the ions supplied behave as electronic promoters, modifying the activity and the selectivity of the catalyst. We used EPOC for designing new environmentally-friendly catalysts for the epoxidation of ethylene in order to produce ethylene oxide at atmospheric pressure with high selectivity to ethylene oxide (EO) without the need for chlorinated hydrocarbons in the gas feed. We have prepared Ag-based composite electrodes as Ag is the most efficient metal for this reaction.

Composite electrodes were prepared from a mixture between a Ag commercial paste and either a pure oxygen ionic conductor, i.e. Yttria-Stabilized-Zirconia (YSZ) or a Mixed Ionic and Electronic Conductor (MIEC), i.e. LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$). These composites electrodes were deposited either on YSZ or on K^+ conducting β-Al_2O_3 membranes. The impact of current applications on the ethylene oxide selectivity was carried out at 300°C while the electrochemical properties of the different Ag-based composite electrodes were investigated by cyclic voltammetry. In addition, TEM (JEOL 2010) and Environmental SEM (FEI QUANTA 650 FEG) were implemented to characterize the nanostructure of the electrodes including *in-situ* observations at 300°C in air.

Composites electrodes were prepared by mixing 75 wt.% of a commercial Ag paste (Metalon® HPS-FG32) with 25 wt.% of a powder of YSZ (TOSOH) or LSCF prepared with the Pechini method. These mixtures were deposited on YSZ or β-Al_2O_3 (Ionotec) dense membranes and calcined at 600°C for 2 h. The as-deposited morphology of these layers shows large micrometric Ag agglomerates mixed with nanometric grains of YSZ or LSCF. A period of activation of around 6 h on stream (C_2H_4/O_2: 3.8%/1.1%) at 300°C was necessary to reach a steady-state activity with an EO selectivity at around 12% for an ethylene conversion of 4%. This activation process was attributed to the transfer of Ag from large Ag agglomerates to the conducting oxide surface in the form of 5-10 nm diameter Ag nanoparticles (Figure 1) due to the high evaporation rate of AgOx at 300°C. This evaporation process was *in-situ* observed in air at 300°C with the ESEM. Therefore, the activation process on stream at 300°C leads to highly dispersed Ag-based composite electrodes containing Ag NPs supported on YSZ or LSCF.

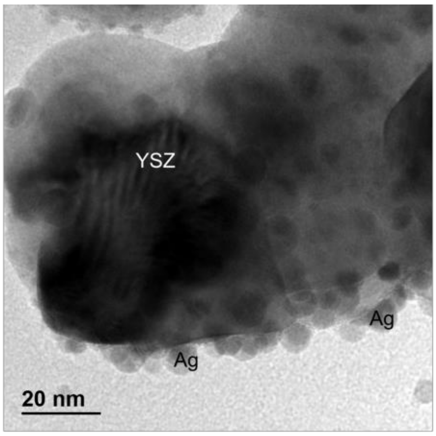

Figure 1: TEM image of the Ag/YSZ composite electrode after catalytic tests at 300°C

The impact of potential and current applications on the EO selectivity was investigated at 300°C according to the nature of the solid electrolyte (O^{2-} and K^+ conductors) and the conducting oxide in the composite (YSZ and LSCF).

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Operating Heterogeneities Along a Direct Borohydride Fuel Cell

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Abstract

Hydrogen is known for its clean combustion (oxidation), which creates neither atmospheric pollutants nor greenhouse gases [1]. It could become a pivotal energy carrier for high energy applications such as transport. However, hydrogen is difficult to store [2] and for low energy applications, a liquid energy carrier could be preferable. The use of hydrocarbons (alcohols, formic acid….) in a fuel cell produces adsorbed carbon monoxide (CO_{ads}) on the anodic catalyst, which acts as a poisoning agent and is difficult to further oxidize to CO_2 [3]. One alternative to hydrocarbons is boron hydride, historically studied as hydrogen storage materials [4], which exhibits high energy density, good solubility in water (55 g per 100 g H_2O) and stability in alkaline medium [5]. BH_4^- electro-oxidation in aqueous alkaline solution (pH = 14) is (in theory) possible at very low potential and generates 8 electrons and borate (BO_2^-) (reaction 1):

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6\,H_2O + 8\,e^- \qquad E^0 = -1.24 \text{ V/SHE} \tag{1}$$

However, this electrochemical reaction is in competition with the catalytic hydrolysis [6,7] (reaction 2):

$$BH_4^- + 2\,H_2O \rightarrow BO_2^- + 4\,H_2 \tag{2}$$

which precedes the possible oxidation of hydrogen ($E \geq -0.83$ V/SHE at pH = 14), which is not necessarily penalizing in terms of performance because it is very fast [8], but can penalize the fuel efficiency.

Here we use an instrumented cell to measure the local current density and local potential between the fuel inlet and outlet in order to understand the operating heterogeneities associated with the increase of hydrogen concentration down the channel direction. Furthermore, the internal currents that occur during the DBFC start-up are characterized.

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Degradation of Pt Catalyst on a Gas-Diffusion Electrode at Conditions Corresponding to High-Temperature PEM Fuel Cell Operation

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As an energy vector in hydrogen economy, H_2 can be efficiently transformed, together with O_2, in fuel cells into the electric energy. Consequently, one of the determining factors of development towards full hydrogen economy is widespread availability of pure H_2. This presents a significant challenge on a large scale, as readily available H_2 is still produced mainly from fossil and bio-fuels and therefore is, inevitably, contaminated to a various degree. One of the transient fuel cell technologies that can utilize H_2 of lower purity for effective electric energy production without complicated purification is high-temperature fuel cell with proton-exchange membrane (HT PEM FC).

Operating within temperature range of 120 to 180 °C brings out much better resistance of Pt catalyst on HT PEM FC electrodes against poisoning, especially by the CO. On the other hand, H_3PO_4-doped membranes based on polybenzimidazole and/or pyridine-type polymers has to be utilized. High operating temperature in combination with extremely corrosive environment of H_3PO_4 has, however, severe impact on Pt catalyst in terms of its degradation. This affects not only HT PEM FC performance, but also its lifetime.

One of the most profound degradation processes affecting Pt catalyst is coarsening of Pt nanoparticles, leading to the decrease of active surface area of gas-diffusion electrodes. Coarsening is a result of several degradation mechanisms, including agglomeration with subsequent sintering and, most importantly, Ostwald ripening. Caused by the difference in surface energy of various nanoparticles, Ostwald ripening comprises dissolution of smaller nanoparticles and redeposition of Pt ions on larger nanoparticles. Dissolution of Pt is determining step in this degradation mechanism. The major factor influencing production of Pt ions is surface state of Pt nanoparticles. Three main reactions occur on Pt surface during polarisation: (*i*) electrochemical Pt oxidation to Pt^{2+} (Eq. 1), (*ii*) electrochemical Pt oxidation to PtO (Eq. 2) and (*iii*) chemical dissolution of PtO to Pt^{2+} (Eq. 3).

$$Pt^{2+} + 2e^- \rightleftharpoons Pt \qquad \text{(Eq. 1)}$$

$$PtO + 2H^+ + 2e^- \rightleftharpoons Pt + H_2O \qquad \text{(Eq. 2)}$$

$$PtO + 2H^+ \rightleftharpoons Pt^{2+} + H_2O \qquad \text{(Eq. 3)}$$

Mechanisms of these three Pt surface reactions are complex and determination of electrochemical kinetics, especially at the conditions corresponding to HT PEM FC environment/operation, is experimentally demanding. Due to these reasons, available data of Pt dissolution at conditions of HT PEM FC operation are scarce. Therefore, the aim of this work is a determination of kinetic parameters of Pt surface reactions and estimation of total Pt dissolution rate at various operating voltages.

Main part of this work consists of 1D mathematical model of Pt dissolution in catalytic layer of gas-diffusion electrode. The basis of the model is taken from previous works [1, 2] and modified accordingly to our system, i.e. concentrated H_3PO_4 at temperature of 160 °C. Model inputs comprise experimental kinetic constants determined by means of cyclic voltammetry on a bulk Pt electrode in combination with simple 0D mathematical model and degradation rates of Pt catalyst on gas-diffusion electrode obtained from potentiostatic tests. All experiments were performed in 99% H_3PO_4 electrolyte saturated with N_2. Change of electrochemically active surface area, total amount of Pt and average Pt crystallite size were the studied degradation parameters. Our model is able to predict changes in Pt nanoparticle size distributions, flux of Pt ions to electrolyte and the surface state of Pt nanoparticles within selected size group.

This study was supported by the Grant Agency of the Czech Republic under project No. 19-02964J.

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Probing the nature of the highly active and strained Pt overlayer in Pt_3Y alloy catalyst for application in low temperature fuel cells.

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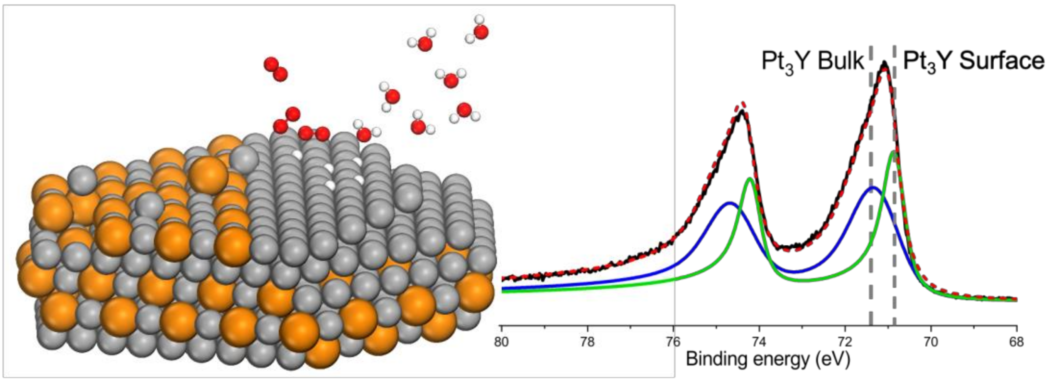
The development of highly active, low cost fuel cell catalyst materials is vital for fuel cell applications in a sustainable future. In low temperature fuel cells, platinum is used to effectively catalyse the oxygen reduction reaction (ORR) but with slow kinetics and at a high price. To reduce the cost whilst increasing kinetics, platinum can be alloyed with other metals such as yttrium[1]–[3]. Pt_3Y has an ORR activity about 7 times greater than Pt metal after acid pretreatment[2]. Pretreatment causes the formation of a protective overlayer of strained platinum on top of the alloy material[4].

Here, a study into the nature of the overlayer in 27 nm thick Pt_3Y films sputtered from an alloy target is presented. Rotating disk measurements of Pt_3Y show that the activity of the catalyst is in agreement with past studies[2], [5]. To elucidate the effect of the pretreatment on the material surface, detailed synchrotron X-ray photoelectron spectroscopy (XPS) measurements of the catalyst surface show the formation of a platinum overlayer. Chemical shifts confirm the formation of a Pt overlayer a few monolayers thick. The majority of yttrium at the surface is oxidized and is removed by acid pretreatment. X-ray diffraction (XRD) measurements indicate very small grain sizes and large microstrain as well as a change in the effective lattice parameter, reflecting the loss of yttrium from the alloy. Understanding more about the de-alloying process and the structure of the formed overlayer is expected to aid in the development of these catalysts for long term application in fuel cells.



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Inline fabrication of porous silicon membranes for energy applications

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In the last decades evidence of climate change led to growing interest in environmentally friendly ways to generate and store energy e.g. with help of photovoltaic cells, batteries and fuel cells. Porous materials play in these applications an important role as porous electrodes [1], membranes [2], antireflection coating [3], or as sacrificial layers in layer-transfer processes [4]. One of the promising materials for energy applications remains porous silicon (PorSi) produced by electrochemical etching of crystalline silicon substrates in hydrofluoric acid [5]. In this work we present our activities on the optimization of the inline fabrication process and the development of the supporting characterization methods.

To form PorSi layers, wafers were anodically etched in a first of the kind experimental inline lab tool developed at Fraunhofer ISE in cooperation with RENA Technologies GmbH. The setup consists of at least three electrolyte tanks, whereas the two side tanks are connected anodic and the middle one connected cathodic. The wafer side facing down is porosified while moving over the anodic tank.

Finite element method (FEM) simulations were applied to optimize the process homogeneity in the inline porosification tool (s. Figure 1).

For characterization of PorSi layers, various characterization techniques have been used, including gravimetric measurements of thickness and porosity and thickness mapping with an optical thickness measurement device. As a non-destructive, fast, and inline-capable method for determination of local porosity and thickness of porous layers, spectroscopic liquid infiltration method (SLIM) [6] with Fourier analysis of the reflectance spectrum was applied (s. Figure 2). In case of fabricating freestanding PorSi layers, scanning acoustic microscopy was used to analyze the delamination of the fabricated PorSi layers.

Figure 3 shows the transfer of a fabricated PorSi layer on a copper foil for battery applications. Our further work is aimed on the development of a fast characterization tool for porous layers and the integration of the inline PorSi fabrication process to existing production lines for batteries.

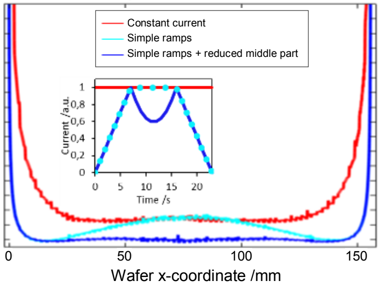

Figure 1: Simulated total charge density on the wafer frontside after one run in the tool for different applied current profiles shown in inset.

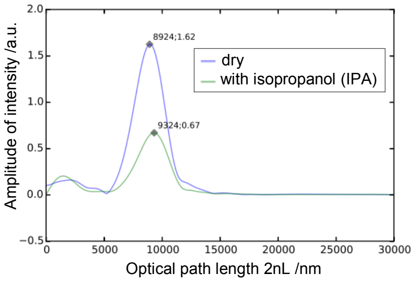

Figure 2: Fourier transformed reflection spectrum from a PorSi layer in dry and filled with IPA states for SLIM analysis.

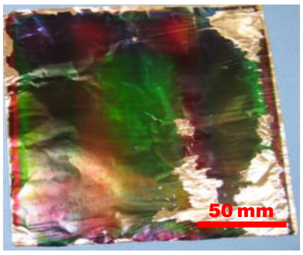

Figure 3: Photo of a 156x156 mm² porous silicon layer with thickness 13 µm transferred to a copper foil.

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Electrochemical Real-Time Mass Spectrometry (EC-RTMS): Time-Resolved Product Analysis during Electrochemical Reactions

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Modern energy conversion technologies must withstand the intermittent supply or varying demand of energy. In this direction, resolving the transient behavior of electrochemical systems under dynamic conditions is of great importance. To monitor such transients, which may be otherwise not present under steady operation, advanced methods are required with temporal resolution that is sufficient to capture the occurring events.

The traditional approaches to determine the potential-dependent product distribution include sample collection in the gaseous and liquid phase during long-term electrolysis (potentiostatic or galvanostatic) and detection/quantification with intermittent analysis methods, (e.g. chromatography, nuclear magnetic resonance etc.) [1]. This approach is excellent for the quantification of production rates, selectivities, or faradaic efficiencies, but the offered temporal resolution is limited. Therefore, processes occurring transiently cannot be captured.

Analysis of gaseous and volatile compounds during electrochemistry in real-time was enabled by differential electrochemical mass spectrometry (DEMS) and its later variations [2]. The application of DEMS in several electrochemical reactions that involve gaseous products provided great, invaluable information on underlying reaction mechanisms. However, the direct determination of non-volatile products (e.g. organic acids) is not feasible, whereas copious fragmentation often requires complex spectra deconvolution [3]. Significant efforts have been made to determine liquid products with electrospray ionization mass spectrometry [4], but the analysis is often hindered by ion suppression effects. In a recent work, selected ion flow tube mass spectrometry was employed which enables the analysis of liquids [5], but the temporal resolution is in the order of several tens of seconds.

We demonstrate here a new, powerful technique for the analysis of both liquid and gaseous products of electrochemical reactions in real-time with remarkable temporal and potential resolution i.e. during a potential sweep or a potential step experiment, along with excellent sensitivity. The methodology is based on the integration of two independent mass spectrometry techniques, after proper modification of their inlets. We present the first applications of the method in the analysis of electrochemical reactions that form multiple products, such as the reduction of CO_2 on copper and the oxidation of several organic compounds. The offered temporal resolution (in the order of one second) and the excellent sensitivity (in the ppb-range) enable the observation of transients in product formation, independent of their vapor pressure, which are not accessible with any of the existing methodologies.

Acknowledgments

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Electrochemical behavior of aromatic compounds on nanoporous gold

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Nanoporous noble metals, with 3D porous networks of interconnected metal ligaments, have received substantial attention in the modern electro-catalysis field owing to their distinct properties such as high surface area, tunable porosity, excellent conductivity, high chemical stability and biocompatibility [1]. Of particular interest is their potential use as electrochemical platforms for detection of organic compounds. Up to now, there have been a number of reports demonstrating their abilities to detect separately many organic molecules. However, little information is available concerning their capability of simultaneous detection of different compounds in mixed solutions.

We will report on electrochemical behavior of benzene and its substituted derivatives on nanoporous gold thin film electrode and the possibility of using it as an efficient platform for simultaneous electrochemical detection of different aromatic compounds [2]. In this study, cyclic voltammetric studies were performed with solutions containing five aromatic compounds of benzene, hydroquinone, catechol, phenol, 2-aminophenol, 2-chlorophenol as well as their mixtures on nanoporous gold. Compared with the compact and flat gold electrode, the nanoporous structure provided enhanced electro-oxidation of hydroquinone, catechol, phenol, 2-aminophenol and 2-chlorophenol and considerable resistance toward electrode fouling in the electro-oxidation of phenol and 2-aminophenol. Interestingly, the oxidation potentials of these aromatics were found to vary depending on the attachment of functional groups to the benzene ring. Especially noteworthy was the finding that nanoporous gold is more advantageous over nanoporous platinum in terms of simultaneous analysis of these aromatics in neutral solutions using the voltammetric technique as the discernable peak potential separation was hardly achievable with the nanoporous platinum electrode.

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Cu-Mo-doped Ceria as Material for Carbon-Air Solid Oxide Fuel Cell Anodes

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Mo-doped ceria (CMO) is a promising material for carbon-air solid oxide fuel cell (CA-SOFC) applications, due to the high tolerance to deactivation by carbon deposition and resistance to sulfur poisoning reported for its components ceria (CeO_2) and molybdenum trioxide (MoO_3) [1-3].

Pure and crystalline CMO nanopowders (ca. 20 nm diameter) have been synthesized using the citrate-combustion method, as an alternative to the solid-state reaction method proposed by Li and Thangadurai [4]. The maximum conductivity values measured by the four-probe method for CMO dense pellets correspond to $1.87\cdot10^{-3}$ S cm^{-1} in air and $9.37\cdot10^{-1}$ S cm^{-1} in 10%H_2/90%Ar at 800°C, which are higher than those reported by these authors.

It has been reported that the addition of copper to SOFC anodes prevents the formation of carbon deposits and sulfur poisoning during the oxidation of carbonaceous fuels [5-7], and also improves the electrical conductivity of ceramic composites. In view of this, commercial copper nanoparticles have been added to the CMO synthesis process to obtain Cu-Mo-doped ceria (Cu-CMO) nanoparticles. The conductivities of Cu-CMO pellets are compared with those of pure ceria and CMO in figure 1, which shows that the addition of copper to CMO increases its electrical conductivity, particularly at high temperatures.

Currently, electrochemical impedance spectroscopy (EIS) tests in symmetric-cells and fuel cell tests (using YSZ electrolytes and LSM-based cathodes) are being conducted to characterize the performance of CMO and Cu-CMO anodes.

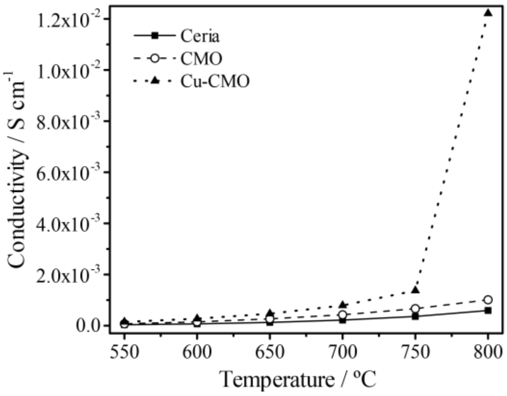

Figure 1. Conductivity of ceria, CMO and Cu-CMO pellets (5wt.%Cu-5wt.%Mo).

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Fabrication of Palladium Nanowires by Centrifugal Electrospinning Method as Electrocatalyst for Low Temperature Fuel Cells

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One-dimensional metal nanowires have received much research efforts due to their potential applications as electrocatalysts in low temperature fuel cells such as PEMFC or DMFC. These 1D nanowires are generally composed of pure platinum (Pt), Pt-based alloy, or non-Pt catalysts. Comparing with the widely used Pt/C catalysts, 1D nanowires may exhibit higher catalytic activity and stability. These characteristics provide a promising way to reduce the loading of precious Pt metal or replace it in the electrode and enhance the durability of fuel cell stack. Several non-Pt materials have been studied as alternative electrocatalysts in low temperature fuel cells. Among these alternatives, palladium has been proposed as a viable candidate since it has similar valence shell electronic configuration as Pt and its reserve is more abundant on earth than Pt. In this study, the centrifugal electrospinning method is employed to fabricate Pd nanowires. The nanowires are produced from a polymer solution containing palladium chloride ($PdCl_2$) as Pd precursor and polyvinyl pyrrolidone (PVP). The effects of system parameters on the morphology of Pd nanowires are evaluated including the concentration of Pd precursor, rotation speed of spinneret, hydrochloric acid concentration, and magnitude of applied electric field. The energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) patterns are performed to analyze the Pd nanowires and the cyclic voltammetry tests are conducted to characterize the corresponding electrochemically active surface area. The Results show the centrifugal electrospinning method can successfully produce Pd nanowires as shown in Figure 1 with minimum mean diameter of 98 nm. The fabrication rate of polymer nanofibers measured in terms of the volume flow rate of polymer solution can reach 25 ml h^{-1} which is significantly higher than that in the conventional electrospinning method generally less than 0.5 ml h^{-1}. The present results demonstrate the centrifugal electrospinning method is an efficient approach to fabricate Pd nanowires, while the mean diameter still needs to be reduced further for practical applications as electrocatalyst in fuel cells.

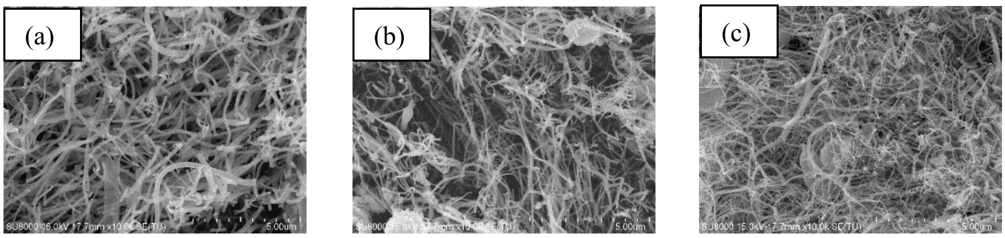

Figure 1. The SEM images of Pd nanowires produced at different hydrochloric acid concentrations; (a) 1 M, (b) 3 M, and (c) 5 M.

Electrochemical on-line ICP-MS in Electrocatalysis Research

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It is difficult to imagine modern electrocatalysis research without advanced techniques used to analyse performance of electrocatalysts. *On-line* inductively coupled plasma mass spectrometry (ICP-MS) is one of such techniques, specially developed to quantify degradation of an electrocatalyst or a support due to dissolution [1]. Extremely low detection limits, going down to parts per trillion (ppt) range, allow precise on-line tracking of catalyst degradation at operational potentials, even when relatively stable noble-metal-based materials are considered. Representative examples are carbon and conductive oxides supported platinum oxygen reduction reaction (ORR) and supported and unsupported iridium oxygen evolution reactions (OER) catalysts.

This work will concentrate on representative *on-line* ICP-MS studies in fuel cells and water electrolysis research. Concerning fuel cells, it will be shown that platinum dissolution is a transient process triggered by surface oxidation or reduction [2]. Examples showing how *on-line* ICP-MS assisted in clarifying the transient platinum dissolution mechanism will be given. Qualitatively, dissolution is independent on the morphology, whether Pt single crystal, polycrystalline Pt, Pt nanoparticles, pure catalyst or alloy are considered. Quantitatively, however, dissolution stability of platinum depends on experimental parameters and properties of the catalyst including its structure, morphology, composition, catalyst loading, support material, etc [1]. Understanding of these dependences is a prerequisite in the design of more stable catalysts. Concerning OER catalysis taking place during the water electrolysis, it will be presented that there is a correlation between Ir dissolution and OER mechanisms [3, 4]. It will be shown that qualitatively new information on the mechanisms can be obtained when on-line ICP-MS is coupled with on-line electrochemical mass spectrometry (OLEMS) and isotope labelling analysis [3, 4]. Based on this correlation, insights on the design of simultaneously active and stable Ir-based OER catalysts will be given.

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Organometallic Complexes for Energy Production and Storage

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Organometallic complexes have intrinsically excellent characteristics as a new class of electrocatalysts for clean energy production in fuel cells and electrolyzers. The state of the art materials for those devices are based on precious metal nanoparticles dispersed on a conductive carbon based supports. Despite the fact that such materials have reached very high performance levels in terms of activity and stability, they still suffer from some intrinsic limitations that contribute to hinder the commercial development of fuel cells and electrolyzers on a large scale. Organometallic-based electrocatalysts may help to overcome such limitations. For example, those devices exhibit remarkably high selectivity for alcohol electrooxidation towards carboxylic compunds of industrial relevance. Additionally, precious metal loadings can be reduced significantly by using single site organometallic catalysts where each metal atom is potentially active. Here we present a Rh organometallic catalyst, [Rh(OTf)(trop$_2$NH){P(4-n-butyl-Ph)$_3$}] (trop$_2$NH=bis(5-H dibenzo[a,d]cyclohepten-5-yl)-amine; OTf$^-$ = $CF_3SO_3^-$ = triflate) that was successfully employed as anode both for Direct Alcohol Fuel Cells, named Organometallic Fuel Cells (OMFCs) and Alcohol Electroreformers, named Organometallic Electroreformers (OMERs). These devices exploit a biomass-derived alcohol (e.g. EtOH, 1,2-propanediol or glycerol) for respectively energy and hydrogen production and contemporaneously, the alcohol is converted in a high-added-value carboxylate, such as lactate. Therefore, we hypothesize the exploitation of OMFCs and OMERs as an essential component of the biorefinery platform. To the best of our knowledge, this [Rh(OTf)(trop$_2$NH){P(4-n-butyl-Ph)$_3$}] complex is the most active organometallic anode for OMFCs and OMERs ever reported. (1)

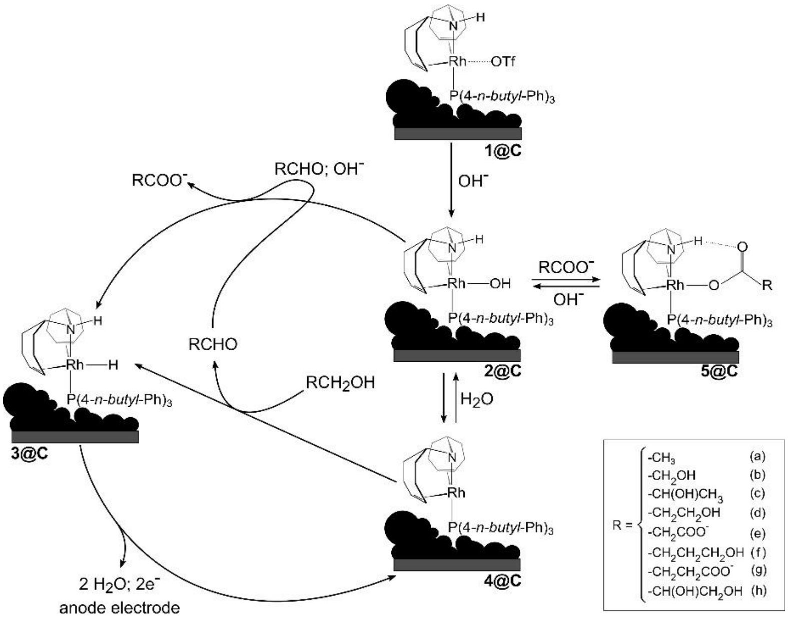

Figure 1: proposed mechanism for the alcohols electrooxidation occurring on the OMFCs and OMERs anodes coated with the [Rh(OTf)(trop$_2$NH){P(4-n-butyl-Ph)$_3$}] catalyst (1@C).

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Performance Evaluation of Fuel Cell Catalysts: GDE vs. RDE measurements

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Catalyst development for proton exchange membrane fuel cells (PEMFCs) has made tremendous progress in recent years. In academic research many examples have been demonstrated of cathode catalysts (electrode with highest overpotential) with extraordinary activity for the oxygen reduction reaction (ORR). Despite these successes, we do not see these catalysts in commercial applications. There seems to be a significant gap between fundamental and applied research and so far, no catalyst ever reached the "predicted" performance in an actual fuel cell device. This indicates that the state-of-the-art testing method, the thin-film rotating disk electrode (TF-RDE) technique needs to be critically assessed and supplemented by more applied testing. In the presentation, I will introduce different concepts of gas diffusion electrode (GDE) setups for PEMFC catalyst testing that combine the strength of TF-RDE measurements (e.g. fast, cheap and straight forward testing) and at the same time alleviate its weaknesses such as low reactant mass transport.

Fe/N Doped Carbide-Derived Carbon/Carbon Nanotube Composite Catalysts for Anion Exchange Membrane Fuel Cell Cathodes

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Non-noble metal catalysts based on carbon nanomaterials doped with nitrogen and abundant transition metals are emerging as prospective catalysts for a number of electrochemical reactions, most importantly for the oxygen reduction reaction (ORR) taking place on the cathode of low-temperature fuel cells [1]. While there is an ongoing debate about the electrocatalytically active site for ORR in this type of catalysts and the mechanism of ORR on these materials, many advances in activity have been made by rationally designing catalysts with a high specific surface area and efficient morphologies for utilisation in fuel cells. As a continuation of our previous works based on nitrogen and transition metal doped CDCs [2,3], we use carbide-derived carbons (CDC, a carbon material made by removing metal atoms from a starting carbide, which has a highly tunable porosity and a high specific surface area) as the carbon base material in this study, which is doped using 1,10-phenanthroline and iron(II)acetate by solvent-free ball-milling and high temperature pyrolysis followed by acid leaching to remove excess iron. A multi-walled carbon nanotube (MWCNT) shell was then created around the doped CDC for addition of mesoporosity, which was further doped using dicyandiamide and iron(II)acetate. Three different CDC-MWCNT composites are compared. A thorough physico-chemical study of the resulting catalysts is presented, including information on the elemental composition via inductively coupled plasma mass spectrometry, porosity by N_2 physisorption analysis and surface elemental composition by X-ray photoelectron spectroscopy. The morphologies created by the MWCNT addition on top of the doped CDCs is also described by scanning electron microscopy. These data are then correlated with *ex situ* activity determined by the rotating disk electrode (RDE) method in alkaline conditions and *in situ* activity in an anion exchange membrane fuel cell (AEMFC). We show that the combination of high ORR electrocatalytic activity of the Fe/N doped CDCs and mesoporosity added by the MWCNTs yields a very efficient AEMFC catalyst which can reach power densities of up to 160 mW cm^{-2} at 50 °C using the Tokuyama A201 anion exchange membrane [4].

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Water Splitting Electrocatalysis at various porous Ni electrodes

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The promise of hydrogen as a sustainable, secure, and clean alternative energy carrier to satisfy the growing global energy demand requires efficient, low-cost, and environmentally friendly production. Water electrolysis to generate hydrogen fuel - preferably driven by renewable energy - is a highly attractive means to produce hydrogen, but advanced electrolyzer systems are required for electrolytic H^2 production to become a commercially viable technology. Lately, new classes of anion exchange membranes (AEMs) have emerged with improved performance over their predecessors, improving the future prospect of commercialized anionic polymer electrolyte membrane water electrolysers (APEMWEs). The prospect of new AEMs for alkaline APEMWEs that could match the performances of cationic exchange membranes in terms of ionic conductivity and longevity has spurred a renewed interest in research to improve catalyst performance for the oxygen evolution reaction (OER) in alkaline electrolyte.

In this presentation we will focus on the electrochemical characterization of arrays of micrometer long Ni nanowires (NWs) (Fig. 1a, 1b and 1c) and mesoporous Ni electrodes synthesized by the dynamic hydrogen bubble templating (DHBT) method (Fig. 1d and 1e). Detailed structural and electrochemical analyses were conducted including HR-TEM and EELS analysis providing information on the chemical state of atoms from quantitative analysis of the signals and electrochemical impedance spectroscopy providing information on the charge transfer resistance and capacitance in the potential region where the oxygen evolution reaction (OER) is occurring. The effect of Fe on the electrocatalytic activity for the OER will also be investigated. By fine-tuning the Fe content of the electrolyte, the OER overpotential under galvanostatic conditions (250 mA cm^{-2}) was reduced to η_{250} = 260 mV and remained stable over the polarization duration.

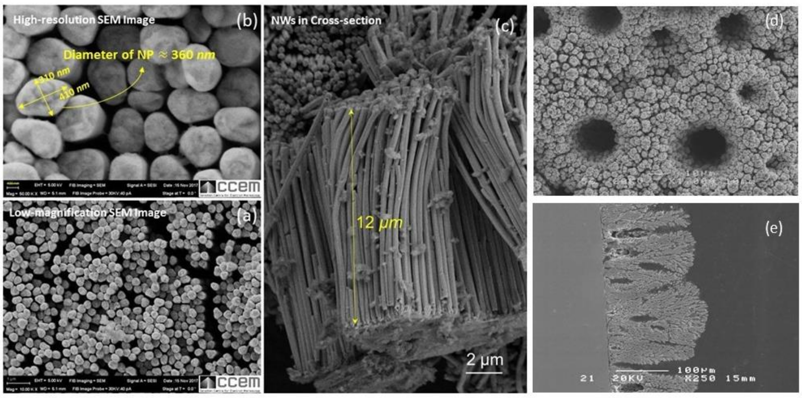

Figure 1 High-resolution SEM images of Ni Nanowires (a, b and c) and mesoporous Ni (d and e) revealing their cross-sectional (c and e) and top views (a, b and d).

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Electrochemical Energy storage in Materials based on Phosphates

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Renewable energy power sources are considered worldwide as alternatives to provide a clean energy and to find new pathways to address the growing demands in energy. Therefore, there are increasingly high demands for energy storage materials with high performance, dominated mainly by Li-ion batteries (LIBs) exhibiting great potential due to their high volume and gravimetric energy density.

In order to develop more powerful Li-ion batteries and to overcome the drawbacks of the existing electrode materials, a great number of electrode materials have been investigated during last few decades. Electrode materials based on phosphates are the best solution to meet the needs for the development of the renewable energies and that of electrical vehicle as they provide more safety and sustainability.

We developed in our research group a multitude of electrode materials for the cathode and anode sides of high energy density lithium ion batteries. The relationship between the crystal structure, the morphology and the energetic performance of the studied phosphates was well established. For instance, the optimization of the synthesis conditions and the electrode composite leads to an outstanding energetic performance of an $Li//Li_{0.5}Ni_{0.5}Fe_{0.5}Ti_{1.5}(PO_4)_3$ electrochemical cell, cycled under different rate in the voltage range of 1.5-3 V vs Li^+/Li.

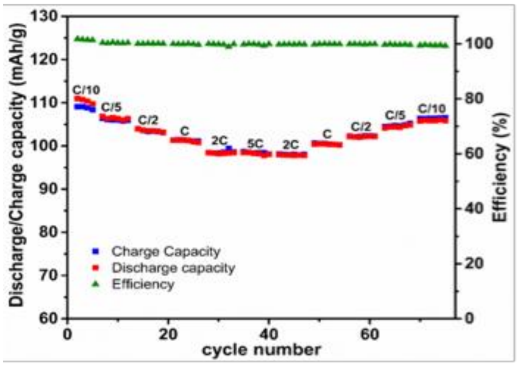

Fig. 1 : Rate capability test of $Li//Li_{0.5}Ni_{0.5}Fe_{0.5}Ti_{1.5}(PO_4)_3$

The current contribution will present an overview of the recently published results on the understanding of the electrochemical energy storage mechanism and the future challenges and actions to develop more powerful rechargeable batteries.

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Creation of Active Sites on Phosphor and Nitrogen Co-doped Rutile TiO_2 for Polymer Electrolyte Fuel Cell Cathodes

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Polymer electrolyte fuel cells (PEFCs) have been expected to replace internal combustion engines in vehicles which operate over 300 miles or carry high loads of buses and tracks [1]. In spite of the worldwide trend to regulate vehicle emissions, the widespread use of PEFC-powered vehicles has not yet been recorded. One of the barriers for the widespread use is the high loading of platinum-cobalt catalysts at the cathode for oxygen reduction reaction (ORR) [2]. Only one type of platinum group metal (PGM)-free catalyst, so-called Fe/N/C, have shown promising initial activity and the most researchers in non-PGM catalyst community have focused on this catalyst type. Particularly after the performance breakthrough with the use of metal organic framework precursor by Dodelet group in 2011 [3], highly active Fe/N/C catalysts whose performance is comparable to that of commercial carbon-supported platinum have been reported by some other groups [4,5]. However, these highly active Fe/N/C catalysts were instable even when they were operated at the lowest voltage in vehicles, 0.6 V [6]. Some debates have been continued for the source of degradation in this community whereas carbon corrosion proceeded in this catalyst type even below 0.7 V owing to the defective nature of carbon species in Fe/N/C.

We have focused on another PGM-free catalyst type, oxides containing group IV metals. The advantage of this catalyst type is high chemical stability whereas the disadvantage is low conductivity to utilize carbon supports [7,8]. The best performance has been obtained from nitrogen-doped zirconia [8] to attract attentions of Dodelet group [6]. However, zirconia is not conductive and thus conductive carbon supports were needed to degrade the performance during the mild operating conditions in PEFC [8]. As titanium oxides and nitrides show higher conductivity than zirconia, we recently developed carbon-support-free titanium-based catalysts [9-12]. In this study, the process to create active sites on recently reported phosphor and nitrogen doped rutile TiO_2 [12] was investigated using two heating steps. The role of the second heating step will be discussed at the meeting.

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Alcohol oxidation with metal-doped Ni-based electrodeposited catalysts in alkaline media

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Generation of sustainable energy remains one of the biggest challenges for the society in order to become fossil fuel-free [1]. Some alcohols can be produced from biomass and are considered a renewable source of clean energy. Consequently, alcohol oxidation reactions (AOR) have an increasing relevance in several renewable energy applications such as fuel cells or clean H_2 production by electrolysis. Finding appropriate catalysts to achieve the AOR with low energetic requirements could lead to the development of profitable applications. Nickel-based materials have been employed for alcohol oxidation due to their low cost and high stability in alkaline media. Incorporation of other metallic atoms is a known method to enhance the catalytic properties. For instance, earth-abundant materials such as NiCo and NiFe materials have been reported for the AOR [2] or water oxidation, respectively. Meanwhile, doping into noble metals such as Pt or Pd has demonstrated higher electrocatalytic activity towards alcohol oxidation at low potentials [3] than earth-abundant materials. However, it is also known that these electrocatalysts are prone to deactivation [4], avoiding the possibility to achieve high current densities during alcohol oxidation. Therefore, many issues are still unresolved and the development of new electrocatalysts with enhanced properties for alcohol oxidation is a constant concern for the scientific community.

In this work, we evaluated several Ni-based bimetallic catalysts generated by a simple and fast electrodeposition method for the oxidation of alcohols in alkaline media.

Firstly, earth-abundant catalysts were generated using Ni films doped with Fe or Co and their catalytical activity towards the ethanol oxidation reaction (EOR) was studied. An opposite effect was found after incorporation of Co or Fe to the catalyst, with Co enhancing the catalytic response and Fe decreasing the activity. Electrochemical studies suggested that Ni atoms are the active sites for the EOR since Tafel slopes were similar on the binary and pristine nickel materials and the electrogenerated Ni(III) seems to be directly involved in the reaction.

Secondly, a PdNi electrocatalyst was generated by a similar method with unprecedented behaviour for the ethanol oxidation in alkaline media. The optimal catalyst showed enhanced activity and kept the ethanol oxidation at high potentials, demonstrating an extraordinary resistance to deactivation. The role of different parameters such as the ethanol and hydroxide concentrations or the mass transfer conditions was studied and their effect on the electrocatalytic response and deactivation process was revealed. Under specific conditions, the electrocatalyst did not show deactivation issues in a wide range of potentials leading to the ethanol oxidation at high current densities and low potentials at a significant rate. This catalyst was also evaluated for the oxidation of secondary alcohols such as isopropanol and lactic acid with promising catalytic activity.

Future work will look into further exploring this PdNi electrocatalyst for efficient H_2 generation by oxidation of biomass-produced alcohols.

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Electrolysis of biofuels

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Electrochemical oxidation of organic fuels is becoming increasing important in the development of new technologies for sustainable production of power and materials. Direct organic fuel cells can increase the efficiency of power generation from biomass, while also providing value added chemicals [1]. Electrolysis of biofuels, such as ethanol, ethylene glycol, and glycerol can be used to produce hydrogen at much lower potentials than water electrolysis, and useful oxidation products such as acetic acid and glyceric acid [2].

Efficient use of biofuels in electrolysis and fuel cells requires anode catalysts with both high activities and high selectivity for the preferred product. High selectivity for the complete oxidation of the fuel to carbon dioxide is required for efficient power and hydrogen generation. The work described here focuses on new catalysts for the oxidation of organic fuels, and experimental methods for determining activities and efficiencies in proton exchange membrane (PEM) electrolysis cells at elevated temperatures.

Activities and stoichiometries for methanol, ethanol, ethylene glycol, and glycerol oxidation at alloy, core-shell, oxide-supported, and commercial catalysts have been compared in multi-anode PEM electrolysis cells. Separation of the measured current into kinetic and mass transport components is used to obtain mechanistic information and stoichiometries [3], while product analysis provides yields of by-products [4]. The results provide projections of fuel cell efficiencies, and energy efficiencies for hydrogen production. The highest projected efficiency for a direct ethanol fuel cell was obtained with an octahedral PtNi catalyst [5].

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Alkaline water electrolysis enhanced by an alternative magnetic field: promises and bottlenecks

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Low-temperature water electrolysis enables to store renewable electricity into hydrogen, the so-called power-to-hydrogen strategy. The present state-of-the-art, proton-exchange-membrane electrolyzers, however remains impeded by its materials' high-cost and low-availability, combined with an insufficient durability on the field [1]. On the contrary, alkaline water electrolyzers are more industrially mature, but their weak power density and complex fluid/thermal management render them incompatible with the intermittent operation desired for renewable energy storage [2]. An industrial endeavor would be to combine the advantages of these two technologies, which shall be possible using alkaline water electrolysis enhanced by an alternative magnetic field. This strategy is based on the magnetic activation of dedicated nanomaterials, that also exhibit electrocatalytic properties. To that goal, FeC-core@Ni-shell nanostructured electrocatalysts have been developed, these materials heating intensely under a high-frequency alternating magnetic field (AMF, to excite the FeC core), while promoting the oxygen (or hydrogen) evolution at their Ni shell. The corresponding OER overvoltage is immensely decreased (by 200+ mV) under AMF excitation in an alkaline water electrolysis flow-cell, while hydrogen evolution overvoltage can be minored by 100 mV. This spectacular enhancement of the reaction kinetics obtained near room temperature evidences that the only the surface temperature of the FeC-core@Ni-shell electrocatalyst is significantly increased under AMF activation, an effect beyond reach in classical approaches of materials sciences and electrochemical engineering. With this technology, one can hope to promote water splitting close to the equilibrium voltage at room temperature, which would however require that an optimized electrolysis cell is designed for operation under AMF activation.

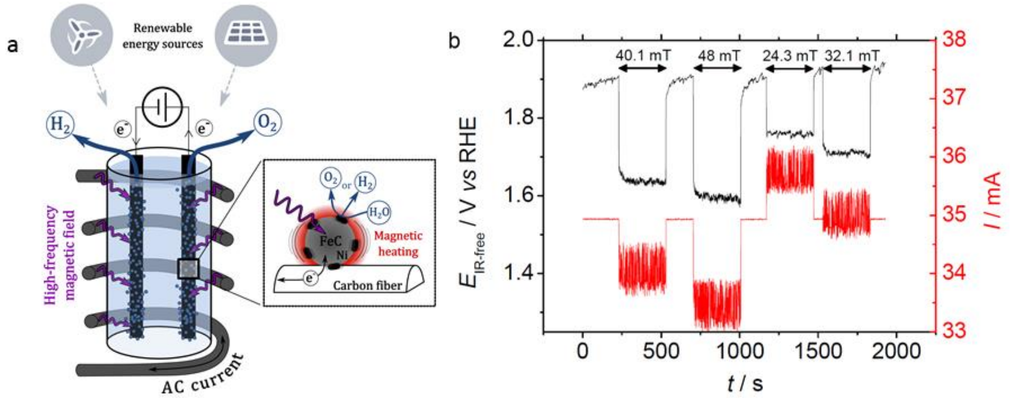

Figure 1: Basics of AMF-activated water electrolysis (a) and example of improvement of the IR-free OER potential measured at ca. 35 mA under various AMF strengths (b). Reproduced from [3] with permission from Nature publishing group.

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Oxidation mechanisms of C1-C2 molecules on platinum, similarities and differences

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Fuel cells appear as an alternative to conventional energy storage/supplying devices. In this technology, hydrogen is regarded as the most probable candidate to use as fuel. However, it presents several problems: it cannot be obtained directly from natural sources, it has a low volumetric energy density and the its widespread distribution would require a deployment of new distribution network. On the other hand, small organic molecules, with one or two carbons, overcome those disadvantages. However, the main obstacle for the use of these molecules as fuels is that their oxidations require higher overpotentials than those measured for the hydrogen oxidation reaction. Thus, more efficient electrocatalysts are needed if effective fuel cells are to be constructed. The rational quest of these new materials requires a deep knowledge of the oxidation mechanism, so that the possible bottlenecks are solved. Among all pure metals, platinum is, the best electrocatalyst for the oxidation of C1 and C2 organic molecules to CO_2. It is normally accepted that the mechanism for the oxidation of these molecules proceeds through a dual path mechanism in which CO is involved. In this communication, it will be shown that the rate determining step is different for each molecule, so that the dependence with the interfacial properties (surface structure, pH and solution composition) are significantly different. To demonstrate those differences, the voltammetric behavior of the formic acid, methanol, ethanol and ethylene glycol on single crystal electrodes will be compared. These results will be analyzed with the aid of the spectroelectrochemical and DFT calculations. The simplest oxidation mechanism is that of formic acid. For this molecule, obtained results and the calculations indicate that the crucial step is the adsorption of the molecule on the electrode surface. If the molecule adsorbs in the right configuration, which is not the most stable one, the reaction will give the final product with a low activation energy by simple dehydrogenation steps. The main problem of this reaction is to avoid the evolution of the adsorbed mode of formic acid to the most stable configuration, which is inactive, and the formation of CO. The methanol reaction, on the other hand, not only requires dehydrogenation steps, but also the transfer of an oxygen atom to form CO_2. In this case, the results show that interaction of the molecule with the surface is weak, and the initial steps of the reaction require the presence of adsorbed OH on the surface. Finally, for C2 oxidation, the most difficult step is the cleavage of the C-C bond, which occurs only on specific sites of the surface. Moreover, the rate for this step also depends on the nature of the substituents in each carbon of the C2 molecule, being much higher for ethylene glycol than for ethanol.

BDD Anodic Oxidation of 6:2 Fluorotelomer Sulfonate and Short-chain Perfluorocarboxylic Acids Products

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Per- and polyfluoroalkyl substances (PFASs) have been extensively used over the last half century for a wide variety of applications due to their unique physicochemical properties [1]. Recently, the use of extremely persistent and bioaccumulative long-chain PFASs was restricted and chemical manufacturers were committed to achieve a > 95% reduction in emissions of perfluorooctanoic acid (PFOA) and its precursors. To meet this goal, long chain PFASs are being substituted by alternative chemicals, such as 6:2 fluorotelomer sulfonic acid (6:2 FTSA). However, biodegradation pathways of 6:2 FTSA lead to short-chain perfluoroalkyl acids, mainly perfluorohexanoic acid (PFHxA), which is highly persistent. Rising concentrations of PFHxA in the environment are expected, as a result of the growing production of 6:2 fluorotelomer-based compounds. Boron doped diamond (BDD) anodic oxidation has already shown outstanding efficiency for PFOA electrolysis in different concentration ranges [2-4].

The objective of the present work is to evaluate the electrochemical degradation and defluorination of 6:2 FTSA and of its degradation products, with the aim of achieving its complete mineralization. Electrolysis experiments were carried out using an undivided electrochemical cell (Adamant) which consists of two parallel compartments made of a central bipolar p-Si/BDD electrode and p-Si/BDD anode and cathode. Each electrode had a surface area of 70 cm^2, summing a total anodic area of 140 cm^2. Feed aqueous solutions (2 L) of 6:2 FTSA (100 mg L^{-1}) or individual perfluoroalkyl acids (PFBA, PFPeA, PFHxA and PFHpA, 100 mg L^{-1} each) were electrolyzed. The applied current density (*J*) was varied in the range 5–600 A m^2. Three electrolytes were tested: Na_2SO_4 (5 g L^{-1}), NaCl (3.5 g L^{-1}), or $NaClO_4$ (9.4 g L^{-1}), their concentrations were adjusted to provide the feed solution with equivalent electrical conductivity. &:2 FTSA ans its degradation products were analyzed using a liquid chromatography-mass spectrometry (triple quadrupole) method.

The results showed excellent 6:2 FTSA electrochemical mineralization (removal rates close to 100%) that was confirmed by the high removal of total organic carbon and defluorination rate (> 90%), with independence of the background electrolyte composition. The main 6:2 FTSA degradation product was PFHxA, but also PFHpA was formed at a lesser extent. These results confirmed that 6:2 FTSA oxidation was preferentially initiated at the hydrogenated carbon attached to the fluorinated part of the alkyl chain. While the electrolysis kinetics of the parent compounds was controlled by diffusion in the aqueous phase, degradation products were always found in trace levels, revealing that oxidation was fast and confined in the proximity of the anode surface. Removal rates were slightly faster as the length of the alkyl chain length was diminished, i.e., the diffusion control regime was favoured as the molecular weight of the perfluoroalkyl acids was reduced. These results give insight to understanding the mechanisms of perfluoroalkyl compounds electrolysis on BDD anodes. Moreover, the use of BDD electrochemical oxidation is shown as an effective technology for the treatment of industrial emissions of 6:2 FTSA and perfluroalkyl acids and for the remediation of environmental matrices impacted by persistent fluorinated chemicals.

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Evaluation of temperature influence on electrochemical processes occurring in the lithium-ion supercapacitor with the use of Dynamic Electrochemical Impedance Spectroscopy

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Lithium-ion supercapacitors (LiC's) belong to the hybrid type, combining the features of lithium-ion batteries and EDLC supercapacitors, which ensures their high power and energy density. The processes occurring in these devices largely depend on their operating temperature [1]. To study dynamic changes of temperature over wide range Dynamic Electrochemical Impedance Spectroscopy (DEIS) was used. This method is a modification of the classical EIS method by replacing classical sequential perturbation with multisinusoidal signal. It allows to test object in dynamic operating conditions due to very short measurement time. DEIS was successfully used for monitoring of fuel cells and batteries [2].

In this work impedance characteristic of LiC were obtained for linear temperature changes in the range from -30 to 60° C for different State of Charge (SoC) levels. All measurements were conducted with DEIS in two-electrode configuration in galvanostatic mode. Obtained results were presented on impedance and complex capacitance diagrams. Analysis of equivalent circuit parameters in the function of temperature allowed to understand which process is dominant for specific conditions. This study allowed for a detailed characterization of the occurring processes and it provided information about the optimal temperature range of LiC operation.

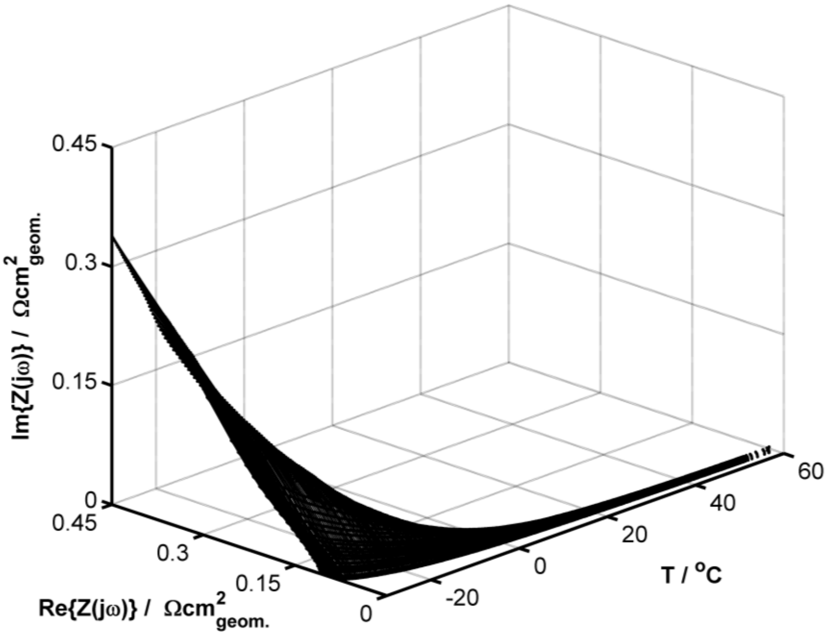

Fig. 1. Impedance diagram for LiC obtained in galvanostatic mode during the dynamic change of temperature for 50% SoC.

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Electrochemical Advanced Oxidation Processes – From $^{\bullet}$OH Radical Mechanism to Modeling and Engineering Aspects

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Electrochemical advanced oxidation processes (EAOPs) have been widely developed in the last 20 years for environmental protection [1,2]. Wastewater treatment represents a challenge since its reuse remain urgent to face the increasing water demand together with the global water stress. EAOPs are promising advanced physico-chemical technologies to answer this issue as complementary process in the wastewater treatment plant (WWTPs), the conventional biological technologies being not sufficient to remove completely the organic pollution, especially the biorecalcitrant micropollutants. EAOPs involve electron as "green" reagent and allow producing continuously and *in situ* strong oxidizing agents such as hydroxyl radical ($^{\bullet}$OH) (E° = 2.8 V / standard hydrogen electrode (SHE)) [3]. This radical has a very short lifetime, in the range of nanoseconds and it has a very high reactivity thanks to its action modes. Until recently, three mechanisms of $^{\bullet}$OH action were noticed [4]: (i) hydrogen atom abstraction (dehydrogenation), (ii) electrophilic addition to unsaturated bond (hydroxylation), and (iii) electron transfer (redox reactions). Last year, a fourth mechanism of action has been highlighted, which consists of the ipso-substitution on perhalogenocarbon compounds such as carbon tetrachloride (CCl_4). This work has been evidenced by EAOPs technologies and will be presented [5].

EAOPs need further studies to be developed at industrial scale. Modeling studies are required for reactor design optimization. The competition between mass transfer and charge transfer has been assessed recently in a paired electrocatalysis process by considering three reaction rate, i.e. anodic oxidation at anode surface, Fenton oxidation (through electro-Fenton process) in bulk solution and mediated oxidation in the bulk and anode surface [6]. This brings new scientific insight compared to the Comninellis' team model developed in the early 2000s [7], since two more reaction rate are considered (Fenton and mediated). Also, the mass transfer constants were depending on the electrolysis time, since the viscosity of solution was increasing with the surfactant degradation. This non-stationary condition makes the reaction orders more complex than the one developed previously [7,8]. Anodic oxidation is favored at higher concentration and the flow-cell design are more suitable than stirred tank reactor for heterogeneous catalytic systems. In addition, a new global current efficiency has been proposed which permit to fit the experimental data in electro-Fenton combined to anodic oxidation process.

Another challenge for the upscaling of EAOPs is the limitation of their drawbacks such as energy requirement and the need for a supporting electrolyte. Thanks to electrochemical microfluidic reactors there is the possibility to reduce ohmic drop and the cell resistance, which reduce the conductivity requirement and the energy consumption. The short inter-electrodes distances involved in the range of 50 to 500 µm allow for transfer intensification and have shown promising results for EAOPs application in wastewater treatment [9]. The optimization of micro-reactor design through mass transfer and specific energy efficiency studies will be exposed as well.

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Hydrogen Evolution on Transition Metal Carbides

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Hydrogen is considered a clean fuel of future because it acts as a green energy carrier and provides a method for storage and transport of energy. However, efficient, pure and low cost production of hydrogen proves challenging. In this regard, Pt possesses extremely high catalytic activity for the hydrogen evolution reaction (HER), though its high price and low Earth-abundance substantially leads to high capital costs in H_2 production by electrolysis. Thus, exploration and rational design of low cost and Earth-abundant non-noble-metal materials with high efficiency and durability will have a significant impact on making electrolyzer technology to be more affordable [1].

The improvement of catalysts for HER has been ascribed to several factors, such as hydrogen binding energy, catalyst surface area, presence of different crystalline phases, composition, changes in the metal-metal interatomic distance and electronic configuration of the catalyst. Active research, carried out to find new economically sustainable hydrogen production, is focusing on water electroreduction catalysed by carbide-based nanomaterials. The great interest of these materials resides in their similar electronic structure near Fermi's level with Pt-group metals. Moreover, these materials were reported to be chemically stable in a wide pH range and resistant to poisoning, as well as to have excellent mechanical durability and high electrical conductivity [1].

In a previous work, the synthesis and physicochemical characterization of Mo_2C as well as its elevated catalytic performance toward the HER were reported (Figure 1) [2]. In the present communication, results for several transition metal carbides (TMCs) will be presented and compared with those for Mo_2C. Furthermore, the performance and mechanism of the HER on TMC catalysts will be explored by differential electrochemical mass spectrometry (DEMS).

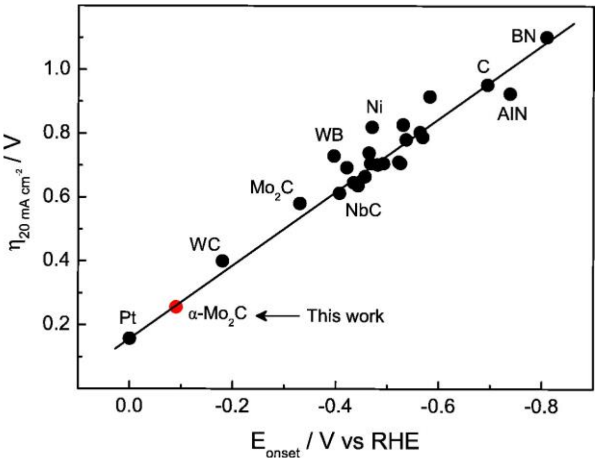

Figure 1. Overpotential for the HER at a current density of -20 mA cm^{-2} versus the onset overpotential for the HER of several catalytic materials [2].

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A comparative study of conventional and laser prepared MMO (Ti/RuO_2IrO_2) anode on the electrochemical oxidation of RB21 dye

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Increase in industrial activity has a direct impact on the environment, especially when concerning highly contaminated effluents, such as those seen for textile industries. The challenges of treating these wastewaters have motivated the advance in wastewater treatment technologies. The present study focuses on the use of mixed metal oxides anodes prepared using CO_2 laser beam as heating source for application in electrochemical oxidation of Reactive Blue 21 (RB21) dye. The Ti/RuO_2IrO_2 anode were synthesized by Pechini method and calcined using a CO_2 laser as reported elsewhere [1] applying a power density of 0.22 W/mm^2 at 270 mm of focal distance. For comparison, the anodes were conventionally produced in a furnace. The performance of the electrodes was analyzed in different electrolytes (Na_2SO_4 and with NaCl addition in different concentrations) and current densities (20, 40 and 60 mA cm^{-2}), besides analyzing the energy consumption and ecotoxicity behavior. Important differences were found considering the variables tested.

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Atomic Layer Deposition of Pt Nano-Particles for Electrocatalysis

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Atomic Layer Deposition (ALD) is a thin film deposition technique based on the chemical reaction of gas phase species on a solid surface. ALD is currently used commercially by the semiconductor industry and thin-film magnetic head industry. There has also been recent interest in using ALD in other application areas, such as photovoltaics and organic electronics. ALD is performed by the sequential exposure of the substrate to two (or more) different gas species separated in time by purging steps. Each gas species reacts with the substrate up to saturation, through a self-limiting reaction mechanism. Due to its self-limiting nature, the main advantages of ALD are the control of film thickness at the atomic scale, high conformity with surface features and high reproducibility. On most metal oxides, the growth starts with small islands (i.e. nanoparticles) and many ALD cycles are required to obtain a completely closed film. Therefore, ALD is ideal for accessing and decorating the entire volume of our porous electrode backbone with Pt nanoparticles [1].

Here we present the advantages of employing ALD of Pt nano-particles in two different concepts of gas phase electrocatalysis: a) the Electrochemical Promotion of Catalysis (EPOC) and b) the co-electrolysis of CO_2-H_2O towards syngas (CO and H_2).

EPOC was investigated over the highly dispersed Pt nanoparticles prepared by ALD, propane oxidation was selected as a model reaction. The electrode backbone in which Pt is deposited is a porous $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}/Ce_{0.9}Gd_{0.1}O_{1.95}$ composite, which offers mixed ionic–electronic conductivity. 100 Pt ALD cycles were selected based on literature studies of Pt deposition on flat Al_2O_3 substrates in which 100 cycles resulted in Pt nanoparticles with an average size of 4.5 nm [2]. The bare electrode backbone shows negligible activity for propane oxidation, while in the presence of Pt nanoparticles a high catalytic activity is obtained above 200 °C. The performance of the Pt-loaded LSM/GDC catalyst was significantly improved by application of small currents ($I < 500$ μA), leading to a 27–33% increase as a function of the open circuit catalytic rate, with apparent Faradaic efficiency values ranging from 1000 to 3860% at 300 °C. The results reveal that by using this novel catalyst design the main bottlenecks that limit EPOC commercialization, i.e., the low dispersion and small surface area of metal catalysts, could be surpassed.

Decoration of noble metal nanoparticles on fuel electrodes for high temperature (CO_2 and/or H_2O) solid oxide electrolysis applications is recognized as a very promising way to enhance their electro-catalytic performance. The deposition of noble metal nanoparticles is typically implemented by wet chemistry such as infiltration [3]. The latter has poor accuracy in terms of reproducibility, conformity and particle size distribution when compared to ALD. Therefore, inspired by the success in EPOC concept we employed ALD of Pt in state-of-the-art $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) fuel electrode [4]. The electrochemical performance of 100 cycles Pt-LSCM increases by up to 30% over the bare LSCM samples due to the enhanced electro-kinetics over the Pt nanoparticles, thus demonstrating the potential of ALD technique in solid oxide electrolysers.

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Pd-based Bimetallic Electrocatalysts for Oxygen Reduction Reaction in Alkaline Medium

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Faster oxygen reduction reaction (ORR) kinetics and less corrosive environment, allowing the use of a wider range of electrocatalysts including non-noble metals, are the major advantages of alkaline over acidic medium [1]. Pd-based electrocatalysts exhibit high ORR activity in alkaline medium, mainly associated to the electronic properties of Pd [2]. These properties are mostly related to the position of the d-band center since it affects the binding energy of the adsorbates participating in ORR [3]. Combining Pd with a second transition metal alters the d-band characteristics of the former, which can enhance ORR activity [4].

In the present work a series of 10 wt.% Pd-M (M: Ag, Ca, Co, Cu, Fe, Ni, Sn, Zn)/C (Pd to M mass ratio equal to 3:1) bimetallic electrocatalysts, denoted as 7.5Pd–2.5M, as well as 10 wt.% Pd/C and 10 wt.% Pt/C reference electrocatalysts, denoted as 10Pd and 10 Pt respectively, were prepared via wet impregnation/co-impregnation [5]. The prepared electrocatalysts were physicochemical characterized employing various techniques (BET, XRD, TEM/SAED, XPS) and electrochemically tested concerning their ORR activity in 0.1 M KOH solution using the thin-film rotating disk electrode technique with a loading of 15 $\mu g_{met}\ cm^{-2}_{disk}$ [5]. Their electrochemically active surface area (ECSA) was determined via CO-stripping [5].

XRD and TEM/SAED analysis revealed bulk alloy formations in the case of 7.5Pd – 2.5Zn and 7.5Pd – 2.5Sn electrocatalysts. XPS confirmed the presence of both Pd^0 and PdO on the surface of all tested Pd-based electrocatalysts. Similarly, the presence of Sn^0 and Ni^0 along with SnO and NiO was identified by XPS on 7.5Pd – 2.5Sn and 7.5Pd – 2.5Ni, respectively. In the case of 7.5Pd–2.5Cu and 7.5Pd – 2.5Zn electrocatalysts, XPS analysis revealed the presence of surface CuO and ZnO, respectively.

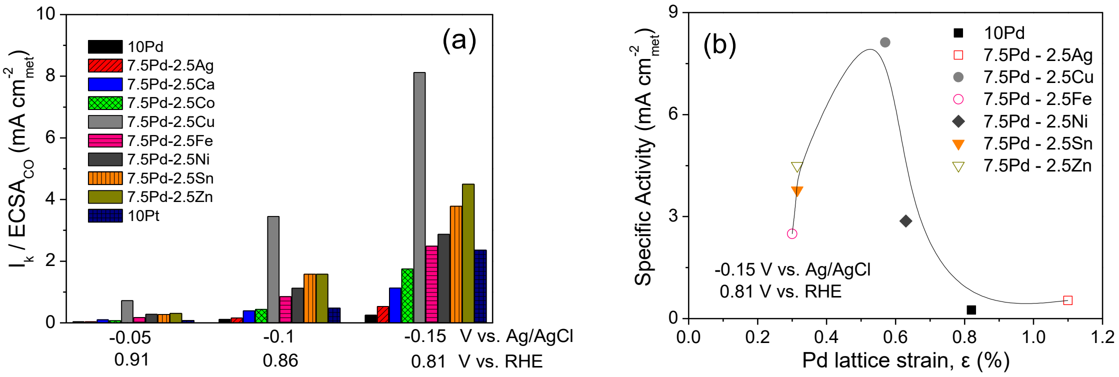

Fig. 1 (a) ORR specific activity in 0.1 M KOH solution at selected electrocatalyst potentials, (b) Correlation between ORR specific activity and calculated (via XRD analysis) Pd lattice strain.

The best ORR electrocatalytic performance in 0.1 M KOH, in terms of both specific (Fig. 1a) and mass activity, was exhibited by the 7.5Pd – 2.5Cu electrocatalyst, its ORR activity being higher than that of the 10Pt reference electrocatalyst. High electrocatalytic activity, in descending order as it concerns specific activity, was also exhibited by the 7.5Pd – 2.5Zn, 7.5Pd – 2.5Sn and 7.5Pd – 2.5Ni electrocatalysts (Fig. 1a). All Pd-based bimetallic electrocatalysts exhibited higher activity than the 10Pd reference electrocatalyst. The enhanced ORR performance of 7.5Pd – 2.5Cu was associated mainly with an optimum Pd lattice strain (Fig. 1b) and, possibly, with the presence of surface CuO.

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Electrochemical Reduction of CO_2 in Gas Phase using Cu/CNT Catalyst Synthesized in Supercritical Medium

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The continuous combustion of fossil fuels has led to an increase in CO_2 emissions into the atmosphere. The electrocatalytic reduction of CO_2 (ERC) is considered as one of the options with larger potential from the economic and technical points of view since it can take advantage of renewable energies as well as idle nuclear/hydro- electric energies to convert CO_2 into gaseous and liquid fuels [1-3]. It consists of the reduction of the carbon dioxide molecule on the cathode of an electrochemical cell thanks to the protons produced on the anode of the cell and the electrons supplied by an external energy source. The initial step (activation of CO_2 molecule, i.e. $CO_2 + e^- \rightarrow CO_2^*$) is the most critical one in the entire electrochemical process and needs to overcome a high overpotential. This overpotential can be lowered in the presence of electrocatalysts, which would depress accordingly hydrogen evolution competing reaction. In this work, Cu nanoparticles were deposited onto CNT (carbon nanotubes) by supercritical fluid deposition to obtain Cu/CNT catalysts. Supercritical fluid deposition is an advanced synthesis method that has demonstrated to lead to homogeneous distribution of small metal nanoparticles on the carbon support (CNT) [3, 4].

The correct deposition of Cu nanoparticles on CNT has been confirmed by ICP, XRD and TEM analysis. As well, TEM micrographs have been used to obtain the particle size distribution. ICP analysis indicated that Cu deposition yield was over 85 %, and TEM images showed that Cu nanoparticle sizes were mainly between 2.0 and 3.5 nm.

The electrocatalytic activity of Cu/CNT catalyst has been studied by electroreduction of CO_2 in the gas phase. Experiments have been carried out in a Polymer Electrolyte Membrane (PEM) type cell with 25 cm^2 surface electrode geometric area [3] working in continuous mode at 0.02 SL of CO_2 /min and 30 ºC. The anolyte used was an aqueous solution (0.5 M) of $KHCO_3$. The experiments were performed at galvanostatic conditions at current density values of 2, 4, 6 and 8 mA/cm^2. CO_2 reduction products have been analyzed by gas chromatography (equipped with SPME (solid phase microextraction) preconcentration system for liquid products). To confirm that the compounds detected came from the conversion of CO_2, blank experiments (with current density applied) were carried out substituting the flow of CO_2 by a flow of N_2.

It has been observed that CO_2 conversion rate was constant (and around $1 \cdot 10^{-2}$ mmol/h) at 2 and 4 mA/cm^2, and then increased linearly with current density from 4 to 8 mA/cm^2, to reach $9 \cdot 10^{-2}$ mmol/h which is a considerable CO_2 conversion rate. However, using values of current density above 8 mA/cm^2 led to operation troubles related to obstruction of the cathodic flow channel, probably due to an excessive anolyte concentration for this cell configuration and the crossover of K^+ through the Nafion® membrane [4]. Regarding the reduction products, at 2 mA/cm^2 only CO was obtained, whereas formic acid was also observed for higher current densities, being CO the main reduction product. In addition, experiments carried out at 8 mA/cm^2 allowed to obtain traces of methane and methanol.

The results found in this work are indicative of the excellent electrocatalytic activity of Cu/CNT obtained by supercritical deposition, since it has allowed to obtain CO_2 conversion rates more than one order of magnitude higher than those reached with Pt/CNT and Pb/CNT reported in previous works [3, 4].

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Polyaniline Treated Pt/TiO_2 with Enhanced Activity and Durability for the Oxygen Reduction Reaction

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Carbon has been seen as an ideal support material for many catalytic systems, including fuel cells. However, carbon support itself also suffers from the possible oxidation, i.e. corrosion under harsh conditions. To improve the durability and increase the activity of Pt electrocatalysts are two long quests for polymer electrolyte membrane fuel cells (PEMFCs). Herein, we report a novel and efficient strategy for preparing oxygen reduction catalyst and improving its catalytic performance by taking advantage of the "strong metal-support interaction" (SMSI) effect between Pt and the non-carbon support. TiO_2 supported Pt (Pt/TiO_2) nanocatalysts were first prepared prior to in-situ polymerization of polyaniline (PANI), followed by thermal annealing at different temperatures. After heat treatment, it is found that anatase TiO_2 support transforms into rutile structure with Magnéli phase Ti_4O_7 on surface, and such a unique rutile@Ti_4O_7 feature enhances the SMSI effect and catalytic performance. Among all results, the electrochemical performance of the catalyst annealed at 950 °C (PANI-Pt/TiO_2-950) possesses the highest specific current density of 0.37 mA cm^{-2} at 0.9 V (vs. RHE). The accelerated stability test also demonstrated that the PANI-Pt/TiO_2-950 exhibits superior stability to Pt/C (JM 20) after 2,000 potential cycles. The enhanced electrocatalytic activity and durability can be attributed to the synthetic approach where the electronic interaction between Pt nanoparticles and reduced TiO_2 support is maximized through annealing while the growth of Pt under elevated temperatures can be effectively suppressed due to the constrained PANI coating. X-ray absorption spectroscopy (XAS) further confirms that a higher electronic density in the Pt 5d-orbital for PANI-Pt/TiO_2-950 can indeed improve the ORR activity, as compared to its commercial and the pristine counterparts. The presented strategy could be easily applied to other electrocatalysts and make non-carbon support materials a feasible alternative for improved performance.

Novel Au/PPy and Cu/PPy Nanocomposites as Electrocatalysts for Borohydride Oxidation

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Sodium borohydride ($NaBH_4$) has application as reducing agent in numerous chemical reactions. Still, in recent decades, one of the most important applications of $NaBH_4$ is as potential fuel in direct borohydride fuel cells (DBFCs)[1]. DBFCs attract attention because of their advantages, such as high open circuit voltage and environment friendly reactants and products [2]. The anodic reaction in DBFC is borohydride oxidation reaction (BOR), which in highly alkaline media (pH 14) is described as follows [3]:

$$BH_4^- + 8\ OH^- \rightarrow B(OH)_4^- + 4\ H_2O + 8\ e^- \qquad E^0 = -\ 1.24\ \text{V vs. SHE} \qquad (1)$$

The anodic catalysts used in DBFC include noble metals (e.g., Au, Pt, Pd, Ag) and transition metals (e.g., Cu, Ni, Co), in pure form or as alloys, typically supported on carbon [2]. Most of these electrocatalysts have good catalytic activity for both electrochemical BOR and borohydride hydrolysis reaction. The fuel loss is increased during borohydride hydrolysis [3]. Thus, it is very important to find appropriate electrocatalysts which are more active for direct borohydride oxidation than for borohydride hydrolysis reaction, being also accessible and not expensive.

In this work, polypyrrole was used as support for metal (Au and Cu) nanoparticles and two electrocatalysts (Au/PPy and Cu/PPy) were tested for BOR in alkaline media. *In situ* polymerization process between metal ions (Au^{3+} and Cu^{2+}) and pyrrole in water and methanol was used for the preparation of Au/PPy and Cu/PPy, respectively. The amounts of Au and Cu in the collected powders were found to be 23.3 and 22.8 wt.%, respectively. The working electrodes were prepared by pipetting 10 µL of the catalytic ink onto a glassy carbon tip and leaving it to dry at 100 ºC overnight.

BOR was investigated in 2 M NaOH + 0.03 M $NaBH_4$ solution by cyclic voltammetry (CV) from the open circuit potential up to 0.5 V vs. SCE at a scan rate of 0.05 V s^{-1}. Au/PPy gave about two times higher current density (ca. 6.5 mA cm^{-2}) than Cu/PPy (2.5 mA cm^{-2}) electrocatalyst during BOR. Influence of temperature on BOR kinetics was examined for both electrodes in the temperature range from 25 to 65 ºC. As expected, increase of current densities with increasing temperature of electrolyte was observed for both electrodes. Thus, current densities of Au/PPy of ca. 13.5 mA cm^{-2} and of Cu/PPy of ca. 7.6 mA cm^{-2} were recorded near 0 V vs. SCE in the CVs run at 0.05 V s^{-1} and 65 ºC. These results were used to calculate apparent activation energy, E_a, by Arrhenius equation [3]. Again, Au/PPy showed better catalytic activity than Cu/PPy in terms of lower E_a, i.e., E_a of BOR at Au/PPy electrocatalyst was evaluated to be 15.5 kJ mol^{-1} whereas at Cu/PPy it was 22.6 kJ mol^{-1}.

Both Au/PPy and Cu/PPy electrocatalysts showed good activity for BOR in highly alkaline media, where Au/PPy showed about two times higher activity as evidenced by higher current density and lower apparent activation energy. It should be emphasized that both electrocatalysts have relatively low cost due to the reduced amount of used metal nanoparticles.

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Nickel-Doped Ceria Bifunctional Electrocatalysts for Oxygen Reduction and Evolution in Alkaline Media

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The oxygen reduction (ORR) and oxygen evolution (OER) reactions are central processes in energy conversion and storage devices where catalysts play a key role. Applications such as rechargeable metal–air batteries or unitised reversible fuel cells require bifunctional ORR/OER catalysts.

Pt/C, Pd/C, Ru, Ir and its alloys have been explored and seen as the most promising electrocatalysts for ORR and OER reactions, but these electrocatalysts are too expensive. Ni electrodes are typically used for OER in alkaline media due to its good stability and corrosion resistance [1]. While Pt-based and Ni-based materials show activity for ORR and OER, respectively, their activity for the reverse reaction is typically lower, suggesting the need for developing bifunctional ORR/OER catalysts. Metal oxides, such as cerium oxide (CeO_2), offer several benefits, which include high corrosion resistance, the ability to modify the metal electrocatalytic activity, and also to co-catalyse reactions through abundant surface hydroxyl groups [2].

Within this study, CeO_2 samples doped with different Ni amounts (5, 10, 15 and 20 wt.%) were prepared and characterized using several different physicochemical techniques [3]. The four prepared materials were tested as bifunctional electrocatalysts for ORR and OER in alkaline medium (0.1 M KOH). Electrochemical measurements were done by cyclic voltammetry (CV), linear scan voltammetry with rotating disk electrode (LSV RDE), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA).

All electrocatalysts showed good electrochemical activity for both ORR and OER. ORR Tafel analysis performed in -0.45 to -0.15 V potential window lead to Tafel slopes in the 88 - 121 mV dec^{-1} range. Number of electrons exchanged during ORR was evaluated to be between 2 and 2.7. OER Tafel slopes were determined to be in the 343 - 440 mV dec^{-1} range. OER activation energies were also determined and found to be between 28 and 43 kJ mol^{-1}. Additionally, the specific capacitance of Ni-CeO_2 electrocatalysts measured at scan rate of 100 mV s^{-1} was found to range from 0.7 to 1.4 Fg^{-1}. The results demonstrate that Ni-CeO_2 can act as bifunctional electrocatalyst for ORR/OER. The effects of composition on catalytic behavior are discussed.

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Influence of the GDL and assembly mode of a PEM cell on the revalorization of ethanol into chemicals

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In recent years bioethanol has become one of the most promising alternatives to traditional fossils fuels. However, the overproduction on a global scale (biodiesel crisis) and also on a national scale (surplus in wine production and industrial waste of alcohol production) have required the search of different strategies for the valorization of this compound. In this research work, the electrochemical reforming process is proposed as an alternative, which present some advantages (less deactivation and selectivity limitations) compared to conventional catalytic processes. Using a polymer membrane electrochemical reactor (PEM cell), in the anodic compartment the oxidation reaction of ethanol takes place, producing protons and organic compounds of industrial interest, while reduction reaction takes place in the cathodic compartment, generating high purity hydrogen. It is well known the viability of light alcohols for the generation of hydrogen through this technology [1]. However, literature on the production of bioethanol-derived chemicals through this technology is scarce. Therefore, the current research is focused on maximizing the production of valuable liquids obtained in the anodic compartment, derived from the ethanol oxidation, apart from hydrogen generation. Some of these compounds are the acetaldehyde, acetic acid and ethyl acetate. Acetaldehyde is an important intermediate in organic synthesis, used as a raw material for the production of acetic acid, acetic anhydride, ethyl acetate, pyridine, medicines or plastics. Industrially, it is obtained from the direct catalytic oxidation of ethylene through Wacker process, which is very intensive in terms of energy, so the electrocatalytic alternative is presented as a more efficiency option. Under this scenario, a study of the influence of the MEA (membrane electrode assembly) configuration by using different GDL (gas diffusion layer) and modes of assembly was carried out. Hence, three cell configurations so called a, b and c were tested. Configuration a) was formed by a GDL of carbon paper also used as a support for the catalytic layer, which is impregnated through the drip method. To conform the MEA it is necessary an assembly step, applying 120 ºC and 1 ton. Configuration b) was formed by a GDL of porous titanium. This material is thicker than carbon paper and provides higher mechanical resistance to the system. The catalytic layer was impregnated directly on the membrane by airbrushing, so this configuration does not need thermal assembly. In the last configuration (c) the GDL was of carbon paper and the catalytic layer was also impregnated on the membrane avoiding the assembly step. Fig. 1 shows a scheme of the proposed configurations. In order to determine the influence of the MEA configuration on the production of valuable organic liquids and hydrogen, different experiments were carried out: linear voltametries (0-1.4V), chronopotenciometries at various levels of intensity, stabilities essays to estimate the total consume and impedance spectroscopy essays. An aqueous solution of ethanol (4 M) was feed to the anodic chamber with a flow rate of 2 ml/min at 80 ºC and 1 atm. Regarding the electrocatalysts, commercial PtRu/C and Pt/C were used as anode and cathode, respectively. Configuration c) proved to be more active in the electro-reforming of ethanol in terms of current density (four times higher, which is related to hydrogen production) and selectivity to valuable chemicals while requiring the least energy consume (24 kWh kgH_2^{-1}).

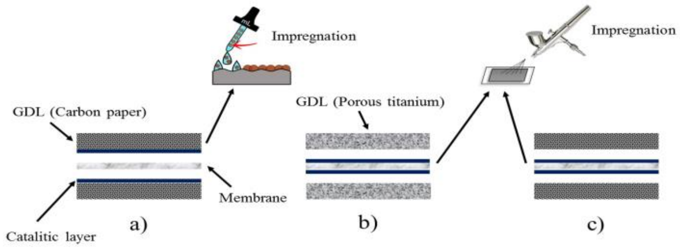

Fig 1. Scheme of MEA configurations.

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Antimonene 2D Single Layers as Supercapacitors.

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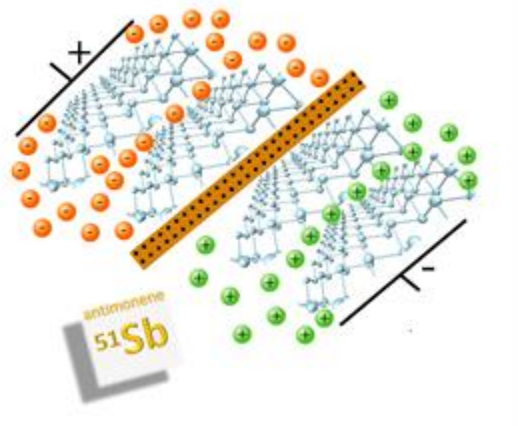
The increasing development of renewable energy sources, as solar and wind power harvesting devices, has required the development of sustainable energy storage technologies in order to satisficed the increasing energy demand. In energy storage devices, nanomaterials are playing a key role in bringing these devices toward practical applications. Therefore, much attention has recently been paid to the development of new nanomaterials, which are expected to allow electrode development with major storage capability. Among nanomaterials, 2D nanomaterials have a high specific surface area suitable for high double-layer capacitance1. Even so 2D nanomaterials have reactive basal planes and edges that can provide pseudocapacitance2. After graphene successful application in different energy storage devices, new 2D inorganic nanomaterial have been developed3, some of them following the graphene structure as a pattern. In recent years, a new family of compounds similar to graphene, base in anisotropic layered elemental materials is calling the attention of the scientific community. One of these new nanomaterials is Antimonene. It consists in one atom type two dimensions structure, each atom is covalently bonded with adjacent atoms to form a puckered honeycomb structure. In the present work, Antimonene is characterized for the first time as a material for applications in energy storage, being applied as an electrode material as the basis of a supercapacitor. Antimonene is shown to significantly improve the energy storage capabilities of a carbon electrode in both cyclic voltammetry and galvanostatic charging. It demonstrates remarkable performance with a capacitance of 1578 F g^{-1}, with a high charging current density of 14 A g^{-1}. The system also demonstrates a highly competitive energy and power densities of 20 mW h kg^{-1} and 4.8 kW kg^{-1}, respectively. In addition to the excellent charge storing abilities, antimonene shows good cycling capabilities over 10000 cycles until the drop-cast material is liberated from the substrate. Hence, this nanomaterial is shown to be a highly promising for energy storage applications.



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Graphene-based Systems for Catalytic Electroreduction of Oxygen

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Due to their unique electrical, electronic and chemical properties, graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (RGO) are used in a wide range of applications e.g. fuel cells, supercapacitors, batteries, and related devices. Being perfect mechanically, thermally and chemically stable two-dimensional platform for metal nanoparticles (NPs), graphene has potential application in proton exchange membrane fuel cell (PEMFC), where the oxygen reduction reaction (ORR) on the cathode meets strict kinetic limitations.

To date, high-area carbon supported platinum or Pt-alloys have shown the highest electrocatalytic activity toward the ORR, however there is an increasing demand to minimize the amount of Pt in fuel cell cathode materials. Besides, to cut down the cost of fuel cell by lowering Pt loading it is important to maintain the long-term stability of Pt catalysts. Pt/C composites have tendency to deteriorate during long-term operation of fuel cell. In harsh PEMFC conditions, Pt particles dissolve, migrate, and grow in size, resulting in the loss of electroactive catalyst surface area. Furthermore, Pt nanoparticles (PtNPs) enhance the corrosion of carbon support shortening the lifetime of fuel cell cathodes. To overcome these challenges, great effort has been made in order to combine PtNPs with graphene and its derivatives for enhancing their electrocatalytic performance.

GO has hydroxyl, epoxy and carboxyl groups at the edges and on the basal plane, which make the GO materials hydrophilic and dispersible in aqueous solutions. Such surface functionalities favor good dispersion of catalyst nanoparticles on RGO carrier increasing the electrochemically active surface area. Moreover, RGO based 2-D platform is used to stabilize supported metal NPs.

The main objective of the present work was to demonstrate a comparative study into the relative effects of graphene-based hybrid nanocomposites on the performance of platinum nanoparticles towards the oxygen reduction reaction in both acidic and alkaline media. For the purposes of comparing the supports, a simple platinum black catalyst is used and the performance is evaluated via direct measurement of peroxide by rotating ring-disk electrode (RRDE) to determine the number of electrons (n) transferred in the ORR. Prepared catalyst materials showed remarkable electrocatalytic behavior toward ORR in both alkaline and acidic media. For comparison, the nanoparticles supported on Vulcan carbon support were also studied.

To examine physical properties of used hybrid materials Raman spectroscopy, infrared spectroscopy (IR), and scanning electron microscopy (SEM) with (EDX) analysis were used. The electrocatalytic properties of the resulting materials toward oxygen electroreduction were investigated using RRDE.

Role of Iron in Pyrolyzed Catalyst for Oxygen Reduction Reaction in Basic Media.

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The study of non-precious metal catalysts (NPMC) for oxygen reduction reaction is crucial for the massification of environmentally friendly energy conversion devices. Among the NPMC, the M-N-C catalysts (M, transition metal) are the most promising catalysts for the ORR in basic and acid media. These materials are prepared by two pyrolysis treatments of carbon, nitrogen and metal precursors, first in inert atmosphere and later in ammonia. In acid media there is an agreement that the ORR follows an inner-sphere mechanism via the O_2 adsorption on the metallic center [1]. However, in basic media the role of metal is unclear, some authors point out an outer-sphere mechanism mediated by the oxidized groups of carbon matrix [2], while others find a relation between the catalytic activity and the presence of metal in the active sites inserted in the structure [3]. In the present study, the presence and participation of the metallic center in ORR in basic media is approached in three ways, by the connection of the formal potential of the catalysts with the onset potential of the ORR, by comparison of the catalytic activity if KCN is present in dissolution, and by the study of Tafel slopes.

The studied MNC catalysts were prepared by pyrolysis process of two iron porphyrins adsorbed on carbon Vulcan [2a]. The presence of iron in the actives sites was performed by XPS and Mössbauer spectroscopy. The XPS characterization shows the presence of Fe-Nx and other nitrogen contributions (as pyrrolic, pyridinic and graphitic) in the final catalysts, and the structure of the Fe-Nx groups are related to FeN4 type moiety according to Mössbauer spectroscopy, which are similar to intact iron porphyrins. By the electrochemical tests, a direct relation between the formal potential (Fe(III/II)) of the pyrolyzed catalyst and the onset potential of ORR is detected, starting the ORR at potentials where Fe^{2+} become to be present in the catalysts. Additionally, the poisoning test shows a decrease in the activity in the presence of KCN, indicating the active role of Fe in ORR. The Tafel slope studies show two slopes, at low and high overpotentials for pyrolyzed and intact FeP´s. This change is also related with the formal potential of the catalysts, showing values of 0.06 $Vdec^{-1}$ in the range of potentials of the Fe(III/II) reduction, and values close to 0.120 $Vdec^{-1}$ when Fe^{2+} is predominant.

The results obtained in this work show the active role of iron in ORR catalysis in basic media, indicating that the ORR in this media follows an inner-sphere mechanism as proposed for intact MN4 complexes. In addition, a direct relationship between the formal potential of the pyrolyzed catalysts and the catalytic activity (expressed as log I at E=cte) is found.

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Schiff Base Complexes as Electrocatalysts for Urea Electrooxidation

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Abstract

Finding alternative energy sources has been of prime interest over the past several decades. Hydrogen (H_2) is considered a leading candidate that is both renewable and gives zero emission. Recently, urea electrolysis has emerged as a promising new method for H_2 generation, making urea itself a potential source of sustainable clean energy. In an electrochemical cell, urea is electrochemically oxidized at the anode into N_2, CO_2, and H^+, whereas water is reduced to hydrogen at the cathode. Theoretically, water electrolysis for hydrogen production requires 1.23 V *v*s NHE, whereas urea electrolysis requires only 0.37 V, generating hydrogen in a very cost-effective way.

Different solid-state electrocatalysts have been studied extensively for urea electrooxidation, but such catalysts are inherently difficult to control, manipulate and study at the atomic level. We aim to develop molecular catalysts that can be fine-tuned relatively easily at the atomic level, and studied in detail using methods that are common for such molecular systems, such as NMR spectroscopy and single-crystal X-ray crystallography.

To the best of our knowledge, no molecular catalysts have been reported to perform the electrochemical oxidation of urea. Herein, we describe our efforts to design, synthesize and investigate nickel-based metal complexes for urea electrooxidation, utilizing imino-phenol ligands. These ligands, containing N and O donors, act as good chelators and can stabilize diverse oxidation states of metal centers. Such an imino-phenol-based complex was studied as an electrocatalyst for urea oxidation, displaying an onset potential of 0.33 V *vs* Ag/AgCl in an alkaline medium. The stability of the molecular system in alkaline media was studied using different spectroscopic methods, such as time-dependent UV-Vis, NMR and Raman spectroscopy. The electrochemical stability of the catalyst was examined using *in-situ* Raman spectroscopy and chronoamperometry. The available data indicates that the complex is the active catalyst for urea electrooxidation, and is stable both chemically and electrochemically under the studied conditions.

Converting mixed plastics into mesoporous Fe-N-C electrocatalyst for energy devices

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The short disposability and high cost of platinum-based catalysts are serious obstacles to the scale-up and commercialization of PEMFCs. To meet the economic requirements of FC technologies, inexpensive and commercially available heteroatom-doped porous carbon materials have proven to be active catalysts for the oxygen reduction reaction (ORR). Moving forward to the development of non-platinum group metal catalysts (non-PGMCs) is clearly a significant challenge [1]. Among non-PGMCs, Fe-N-C materials have attracted particular interest, as alternative to Pt-based materials, due to their high activity, selectivity and good tolerance to poisoning. It was observed that the catalytic performances are influenced by: (a) presence of superficial Fe-N_x sites [2], (b) 3D-hierarchical structure in terms of surface area and porosity and (c) the degree of graphitization. Recently, many researches focused on the development of synthesis transforming non-conventional polymeric precursors including refined biomass and recycled polymers [3], undertaking the goal of adding cost-valued and sustainable routes to fuel cell catalysts.

In this paper non-conventional polymeric precursor materials (Polyethylene, PE and Polyurethane, PU) were employed as suitable N-doped carbon supports for preparing Fe-NMC catalyst. The first step was the dispersion of polyurethane and iron precursor inner suitable polyethylene matrix through mechanical mixing. A two-stage pyrolysis treatment was chosen to obtain the final material. At first it was subjected to a fast pyrolysis to obtain a crude product, which is further heated to improve the graphitization degree. This catalyst was also activated in hot H_2SO_4 to improve catalytic performance versus ORR [4]. The obtained catalyst was fully characterized by RRDE technique for understanding the activity and the selectivity of the material. Figure 1a showed as the activation treatments allowed to obtain more stable limiting current and more positive semi-wave potential ($E_{1/2}$). Furthermore, the pyrolysis temperature was found to deeply affect the activity of the material, in this case (Fig.1b) the best temperature is 700 °C.

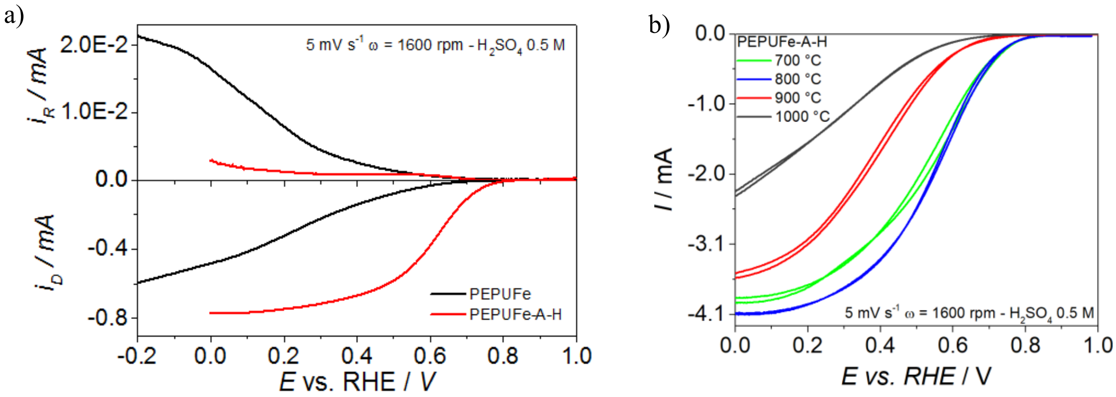

Figure 1: LSV at RRDE analysis: effect of (a) of activation treatments and (b) of temperature.

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Electrochemical Promotion of Propylene Combustion on Ag Catalytic Coatings

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Catalytic combustion as a process used for removal of hydrocarbons from automotive gas exhausts or for energy production has been widely implemented on supported PGM (Platinum Group Metals) based catalysts[1]. Since PGMs are very costly and rare, there is a strong need for an equally effective and less expensive catalyst. The electrochemical promotion of catalysis (EPOC), is a promising concept to in-operando boost catalytic processes in a reversible and controlled manner[2]. The aim of this study was to develop Ag-based electrochemical catalysts for low temperature propylene deep oxidation. EPOC of propylene combustion has been carried out in the literature but mainly on Pt catalytic films[1,3], while this phenomenon was attributed to the modification in the propylene chemisorption[3].

Nanostructured electrochemical catalysts were prepared by screen-printing and reactive Physical Vapor Deposition (PVD) method. Thickness and porosity of Ag coatings were modified by changing the deposition parameters (duration and pressure for PVD, nature of the ink and calcination temperature for screen-printing) to optimize the catalytic properties. Catalytic and electrocatalytic tests have been carried out in a quartz reactor[1] which operated under continuous flowing conditions at atmospheric pressure. The catalytic activity was monitored in a temperature range of 100 to 400°C under lean-burn conditions, as encountered in Diesel exhausts. The most active Ag films were also evaluated under closed circuit conditions (± 2V) in order to measure the effect of polarization between the Ag working electrode and an Au reference electrode. Both electrodes were exposed to the same atmosphere in a single chamber configuration.

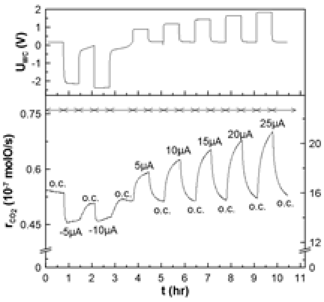

Figure 1. Transient effect of applied currents on U_{WC} as well as on the catalytic rate of CO_2 production and on C_3H_6 conversion (T = 300 °C, 0.1% C_3H_6, 3.6% O_2, 3 l/h).

Values of Faradaic efficiencies in the range of 300 were obtained while the conversion could be tailored from 14 to 21% (Fig. 1). Negative current applications lead to the decrease of the CO_2 production while positive current application corresponds to a pronounced increase of the catalytic performance. Upon positive current applications, the rate enhancement ratio increases with the intensity of the current. This indicates that the coverage of promoting ionic species ($O^{\delta-}$) increases with the current, then producing more weakly bonded oxygen species coming from the gas phase[4]. This study reports, for the first time, that the catalytic activity for propylene of Ag coatings deposited onto YSZ can be tailored by current applications in a non-Faradaic manner. The predominant impact of current applications is to modify the reactivity of oxygen present on the Ag surface. Positive current applications increase the propylene conversion by producing more reactive oxygen species. This beneficial effect is more pronounced in an oxidizing atmosphere, where the oxygen coverage on Ag is high. This demonstrates that EPOC can enhance catalytic properties of Ag coatings for the abatement of propylene in air.

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Theoretical modelling to evaluate the influence of the electrode kinetics over the catalyst efficiency

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The interest of molecular catalysts to enhance relevant reductive or oxidative reactions is out of question with examples such as water oxidation/reduction, hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), CO_2 reduction…[1] In order to quantify and understand the overall efficiency of such catalysis, in this work rigorous analytical explicit expressions have been deduced for the current response and for the concentration profiles of the species involved in a first order catalytic mechanism (Scheme 1), considering finite electrochemical and (pseudo)first order chemical kinetics, and the use of single pulse electrochemical techniques and spherical microelectrodes [2,3].

$$O + e^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R(+Y) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O(+Z)$$

Scheme 1. Non-nernstian (pseudo)first order catalytic reaction mechanism.

Also, compact simpler expressions for the current response, the concentration profiles and the spectroelectrochemical signals have been obtained from the rigorous ones making $(k_1+k_2)\ t >>> 1$. These latter expressions can also be applied to differential voltammetric techniques such as double differential pulse voltammetry (DDPV), differential multipulse voltammetry (DMPV) or square wave voltammetry (SWV), and its applicability is analysed under different conditions.

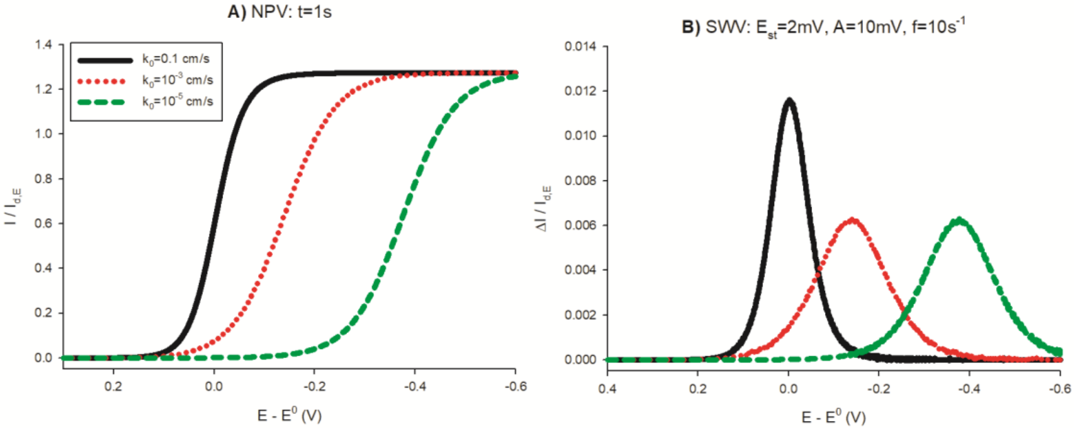

Figure 1. Influence of the electrochemical kinetics for an irreversible catalysis (K=0) and considering the use of a spherical microelectrode (r_0=10μm). Other conditions: D=10^{-5} cm^2/s, $(k_1+k_2)\ t = 2.5$.

From the theoretical solutions obtained, a comprehensive analysis of the voltammetric and spectroelectrochemical responses will be carried out for the evaluation of the efficiency of the catalysts as a function of the mass transport conditions (i.e., electrode size) and the electrochemical and chemical kinetics and thermodynamics (as an example, see Figure 1). Most suitable techniques, experimental conditions and data treatment procedures for quantitative characterization of systems will be discussed. The utilization of differential techniques are advantageous since well-defined peak-shaped signals are obtained and the peak-position can be employed to estimate the electrochemical kinetic constant values (k_0). Finally, the direct monitoring of the extent of the chemical reaction layer under stationary conditions via spectroelectrochemical measurements will be examined for the quantification of the catalytic performance.

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Acknowledgments

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Generation of Hydroxyl Radicals and Electro-oxidation of Emerging Pollutants on Pt-doped SnO_2-Sb Electrodes

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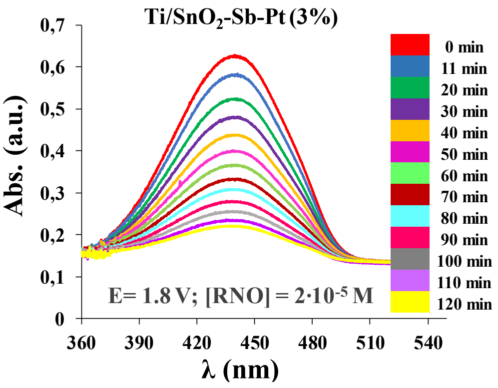
Emerging pollutants, including various types of chemicals found in pharmaceuticals, cosmetics, pesticides, industrial products, etc., present potentially-serious risks to human health and ecosystems. Hence, it is necessary to develop efficient and reliable methodologies for their elimination. The anodic oxidation is one of the most promising methods for the degradation of these compounds [1]. In this field, most studies have been carried out with BDD, to now, the most efficient electrode for the generation of highly-reactive hydroxyl radicals (•OH). On the other hand, Pt-doped SnO_2-Sb anodes constitute an attractive cheaper alternative for the electrochemical treatment of phenolic wastewaters [2], and their electrocatalytic response has been recently discussed [3]. Despite that, the capability of these anodes for •OH generation or for the removal of emerging pollutants has not been studied yet.

In this work, the generation of •OH and the abatement of various emerging pollutants (diclofenac, paraquat and glyphosate) on Ti/Pt, Ti/SnO_2-Sb and Pt-doped Ti/SnO_2-Sb electrodes (3-13 at. % Pt) have been studied. Moreover, the performance of these anodes is compared to that of BDD. The different SnO_2-based anodes were prepared onto Ti substrate by the thermal decomposition method [2]. The •OH radicals were determined by reaction with N,N-dimethyl-p-nitroso aniline (RNO) and using the spectrophotometric method at constant potential [4]. The elimination of pollutants was carried out by galvanostatic electrolysis in an undivided filter-press cell and their concentration and/or that of by-products was followed by different techniques (UV-vis, ionic chromatography, COD, TOC).



The results indicate that the incorporation of Pt increases the electrocatalytic activity of SnO_2-Sb electrodes to the generation of •OH radicals (see for example in the figure the activity of these radicals to react with RNO, i.e. to decrease its absorbance). These radicals enable to oxidize 85-90 % of diclofenac (in 3 h) and paraquat (in 5 h) solutions (200 ppm, 0.2 L). In the case of refractory glyphosate, while Ti/SnO_2-Sb-Pt(3%) only oxidizes this compound, Ti/SnO_2-Sb-Pt(13%) produces also its mineralization. Although less efficient than BDD, this work demonstrates that these cheaper electrodes overall exhibit good activity towards the elimination of the studied emerging pollutants.

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Electrochemical activation of catalysis for hydrogen production via ethanol steam reforming

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The search for sustainable energy systems has encouraged the development of hydrogen-based technologies to reduce the impact of non-renewable sources. Methane steam reforming has conventionally been the main route for hydrogen production. However, in order to not increase the amount of greenhouse gases, the utilization of alcohols derived from biomass is one of the promising solutions for the free-carbonaceous hydrogen production. Among bio-alcohols, ethanol is drawing attention due to its favorable features such as safety in storage, handling and transportation.

The phenomenon of electrochemical promotion of catalysis (EPOC), discovered by Stoukides and Vayenas, has recently shown to be an alternative way to promote and enhance catalytic reaction rates. This phenomenon has been shown to be an useful tool to modify the reversible oxidation state of a catalyst, to prevent poisoning effects or even to regenerate the catalyst from carbon deposition during the course of the catalytic reaction.

The application of the EPOC phenomenon in hydrogen production via ethanol steam reforming was studied in this work. For that purpose, different electrochemical catalysts based on Pt, Pd and Ni metals were prepared, characterized and tested under different reaction conditions. An electrically continuous metallic film was deposited by impregnation, spin-coating or sputtering on a K-βAl_2O_3 (Ionotec) solid electrolyte disc using Au as counter and reference electrodes.

A wide variety of experiments were carried out in different reaction conditions. As an example, Figure 1 a) shows a strong promotional effect induced during the negative polarization step. It allows to increase the hydrogen production rate in more than 3 times vs. the unpromoted catalyst surface (V_{WR}= 2V). The enhancement is attributed to an increase of intermediate chemisorbed species (ethoxy molecules) and its further dehydrogenation (Figure 1 b)).

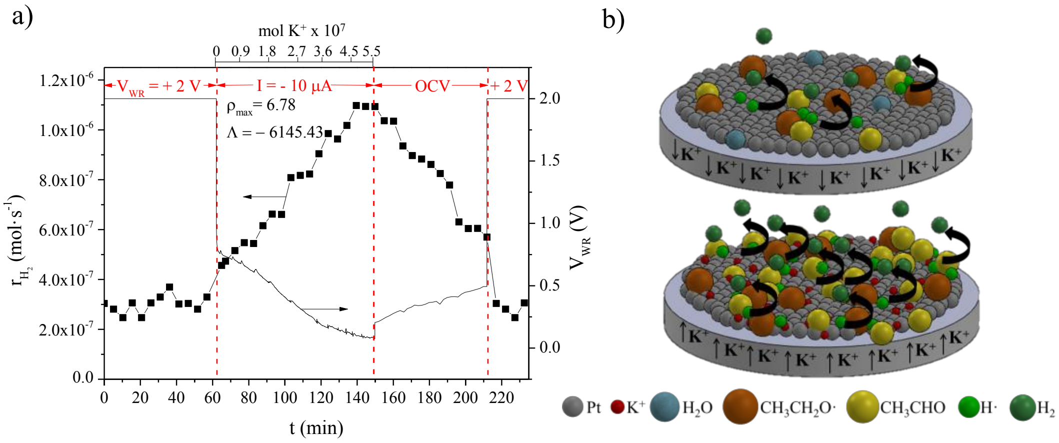

Figure 1. a) H_2 production rates upon different potentiostatic-galvanostatic transitions. EtOH/H_2O = 3%/9%, Ar balance. T = 500 ºC. Catalyst: impregnated Pt; b) Mechanism reaction scheme on the Pt catalyst surface under unpromoted and promoted states.

Nevertheless, under open circuit conditions, potassium ions were removed from the catalyst surface (thermal back-diffusion, sublimation…), decreasing H_2 production rate. The final application of 2 V forced the fast migration of K^+ promoters back to the solid electrolyte, leading to a strong decrease in the hydrogen production reaction until the unpromoted catalytic activity was again attained, achieving a complete reversible EPOC effect. This fact points out the fully reversible character of the observed promotional effect as well as the stability of the catalyst film during the different polarization steps, i.e., achieving the same catalytic activity at the beginning and at the end of the experiment.

Electrochromic "green" smart devices based on spiropyran-merocyanine system

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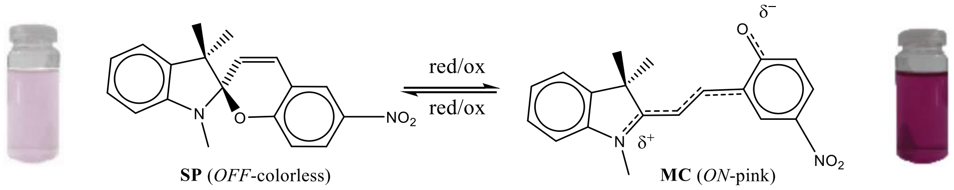
The design of smart molecular systems using green materials is a topic of great importance for the construction of novel and ecofriendly dynamic materials. Among them, their use in smart windows has emerged as a key technology to reduce energy consumption in buildings, which accounts for ca. 33% of global energy usage. Nowadays, most current commercial smart windows are made of metal oxide-based electrochromic coatings, [1] although their high fabrication costs prevent massive use. Alternatively, organic electrochromic compounds offer lower costs and facile processing, which together with their higher coloration, faster response and synthetic color tunability have prompted their application in smart windows. [2] One of the most promising families of halo-photo-electrochromic devices are spirobenzopyran derivatives due to its versatility to convert from its Spiro form (**SP**, closed isomer colorless, OFF state) to a Merocyanine form (**MC**, open isomer, pink color, ON state) through an isomerization mechanism upon irradiation at specific wavelengths. [3] Despite of their halo and photochromic properties are widely investigated, their electrochromic behavior is scarcely studied. [4] Hence, the aim of this study is to demonstrate that the mechanism of isomerization of the spirobenzopyran derivative 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole can undergo bidirectional switching by applying exclusively an electrical stimulus (Scheme 1).



Scheme 1.

The current work aims to establish the electrochemical properties and the electrochemical mechanism for the reversible conversion between the SP and MC states (OFF-ON). Besides, a new approach towards the development of (photo)electrochromic devices (ECDs) for the preparation of smart windows using solid state electrolytes based on green solvents and low-cost, high-throughput fabrication methods, such as screen-printing, is described.

Acknowledgments

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A facile protocol for alkaline electrolyte purification and the influence of Fe impurities on a Ni-Co oxide catalyst for the oxygen evolution reaction

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It is well established that Fe contaminations in the electrolyte can affect the catalyst performance of Ni-based materials for the oxygen evolution reaction (OER) [1]. Using a novel purification method for the complete removal of Fe traces from the electrolyte, with the use of a high surface area Nickel foam impregnated with a MoS_2 catalyst which served as the working electrode, we investigated the activation behavior and performance of a Ni-Co-based OER catalyst in both Fe-free and Fe-contaminated commercial KOH solution. For this purpose, we utilize an electrochemical flow cell (EFC) in combination with an Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) [2-3] (Fig. 1), in order to detect possible catalyst corrosion during the electrochemical measurements.

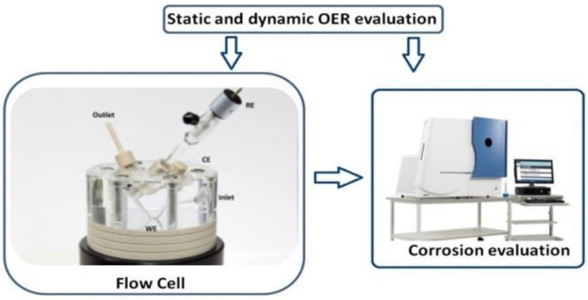

Fig. 1 Flow cell design and combination with ICP-OES for performance and corrosion evaluation of OER catalysts.

Interestingly, after 100CVs of catalyst activation between 0.7-1.6V_{RHE} and during a 2h chronopotentiometry stress test at 10mA/cm^2 the catalyst shows different behavior in Fe-contaminated and Fe-free solution (Fig. 2a). In the first case considerable Fe removal from the electrolyte (Fig. 2b red line) and subsequent incorporation on the catalyst was observed explaining the significant activity increase (Fig. 2a black lines), defined as the maximum current density at E=1.7V_{RHE}, contrary to what is expected during stress measurements. In the latter case significant activity decrease was observed during the stress test due to the lack of the Fe effect on the catalyst (Fig. 2a red lines). On a separate experiment (not shown here), during catalyst activation between the same potential range, a NiOOH structure was formed both in Fe-free and Fe-contaminated electrolyte, which has been previously identified as the active site for the OER. However, the activity of the catalyst is significantly decreased in Fe-free electrolyte indicating that the formation of the aforementioned NiOOH structure is irrelevant with the catalyst activation in the case of an Fe-free solution.

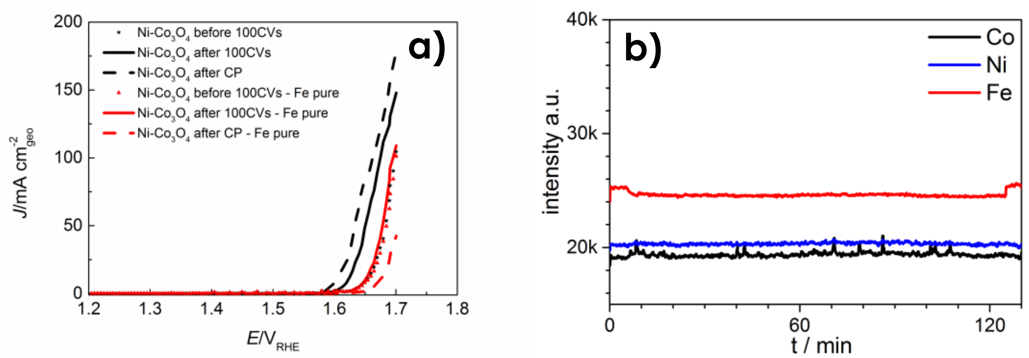

Fig. 2 a)Ni-Co_3O_4 activity comparison at different steps of the electrochemical investigation. b) ICP-OES profile of the Ni-Co_3O_4 catalyst during a 2h chronopotentiometry stress test at 10mA/cm^2, additionally revealing Fe removal from solution.

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A Bifunctional Ni-N-doped Carbon-Supported Copper Electrocatalyst for CO_2 Reduction

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Industrial catalysis relies in many cases on the use of bifunctional catalysts, consisting of supported metallic or bimetallic particles. In such systems, both the metal and the support catalyze different reaction steps. Yet in electrocatalysis, carbon is often used as carrier, but rather because of its relative inertness (among others), which of course rules out bifunctionality. Luckily, the chemistry of carbon is so rich that it can even be adapted - notably via nitrogen and metal-nitrogen doping – to the extent of catalyzing electrochemical reactions such as the oxygen reduction reaction and CO_2RR to CO.

Copper on the other hand is also unique because it can catalyze the reduction of CO_2 and CO to hydrocarbons. The major products formed on Cu NPs are methane and ethylene, with the C_1/C_2 ratio depending on the particle size, electrolyte and carbon's morphology. Interestingly, it is well known that a pathway to C_2 products exists which involves the dimerization of CO at low overpotentials. High faradaic efficiencies and current densities to ethylene, the major C_2 product of the pathway, have been obtained on Cu by virtue of this important insight and by optimizing the processing conditions. Ethylene production is feasible in part because on Cu, the onset potential of CO formation is lower than that of ethylene by several tenths of millivolts. This provides both the necessary higher local pH and surface CO concentration, because the conversion to CO produces two moles of OH^- per mole CO formed.

We argue that both local alkalinity and CO could be provided by a suitable CO generating support. While carbon black produces only up to 25% CO at low current densities in the interval [-1.1,-0.9]V vs. RHE, we have observed experimentally that in 0.1M $KHCO_3$, Ni-containing N-doped C reaches its maximum CO productivity (~ 0.78 mg cm^{-2} ; -2.7 mA $cm_{DL,norm}^{-2}$; > 90% FE_{CO}, See Figure) at the onset of ethylene production on Cu. Thus, we hypothesized that at the interface of Cu NPs and Ni-N-C the local environment will be more favorable for ethylene production compared to plain carbon black supported Cu NPs.

In this work, we discuss the conceptual framework for the application of a Ni-N-C supported Cu catalyst, both in batch and in CO_2 electrolyzers. Then, we proceed to the characterization of a Cu-Ni-N-C catalyst prepared through a chemical ammonia deposition-precipitation method. Finally, the electrochemical performance of the catalyst is closely examined. At -1.1V vs. RHE, a doubling of the C_2/C_1 ratio is observed, accompanied by an increase of the partial ethylene current density compared to the reference Cu-C material.

Is it synergy? A balancing act between metal and support? In what follows, these questions will be explored.

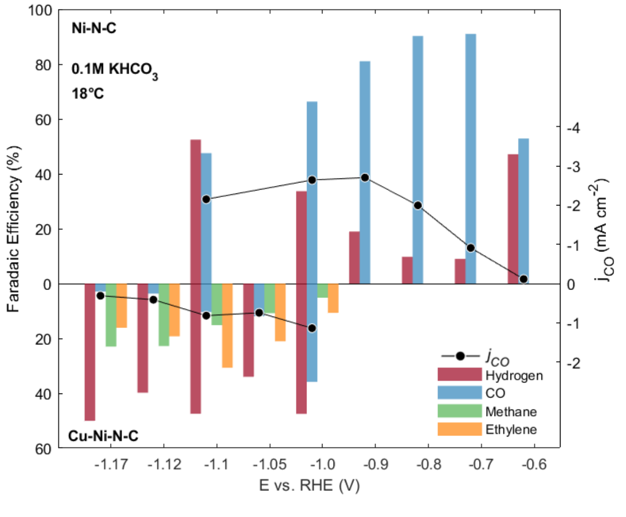

Figure 1 Faradaic Efficiency and partial CO current density as a function of electrode potential (iR-corrected) in 0.1M $KHCO_3$

Development of Gas Diffusion Electrodes for the non-aqueous Electrochemical CO_2 Reduction to Oxalic Acid

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Introduction

The electrochemical CO_2 reduction is increasingly getting attention as a means to store energy chemically (e.g. through methane, formate) and to produce value-added chemicals (e.g. CO, methanol, oxalic acid) from CO_2 waste streams. One challenge in the electrochemical reduction of carbon dioxide is the relatively low solubility of CO_2 in water of $c \approx 33\ \mathrm{mmol \cdot L^{-1}}$. The low local concentration of CO_2 reduces the achievable current densities of the reaction due to a mass transfer limitation using conventional electrodes. Once the limiting current density i_{limit} is exceeded, the observed side reaction is the water reduction in aqueous electrolytes (hydrogen evolution reaction, HER). Several possibilities have been proposed to increase $i_{\mathrm{limit.}}$ This includes the electrochemical reduction at high pressures, the use of alternative solvents and the application of gas diffusion electrodes (GDEs). GDEs are highly porous three-dimensional electrodes, in which a three-phase boundary, consisting of the solid electrode (catalyst and support), the liquid electrolyte and a gas phase, is formed during the electrochemical reaction [1]. As opposed to submerged electrodes, porous gas diffusion electrodes (GDEs) allow for the formation of the interfacial area between liquid and gas within the material of the electrode and thus can largely reduce mass transfer limitations and enhance the corresponding current densities [2]. While GDEs are already commercially applied (PEM fuel cells, chloralkali process) and are commonly applied in the electrochemical CO_2 reduction in aqueous media [3], there is still need for research exploring applications in non-aqueous solvents.

Electrochemical CO_2 reduction in non-aqueous media

While water is a favorable reaction medium in many aspects, the use of organic solvents has several advantages. With the application of organic solvents, the solubility of CO_2 can be increased drastically (ca. 5-fold for methanol, 10-fold for acetonitrile). In addition, the production of alternative, value-added reduction products such as oxalic acid (compare figure 1) are possible. In aprotic solvents, a direct C-C coupling through the dimerization of CO_2 radical anions are accessible [4]. Many organic solvents are less susceptible to a cathodic reduction compared to water, which provides a larger potential window while avoiding the, in aqueous electrolytes competing, HER.

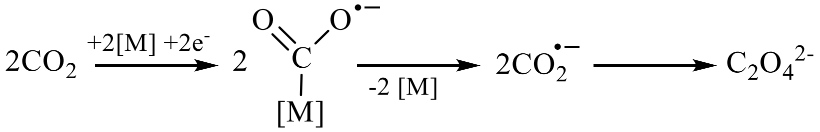

Figure 1: Proposed reaction mechanism for the formation of oxalate in aprotic solvents [4].

Challenges for the application of GDEs in non-aqueous media

- Investigation into the effect of different organic solvents on the catalyst activity, product selectivity.
- Screening of organic solvents based on their conductivity, CO_2 solubility, toxicity, viscosity.
- Adjustment of wetting properties of GDEs (hydrophobicity, wettability, porosity) for specific solvent requirements to ensure a stable three-phase boundary during the reaction to facilitate an ideal mass transport for carbon dioxide.
- Development of a compatible anode oxidation reaction.

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Analysis of discontinuous experiments on electrochemical ClO_2 generation

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Minimization of hazardous by-products during disinfection is a research subject sustained interest. Although active chlorine is a powerful disinfectant with good long-term activity, it is known for forming a large variety of chlorinated by-products. In contrast, chlorine dioxide is known for lower by-product formation, and can replace, at least partially, chlorine in many applications. Unfortunately, producing and handling chlorine dioxide on site is not comfortable. Therefore, easier methods are under research – possible to be applied in small-scale disinfection [1]. Whereas ozonation of chlorite solutions is still accompanied by a series of problems, electrolysis of diluted chlorite solutions shows very high efficiency close to 100% [2].

$$ClO_2^- \rightarrow ClO_2 + e^- \qquad (1)$$

Consequently, many discontinuous experiment were performed for better understanding and quantifying the process in mostly undivided electrochemical cells containing 100 – 160 ml chlorite solution at mM concentration level. Analysis was carried out using UV spectroscopy (*Analytic Jena*). Chlorite concentration, temperature, electrode material, pH, and current load were varied for finding optimized operating parameters and eliminating as best as possible parasitic reactions such as shown in reactions 2 and 3:

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O \qquad (2)$$
$$ClO_2^- + H_2O \rightarrow ClO_3^- + 2H^+ + 2e^- \qquad (3)$$

Also, other reactions seem possible.

Indeed, ion chromatography (*Metrohm*) showed low-intensive chlorate formation. Perchlorate was not found in any experiment.

It must be stated, that also in case of current disinfection practice, formation of chlorate, both for chlorine- and ClO_2-based disinfection, cannot be completely excluded and must be tolerated to small extent.

Furthermore, it could be found that the influence of parasitic reactions can be taken into account by a mathematical model. It fits the practical ClO_2 concentration vs. time curves with good accuracy.

Additional research activities are necessary for clarification electrochemical kinetic details.

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Sulfur-impregnated CeO_2-Sn nanowires as effective cathode for lithium-sulfur batteries

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In recent years sulfur has attracted attention in the world of electrochemistry, since the Li-S battery has a specific theoretical capacity of 1673 mAh g^{-1} and a theoretical energy density of 2500 Wh kg^{-1}, 10 times more than that of the current Li-ion battery [1]. The implications of Li-S inheriting the battery crown stretch beyond technology because of the materials used. Much publicized is the fact that this technology repurposes the elemental sulfur waste product generated by refining petroleum. While this will surely make the battery cheaper to produce, what effect could it have on the environment? If Li-S technology successfully replaces Li-ion, the battery industry will have heavy demand for sulfur. In addition, sulfur is an abundant, low-cost and non-toxic material. It is well known that during the discharge, elemental sulfur (S_8) is reduced to form Li_2S at approximately 2 V (vs. Li/Li^+) by forming polysulphides (PS) of the Li_2S_n type ($2 \leq n \leq 8$). However, there are several challenges to improve the sulfur electrochemical reactions, which is the bottleneck that is currently stalling the commercialization of this type of technology. Since of the electronic and ionic insulating nature of sulfur, the electrochemical response is poor and the access to the active material is low. In addition, the process of lithiation of sulfur-based materials, a volumetric expansion of approximately 22% is expected because of the difference in volumetric density between Li_2S and S_8 (1.67 gcm^{-3} vs. 2.03 gcm^{-3}, respectively). This can lead to ruptures in the cathode and thus to a lower cyclability, leading to a short life of the battery. Another important issue to avoid is the dissolution and diffusion of PS in the electrolyte (shuttle effect) which results in a mass loss of active material and leads to a constant decrease in the capacity of the battery and the contamination of the whole system.

Here, we report an effective sulfur-host material based on cerium oxide nanowires doped with a 10% of Sn, embed in a reduced graphene oxide matrix. In Figure 1 we show the galvanostatic charge/discharge profiles at different current densities performed on the composite prepared. The specific capacities were determinated considering the sulfur mass content obtained by TGA analysis. It is possible to see the well-definition of the typical plateaus corresponding to the discharge-charge processes as well as the excellent reversibility of the them even in the 500º cycle performed. The new material synthesized was also characterized by cyclic voltammetry, electrochemical impedance spectroscopy, charge/discharge cycling and rate capability performance.

Finally, we determinate the effect of the doping of the CeO_2 with different cations (Ni, Co, Mn) in the ability to retain the PS during the discharge/charge processes.

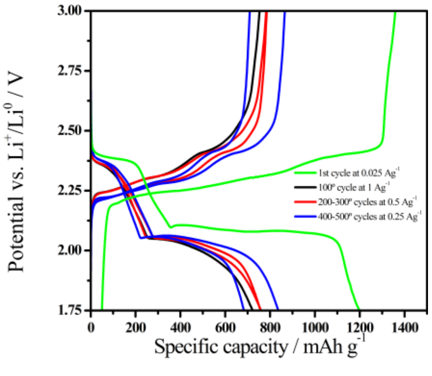

Figure 1. Galvanostatic charge/discharge profiles of the CeO_2-Sn/GOr/$S_{(30\%)}$ at different current densities

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Bi modified Pt and Pd nanostructures as outstanding catalysts for biomass (electro)conversion and hydrogen cogeneration

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The conversion in aqueous phase of alcohols, polyols and carbohydrates from biomass into value-added products has been extensively studied since the end of the twentieth century[1-4] All oxygenated species derived from bio-sourced polyols and carbohydrates are recognized to have important industrial interests[2,3], and selectively controlled oxidation reactions are therefore very promising ways to synthesize building blocks for, as examples, surfactants and polymers. To improve the selectivity, catalytic and electrocatalytic methods have then been developed. In this context, platinum-bismuth and palladium-bismuth materials have been extensively studied for several decennia owing to their high catalytic activity towards controlled electrooxidation reactions of alcohols, polyols and carbohydrates.[5,6,7] Several explanations were given to explain this unique catalytic behavior of PtBi and PdBi catalytic materials, such as the strong affinity of bismuth ad-atoms for oxygen species[8] and the bifunctional mechanism[9], the lower poisoning of PtBi catalysts by carbon monoxide (CO_{Ads})[10] or strongly bound intermediates occupying multiple surface sites[11], etc.

The understanding of the PtBi and PdBi catalytic behaviors for electrooxidation reactions is therefore of paramount importance for their optimization in terms of conversion yield, selectivity and efficiency. To achieve this, it is necessary to know the exact structure of the catalytic materials. This can be achieved by modeling the nucleation and growth process of PtBi and PdBi nanoparticles to obtain information on the final structure and by comparing these results with experimental ones obtained from a comprehensive characterization of the catalytic materials. Such information could help to design the best material in terms of composition and structure. In this contribution, we will use molecular dynamics simulations to study the growth of Pt_xBi_{10-x} and Pd_xBi_{10-x} clusters under conditions close to those encountered in classical low temperature chemical or physical synthesis methods, such as the water-in-oil route or plasma sputtering route, respectively. The simulation results will be compared with physicochemical characterizations of synthesized Pt_xBi_{10-x} and Pd_xBi_{10-x} ($x = 0$, 0.1 and 0.2) materials. The electrocatalytic behaviors, in terms of activity and selectivity, of the Pt_xBi_{10-x} and Pd_xBi_{10-x} will be presented, and a a discussion on the relationship between composition/structure of the Pt_xBi_{10-x} and Pd_xBi_{10-x} catalytic materials and activity/selectivity for glycerol and glucose electro-oxidation will be proposed.

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Electrocatalytic Nanoreactors of Mixed-Metal-Oxide Supported Noble Metal Particles: Enhancement of Oxidation of Simple Organic Fuels

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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.

Hybrid Inorganic Materials of Defined Structure and Catalytic Activity for (Photo)Electrochemical Energy Conversion, Generation of Fuels and Charge Storage

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Our research interests aim at establishing structure/property relations leading to rational designs of functionalized materials for efficient electrocatalysis and electrochemical energy conversion and storage. Graphene is, in principle, a promising material for consideration as component (support, active site) of electrocatalytic materials, particularly with respect to reduction of oxygen, an electrode reaction of importance to low-temperature fuel cell technology. Different concepts of utilization, including nanostructuring, doping, admixing, preconditioning, modification or functionalization of various graphene-based systems for catalytic electroreduction of oxygen are elucidated, as well as important strategies to enhance the systems' overall activity and stability are discussed.

There has been growing interest in the electrochemical reduction of carbon dioxide, a potent greenhouse gas and a contributor to global climate change. Given the fact that the CO_2 molecule is very stable, its electroreduction processes are characterized by large overpotentials. To optimize the hydrogenation-type electrocatalytic approach, we have proposed to utilize nanostructured metallic centers (e.g. Cu, Pd or Ru) in a form of highly dispersed and reactive nanoparticles generated within supramolecular network of various polytungstate systems. Among important issues are the mutual completion between hydrogen evolution and carbon dioxide reduction and specific interactions between coordinating centers and metallic sites. Upon incorporation or modification of various noble metal nanostructures with ultra-thin polyoxometallate films, highly reactive and selective systems not only toward reductions of carbon dioxide and oxygen but also oxidations of simple organic fuels (formic acid, methanol or ethanol) have been obtained. Another possibility to enhance electrocatlytic reactions is to explore direct transformation of solar energy to chemical energy using transition metal oxide semiconductor (WO_3, Cu_2O) materials (e.g. toward water splitting or photoelectrochemical reduction of carbon dioxide mostly to methanol).

The potential materials for solid-state electrochemical applications including charge storage 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. The emphasis is on the elements of dynamics for the efficient delivery of charge and on reactivity of the 'redox conducting' (certain polyoxometallates or metal oxide) materials. The effective (apparent) diffusional mechanism is critical to the success of effective charging-discharging in solid or semi-solid state.

Implications of Poor Mass Transport on Selectivity, Activity and Efficiency of High Surface Area CO_2 Reduction Electrocatalysts

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Short term impacts of climate change may not be catastrophic but certainly will be expensive. This most likely will lead to transition to renewable electricity sources sooner than anticipated. Although batteries are an excellent platform for electricity storage, there will be need of high energy density fuels for not only air transport vehicles ,heavy duty ships and trucks but also seasonal storage. Room temperature electrochemical conversion of CO_2 can directly utilize electricity and protons by passing the need of energy transformation and hydrogen production required for most of the thermo-catalytic routes.

Electrochemical CO_2 reduction is under heavy investigation over the last decade which lead to tremendous improvements in understanding of the reaction mechanisms and performance of the electrocatalysts. These improvements are mostly result of the deployment of high surface area nanostructured electrodes and improved theoretical models. Currently, there are nearly countless number of papers producing selectively CO, ethylene and formic acid. In this talk, we will discuss that whether high selectivity on these elaborate structures is fact or fiction. We will present the quantitative measurements and analysis of near surface concentrations of molecules and adsorbed reaction intermediates by using in-situ surface enhanced infrared absorption spectroscopy (SEIRAS) on Cu electrodes(Figure 1a). The results are supported and compared by a computational model that predicts the surface concentrations of molecules participating in both electrocatalytic and homogenous reactions. Online GC analysis, combined with in-situ SEIRAS results strongly suggest that the local environment has a large impact on the selectivity of the Cu electrocatalyst. The serious implications of the poor mass transport on the overall energy efficiency, kinetic analysis and mechanistic interpretation of the CO_2 reduction electrocatalyst will be presented and discussed.

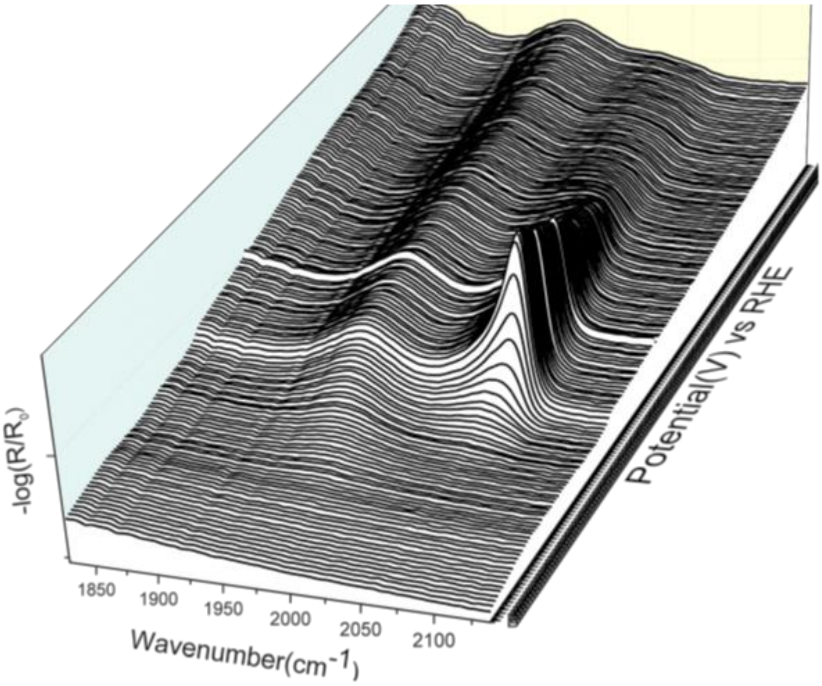

Figure 1: Potential dependence of CO adsorption onto copper electrode.

Highly effective and reusable sulfonated pentablock copolymer nanocomposites for water purification applications

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Hybrid polymeric membranes have been prepared to be used as adsorbent or photocatalyst for dyes (Methyl Orange-MO and Methylene Blue-MB) removal from water [1-2]. The investigated polymeric material is Nexar^{TM} polymer [3], a sulfonated pentablock copolymer (s-PBC), whose structure is formed by tert-butyl styrene, hydrogenated isoprene, sulfonated styrene, hydrogenated isoprene, tert-butyl styrene (tBS-HI-SS-HI-tBS), characterized by high hydrophilicity and a structure for which they are stable in water but they can adsorb it. Graphene oxide (GO), and photocatalysts as titania or bismuth oxide have been added to the polymers to increase their mechanical and thermal stability, their adsorption efficiency and to confer them a photocatalytic activity [3-4]. All the investigated materials showed more than 90% efficiency in removing MB only by absorption. For what concearn MO, Nexar GO composite showed the same efficiency but less toxicity in dye photodegradation with respect to the composite with titania. Furthermore, in the case of the composite with bismuth oxide, the formation of the Bi/Bi_2O_3 mixture confers to the polymer a photocatalytic activity under visible light as shown for MO degradation [4].

For all the investigated materials, it has been confirmed that the use of polymeric nanocomposites is to be preferred with respect to nanomaterials directly dispersed in water; since these can be easily removed at the end of the process wihout any dispersion of particles in the enviroment and they can be regenerated and used again. The comparison between the activity of nanomaterials dispersed in water with the activity of the same amount of nanomaterial but dispersed in the polymeric matrix also evidenced a synergic effect of the polymer in increasing the degradation activity of the filler [1-4].

The hypothesis of using sulfonated pentablock copolymer nanocomposites in water purification application is finally confirmed.

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Electrochemical tuning of CO_2 reactivity in ionic liquids: from oxalate to carboxylation products

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Global warming due to the emission of greenhouse gases, especially carbon dioxide (CO_2), has a significant effect on the climate change and has become a widespread concern in the recent years. Carbon capture, utilization, and sequestration (CCUS) strategy appears to be effective in decreasing the carbon dioxide level in the atmosphere[1]. Thus, the ability to transform this gas into valuable commodity chemicals through the construction of C-C bonds is a very attractive strategy. Despite a great progress in this field, there are still major limitations in commercializing CO_2 capture and valorization methods. High capital costs of for the CO_2 capture, low absorption and desorption rates (which require large facilities), solvent losses due to evaporation, and the use of corrosive and toxic solvents are among main obstructions.

Recently, CO_2 capture and valorization with ionic liquids (ILs) has appreciably attracted researchers' attention. The properties of ILs such as negligible vapor pressure and their affinity to capture the CO_2 molecules make them a feasible alternative for currently available solvents[2–6]. Moreover, ILs have a very attractive properties from an electrochemical point of view, moderate to high conductivities and large electrochemical windows. In the current communication, it will be analyzed the influence of the potential applied, the nature of the cathode and the electrolyte using different organic mediators, such as nitro and cyano aromatic derivatives, to promote the electrochemical activation of CO_2. Hence, the products obtained from the electroreduction of CO_2 can be easily tune from oxalate to carboxylation products, after the reduction of organic mediators containing good leaving groups in function of the potential applied. It is worthy to highlight that carboxylic acids and their derivatives have wide application in pharmaceuticals and advanced materials[7], and can be potentially easily through a carboxylation reaction between a carbon nucleophile and reaction of CO_2.

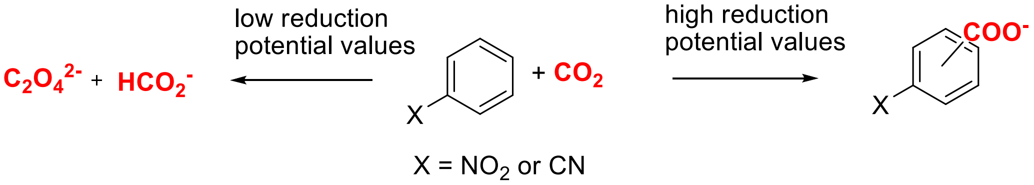

Figure 1

Acknowledgments

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Understanding Electrolyte Effects on Magnesium Electrode Plating/Stripping

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Recently, there has been significant research into magnesium batteries due to their potential as a beyond Li-ion technology. This is due to a number of beneficial properties of the Mg negative electrode, including high volumetric capacity, twice that of metallic Li, (Figure 1) and lack of dendritic growth on cycling.[1,2] However, current electrolytes are insufficiently stable to the Mg electrode, leading to reduction of the electrolyte and formation of an interphase, which is detrimental to performance.[3,4] The electrode performance will also be affected by the electrochemical mechanism of Mg plating/stripping and the solvation environment of the Mg^{2+} ion. To advance the development of Mg negative electrodes, it is crucial to understand both the fundamental electrochemistry occurring during cycling of Mg electrodes, and how the interphase forms.

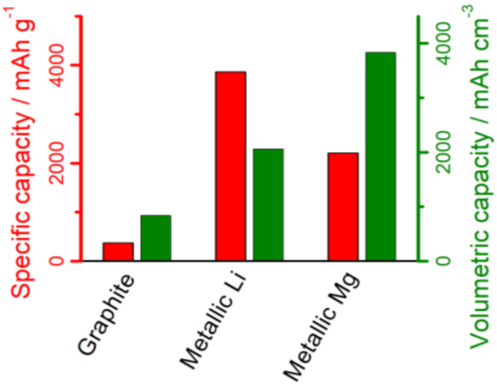

Figure 1: Capacities of various battery anodes

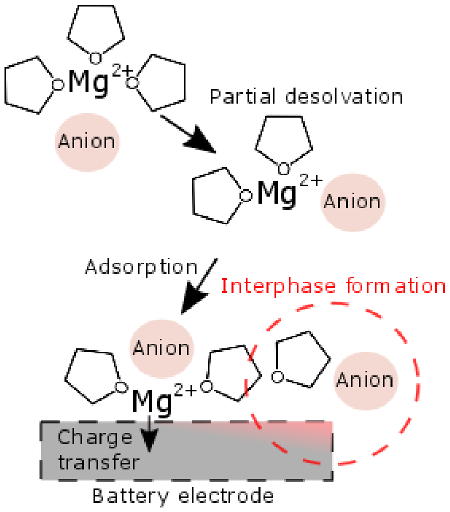

Figure 2: Schematic of the simplified processes occurring at Mg battery interfaces.

Various fundamental steps are involved in the plating of Mg^{2+}, including partial desolvation and adsorption of Mg^{2+} on the electrode surface, before charge transfer takes place (Figure 2).[5] Here, we discuss the influence of the salt anion and solvent on these fundamental steps, using Mg^{2+} and Cu^{2+} salts to understand plating of divalent metal cations. Replacing Mg with Cu allowed the desolvation and adsorption processes to be studied in the absence of an interphase. This was compared to Mg plating, where the interphase affects the fundamental steps, particularly adsorption of Mg^{2+} on the electrode surface. The results of this work will inform the development of future electrolytes of the properties required to improve electrochemical performance and facilitate efficient Mg plating/stripping.

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Tracking and Modeling of PtCu Nanoalloy Dealloying at the Atomic-Scale: Spot the Difference "Game" at the Atomic Level

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Nanoparticles catalytic performance is determined by exact and specific atomic structure, composition and morphology of its surface and near-surface area: also referred to as the structure-activity relationship. The materials nanoscale architecture is tailored by many parameters of the nanoparticle synthesis, post-synthesis annealing and activation (dealloying) steps. Therefore predicting, understanding and finally designing of nanocrystals structuring processes at the atomic-scale is far from straightforward. Much progress has been achieved with respect to the synthesis procedure of the so-called as-synthesized nanoparticles. However, when particles get exposed to real conditions and a process of activation, such as dealloying that is actually forming the final active centers of electrocatalysts, much is still to be learned. As-synthesized material and activated material usually differ significantly, especially in the case of Pt-alloys where selective leaching of the less noble metal occurs.[1] Advancements in the scanning transmission electron microscopy together with groundbreaking identical location approach have made it possible, for the first time, to track the evolution of the same individual partially ordered $PtCu_3$ shaped nanocrystals during materials processing. Specifically, Figure 1 exemplifies the development of a polyhedron containing six {100}, 12 {110} and eight {111} facets at atomic-scale resolution before and after dealloying, thus providing unprecedented insights into this critical processing step. It is shown that anisotropic facet etching is occurring resulting in unexpected disappearance of the most stable {111} plane at the expense of the growth of a less stable {110} plane (Fig. 1). Such atomic-scale dealloying mechanism is supported by Monte-Carlo simulations [1] and online dissolution measurements. Our novel advanced multidisciplinary approach paves the way to the atomic-scale understanding of the dynamic structural and morphological evolution of nanostructures and thus deeper understanding of the structure-stability relationship. Combined with other nanoscale events, such detailed observations on atomic scale can advance our understanding of catalysts dealloying phenomena as one of the perspective top-down nanofabrication and activation treatment methods.

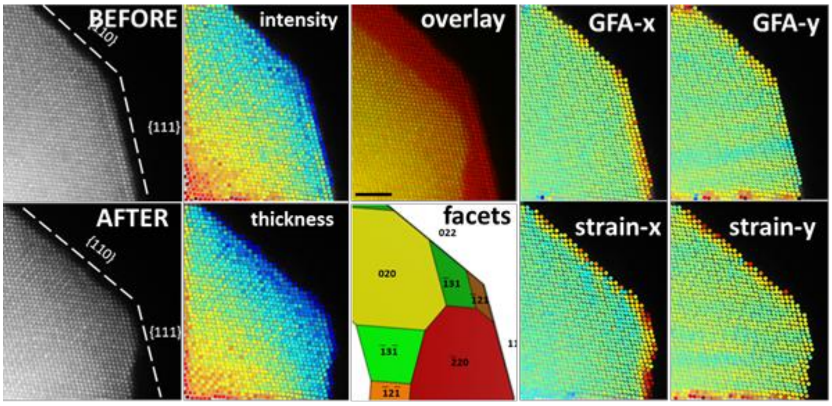

Figure 1: STEM ADF images of PtCu/C before and after *dealloying*. Next are intensity (thickness) profiles, overlayed STEM ADF images and below model crystal morphology and finally geometric phase analysis (GPA) of strain.

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Electrochemical promotion of CO_2 hydrogenation over free standing and supported Ru nanoparticles deposited on proton conductor electrolyte

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In this study we investigate the reaction of the carbon dioxide (CO_2) hydrogenation through the Electrochemical Promotion of Catalysis (EPOC) effect [1]. CO_2 is the most abundant exhaust gas in the atmosphere, it is almost related to any anthropogenic activity and contributes strongly to the greenhouse effect [2]. We have all been faced with global warming over the last few years, which is manifested globally through extreme weather conditions. A global aim is therefore to reduce, capture and exploit CO_2, thus leading to a more friendly environment for everyone. In recent years, particular emphasis has been placed on the conversion of CO_2 to useful chemicals and fuels, such as methane or synthesis gas (CO and H_2) to produce higher hydrocarbons through the Fischer-Tropsch reaction [2,3]. This study combines this idea with the EPOC effect in order to enhance the catalytic rate of CO_2 hydrogenation, but also to change the selectivity of the reaction depending on the desired final product. This effect is based on the modification of the work function of a metal, which also serves as working electrode in the EPOC experiments, leading to an alteration in the chemisorption bond strength of the reactants [1,4-7]. This effect is observed when small currents or potentials are applied to a catalyst/working electrode deposited on a solid electrolyte [1]. In the present study, free standing Ru nanoparticles, supported Ru nanoparticles on Co_3O_4, as well as pure Co_3O_4 semiconductor were used. These three catalytic systems exhibit significant differences in both their product selectivity and their electrochemical behavior. The use of Co_3O_4 as the catalyst support for metal nanoparticles has been very recently shown [8] to lead to successful electrochemical promotion of nanodispersed metal catalyst particles for methane oxidation and appears, on the basis of preliminary kinetic data, to be also very promising for electropromoting the CO_2 hydrogenation reaction.

ACKNOWLEDGMENTS

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New concept and design for the scale up of electrochemical promotion of catalysis via triode operation of fuel cells

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The susceptibility of state of the art Pt-based carbon supported catalysts to CO poisoning is a well-known major problem of the low temperature fuel cells. Up to a few ppm of CO in the anode feed leads to degradation of the anodic electrode and consequently to a severe drop of the cell performance, since CO is strongly absorbed on the Pt-based electrodes and blocks any further H_2 adsorption [1]. This phenomenon is hard to be avoided as H_2 which is the most often used fuel in low temperature fuel cells applications is mainly produced by reforming processes of hydrocarbons or liquid alcohols, resulting in significant amounts of CO in the product stream.

Triode operation of fuel cells is an alternative approach for enhancing fuel cells power output under severe poisoning conditions which lead to high overpotentials. This innovation developed in 2004, applied firstly on SOFCs and later on PEMFCs [2]. In a triode fuel cell in addition to the anode and the cathode, there is a third auxiliary electrode in contact with the solid electrolyte (e.g. polymer electrolyte membrane in the case of PEMFCs). This electrode forms together with the cathode, a second (auxiliary) electric circuit operating in parallel with the conventional main circuit of the fuel cell. The auxiliary circuit runs in the electrolytic mode, pumping ions (i.e. protons in the case of a PEMFC) from the cathode to the auxiliary electrode. In this way, imposition of a potential difference between the auxiliary electrode and the cathode permits the primary circuit of the fuel cell to operate under previously inaccessible, i.e larger than 1.23 V, anode – cathode potentials. This ability introduces a new controllable variable in fuel cell operation and can lead to significant reduction of the power output of a fuel cell, and can also decrease overpotential losses at the anode and cathode electrodes, leading to an enhancement of the overall thermodynamic efficiency. It can also affect the rate and selectivity of catalytic reactions when a reaction gas mixture is fed at the anode and cathode. Two parameters are used to quantify the performance of a triode cell, i.e. the power enhancement ratio, ρ (= P_{fc} / P_{fc}^{o}) and the power gain ratio Λ (= $\Delta P_{fc} / P_{aux}$), where P_{fc}, P_{fc}^{o} is the power in triode and conventional mode respectively, P_{aux} ,is the power sacrificed in the auxiliary circuit and ΔP_{fc} the increase in the fuel cell power output. In previous study, mathematical model was developed to describe the triode operation and the key operation parameters [3]. The same type of cells can be used to carry out electrochemically promoted catalytic reactions (as pre-reactor for CO diminution and CO2 production via the WGS reaction).

In the present study, the triode fuel cell performance has been investigated under various fuel cell temperatures (under fully hydrated membrane) for various CO poisoning conditions at the anode. Results have shown that increasing temperature during pure hydrogen anode feed, triode operation is more pronounced, while the opposite behavior is observed under CO-poisoning conditions.

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Towards a sustainable technology for H_2 production: Direct lignin electrolysis in a continuous-flow PEM reactor

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1. INTRODUCTION

To this date it is well known that H_2 is an excellent energy carrier, which is expected to play a key role in near-future energy systems. Water electrolysis has gained much attention lately, since it allows to produce pure H_2 quick and conveniently. Its main drawback is related to its high electrical energy requirements, which makes the process economically unattractive [1]. In this sense, the electrolysis of organic molecules (methanol, ethanol [2], bioethanol [3], etc.) allows to produce pure H_2 with much lower power demands. Lignin is one of the most abundant bio-polymers in nature. Nowadays, about 50 million tons of lignin are produced annually as a waste stream of the Kraft pulping industry for cellulose production [4]. In this study we propose, for the very first time in literature, to perform the direct electrolysis of lignin-based solutions in Polymer Electrolyte Membrane reactors under continuous operation mode to produce pure H_2.

2. RESULTS AND DISCUSSION

Figure 1a shows a basic scheme for the PEM electrolysis operation. Briefly, considering the alkaline membrane as a pure OH^- conductor, the application of positive polarizations leads to the electro-reduction of H_2O in the cathode, with the subsequent production of pure H_2 and OH^- ($H_2O + 1\ e^- \rightarrow OH^- + ½\ H_2$). The OH^- ions will then migrate, through the polymeric membrane, to the anode, leading to the electro-oxidation of the lignin ($\text{Lignin} + OH^- \rightarrow \text{Lignin-ox} + e^-$), and therefore to the production of lignin oxidation products (denoted as "lignin-ox"). When water is introduced in the anode instead of lignin, O_2 evolution takes place ($2\ OH^- \rightarrow ½\ O_2 + H_2O + 2e^-$).

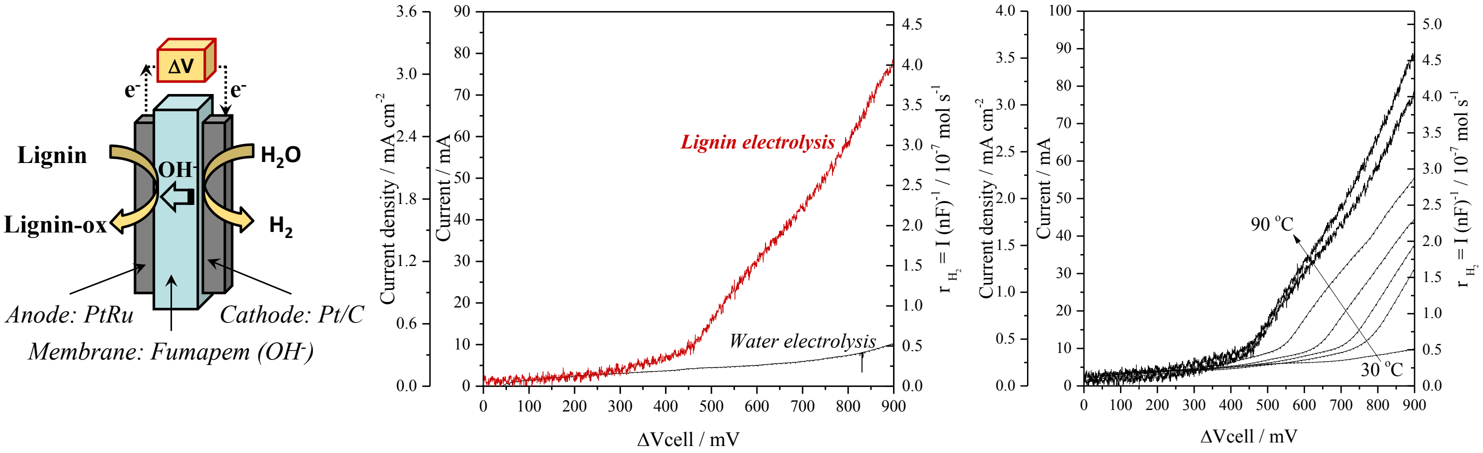

Fig 1. a) Scheme of the overall lignin electrolysis process in a PEM reactor working in continuous-flow mode; b) Influence of the presence of lignin in the anodic compartment at 80 °C; c) Influence of the reaction temperature during lignin electrolysis. Anode: Lignin 10 g L^{-1} in NaOH 1 M, 2.5 ml/min (lignin electrolysis), or NaOH 1 M, 2.5 ml/min (water electrolysis). Cathode: NaOH 1 M, 2.5 ml/min.

The comparison between water and lignin electrolysis (Fig. 1b) clearly demonstrates for the very first time that the addition of lignin to the anode leads to a significant production of pure H_2 in the cathode. These results can be explained based on the lignin electro-oxidation at the anode, which allows to dramatically decrease the energy requirements compared to water electrolysis. In addition, the influence of the reaction temperature was studied (Fig. 1c), demonstrating that an increase of the reaction temperature gives rise to an enhanced production of pure H_2. It could be mainly attributed to the enhanced kinetics of the electrochemical reactions involved in the electrolysis process.

3. CONCLUSIONS

In this study we have demonstrated, for the first time, the possibility to advance a step forward for the development of a sustainable technology (electrolysis) towards the valorization of biomass-derived resources (lignin waste) for the production of pure H_2.

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Bismuth-Tin Nanoparticles as Electrocatalysts for the Electrochemical Denitrification Process

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Anthropogenic factors are responsible of serious imbalances in the natural nitrogen cycle. Consequently, nitrates (NO_3^-) concentration in surface and ground waters has augmented considerably during the last decades, which implies negative environmental impacts like eutrophication and a risk for human health in drinking water. NO_3^- can be reduced to nitrite (NO_2^-) in living organisms, which may cause methemoglobinemia, liver damage or even cancer. Accordingly, the legislation of different countries limits considerably the NO_3^- content in drinking water [1] and, therefore, efficient denitrification strategies are needed.

In this regard, electrochemical denitrification is a very promising technique to remove NO_3^-, when compared to other available technologies like reverse osmosis or ion exchange membranes, due to its advantages: no chemicals addition, no sludge production, environmental compatibility and inexpensive infrastructure. The electroreduction of NO_3^- pursuits its complete conversion to innocuous N_2 gas but, unfortunately, other non-desired secondary products such as N_xO_y, NH_2OH, NH_3 and NH_2NH_2 are also possible. According to recent studies, the most active and selective electrocatalysts reported for this process are combinations of Pd or Pt with at least one more metal (PdSn, PtCu, PtSnAu…) but they are not cost-effective for practical applications [1, 2]. On the other hand, cheap metals like tin (Sn) and bismuth (Bi) have also shown interesting rates of reduction and selectivity to N_2 [3].

In this contribution, the electrocatalytic performance of Bi-Sn nanoparticles was evaluated for the electrochemical denitrification process. For that, 10-12 nm Bi, Sn and BiSn (Bi:Sn ratios 80:20, 60:40, 40:60, and 20:80) nanoparticles were synthesised and supported on a carbon black using a simple, fast and scalable method at room temperature. The prepared materials were physiochemically characterised by TEM, XRD and XPS and, subsequently, air-brushed onto a Toray Carbon Paper. Voltammetric studies and electrolysis experiments were carried out in order to find the most active nanoparticulated material towards the complete removal of NO_3^-. The results obtained indicate that the $Bi_{60}Sn_{40}$ electrocatalyst is the most convenient one for this process. Interestingly, in terms of selectivity, the analysis of the products both in solution (using spectrophotometric methods) and in the gas phase (by gas chromatography coupled to a thermal conductivity detector), shows that N_2 is the main product of the electrochemical denitrification process.

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Kinetic Scaling Relations: A Novel Approach Exemplified with the Oxygen Evolution Reaction over Transition Metal Oxides

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Renewable energy needs to be stored to match demand. The obvious choice is electrochemical water splitting to produce the energy vector H_2, where the sluggish oxygen evolution reaction (OER) at the anode limits the efficiency of this process **[1]**. Due to its high stability and reasonable activity in the OER, IrO_2-based anodes are considered as benchmark in acidic water electrolysis. However, even for single-crystalline $IrO_2(110)$ anode the kinetic bottleneck has not been resolved, thereby hampering a rational search for alternative materials. Here, we apply the approach of constructing the free energy diagram along the reaction coordinate **[2,3]** in order to identify the rate determining step (rds) in the OER over an $IrO_2(110)$ model anode in acidic media. The free energy diagram as function of the applied electrode potential is compiled on the basis of experimental Tafel plots and ab initio Pourbaix diagrams from the literature.

The widely accepted reaction mechanism for the OER in acidic media consists of four proton-coupled electron transfers, in which the OH, O and OOH adsorbate need to be stabilized on the electrocatalyst's surface **[4]**. The formation of the OOH adsorbate is widely accepted to govern the performance of transition metal oxides in the OER, which has been proven for the case of $RuO_2(110)$ **[2,5,6]**. However, quite in contrast to common perception, the free energy diagram along the reaction coordinate ultimately reveals that the rds for the OER over $IrO_2(110)$ at high overpotentials ($\eta_{OER} > 0.40$ V) is identified with the decomposition of the OOH adsorbate under the formation of O_2 **[7]**.

In order to understand the different OER kinetics of $RuO_2(110)$ and $IrO_2(110)$, we establish a novel approach, in which the free energy diagram in the high overpotential regime ($\eta_{OER} > 0.40$ V) is conjoined with the concept of linear scaling relationships based on ab initio thermodynamics. This procedure facilitates us to derive *kinetic scaling relations*, which allow predicting the kinetic bottleneck (rds) of the OER over any transition metal oxide electrocatalyst in the high overpotential regime by a single descriptor, namely the free formation energy of the oxygen adsorbate on the anode surface **[7]**. It turns out that either the formation of the OOH adsorbate constitutes the rds (strong O-binding) or, for weakly bound surface oxygen, the decomposition of the OOH adsorbate is reconciled as rds in the high overpotential regime, thereby explaining the different OER kinetics for $RuO_2(110)$ and $IrO_2(110)$.

So far, linear scaling relationships have been used to construct Volcano plots, in which researchers discussed the "activity" in terms of the thermodynamic overpotential **[8]** as function of a thermodynamic binding energy (descriptor), such as the free formation energy of oxygen **[1,4,8]**. However, Volcano relations fail in certain cases to describe the activity trends of electrocatalysts correctly **[7,9]**. The combination of linear scaling relationships with the free energy diagram approach in terms of *kinetic scaling relations* does not reveal direct information on the activity of the electrocatalyst, but it allows determining the kinetic bottleneck in the high overpotential regime based on a single binding energy, which is accessible to simple ab initio thermodynamics calculations or to experimental cyclic voltammetry. This correlation augments computational researchers in materials screening to investigate directly how the transition states of the rate-determining OOH formation or OOH decomposition within oxygen electrocatalysis can be stabilized in order to increase the catalytic activity.

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Cathodic disintegration as an easily scalable method for the production of Sn and Pb based catalysts for CO_2 reduction

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The electrocatalytic conversion of CO_2 is of considerable interest nowadays due to the possibility of using energy from renewable sources to convert this ubiquitous and rather inert waste product to value added chemicals and fuels [1]. Among the possible products yielded from this reaction, formate is of particular interest because of its possible use as a liquid fuel precursor and hydrogen carrier for fuel cells applications [2], the pre-existing market as a preservative in animal feed and production of leather and the low amount of electrons needed for its conversion from CO_2. Typically, metals such as Sn, In, Pb, Hg and Bi show better catalytic activities to convert CO_2 into formate [3] and best results are obtained in Gas diffusion electrode (GDE) configurations. GDEs allow to overcome problems such as mass transport limitations arising from the low solubility of CO_2, that is a common drawback to achieve high reaction yields at high current densities.

In this work, we study the process of disintegration of Sn and Pb cathodes under cathodic polarization [4,5] to quickly and cheaply produce catalysts that can be readily transferred on a GDE as a coating, to catalyze the electrochemical conversion of CO_2 to formate. The disintegration reaction is thought to proceed through the destruction of the cathode under conditions of intense hydrogen evolution and is able to disintegrate a $Sn_{50}Pb_{50}$ alloy retaining the composition.
The catalysts produced with this method were tested on a 10 cm^2 GDE and perform well in industrial conditions, with Sn being the best one at an applied potential of -2.6V vs Ag/AgCl with a partial current density towards formate of 1.44 kA/m^2 and a faradaic yield of about 60%.

These findings open up the possibility to quickly produce particulated catalysts (with high surface area and easily transferrable to GDEs) and screen Sn-Pb alloys of different compositions (and/or other materials and alloys) potentially yielding good performing catalysts for the reaction of interest. Moreover, understanding the dynamics of the reaction by studying it further could allow for the tuning of important parameters such as particle size distribution and orientation.

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Electrocatalytic synthesis of organic carbonates

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Many industrial chemical processes involve a high-energy demand (often still derived from fossil fuels), toxic reactants, and the production of high amounts of waste. Therefore, the development of more efficient, less hazardous technologies, based on renewable energies, has become one of the most challenging topics for chemical synthesis. For achieving these goals, the combination of catalysis with electrochemical methods, that is, electrocatalysis, can play a very important role [1]. With electrochemical methods, toxic and dangerous chemicals can be replaced with clean electrons, the efficiency and selectivity of the reactions can be tuned by choosing the applied potential, and more importantly, the energy used can come from renewable sources like wind or solar.

Organic carbonates are important chemical building blocks used in many industrial synthesis reactions, such as synthesis of polycarbonates. [2, 3] Because of the high demand of these compounds, the development of new sustainable methodologies (direct synthesis, less waste reagents, green energy) is much desired, especially in a moment that electrochemical production processes using gas diffusion electrodes are already established in chemical industry, as for example, the oxygen-depolarized cathodes in HCl electrolysis [4].

In this work, we report a fundamental mechanistic study of the electrochemical oxidative carbonylation of methanol and phenol with CO for the synthesis of dimethyl carbonate (DMC) and diphenyl carbonate (DPC), respectively. In-situ spectroelectrochemical techniques were applied to these electrosynthesis reactions in order to reveal intermediates and to shed light into the reaction mechanism. Fourier transformed infrared spectroscopy (FTIR) was used with different electrode materials (Au, Pd, Pt, and Ag) to assess the effect of the electrode material on the reaction and the dependence of products and intermediates on the applied potentials. For the first time, the reactions were shown to take place on the metallic catalysts without need of oxidized metals or additives. Moreover, it was observed that the DMC is only formed when the electrode can decompose/oxidize MeOH to form (adsorbed) methoxy groups that can further react with CO to dimethyl carbonate. Furthermore, the electrode needs to adsorb CO not too strongly; otherwise, further reaction will be inhibited because of surface poisoning by CO [5]. In the case of DPC, it can be obtained on Au electrodes at low overpotentials (0.5 V vs Ag/AgCl) through an indirect electrochemical path where DMC is synthesized and readily converted to DPC in an "electro-transesterification" step, at room temperature [6].

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New Understandings on the Mechanism of the Oxygen Reduction Reaction on Pt Single Crystal Electrodes

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The complete understanding of the oxygen reduction reaction (ORR) is crucial for the development of energy conversion technologies such as fuel cells and lithium-air batteries. However, despite many experimental and theoretical studies performed during the last years contributed to expand the knowledge about this reaction, its detailed mechanism has not been totally elucidated yet. It was demonstrated that H_2O_2 is a reaction intermediate under certain conditions, and therefore studies of the hydrogen peroxide reduction and oxidation reactions (HPRR/HPOR) are important for a better understanding of the ORR.

In this work we summarize the most recent advances in the understanding of the ORR and HPRR mechanisms on well-defined Pt surfaces. Firstly, the ORR was studied on different Pt single crystal electrodes at different pH values in the absence of specific anion adsorption [1]. It was observed that the limiting current density decreases as the pH is increased from 3 to 6. This behaviour is not observed for the HPRR [2] and therefore other intermediate different from H_2O_2 was proposed to be formed [1]. The study of the ORR in presence of Br^- anions also pointed out the existence of this other intermediate, especially for neutral pH values since there is no inhibition for the ORR while the HPRR is considerably inhibited by adsorbed bromide [3]. The ionic strength of the solution also has different effects towards the ORR and the HPRR [3]. Recently, $OOH^{\bullet}$ species has been identified during the ORR by Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy (SHINERS) technique [4]. In light of these results, a mechanism for the ORR in the different studied conditions is proposed (Figure 1).

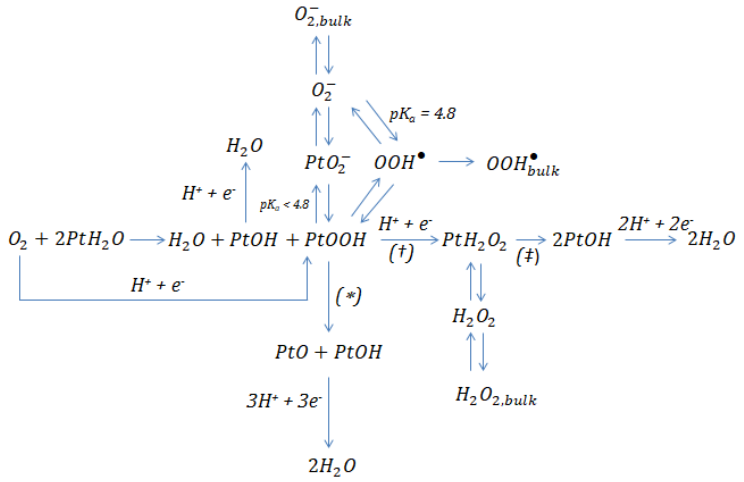

Figure 1. Proposed scheme mechanism for the ORR on Pt electrodes. *(*)* Predominant at 2 < pH < 3 and high ionic strength. Unaffected by Br_{ads}. *(†)* Favoured at very acidic pH and low ionic strength. *(‡)* Hindered in presence of Br_{ads}.

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Sustainable Electrochemical Extraction of Lithium Chloride from Natural Brine

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In the past 25 years lithium ion batteries have changed the way we communicate with cell phones and in the next 25 years electric vehicles are expected to change our everyday mobility with the electric car. If lithium will enable renewable energy storage lithium extraction should be sustainable. In this presentation we will focus on the electrochemical sustainable extraction of lithium chloride form natural brine.

The spontaneous electrochemical extraction of lithium chloride from natural brine of high altitude salt flats in northwest Argentina and recovery in a dilute electrolyte has been demonstrated in two experiments.

i) A highly selective $LiMn_2O_4$ insertion cathode and polypyrrole anion selective anode (salt capturing).
ii) An $LiMn_2O_4$ anode and lithium deficient $Li_{1-x}Mn_2O_4$ cathode separated by anion selective membrane (selective ion exchange).

The entropy driven transfer of LiCl from concentrated brine to a dilute recovery electrolyte has been experimentally studied by ion pumping and the LiCl activity measured in natural brine.

An electrochemical reactor for the extraction of lithium from natural brine has been designed. It comprises two 3D porous packed bed electrodes and (i) a porous separator filled with electrolyte or (2) an anion selective membrane. The electrodes are filled with conducting petroleum coke particles covered respectively with $LiMn_2O_4$ selective to chloride ions and (i) polypyrrole selective to anions or (ii) Li^+ deficient $Li_{1-x}Mn_2O_4$. The reactor operates (i) in two steps: First the porous electrode and separator are filled with natural brine to extract Li^+ and Cl^- by intercalation and adsorption, respectively. Then, after rinsing with water the reactor is filled with a dilute LiCl recovery solution and LiCl is recovered by reversing the electrical current. While the first step is spontaneous, the second one requires energy from solar panels to drive the electrolysis. Alternatively, in (ii) a continuous process of lithium extraction at the $Li_{1-x}Mn_2O_4$ cathode and lithium release at the $LiMn_2O_4$ separated by the anion selective membrane takes place. After completion, and rising with water the brine and recovery solutions are exchanged and the lithiated electrode becomes anode while the delithiated electrode is the cathode to continue the extraction.

The evolution of lithium chloride concentration in the recovery electrolyte has been followed by a lithium selective electrode, while the reactor total voltage and each electrode potential with respect to a Ag/AgCl; 3 M KCl reference electrode were continuously monitored by high impedance potential followers.

The effect of lithium chloride concentration in natural brine, applied current density and reactor geometry have been studied in scalling up the lithium chloride extracting reactor, while the extraction efficiency and charge capacity were evaluated.

A mathematical model for the reactor comprising the Nernst-Planck equation and the battery intercalation model has been developed. The model was solved using the finite element method under the COMSOL® multiphysics environment in order to obtain the electrostatic potential and the ion currents and concentrations across the systems. Unlike the asymmetric $LiMn_2O_4$ /activated carbon supercapacitor, in the lithium extracting reactor the total LiCl concentration decreases in the extraction step and increases in the recovery step. A good agreement between the experimental and simulated potential difference vs. time at constant current validates the model of the reactor.

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Identifying the bifunctional mechanism of Pt-SnO_2 for CO electro-oxidation

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Carbon monoxide oxidation is at the core of fuel cell anodic catalysis, because CO poisons Pt surface and deactivates other anodic reactions, as an impurity from reformate gas and a main intermediate from the incomplete oxidation of fuel molecules (methanol, ethanol, etc.)[1]. Among CO-tolerant catalysts, Pt-Sn alloys stand out, due to a combination of bifunctional effects, ligand effects and ensemble effects[2]. Although the last two effects come from the alloyed Sn, the first one may not. Our recent studies on Pt_3Sn bimetallic nanoparticles[3-4] suggest that the onset potential of CO oxidation is not proportional to the extent of alloying and still as low as ~0.4 V_{RHE} on nanoparticles with a large fraction of SnO_2 (>92 at% out of total Sn). Thus, a bifunctional effect from SnO_2 may be active on Pt-SnO_2.

In this work, a Pt-SnO_2 nanoparticle catalyst supported on carbon (Pt-SnO_2/C) is synthesized with careful consideration to avoid the formation of Pt-Sn intermetallic bonding. The structure of Pt-SnO_2/C and the absence of alloyed Sn are interrogated by XRD and detailed XAS analysis. The CO oxidation is strongly promoted on Pt-SnO_2/C with the onset potential of ~0.3 V_{RHE}, which is reproduced on mixtures of Pt/C and SnO_2 nanoparticles, and SnO_2-modified Pt electrodes. The CO oxidation on Pt-SnO_2 occurs at low overpotential with fast kinetics, such that the diffusion of dissolved CO become the rate-determining-step beyond ~0.45 V_{RHE} (Figure 1 left). By identifying a redox couple of Sn^{IV}/Sn^{II} on the SnO_2 surface, the bifunctional mechanism of Pt-SnO_2 is proposed to originate from a co-catalysis of SnO_2, on the surface of which Sn-OH is consumed by reacting Pt-CO_{ads} at the interface and regenerated by dissociating water (Figure 1 right).

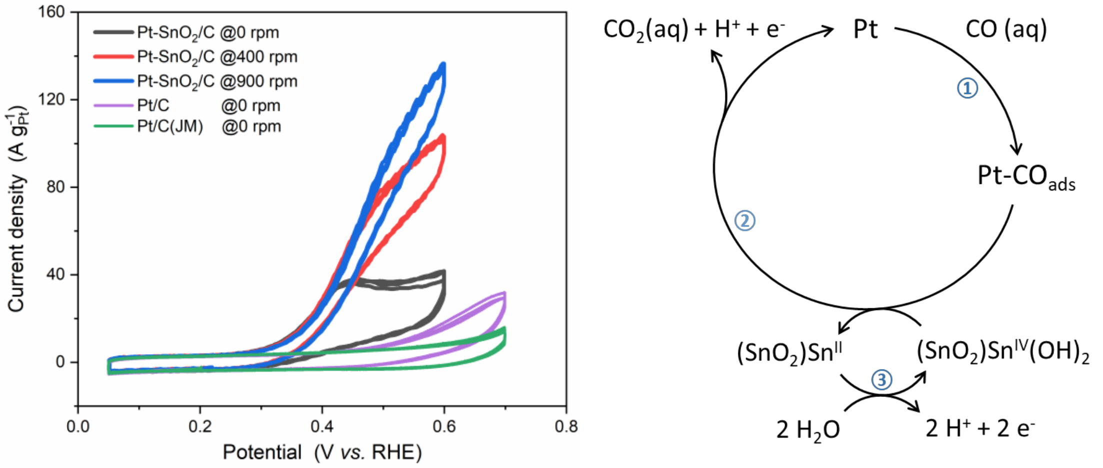

Figure 1 (left) CO oxidation voltammograms of Pt-SnO_2/C, Pt/C and Pt/C (JM) in actively CO-purged 0.1 M $HClO_4$ solution with a scan rate of 20 mV s^{-1}. The rotation rates are indicated in the figure legend. **(right)** Catalysis cycle of Pt for CO electro-oxidation with the co-catalysis of SnO_2.

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How Small: Selecting the Right Size of Pt Nanoparticles to Improve Their Oxygen Electroreduction Mass Activity

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One of the key factors limiting the widespread applications of fuel cell technologies is the cost of the electrocatalysts utilized in catalyzing the oxygen reduction reaction (ORR) at the cathode side. More specifically, only platinum based electrocatalysts have shown sufficient activity; however, due to the scarcity and cost of Pt, it is of a particular interest to increase their activity per mass. Reducing the platinum loading and increasing the mass activity of nanostructured electrocatalysts are major challenges toward efficient oxygen electroreduction (ORR) in proton-exchange-membrane fuel cells. We tackle these challenges by combining theory and experiment to fabricate pure Pt nanoparticles with optimal size. Optimal nanoparticle sizes are predicted near ~1, 2, and 3 nm by computational screening.

To corroborate our computational results, we have addressed the challenge of ~1 nm sized Pt nanocluster synthesis with metal organic framework template approach. The produced electrocatalyst was characterized by high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy and its oxygen reduction activity was measured using a rotating disk electrode setup. The observed mass activities (0.87 A/mgPt) coincide with the computational prediction (0.99 A/mgPt) with respect to the error interval, which represents one of the highest mass activities reported among pure Pt catalysts for the ORR.

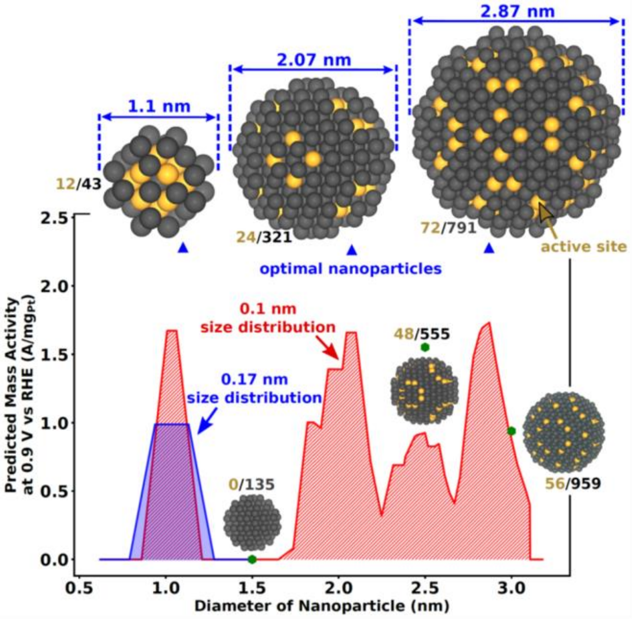

Figure 1. Predicted mass activities plotted versus nanoparticle diameters. Optimal nanoparticles (blue triangles) are identified at diameters of 1.1 nm, 2.07 nm, and 2.87 nm. Three less active nanoparticles (green hexagons) are exemplified at 1.5 nm, 2.5 nm, and 3 nm. The red and blue curves show predicted mass activities for nanoparticles with 0.1 nm and 0.17 nm size distribution, respectively.

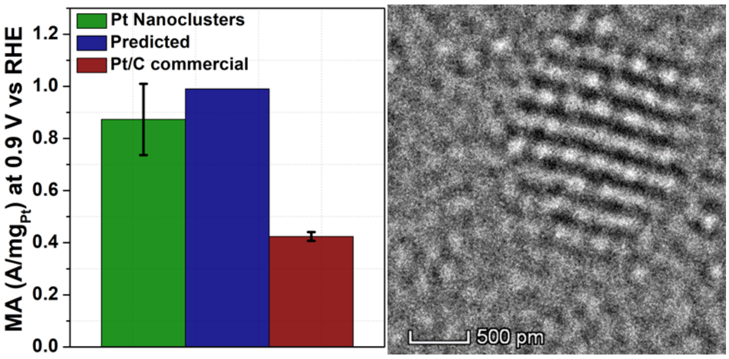

Figure 2. (On the left) Mass activity of Pt nanoparticles compared with commercial Pt/C catalyst at 0.9 V vs RHE. We also showed the predicted mass activity for 1.1 ± 0.17 nm sized Pt nanoclusters. (On the right) HR-TEM images of Pt nanocluster.

De-alloy PtCu/C Electrocatalysts in Electrochemical Cell and in Membrane-Electrode Assembly

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Doping of platinum with d-metals has been considered for a long time as an effective way to increase the activity and stability of nanostructured electrocatalysts used in hydrogen-air and direct methanol fuel cells with a polymer proton-exchanged membrane. To date, an understanding has emerged that the composition and structure (architecture) of bimetallic nanoparticles that make up the active component of a catalyst differ significantly for the "as-prepared" initial state and the "during operation" state of the catalyst. In this connection, attempts to obtain high-alloyed PtM_x/C materials, the subsequent treatment of which allows to obtain PtM_{x-y}/C electrocatalysts with a developed surface, high activity and stability, are of considerable interest.

This paper discusses the results of our research related to the preparation and study of PtM/C alloy/de-alloy catalysts containing nanoparticles of i) a uniform alloy or ii) a gradient architecture in which the concentration of platinum atoms gradually increases in the direction from core to surface [1-3].

A comparative study of the degradation features of the synthesized bimetallic PtCu/C and commercial Pt/C catalysts with a close Pt content under conditions of a multiple repetition of potential sweeps in the 0.6-1.0 V ("soft" regimen) and 0.6-1.4 V ("hard" regimen) range revealed higher stability of bimetallic systems. The specifics of electrochemical behavior and increased stability of PtCu/C catalysts are associated with the size of PtCu nanoparticles, and further evolution of their composition and structure (architecture). A "firmly bonded" copper, left in the de-alloyed nanoparticles, promotes platinum activity in the ORR. Therefore, their specific activity, and for the "gradient" catalyst both specific and mass-activity, are higher than that for the NPs of Pt/C catalysts. During the subsequent multiple cyclic alteration of the potential, the rate of copper selective dissolution is greatly retarded. Perhaps the presence of the Cu atoms at the NP/carrier interface slows down carbon oxidation. The characteristics of the initial "gradient" PtCu/C catalyst architecture provide the most favorable conditions for its evolution, which in turn, determine the combination of high ESA, stability and specific catalytic activity in ORR, related, *inter alia,* to a relatively high residual concentration of Cu (Fig. 1a).

Several $PtCu_{x-y}/C$ materials subjected to pre-treatment in acids demonstrated high activity characteristics and, especially, stability compared to commercial Pt/C when tested in membrane-electrode assembly (Fig.1b). A poisoning of the polymer membrane with copper cations did not occur.

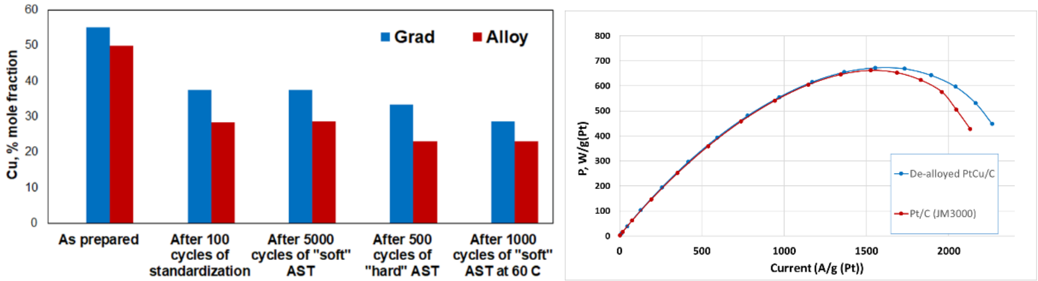

Figure 1. (a) The change of alloy and "gradient" PtCu/C catalysts composition for different accelerated stress-test protocols (AST) and (b) load curves for membrane-electrode assembly containing $PtCu_{x-y}/C$ and Pt/C materials in catalytic layers.

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Single-Crystal Titania (Anatase, Rutile and Brookite) Electrodes: Energy and Environment Fundamentals

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Rutile TiO_2 single crystal electrode introduced by Boddy (1967), Fujishima and Honda (1972) has been a standard for fundamental (photo)electrochemical studies of titania, as long as TiO_2 (anatase) single-crystal electrode has been disclosed in 1996 [1]. Technical difficulties in obtaining good-quality and large-size anatase single crystals by laboratory syntheses are often bypassed by using commercial single crystals. Except for rutile, these crystals are of natural origin, hence, of potentially problematic purity. Nevertheless, certain materials of this kind still exhibit adequate electrochemical properties which can be correlated with those of the laboratory-grown standards. The relevant data have been acquired for anatase with the (101), (100) and (001) exposed surfaces, as well as for brookite (100) single crystals. A concerted application of electrochemical and XPS/NAP-XPS experiments, confronted with theoretical (DFT) modelling could rationalize some contradictory data about the electronic structure of such materials. These findings provide salient inputs for solar energy conversion both in dye-sensitized [2] and in perovskite [3,4] photovoltaics, energy storage in Li-ion batteries [5] as well as in the production of solar fuel (water splitting, CO_2 reduction) and in environmental photocatalysis. Such a general approach to titania electrochemistry is certainly attractive, but inherently problematic, at the same time. The reason is, that the mentioned applications employ a broad palette of polycrystalline, porous, nanotextured and mesosocopic materials. A generic example is the anatase-rutile mixture, P25 from Evonik (Degussa). The unique properties of P25 in photocatalysis are sometimes correlated with the specific band alignment between anatase and rutile near the conduction band edge. However, these problems are far from clearly understood. There are actually five different possibilities of band alignment between anatase and rutile, and one can find supporting arguments for each variant in the literature [4]. In general, nanocrystalline materials may possess properties which do not, and even cannot conceptually exist in bulk single-crystal electrodes. For instance, the classical Gärtner-Butler model of the semiconductor/electrolyte interface need not be appropriate for the description of practical materials and electrodes. The virtual absence of space-charge layer (band-bending) in certain nanocrystalline electrodes must be taken into account for correct interpretation of electrochemical experiments, too. Problems interconnected with electrochemical impedance spectroscopy (Mott-Schottky plots) are particularly appealing in this context. **Acknowledgement**: This work was supported by the Czech National Science Foundation (contract No. 18-08959S).

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Why Breaking Scaling Relations Does Not Necessarily Lead to Better Electrocatalysts

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The adsorption energies of a great variety of species on heterogeneous and homogeneous catalysts have been shown to be linearly dependent [1, 2]. On the one hand, such scaling relations are beneficial as they significantly simplify the elaboration of computational electrocatalysis models. On the other hand, they lower the number of free parameters in multistep electrocatalytic reactions, which may impose limits to the optimization of electrocatalysts.

For example, the scaling relation of *OOH vs *OH supposedly slows down the oxygen evolution and reduction reactions (OER, ORR) [3, 4]. While the optimal separation between the adsorption energies of these two intermediates is 2.46 eV, on most catalysts it is ~3.20 eV. Thus, it is currently believed that the breaking of such scaling relation is vital to the substantial enhancement of OER/ORR electrocatalysts.

In this talk, I will put this widespread idea to the test using a large collection of data from the literature. The results indicate that breaking the scaling relation of *OOH vs *OH is a necessary but not sufficient condition to optimize OER/ORR electrocatalysts.

As an alternative, I will introduce the "electrochemical-step symmetry index" (ESSI), the minimization of which results in low calculated overpotentials [5]. ESSI can also be used in conjunction with experiments to rationalize activity trends and provide guidelines for the optimization of electrocatalysts [6].

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Tailoring Pseudocapacitor Electrode Microstructures for Improving their Performance by Colloidal Strategies

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In the last decades, the design of well-defined nanostructured functional thin films and ceramic nanocomposites has attracted substantial interest within the scientific community owing to their promising properties, compositions, structures, and functions for energy applications.

Many attempts to improve the response of the electrodes are based on strategies to induce a better reactant–catalyst contact through the design of complex structures with large surface-to-volume ratio. The structuring and electrochemical activity can be controlled by tuning the physical properties (particle size, crystalline phase, preferred orientation) but also by shape forming of the ceramic material host (e.g. soft or hard templating).

The processing of ceramic films through the use of the colloidal techniques allows nanostructures tailoring, strengthening the control over specific properties. Moreover, colloidal chemistry allows the fabrication of specific building blocks such as full inorganic or hybrid core-shell structures that can be shaped in a film. Understanding the behavior of nanoparticles (NPs) in the liquid media is mandatory to prepare stable and disperse suspensions suitable for colloidal coating methods such as the Electrophoretic Deposition. Moreover, the adsorption of surface modifiers onto NPs, apart to its role as stabilizers, results in a colloidal strategy to shape inorganic/organic core-shell structures. It has been demonstrated that the Layer-by-Layer (LbL) technology, understood as the alternate absorption of cationic and anionic polymers onto the particle surface, determines NPs assembly in 3D pseudocapacitors electrodes (Figure 1a)[1]. However, other approaches including NPs heterogeneous precipitation in a stable suspension (Figure 1b)[2] and surface neutralization in a colloidal heterocoagulation (Figure 1c)[3], have been explore to shape inorganic/inorganic core-shell nanostructures using surface modifiers as ligants or stabilizers. In this work, those colloidal strategies have been used to build up by EPD the electroactive microstructure of Ni-based pseudocapacitors. Step-by-step inorganic core-shell formation, their stability and EPD kinetics, as well as the electrochemical performance of the electrodes will be described.

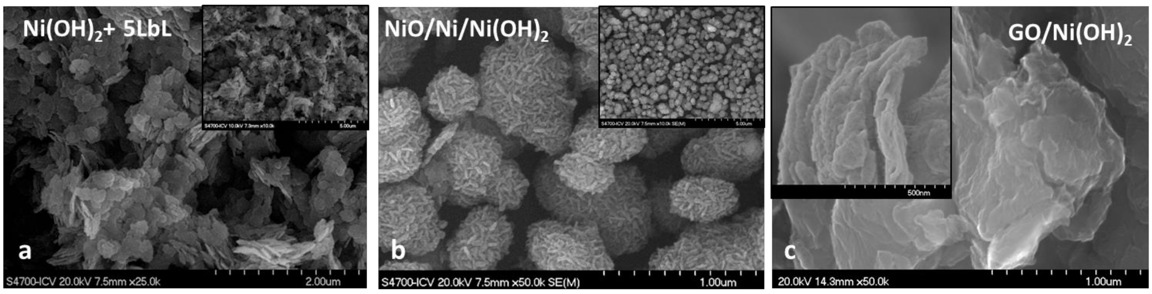

Figure 1. A detail of the Ni-based electrodes shaped by EPD of LbL core-shell (a)[1], core-shell synthesized by heterogeneous precipitation US assisted (b)[2], and by particle surface charge neutralization of GO nanoflakes (c)[3]

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Ammonia Electro-oxidation on Nanoparticulated Molybdenium Carbide Supported Platinum

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Ammonia electro-oxidation(AEO) has received considerable attention for its applications in ammonia low temperature fuel cells (AFC),[1]production of high-purityhydrogen,[2] electrochemical removal of ammonia in wastewater[3] and fabrication of electrochemical sensors[4]. Ammonia is a carbon-free energy carrier, with higher hydrogen storage capacity (17.7 wt%), oxidation charge, energy density(3000Wh kg^{-1}) and low production coast (1.2 \$/kWh and 3.8 \$/kWh for ammonia and methanol respectively)in compare to methanol.Moreover, ammonia decomposition generates hydrogen, another energy vector,which theoretically should cost less than the one from water electrolysis[5]. These advantages make ammonia a promising fuel for low/medium-temperature AFC to combat the global challenges of carbon emission and fossil fuel depletion.To date, the most effective catalyst for AEOhas been platinum and its alloys with other noble metals such as Ir.The high cost and scarcity of these catalysts areof major technical challenges which limit the commercialization of AFC. Therefore, significant efforts devoted to developing catalysts with low-loading of Pt. Herein for the first time to our knowledge, we employed and demonstrated that high surface area MoC-promotes Pt and the composite is an intriguing candidate considered as a high efficient catalyst for AEO at ambient temperature.

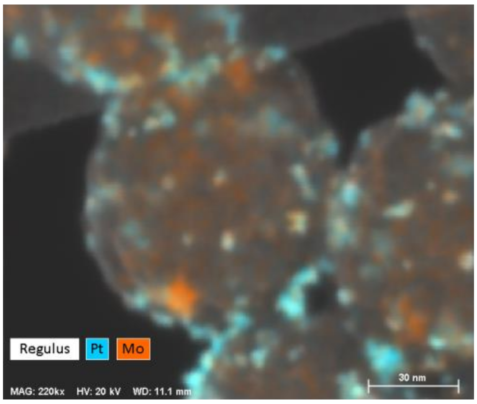

Figure1. STEM image of Pt/MoC

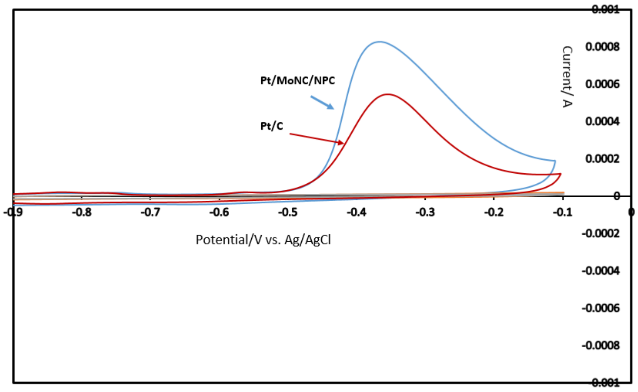

Figure 2. Cyclic voltammograms of ammonia oxidation of Pt supported composite of molybdenum carbide nitride and Pt/C.

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Ni-N_x as promising active sites to obtain CO electrochemically from CO_2: batch vs. flow cell.

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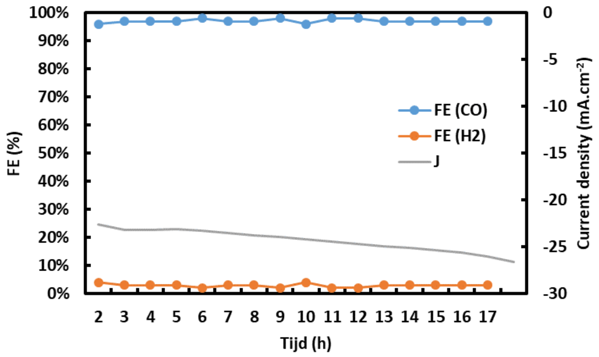
Renewable energy sources can offer a solution for **excessive emissions of greenhouse gases** and to the expected **decrease in availability of fossil fuels** in the near future. Both problems would find a common solution if we were able to develop energy-efficient processes to convert (low concentrated) CO_2 streams into fuels and useful chemical products, ensuring a positive economic and environmental balance. One possible strategy is to use **H_2O and CO_2** as renewable feedstock for the production of carbon monoxide, employing excess electricity generated by renewable power sources to drive the reactions. The **electrochemical CO_2 reduction** (ERC) is currently the most feasible pathway as it benefits from a relatively high efficiency and product selectivity, which can be tuned towards a desired product by adapting the operating potential [1]. Furthermore, they can also be driven by renewable energy having the additional advantage that no extra CO_2 is liberated [2,3].

Whereas, currently Ag is the most commonly applied material to reduce CO_2 electrochemically to CO, its extensive cost and insufficient performance (activity, selectivity and/or stability) seriously limit up-scaling and thus commercialization [4]. For this reason, a cheaper alternative is proposed here in the form of **N-doped graphitic carbons containing non-noble Ni centers.** The electrocatalysts were prepared through an easily up-scalable and easily tunable method based on the pyrolysis of Ni-containing N-doped carbons [5]. The polyaniline-based electrocatalysts were synthesized by varying the loading of Ni and N. The performance of these electrocatalysts in the ERC was first evaluated in an in-house designed measurement cell (H-type cell) with an aqueous 0.1M $KHCO_3$ solution as electrolyte. The electrocatalytic activity (**current densities)** and selectivity (**Faradaic efficiency**) was screened initially in this kind of setup with a combination of **chrono-amperometry and in-situ gas chromatography** to get an in-depth knowledge on product distribution.

The nature of the metal center, the N configuration and their final content proved to strongly influence the electrocatalytic performance, especially in terms of current density and selectivity to CO. Ni-N-AC-B1 synthesized with a high relative amount of nitrogen and nickel, was identified as the most promising candidate for this reaction based on its partial CO current (4.2mA.cm^{-2}), its overpotential (0.57 V) and its Faradaic efficiency to CO (> 99%). This results in unprecedented values for the current density per g active sites (690 A.g^{-1} active sites), which makes us believe that by simply increasing the number of available active sites by increasing the Ni and N content in the initial synthesis mixture it is possible to further improve performance well above any reported data.

Finally, Ni-N-AC-B1 was also evaluated in an in-house designed gas-diffusion electrode-based flow-cell (left figure) to investigate its applicability in an actual electrolyzer. To the best of our knowledge this is the first time that this kind of materials has been investigated in this kind of setup further highlighting the importance of this work. At -0.9 V vs. RHE a constant FE of > 95% was recorded for more than 16h together with a current density of approximately -25 mA.cm^{-2}, further evidencing their promise as potential candidate for the ERC to CO (right figure).



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Tuning and Design of Active Bifunctional Electrocatalysts with Transition Metal Dichalcogenides Using Single Atom Doping and Two-Dimensional Heterogeneous Interfaces

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Single atom catalyst is designed to achieve high catalytic activity while extremely minimizing precious metal loadings for electrochemical energy conversion and storage applications. Using first-principles density functional theory calculations, we screen 48 combinations of single atom catalysts anchored at defective monolayer transition metal dichalcogenides (A1/TMD; A = Ni, Cu, Pd, Ag, Pt and Au; TM = Mo, W, Nb and Ta; D = S and Se). With established methodologies, we identify five best catalysts for each of oxygen reduction/evolution and hydrogen evolution reactions among the stable candidates. A scaling relation between the Gibb's free energy for intermediates is figured out to understand the governing mechanism of single atom catalysts with varying transition metal dichalcogenides supports and to introduce key descriptor. Pt1/MoS2 is proposed as the best bifunctional catalyst for oxygen reduction/evolution reaction. In addition, Pt1/NbSe2 and Pt1/TaS2 are promising candidates for oxygen and hydrogen evolution reactions. Treating the support itself as an active site for hydrogen evolution reaction, Pd1/NbS2 and Pt1/NbS2 are proposed as potential bifunctional catalysts toward oxygen reduction and evolution reaction, respectively. Conceptual design principle via high-throughput screening of single atom catalyst is demonstrated as a great approach to determine active and durable bifunctional single atom catalysts.

Using first principles DFT calculations and AIMD simulations, we establish a database for catalytic properties of two-dimensional metal-dichalcogenides (2D-TMDs) toward the hydrogen evolution reaction (HER). In addition to conventionally known active sites of edges, we propose that terrace sites can be substantially activated for the HER even without incorporating defects or heteroatom doping. The key idea is to design a heterogeneous 2D-TMD with a bilayer of catalyst/support configuration. We identify the best candidates, NbS2/HfSe2, NbS2/ZrSe2, and TaS2/HfSe2, via high-throughput computational screening of 256 different heterogeneous 2D-TMDs. The expected HER activity is estimated to be comparable to or even better than that of the conventional Pt/C catalyst. It is shown that the Gibbs free energy of hydrogen adsorption can be tuned to an optimal value of 0 eV using heterogeneous 2D-TMD materials. Careful analysis of the first principles database for 2D-TMDs leads to capturing a universal descriptor for the HER activity of 2D-TMDs regardless of hydrogen coverage and active sites: the adhesion energy difference of the catalyst/support TMDs before and after the hydrogen adsorption. The descriptor is linearly correlated with hydrogen adsorption energy. Our design principle for highly functional 2D-TMD catalysts for the HER is, thus, to identify a heterogeneous 2D-TMD of an optimum hydrogen adsorption energy based on adhesion energy difference, which can be accurately and quickly performed via the analysis of the first principles database and validation through experimental measurements.

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Electrochemically-mediated amine regeneration for CO_2 capture: Experimental and modeling analysis

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With the increasing evidence that global warming is correlated with carbon dioxide (CO_2) emissions, the development of cost-effective, large-scale and energy-efficient CO_2 capture technologies is critical. Thermal amine scrubbing is the most developed of these technologies, but is expensive to retrofit into existing power plants. Our group has proposed an Electrochemically Mediated Amine Regeneration (EMAR) process that can operate at temperatures under 60 °C [1, 2]. In an EMAR process, the CO_2 rich stream is exposed to electrochemically-generated copper ions (i.e., $Cu = Cu^{2+} + 2e^-$) to drive the dissociation of amine and CO_2 towards CO_2 desorption. Once the gas is flashed off, the lean loading stream is regenerated via the electrochemical plating of copper from the copper-amine complex ($Cu^{2+} + 2e^- = Cu$). A background electrolyte (e.g., $NaSO_4$) is used to minimize resistive losses in the electrochemical cell. This electrochemical modulation of the concentration ratios of cupric ion to amine could afford a rather efficient, energy-saving and absorption-based CO_2 separation process.

The EMAR approach offers several advantages compared to other thermally-driven amine-based processes for the capture of CO_2. Unlike the thermal processes, EMAR can be operated at low temperatures, thereby minimizing thermal amine degradation. It also offers the possibility to desorb CO_2 at moderate pressures, minimizing the downstream compression costs for CO_2 storage. The modular nature of EMAR, as an electrochemical cell, makes it easier to scale up and to operate with fluctuating loadings.

We studied the kinetics and thermodynamics of the EMAR process. With a rotating disk electrode and using the Tafel expression of the kinetics, we investigated several combinations of metals (the complexing agent), amines and background electrolytes. Among them, an EMAR system based on copper (i.e., Cu/Cu^{2+}), ethylenediamine, and sodium sulfate electrolyte was promising. In order to describe the thermodynamics of the system, twelve aqueous speciation reactions are solved simultaneously together with the extended Debye-Hückel activity coefficient model. These kinetics and thermodynamics data can give useful insight into the design of an optimized system.

We also studied the importance of the electrode material and morphology on the EMAR electrochemical performance. In our recent investigation, we used carbon-based electrodes, and compared the performance with the originally-used copper plates. The results showed that the EMAR performance in terms of polarization behavior, coulombic efficiencies and gas desorption rate could be improved through the use of carbon-based electrodes.

The presentation will describe the EMAR process in detail and with updated performance results obtained in the lab-scale setup. The presentation will also highlight the challenges of the EMAR process as well as the various steps being undertaken in order to further improve the efficiency of the process.

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Investigating coupled Electron-Proton storage at nanostructured TiO_2 electrodes under mild aqueous conditions

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There is currently strong societal demand for the development of rechargeable batteries that meet stringent criteria in terms of cost, safety, toxicity and ecological impact, particularly for scalable grid storage systems required by the development of renewable but intermittent energy sources.[1] This has led to a renewed interest in aqueous electrolytes, especially since recent studies have demonstrated that the main limitation related to the low electrochemical thermodynamic stability window of water could be overcome with the use of water-in-salt electrolytes.[2] This has also led to search for aqueous intercalation-type electrodes beyond Li-ion, which geo-availability, cost and aqueous solubility are problematic issues.[3]

In this context, we have investigated the ability of the proton-ion (*i.e.* H^+) to insert reversibly within amorphous nanostructured TiO_2 model electrodes upon reductive electrochemical conditions. We have notably demonstrated that coupled electron-proton storage can occur massively and rapidly not only under strong acidic conditions, but also more interestingly under neutral *p*H conditions in the presence of a weak acid proton donor AH, according to the following reaction mechanism:[4]

$$TiO_2 + x\,e^- + x\,AH \leftrightarrow TiOOH_x + x\,A^-$$

The process was modeled according to a three-step diffusion-reaction mechanism,[5] allowing us to determine the apparent solid-state diffusion coefficient of proton within the metal oxide lattice. The value we have obtained is higher than that usually reported for Li^+ in anatase TiO_2, which is as expected on account of the smaller size of H^+ compared to Li^+. Under optimized storage conditions, a x value of 0.4 was reached, close to the 0.5 maximal value of Li^+ insertion in anatase TiO_2. More recently, we have demonstrated that coupled electron-proton charge storage at mesoporous metal oxide electrodes can be generalized to a wide range of organic as well as inorganic weak acids, under appropriate adjustment of the pH and potential window. Collectively, these results suggest that the proton could be a good substitute for Li^+ in the development of rechargeable aqueous batteries with potentially high rate capabilities.

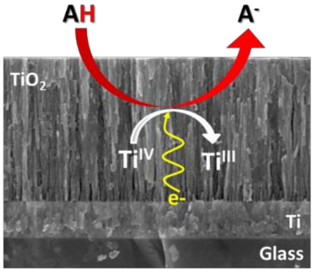

Fig 1. Schematic representation of the faradaic charging process occurring at the model TiO_2 electrodes.

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Early Stage Design of Electrochemical Cells in the Digital Age

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Electrochemical technologies are developing rapidly, with often the material scientists providing a wide and confusing variety of possible electrode or electrolyte designs. Researchers at the next higher levels, i.e. technical electrodes or single cells, need to decide for a small sub-set of materials, study interaction of the materials, and optimise the processes in the electrode and cell for high performance. This serial bottom-up process leads to slow technology development, as electrode and cell level researchers often wait for a certain maturity and preselection of materials, whereas material researchers cannot take possibly crucial technical constraints and demands from the higher levels into account. Early stage design of electrochemical cells in parallel to material design is therefore a key to accelerate technology development and to bring important constraints from higher levels to the material side. Here, model-based analysis is a preferable method over experiments, as optimal materials may yet not be available, and it is a long, often tedious path to get them experimentally well performing at cell level. Furthermore, model-based analysis allows to focus on the processes and questions of interest by omitting irrelevant details or purposely modifying material properties, cell designs and even reaction or transport processes to check their impact.

This talk will illustrate how to conduct early stage design using mechanistic models, and how important constraints and thus recommendations for researchers at other levels can be derived. Models are low dimensional and with a minimum amount of details to focus on the main processes and the resulting constraints, and thus derive conclusions with a wide range of applicability. This allows to answer questions such as which conditions and material properties enable sufficient availability of reactants, and which combination of materials promises the highest performance.

The first part of the talk will focus on stable operating ranges for electrochemical cells and their implication for material design. At the example of alkaline cells like the Zn air and alkaline membrane fuel cells, it is shown how water and carbon dioxide need to be carefully controlled to prevent failure of the cell. Models reveal the crucial impact of environmental and operating conditions on the stable operating range, and the resulting demands to tailor material properties.
The second part of the talk will focus on how the design of electrochemical cells and electrodes can be optimised towards higher performance.

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Influence of Electrolyte Flow Rate on the Performances of a Polysulphide/Iodide Redox Flow Battery

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Reliable and sustainable utilization of energy resources with an intermittent nature such as wind and solar energies requires an efficient energy storage technology. Redox flow batteries (RFBs) can be used for this purpose, but there is a need for low-cost, high energy- and power- density systems. The Polysulfide/Iodide (PS/I) RFB reported in the literature [1, 2] has low cost electrolyte, facile kinetics and high energy density making it an attractive option. However, detailed investigation of the operating conditions are needed to characterize and optimize the performance of the technology. In the present work, experiments were conducted using an electrochemical flow cell with an active geometrical area of 210 mm^2. Two graphite plate (Entegris, pyrolytic bipolar plate) with an interdigitated flow-field were used as current collectors.

Electrochemical methods including as galvanostatic charge-discharge, polarizations studies, and electrochemical impedance spectroscopy (EIS) were conducted at different flow rates for both current density of 10 and 15 mA.cm^{-2} to explore the effect of flow rate and on the performance of PS/I RFB. The influence of the electrolyte flow rate (5 to 50 ml min^{-1}) on the charge-discharge efficiency, the discharge capacity, and the maximum power density of the PS/I RFB was investigated. Precipitation of potassium tri-iodide on the membrane and positive electrodes during charging was observed as well as polysulfide cross-over through the Nafion membrane. SEM-EDS and UV-Vis characterization were performed to investigate the effects of electrolyte concentration and flow rate on these two phenomena. The flow rate was observed to influence both concentration loss and precipitation of potassium-triiodide. As shown in Fig.1, these competing effects led to a maximum in the energy efficiency as the flow rate was increased for an electrolyte concentration of 3 M.

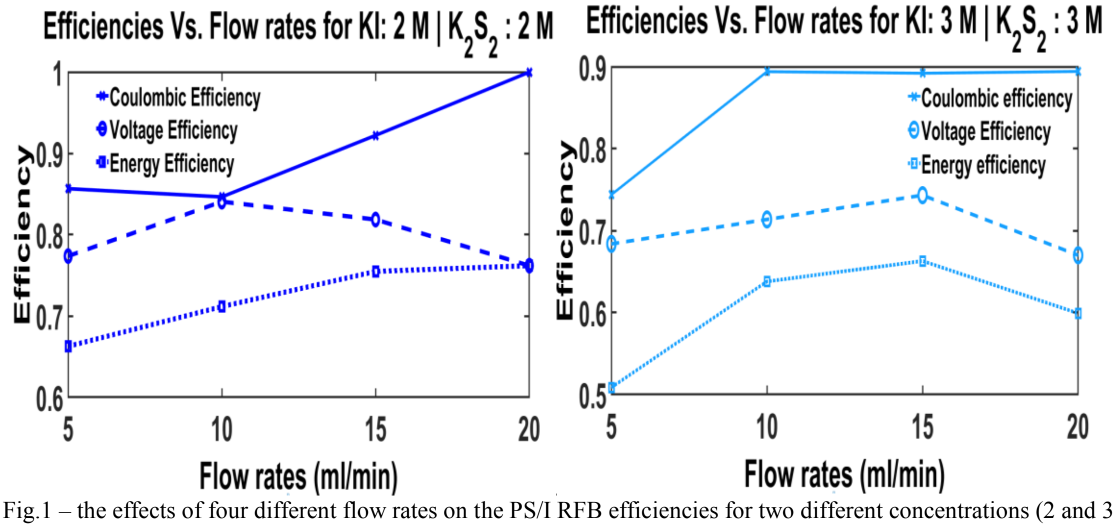

Fig.1 – the effects of four different flow rates on the PS/I RFB efficiencies for two different concentrations (2 and 3 M) of potassium iodide and potassium polysulfide

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Silica Templated Polyaniline Derived Mesoporous Carbons as Electrode Material for the Positive Half-Cell in All-Vanadium Redox Flow Batteries

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State-of-the-art electrode materials for all-vanadium redox flow batteries are carbon-based. The properties of the carbon determine its possible use as an electrode material. Graphitization of carbon and functional groups at the surface determine the kinetics of the VO^{2+}/VO_2^+ redox reaction (positive half-cell) and the wettability influencing the respective usage of the carbon surface.

However, the impact of certain carbon properties achieved by different post-treatments, e.g., thermal oxidation, on the VO^{2+}/VO_2^+ redox reaction (positive half-cell) are controversially discussed which is due to the following reasons:
1) Kinetic data for the VO^{2+}/VO_2^+ redox reaction determined by conventional cyclic voltammetry measurements depend on the electrochemical active surface area and therewith on the wettability of the carbon surface. Any change in surface functional groups affect both kinetics and wettability. Thus the determination of the reaction kinetics requires measurements which account for the active surface area. [1]
2) The electron transfer kinetics can be limited by the reaction in the Helmholtz layer or by the electron transfer in the carbon due to the presence of a space charge layer. The latter is determined by the degree of graphitization which correlates for graphitic-like materials to the sp^2-C content. Any treatment of the carbon surface impacts both sp^2-C content and surface functionalization depending on the graphitization degree of the carbon. [2] However, the sp^2-C content is rarely investigated in the literature.

In this work, the kinetics of VO^{2+}/VO_2^+ redox reaction is investigated for various mesoporous carbons, produced via carbonization of a SiO_2/Polyaniline composite and subsequent removal of the SiO_2 template via etching with NH_4HF_2.[3] The effect of different carbonization temperatures on the speciation of surface functional groups (N-, O-, F-groups) as well as on the sp^2-C content is investigated by near edge X-ray absorption fine structure and X-ray photoelectron spectroscopy quantitatively. These results are correlated to the kinetic constant of VO^{2+}/VO_2^+ redox reaction derived from electrochemical impedance spectroscopy measurements for various amounts of carbon on a GC-disk in V^{4+} electrolyte.

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Monitoring the State of Charge (SOC) of All Vanadium Redox-Flow Batteries (VRFB) to identify crossover and degradation of electrolyte

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To store renewable energies redox-flow batteries (RFB) are a promising and emerging technology. For the characterization and optimization as well as the operation of RFB-systems the reliable detection of the state of charge (SOC) of the battery during its charging and discharging is essential.

At a VRFB test setup different methods e.g. measuring potential and density of the electrolyte [1] and UV-Vis spectrometry have been investigated for the *in situ* determination of the SOC as well as the detection of electrolyte crossover and degradation. These methods can also be transmitted to new electrolyte formulations e.g. organic electrolytes.

Measuring the open circuit potential (OCP) is a simple and cost-effective monitoring method. Monitoring the OCP of the positive and the negative halfcell has been tested concerning the applicability for continuous measurement of SOC during charging and discharging processes. The distinct determination of the SOC for both halfcells is also suitable to identify electrolyte crossover in the VRFB-system (Fig.1). Furthermore the degradation of the VRFB-system especially ageing of the electrolyte shall be estimated from these results.

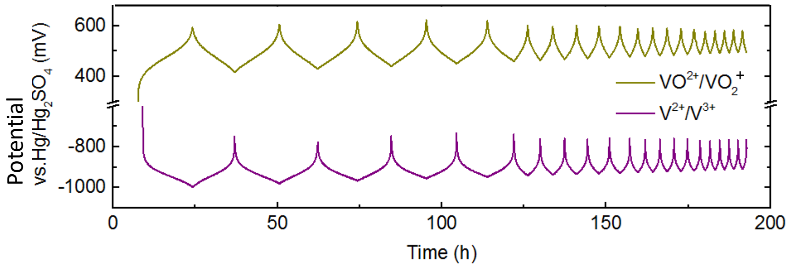

Fig.1: OCP Monitoring of positive (VO^{2+}/VO_2^+) and negative (V^{2+}/V^{3+}) half cell. Crossover and degradation of the electrolyte are pointed out by potential shifts and shortened charging and discharging cycles.

This work is done within the joint research project “DegraBat”.

“DegraBat” is funded by the German Federal Ministry of Economic Affairs and Energy (BMWi) within the government’s funding initiative energy storage.

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Management of Green Energy to Power Electrochemical Processes for the Treatment of Polluted Soils and Wastewater

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Nowadays, the massive use of synthetic organic chemicals over the last century has left soils and water effluent polluted by hazardous compounds. One of main techniques to remove these compounds from the environment are the electrochemical technologies. Among them, electrooxidation of wastewater and electokinetic remediation of soils have been widely studied to remove organic compound achieving high efficiencies. These technologies need as unique reactive, the electron. Nevertheless, this make necessary the use of a power source. In order to increase the sustainability of these technologies and make them more environmentally friendly, their direct coupling with a renewable source, as the solar energy, is proposed. However, the main drawback of the green energies is their intermittence and unpredictability. Consequently, their prediction and storage are key points to study.

Considering the previous statements, this work is focus on the development of a software tool to predict the solar radiation and manage the solar energy to power an electrooxidation reactor. Besides, the management of this energy includes its storage in electrochemical devices as redox flow batteries (RFBs). An RFB was selected due to its flexible design (independence between energy and power). Therefore, a simple and robust simulator with different sections has been developed. All the sections of this software tool have different models which have been empirically or theoretically formulated. Besides, several parameters have been estimated and adjusted using experimental results. Finally, the final model has been validated.

The first section predicts the solar radiation using two different time horizons with the aim of adjusting this variable with the time. After that, the solar power is managed in the second section depending on the amount of dissolved organic carbon (DOC) presents in the effluent to be treated. A percentage of the total power is derived towards the electrooxidation reactor and the rest is storage in a vanadium redox flow battery (VRFB). Thus, if enough power is not generated to supply directly the electrooxidation, the VRFB is discharged in order to power the electrolysis process. Moreover, the flow rate fed to the reactor could be adjusted according to the power with the aim of increase the removal efficiency of the process. Thus, this software tool is able to manage in real time the power generated from a solar panel to carried out the treatment of a wastewater effluent polluted with an organic compound.

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Assembling and Performance Comparison of Different Cathode Chemistries Utilized in All-Solid-State Lithium-Sulfur Batteries

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Solid electrolytes are considered to be utilized in next generation lithium-ion battery systems. Compared to conventional lithium-ion batteries, these systems enables cells with higher energy density along with free of flammability risks. Among various kind of solid-electrolytes, sulfur based electrolytes are promising to be adopted into lithium-ion batteries by virtue of their high ionic conductivity on the order of liquid electrolytes.

Sulfur is at the focus of lithium-sulfur batteries with its theoretical capacity of 1672 mAh/gr. Yet challenges arising from the insulating nature of sulfur and well-known polysulfide shuttle problem hindered its adoption into batteries capable of long cycling. However, studies showed that cell chemistry of solid-state lithium-sulfur batteries are different from conventional cells utilizing liquid organic electrolytes which eliminates the formation of polysulfides.

In this study, we constructed all solid-state lithium-ion battery (ASSLIB) where lithium and $Li_7P_3S_{11}$ utilized as anode and solid electrolyte respectively. We first checked the compatibility of anode-electrolyte interface through chronoamperometry and chronopotentiometry techniques. Then, sulfur based quaternary composite cathodes were synthesized through three distinct chemistries namely, melt-quenching method, sulfur-amine chemistry and sulfur-reduction from $Na_2S_2O_3$. Electrochemical performance of different cathode chemistries were compared. Our results indicate that ASSLIBs assembled with cathode utilizing $Na_2S_2O_3$ reduced sulfur showed best electrochemical performance and cycling. We have proposed the underlying mechanism as the smaller and uniform sulfur distribution enabled by reduction chemistry which facilitates better charge transfer at the cathode. We have also argued the performance limits and bottlenecks of batteries constructed with liquid and solid electrolytes having same cathode chemistries.

Three-dimensional Manganese Oxide aerogels for oxygen reaction reduction in high performance Al-Air batteries.

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New concepts like smart cities, battery to greed, etc. are becoming reality, and many new devices for different applications are going to be implanted in cities, roads, etc. Many experts claim that in the future the battery market is not going to be dominated just by one type of cell but by a mix were different technologies will have their niche markets. Metal-air batteries have been studied from long time ago, but in the last years due to the discovery of new materials have gained a lot of interest. These devices have been targeted as a promising technology to meet the energy requirements for energy-demanding devices [1]. The aluminium is a cheap, extensively used and easily accessible metal and it is a promising power source. Besides, the alloys processing and recycling are well-known processes. The theoretical specific capacity of Al is of 2.98Ah/g, and against an air cathode in aqueous electrolytes gives a potential of 1.5V. Aluminium is low cost and environmentally friendly, and possesses high theoretical energy density (4300 Wh g-1). However, the industrial application of metal-air batteries is limited because of low current density and high overpotential exist in the cathodic catalyst.

The oxygen reduction reaction (ORR) is the heart of metal–air batteries: oxygen molecules are reduced by electrons from the current collector and combine with metal dissolved in the electrolyte during discharging. The development of catalytic materials for the ORR is one of the major challenges in electrochemical energy conversion and storage technologies such as fuel cells and metal–air batteries [2-3]. High efficiency is highly desirable for the commercial success of environmentally friendly energy conversion devices. Among the non-precious metal alternatives, manganese oxides have received intensive attention because of their high elemental abundance, low cost and toxicity and appreciable activity, when integrated with a conductive-based support material such as graphene, carbon nanotubes or black carbon. However, bulk MnO_2 only delivers moderate catalytic performance because of the lack of open channels for oxygen gas access and transport. The ORR activity is affected by many factors; the particle size, morphology as well as on the phase of the Mn oxide. Three-dimensional macroscopic assemblies, such as aerogels and xerogels, represent a category of materials that features low densities large open pores high inner surface areas, and superior physical and chemical properties.

In this study, the catalytic activities of MnO_x both aerogel and xerogel materials with different morphologies and composition have been characterized by XRD, FT-IR and Raman spectroscopy. The evaluation toward ORR using Rotating Disk Electrode technique was carried out. The MnO_2 supported on a glassy carbon electrode (GCE) commercial or synthesized by other process was compared in order to evaluate the influence in the ORR. The performance of Aluminum-Air battery in gel alkaline media under ambient air condition and the stability in this battery was also evaluated.

Acknowledgments

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Tailoring Electrolyte Additives for Advanced Mg-Ca Anode in Aqueous Mg-air Battery

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Mg-air primary batteries represent one class of niche power sources. These batteries have attracted much attention as promising electrochemical energy storage and conversion devices due to their high performance, safety, low cost and low toxicity. Besides, Mg-air batteries can be mechanically rechargeable by replacing the anode material, which make them attractive candidates for electric vehicles, portable devices, remote devices and military applications.

However, during the discharge process the utilization efficiency and battery capacity decreases due to Mg anode self-corrosion and formation of discharge products (i.e., $Mg(OH)_2$ /MgO), which hinders the contact of the reactive surface and electrolyte. The possible solution to enhance the battery performance is to control the self-corrosion of the anode by optimizing of the electrolyte composition and careful selection of the anode material. The first steps towards optimization of the anode composition and choice of the electrolyte additives have been shown recently [1, 2].

In this work, the discharge performance of Mg-air batteries with advanced Mg-Ca anode was boosted by adding complexing agents into the electrolyte. The effect of electrolyte additives on the corrosion behavior and discharge properties of Mg-Ca anode was investigated via hydrogen evolution tests and half-cell measurements. Electrochemical impedance spectroscopy (EIS) was performed to evaluate the effect of different additives on various discharge activity of Mg-Ca anode induced by different additives. Lastly, basic characteristics of Mg-air battery in selected additive solution were tested and compared to bulk NaCl solution.

The results show that the addition of complexing agents can efficiently increase the cell voltage and specific energy of Mg-air battery. The formation of insoluble precipitates on the electrode was minimized, and the dissolution of magnesium anode was less prone to so called chunk effect.

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Plasmon-enhanced Raman spectroscopy for the analysis of some electrocatalytic systems and lithium batteries

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By using plasmonic nanostructures, even the Raman spectra of sub-monolayer quantity of molecules at electrochemical interfaces can be detected. We have made use of this ability, plasmon-enhanced Raman spectroscopy (PERS) including SERS/SHINERS with ultra-high sensitivity to study various electrocatalystic systems, including single crystal electrodes, electrocatalysis and lithium batteries, which will be discussed in details.

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Electrodialytic Recovery of Cobalt from Spent Lithium-Ion Batteries

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Recycling lithium-ion batteries has an increasing interest for economic and environmental reasons. Disposal of lithium-ion batteries imposes high risk to the environment due to the toxicity of some of their essential components. In addition to this, some of these components, such as cobalt, natural graphite and phosphorus, are included in the list of critical raw materials for the European Union due to their strategic importance in the manufacturing industry. Therefore, in the recent years, numerous research studies have been focused on the development of efficient processes for battery recycling and the selective recuperation of these key components.

$LiCoO_2$ is the most common material use in current lithium-ion batteries cathodes. In the current work, an electrodialytic method is proposed for the recovery of cobalt from this kind of electrode. In a standard electrodialytic cell, the treated matrix is separated from the anode and the cathode compartments by means of ion-exchange membranes. A cation-exchange membrane (CEM) allows the passage of cations and hinders the passage of anions, while the behaviour of anion-exchange membrane (AEM) does the opposite. A three-compartment electrodialytic cell has been designed and assembled, as depicted in the figure. In the central compartment, a suspension of $LiCoO_2$ is added.

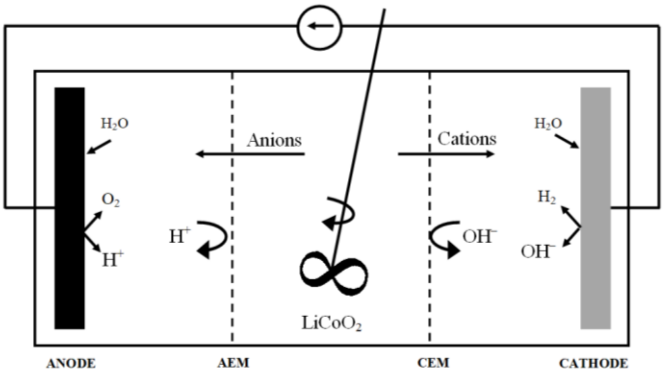

Figure: Scheme of the electrolytic cell for the recovery of cobalt from spent lithium-ion cells.

Different extracting agents, such as EDTA, HCl and HNO_3, are tested to enhanced the dissolution and the selective extraction of the target metal. Dissolved cobalt-containing complexes migrate towards the cathode or the anode compartments depending on the ionic charge of the complexes. While cobalt extraction via extracting agents is an expensive treatment, as it requires the constant addition of chemicals, an efficient electrodialytic cell could allow the recirculation of the extracting agents and the economical optimization of the process.

Acknowledgements:
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Theoretical and Experimental Study of Chromium (III) Oxide-Based Materials as Catalysts for ORR.

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Noble metals, such as Pt or Pd, are considered the most efficient materials to be used as catalysts for the oxygen reduction reaction (ORR). These catalysts have been employed widely in fuel cells. However, its high cost and low availability make necessary the study of new cheaper catalysts for ORR. The most studied elements to replace noble metals as catalysts in the ORR are the transition metals.

In this work, use of chromium (III) oxide supported on different carbonaceous substrates has been analyzed as catalyst materials for ORR. Initially, spectroscopic and electrochemical characterization of these electrodes will be shown together with the zinc-air batteries discharges using Cr_2O_3-based materials as positive electrodes.

The main part of this communication will be to show the Rotating Disck Voltammetric studies of Cr_2O_3 nanoparticles as well as chromium (III) oxide supported onto graphite, graphene, and graphene oxide. Values of n ranging from 2 to 4 were obtained, indicating different ORR mechanisms depending on the Cr_2O_3-based material used.

Finally, the experimental results has been modeled using an EC' (electrochemical-catalytic) mechanism reaching a good agreement between theoretical and experimental results. Both theoretical and experimental results will be discussed in depth.

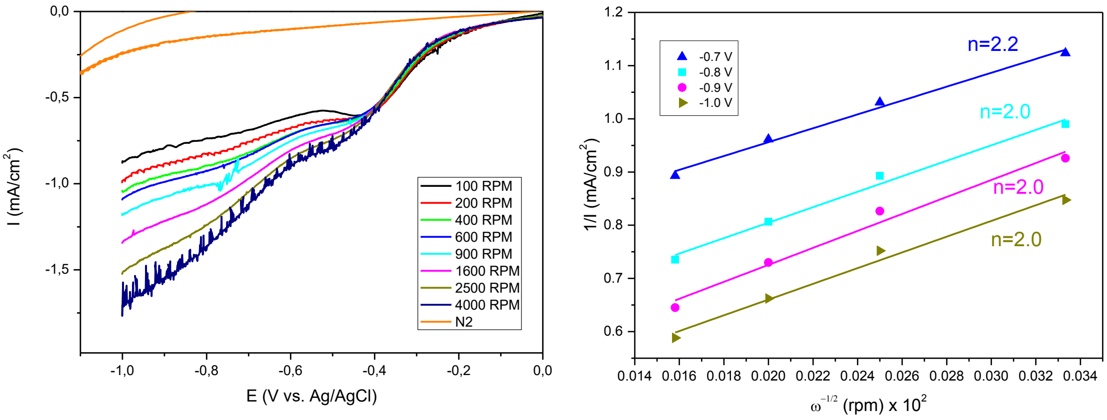

Figure 1. a) ORR study of Cr_2O_3 + graphene and b) Koutecky-Levich plot at different voltage values

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Efficient Barriers Towards Vanadium Crossover in Redox Flow Batteries

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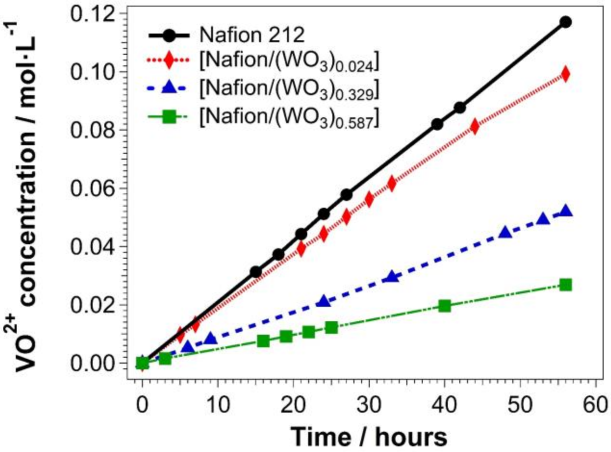
A new family of hybrid inorganic-organic ion-exchange membranes (IEMs), indicated as [Nafion/$(WO_3)_x$], is prepared by dispersing different loadings (x) of tungsten oxide (WO_3) nanofiller in Nafion® [1]. WO_3 exhibits excellent properties, that could be exploited for applications in electrochemical devices [2,3]. Indeed, WO_3 is stable in sulfuric acid media and has a lower cost in comparison with other metal oxides. IEMs for application in VRFBs must exhibit a facile proton migration. At the same time, they must inhibit the permeation of the redox-active vanadium-based species that leads to a low cycling efficiency and a fast capacity decay owing to self-discharge. Morphology studies carried out by scanning electron microscopy (SEM) and micro-Raman investigations reveal that one side of each hybrid IEM exhibits a high concentration of the WO_3 nanofiller. The time-dependent concentration changes of VO^{2+} species in H_2SO_4 solutions across the hybrid IEMs [Nafion/$(WO_3)_{0.024}$], [Nafion/$(WO_3)_{0.329}$], and [Nafion/$(WO_3)_{0.587}$] are compared with that of Nafion 212, that is used as the reference (see Figure). The performance of the hybrid IEMs is tested in a single-cell vanadium redox flow battery (VRFB). In comparison with Nafion 212 reference, at the same current density of 50 $mA \cdot cm^{-2}$, [Nafion/$(WO_3)_{0.587}$] demonstrates: (i) a higher coulombic efficiency (93% *vs.* 88%); a higher energy efficiency (75% *vs.* 65%) and a higher capacity retention (62% *vs.* 42%); this demonstrates a reduced crossover effect.



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Performance stability of negative electrode in vanadium redox flow battery

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Vanadium redox flow battery is a safe, durable and recyclable stationary energy storage technology for large-scale applications. The long-term durability originates from vanadium chemistry and absence of phase changes within electrode reactions. However, the life-time of battery stack can be significantly affected by the choice of inner stack components and operational conditions. In particular, the decrease of catalytic activity of negative graphite felt electrode has been recently reported[1-2].

In our contribution, we systematically study the durability of graphite felt negative electrode under operational conditions of vanadium redox flow battery. First part of the study focuses on the long-term stability under constant current charge-discharge cycling. The effect of graphite felt precursor and thermal activation on the performance stability was investigated for different cut-off voltages of the battery cycling and temperature of operation. The electrochemical impedance spectroscopy and load curve measurements were used to evaluate the performance stability during the cycling. For all the experiments with non-activated felt negative electrodes, the continuous decay of the battery performance was observed leading to the decrease of cycle energy efficiency from 80 to 60 % during 2000 cycles, which can be clearly correlated to the increase of the charge transfer resistance of negative electrode reaction. Contrary to that, only minor performance loss (up to 1 %) was observed for the cells with activated negative felt electrode under identical conditions. The *post mortem* characterization of the electrodes revealed the changes in electrode surface functionalization (by XPS) as the main cause of the negative electrode deactivation.

In order to get closer insight into the deactivation phenomena taking place during the battery operation, the single-electrolyte battery concept[3] was adopted and further developed to evaluate the electrode durability under stable and more defined conditions. Under open-circuit conditions, we observed a significant chemical deactivation of the felt and the deactivation rate depended on the electrolyte state of charge. Under current load conditions, in general, stronger deactivation was observed for charging process and higher currents. These results were again correlated with changes in electrode surface functionalization.

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Electrochemical and structural properties of graphene-like graphite for the anode material of lithium-ion battery

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Introduction

Graphene has been expected as an anode material for lithium-ion batteries with large capacity and good rate capability. However, quite large surface area of graphene brings about poor Coulombic efficiency. To solve this intrinsic difficulty, we have recently introduced graphene-like graphite (GLG) as a new candidate for the anode material [1 – 2]. Since the GLG has low specific surface area, it shows improved Coulombic efficiency compared to graphene. In addition, it shows the comparable capacity and rate capability to graphene. However, origin of these superior electrochemical properties has not been fully understood. In this study, we conducted structural analysis of GLGs together with electrochemical measurement to investigate the unique features of GLGs.

Experimental

Graphite was oxidized with Brodie's method to form graphite oxide, then thermally reduced at 700ºC under vacuum to synthesize GLG. The GLG was mixed with acetylene black and polyvinylidene fluoride on copper foil to obtain composite electrodes. Charge-discharge measurement was conducted with lithium metal as reference and counter electrodes in 1 mol dm^{-3} LiClO$_4$/ethylene carbonate + dimethyl carbonate. During charge-discharge cycling, X-ray diffraction was measured to analyze its structural variations.

Results and discussion

Figure 1 shows the charge and discharge curves of GLG. Even the GLG showed irreversible capacity at the initial cycle, it was much smaller than that of graphene. The discharge capacity at the initial cycle reached to 550 mAh g^{-1}, which was much larger than that of graphite. After the 2nd cycle, GLG showed good Coulombic efficiencies. Figure 2 shows variations of XRD patterns of GLG during charge-discharge cycling. After the 1st charge, the peak shifted to the lower value, indicating increment of interlayer spacing accompanied by Li$^+$ intercalation. However, after the 1st discharge, the pattern did not return to the initial state, indicating irreversible structural change of GLG. On the other hand, the pattern showed reversible variations during the 2nd cycle, indicating the structure of GLG reversibly changed. After the 10th charge, GLG showed a broad peak around $2\theta = 26$º, which was the similar 2θ-value to the pristine GLG. It indicated that the GLG was amorphized during repeated cycles, and Li$^+$ was intercalated without increasing interlayer spacing of GLG. This result shows good agreement with the good cycleability during the following cycles observed in Fig. 1.

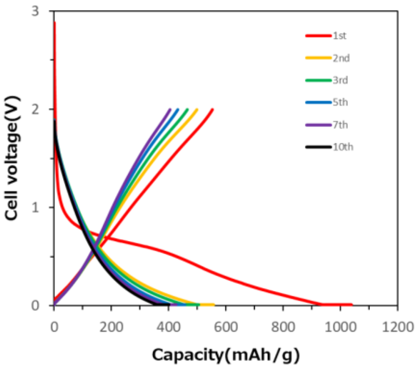

Fig. 1 Charge-discharge curves of GLGs.

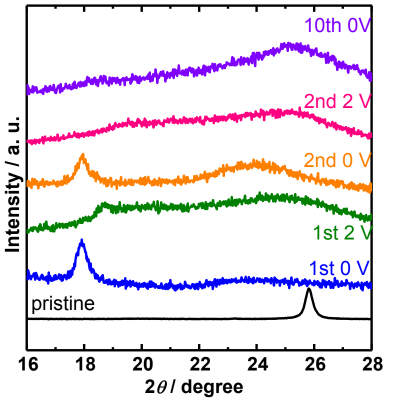

Fig. 2 XRD patterns of GLG during cycling.

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The Effect of Impurities on the Redox Reactions for the All-Vanadium Redox Flow Battery

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The electrolyte is a major component of the cost of vanadium redox flow batteries (VRBs), and the required purity of the vanadium electrolyte can contribute significantly to the cost of the vanadium electrolyte [1]. Understanding the effects of metal impurities on the electrode kinetics may support the development or application of lower cost, less pure vanadium electrolyte resources [2]. In this study, the influences of three important metal impurities present in vanadium ores: iron, aluminum and manganese, on the performances of VRBs have been investigated using the electrochemical studies.

A three electrodes system including carbon paper, platinum wire and saturated calomel electrode (SCE) as a working, counter and reference electrode, respectively, was utilized to conduct cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments. According to the typical vanadium electrolyte compositions, electrochemical characterization was carried out for both positive and negative electrolytes at a vanadium concentration of 1.6 M and sulfuric acid concentration of 3 M as supporting electrolyte. Vanadyl sulfate ($VOSO_4$) was used to prepare the positive electrolyte, and the negative electrolyte was prepared through electrolytic reduction of $VOSO_4$ in an electrochemical flow cell. The effects of five different concentrations (0.02, 0.04, 0.06, 0.08 & 0.1 M) for each impurity were studied through CV and EIS experiments.

The CV results shown in Fig. 1 indicate that gas evolution will increase with increasing concentrations of the metal impurities. The standard rate constants in the presence of impurities were estimated using CV and EIS tests. The Nicholson-Shain approach was used to find the charge transfer kinetics from the CV data. An equivalent circuit model was also fitted to the EIS data to estimate the influences of impurities on the electrode kinetics. Moreover, the effects of impurities on the diffusion behavior of the vanadium species were investigated using Randles-Sevcik analysis. In order to explore the effects of impurities on the efficiencies of VRBs at different current densities, a redox flow cell will be used and galvanostatic charge-discharge experiments will be reported.

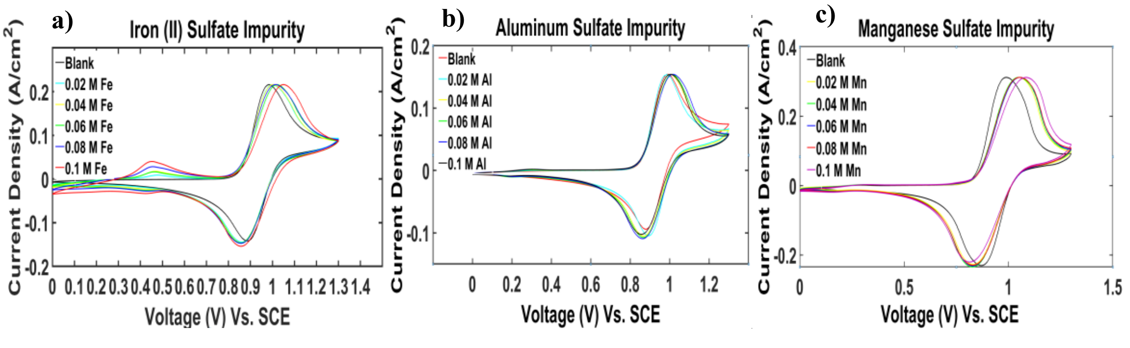

Fig. 1. Cyclic voltammetry for different concentration of impurities: a) Iron sulfate b) Aluminum sulfate c) Manganese sulfate.

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-N=C- based materials for electrochemical energy storage

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Organic based batteries represent an affordable and abundant alternative to conventional batteries based in inorganic materials. Thus, they are key for the development of large-scale electrochemical energy storage where energy density is not a constrain. In addition to their abundance, organic electrodes are very versatile since their redox voltage can be tuned by changing the conjugation length or by the presence of functional groups with different electron donating or withdrawing ability [1].

Among organic and metalorganic materials, those containing >C=N- units, although less explored than other organic functionalities, are showing promising performance for their application in EES systems. Indeed -C≡N- containing metallorganic compounds, such the Prussian Blue and its analogues [2] are excellent cathodes for Na-ion and K-ion batteries and they have been broadly reported and patented by Alveo Energy or SHARP America [3].

In this presentation, I will show several examples of recent developments in which pi conjugated/>C=N- based electrode materials show good electrochemical performance for rechargeable batteries. They will cover from the polymeric Schiff-bases [4] to hybrid oligomeric Schiff bases with carboxylate end-groups [5], both systems able to store Na ions at voltages low enough to be used as anodes in Na-ion batteries. Current understanding of their mechanisms of Na insertion in organic media will be discussed against the Na insertion mechanisms into carbonyl units [6].

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HIGHLY WATER-SOLUBLE ORGANIC DYES AS POTENTIAL SINGLE COMPONENT ELECTROLYTES FOR REDOX FLOW BATTERIES

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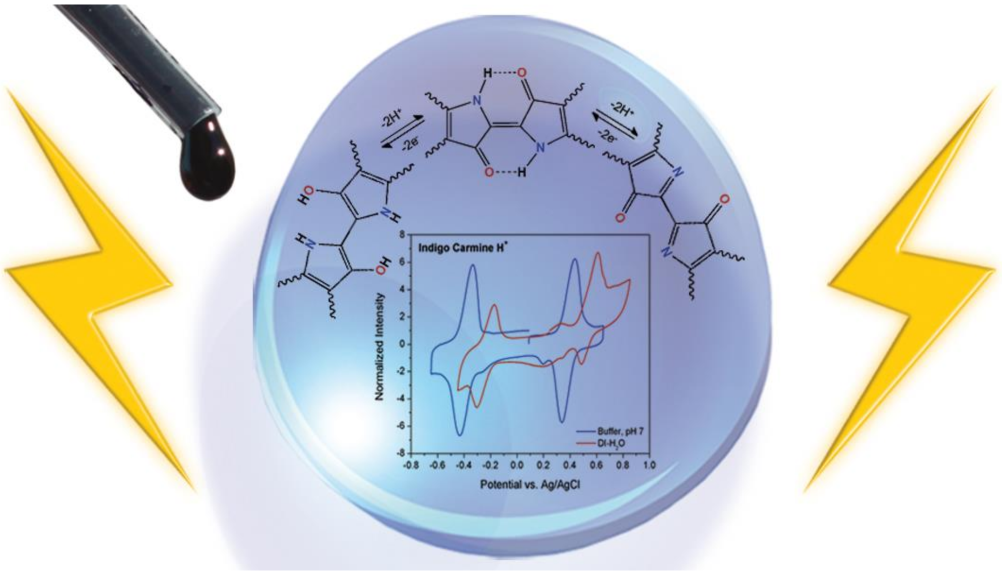
Indigo and anthraquinone derivatives, which are extensively used in industrial dye applications, contain electron density donor (–NH– or –OH) and acceptor (>C=O) groups linked by conjugated bonds in their molecular structure, which are responsible for their deep shades. We found that with a proper choice of aqueous electrolyte these dyes are able to both reversibly oxidize and reduce, developing two-sets of fast two proton–electron transfers separated by ∼1 V. These large flat molecules are poorly soluble due to extensive "π" stacking, and the classical strategy of appending a sulphonate ($-SO_3Na$) group appeared insufficient to reach ≈1 M. Herein, we have further boosted the solubility of these dyes in water up to 1.6 M by replacing Na^+ with an organic cation such as tetrakis (hydroxyethyl)-ammonium $[N(CH_2CH_2OH)_4]^+$ or tetrakis (hydroxymethyl)-phosphonium $[P(CH_2OH)_4]^+$ that are non-chelatable and very hygroscopic while maintaining a reversible charge transfer and a large electrochemical potential window in dilute protic acids (0.1 M $HClO_4$), or in neutral pH buffered aqueous solutions (Britton–Robinson buffer). The corresponding pure salts melt even near ambient temperature. Our findings imply that the same electroactive material could be used as a catholyte and an anolyte in a 1 V symmetrical redox flow cell at neutral or close to neutral pH, with all its advantages in terms of cell corrosion and membrane requirements.



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Towards high-energy alkaline flow batteries

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Ferrocyanide ion-based alkaline redox-flow batteries are considered promising alternatives to traditional redox-flow batteries that are based on high cost and strategic metals and corrosive acidic media. Ferrocyanide has been used as active species in the positive side of a variety of redox-flow batteries, e.g. anthraquinone/$K_4Fe(CN)_6$[1] and phenazines/$K_4Fe(CN)_6$[2]. However, in all these cases, energy density is limited by the low solubility of ferrocyanide in alkaline media (0.4 M equivalent to 10 AhL^{-1}). In contrast, electroactive solid species that are frequently used in non-flow batteries are able to store more charge per unit volume than soluble electroactive species, e.g. $Ni(OH)_2$ has a volumetric capacity of 1180 $Ah{\cdot}L^{-1}$, which is two orders of magnitude higher than that of a ferrocyanide solution. However, solid materials cannot be used in flow batteries as there is no electrical contact between the electrode and the solid located in the external tank.

In this talk, we will show that soluble electroactive species can be also used as molecular wiring to store energy is solid electroactive materials breaking the boundary between liquid and solid energy storage. The concept is demonstrated for a system in which ferrocyanide- ferricyanide is used as electroactive specie that transfers charge between the electrode and the solid ($Ni(OH)_2$) located in the external tank[3] (Figure 1a). By adding solid material, volumetric capacities of >25 Ah L^{-1} are achieved with a utilization rate of $Ni(OH)_2$ of ca. 40 %. We demonstrate the concept in two type of ferrocyanide-ion flow batteries: quinone-ferrocyanide (Figure 1b) and phenazine-ferrocyanide. For the latter, energy densities of >15 Wh L^{-1} are demonstrated representing the highest value for an alkaline flow battery.

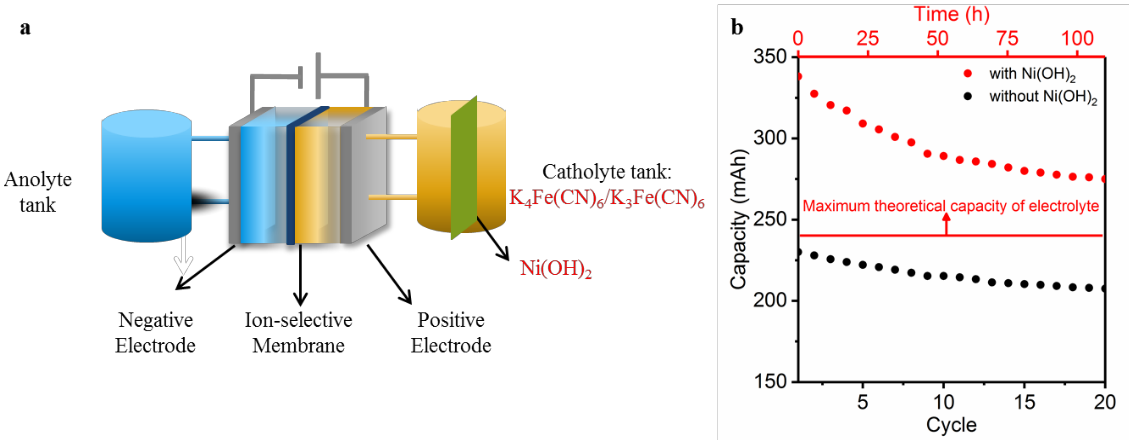

Figure 1 **a** Scheme of a redox-flow battery based on the use of ferrocyanide-$Ni(OH)_2$ in the positive container. **b** Reversible stored charge during the first 20 cycles of a 2,6-dihydroxi- anthraquinone // ferrocyanide flow battery in the absence (black circles) and in the presence (red circles) of solid $Ni(OH)_2$ in the external positive container.

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Lithium Air Flow Battery for Next Generation Energy Storage Applications

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To be succeeding in the electric vehicles, high energy density batteries need to be produced with low cost and safe. Although lithium ion batteries has been reached a great commercial success to mobile devices, their low energy densities (200 Wh/g) and high cost values are limited them to use in electric vehicles. Even though, lithium air batteries have 11.680 Wh/kg theoretical energy density, the energy density can be obtained in range of 600 Wh/kg - 1500Wh/kg in the practical applications [1]. Lithium air batteries using aprotic electrolyte has first reported in 1996 by Abraham and Jiang. There are three basic issues encountered in lithium air batteries; (1) Li_2O_2 and Li_2O compounds deposited more on the higher oxygen flow places, which cause inhomogeneity distribution of the oxygen and result in clogging of the porous and prevent the passage of oxygen through the cathode. Therefore, the cathode cannot show reaction with its all volume and obtain a low energy density. (2) The another reason is that it has not been found an effective catalyst, leading to obtained low energy efficiency and poor cyclability. (3) Another problem, since the liquid electrolytes which has low oxygen diffusivity, the lithium air batteries works under low current density cause obtaining low power density [2]. Recently, researchers have focused on metal-air flow battery system to cope with such issues [3, 4].

In this work, we aimed to obtain higly reversible lithium air flow battery system which will overcome the such issues observed in current air batteries. For this aim, we designed a home-made dual electrolyte lithium air flow cell system which consists of three different parts. First part is the cell where there are anode, cathode, electrolytes and membranes. Second part is electrolyte container which includes aqueous LiOH electrolyte and the last part is pump which assure flowing of the electrolyte from container to cell. The cell was assembled with lithium anode, lithium ionic conducting glass ceramic (LATP) membrane and GDL (sigracet, 24BC) cathode. In this dual-electrolyte cell, lithium ion containing none-aqueous electrolyte situated between Lithium anode and LATP membrane, lithium ion containing aqueous electrolyte added between cathode and LATP membrane. The aqueous electrolyte was stored in a container and provides an electrolyte circulation from container into the cell by a pump. At the same time, oxygen was pumped into the aqueous electrolyte and oxygen was reached to the cell through the aqueous electrolyte. The flow system of the battery such as oxygen flow, electrolyte flow and oxygen volume fraction into the cell was optimized using ANSYS Fluent software. The fabricated lithium air flow battery was tested at the potential window from 2.4 V to 4.5 V at different current density. The obtained results show that the lithium air flow battery system might be an alternative and suitable for storing energy in mobile and stationary applications.

Acknowledgments

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Electrochemical Reactions of Heat-treated Lithium Metal

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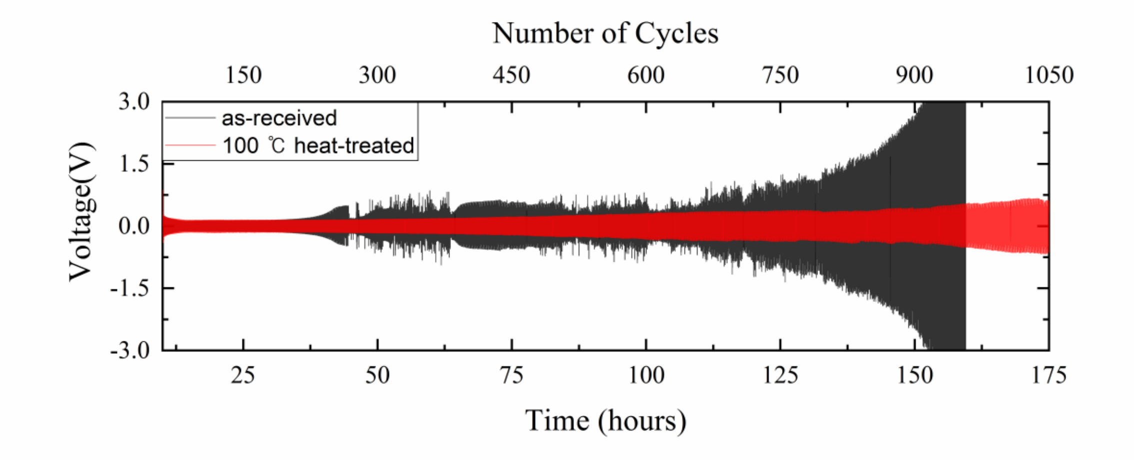
Recently, the emerging market of the electric devices triggered the development of advanced energy storage systems. In this respect, lithium batteries (LIBs) appeared the most promising among the various candidates due to their high theoretical energy and long calendar life. In that way, lithium metal has attracted considerable interest as a negative electrode material because of its high energy density (gravimetric and volumetric capacities of 3860 Ah kg^{-1} and 2060 Ah dm^{-3}, respectively) and low standard electrode potential (–3.045 V versus standard hydrogen electrode). However, even though lithium metal battery receives the attention as a next-generation lithium secondary battery, the formation of lithium dendrite hindered the commercialisation.

This research involves the use of as-received and heat-treated lithium metal foil before running impedance tests with the objective to identify changes over the lithium surface; these procedures help in the understanding of dendritic lithium generation and changes that occur over the surface. Electrochemical impedance spectroscopy (EIS) was used to measure the impedance of Li/Li symmetric cell at 25 ºC in a thermal chamber, and Zibe (ZMAN v.2.4) was used to fit EIS data and find an equivalent model for the cell. Electrochemical analysis of lithium was examined using Li/Li symmetric cell and $LiPF_6$ EC/EMC 1:1 (w/w) as an electrolyte solution to evaluate the evolution of Li deposition-dissolution until cell decay.

This research found that lithium metal after subduing to different temperatures between 25 and 100 ºC generates a series of sub-products that function as a protective film of the surface. Additionally, EIS results show an increment of the internal resistance in 120 ohms, arguing that these changes in the film protects the lithium metal during the deposition-dissolution of lithium against shortcut, afterwards scanning electron images (SEM) reveal concise differences in both samples, in which they showed that such improvement was due to such products. This assumption was later checked in Figure 1 with a Li deposition-dissolution at 1 mA cm^{-2} with a charge amount of 0.25 mAh cm^{-2} for each half cycle in which as-received lithium foil shown unstable dendritic growth against heat-treated lithium metal foil resulting in cell failure.

The results found a relation that the steady increase in overpotential as the cell nears failure is a result of electrolyte penetration through the lithium foil surface and production of inactive Li material on the surface.



This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20184030202130).

Photoelectrochemical solar fuel production using organic semiconductors

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Organic semiconductors are well-established as high-performance and easily-processed materials for inexpensive and scalable solar energy conversion in organic photovoltaic (OPV) devices, but their promise in the economic conversion of solar energy into chemical energy (solar fuels) has only recently been recognized. In this presentation, I will discuss the main approaches for employing organic semiconductor-based devices towards solar H_2 generation via water splitting and review the state-of-the-art.[1] OPV-biased water electrolysis has advanced significantly, now exceeding 6% solar-to-hydrogen conversion efficiency. However, the direct water splitting by an organic semiconductor in a photoelectrochemical cell, which has attractive advantages, remains limited by the intrinsic stability of organic semiconductors with direct junctions with aqueous electrolyte. I will further present experimental insights into the operational stability of donor:acceptor bulk heterojunction photocathodes with an organic/water interface via the photoelectrochemical reduction of sacrificial electron acceptors that identify the key factors that govern long-term photoactivity (>12 h). These insights can be extended H_2 evolution reaction catalyst overlayer design and to set a new benchmark for organic photocathodes for solar fuel production.

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Next generation plating on plastics process without hexavalent chromium and palladium

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1. Introduction

A general pretreatment for plating on plastics(POP) is known that the surface of the ABS resin is etched by a chromic acid solution and then catalyzed by palladium-tin colloid.

Thereafter, an activation treatment for removing tin is performed, and electroless plating is formed.

However, the above method has a problem of using harmful chromic acid and expensive palladium. In addition, since it is necessary to separately perform the catalyst application step and the activation treatment step after performing the etching step, the entire processing step becomes long, and analysis and management of each chemical solution becomes complicated.

Considering productivity and management, it is desirable to shorten the processing step as much as possible.

In this research, we developed a new plating method that can shorten the processing step without using harmful chromic acid and expensive palladium.

2. Experimental

As an alternative to chromic acid, we used permanganic acid. It is known that permanganate has a high redox potential compared to chromic acid (see below).

・$HCrO_4^- + 7H^+ + 3e^- = Cr^{3+} + 4H_2O$ ・・・ + 1.33 V
・$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$ ・・・ + 1.51 V

As an alternative to palladium, we used silver as a cheap precious metal. The processing steps considered are shown in Table 1.

Table 1 Plating Process

Steps	Temperature	Time
Etching & Catalyzing	68 °C	15 minutes
Remove Mn	35°C	30 seconds
↓ Water Rinse		
Electroless Nickel Plating	30°C	10 minutes

By immersing the ABS resin in permanganic acid solution containing Ag (I), etching and catalyzing can be performed at the same time. Thereafter, in order to remove manganese on the surface, it was immersed in an aqueous solution containing chloride ions.

After water rinsing, it was immersed in an electroless nickel plating solution to form the nickel film on the ABS resin.

Thereafter, strike nickel plating was formed to 2 µm and electrolytic copper plating was formed to 50 µm. Then, the adhesion of the plating film was confirmed by a peel strength test.

3. Results

The peel strength from the permanganic acid-silver process (Mn-Ag process) is 12.1 N/cm, and that from the chromic acid-palladium process (Cr-Pd process) is 11.9 N/cm shown as Figure1. The adhesion of Mn-Ag process is equivalent to the conventional Cr-Pd process.

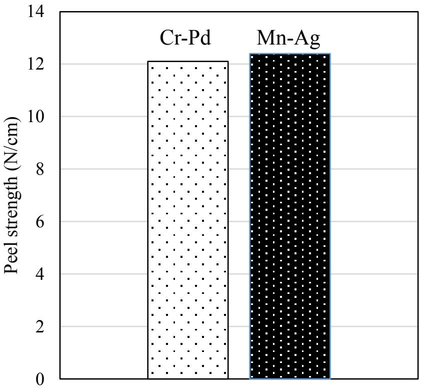

Figure 1 Results of the peel strength test

4. Conclusions

We found that adsorption of silver catalyst and etching of the resin can be performed at the same time by immersing the ABS resin in permanganic acid solution containing Ag (I). This makes it possible to significantly shorten processing step compared with the conventional process without using harmful chromic acid and expensive palladium.

Pressurized CO_2 Electrochemical Conversion to Formic Acid: From Theoretical Model to Experimental Results

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To curb the severely rising levels of carbon dioxide in the atmosphere, new approaches to capture and utilize this greenhouse gas are currently being investigated. In the last few years, many researches have focused on the electrochemical conversion of CO_2 to added-value products in aqueous electrolyte solutions. In this backdrop, the pressurized electroreduction of CO_2 can be assumed an up-and-coming alternative process for the production of valuable organic chemicals [1-3]. In this work, the process was studied in an undivided cell with tin cathode in order to produce formic acid and develop a theoretical model, predicting the effect of several operative parameters. The model is based on the cathodic conversion of pressurized CO_2 to HCOOH and it also accounts for its anodic oxidation.

In particular, the electrochemical reduction of CO_2 to formic acid was performed in pressurized filter press cell with a continuous recirculation of electrolytic solution (0.9 L) at a tin cathode (9 cm^2) for a long time (charge passed 67'000 C). It was shown that it is possible to scale-up the process by maintaining good results in terms of faradaic efficiency and generating significantly high concentrations of HCOOH (about 0.4 M) [4]. It was also demonstrated that, for pressurized systems, the process is under the mixed kinetic control of mass transfer of CO_2 and the reduction of adsorbed CO_2 (described by the Langmuir equation), following our proposed reaction mechanism [5].
Moreover, the theoretical model is in good agreement with the experimental results collected and well describes the effect of several operating parameters, including current density, pressure, and the type of reactor used.

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Electron-Coupled Proton Buffers for Water Splitting and Flow Battery Applications

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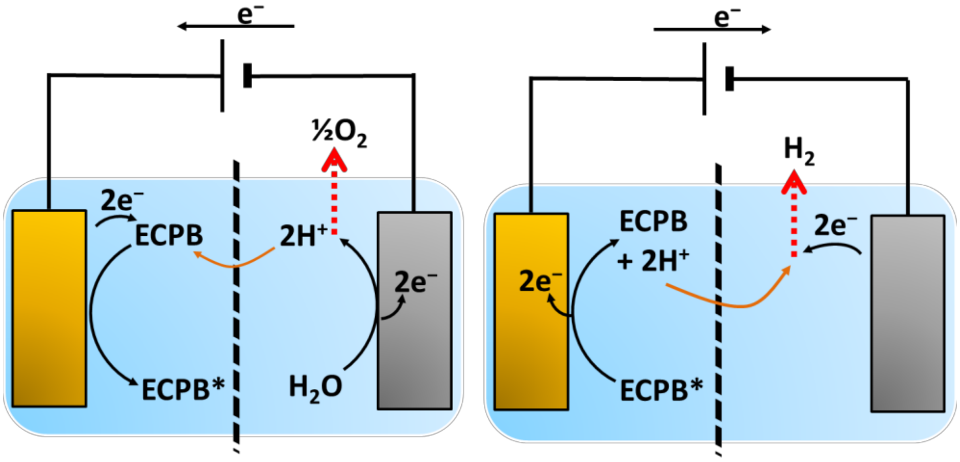
There has been much interest recently in electrocatalytic water splitting for storing intermittent renewably-generated power (e.g. solar) as chemical fuels such as hydrogen (1). In this talk, we shall investigate new device architectures for water splitting that use Electron-Coupled-Proton Buffers (ECPBs, see Figure) as redox mediators (2), allowing oxygen and hydrogen production to be separated in both space and time. The advantages of this approach for harnessing intermittent power sources will be explained, such as the production of ultra-pure product gases (3,4) and the potential benefits of using such a system in a more diffuse, solar-driven hydrogen production platform (5). Finally, the application of this technology to redox flow batteries with remarkably high energy densities will be discussed (6).



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Electrodeposition from Lean Electrolytes using Direct and Pulse Currents

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The use of chemicals for metal deposition, which can control deposit properties, are being increasingly scrutinised for their impact on the environment. The Printed Circuit Board Industry typically requires copper deposits to have certain attributes, such as low electrical resistance coupled with good mechanical properties. Such specific properties are imparted by using bespoke electrodeposition processes where acid concentration and metal ions are prescribed through experience, typically 2.0 M H_2SO_4, and 0.6 M $CuSO_4$, and small amounts of additives.

Some recent work has shown that that micro-scale copper features, such as those required in PCBs, can be deposited using an acid-free, low copper ion concentration. Therefore, current modulation could become a significant factor in modification of deposit properties when additive levels are low. This research also showed that lower concentrations of commercial plating additives are needed to improve deposit properties, so that they are suitable for industrial applications.

This work examines the effect of lowering both additives, metal ions and supporting electrolyte in industry recommended electrolytes. These electrolytes, which can be classified as “lean” electrolytes, still need to achieve industry recommended standards. We describe the steps taken to achieve industry targets for electrodeposited copper for fabrication of copper lines in printed circuit boards. Film of copper which were 25 μm in thickness have been plated on stainless steel substrates from electrolytes containing only cupric ions, chloride and commercial additives. These electrolytes contain different concentrations of additives ranging from 17% to 200% of the levels recommended by the supplier. Both direct and pulse currents have been used for this purpose and material properties have been measured. Pulse currents are used because it is known they can modify deposit morphology and properties.

The grain size, morphology and crystal structure of the deposits have been measured and interpreted in terms of process parameters. In particular, the effects of additive agents and pulsing current have been decoupled. Mechanical and electrical properties of the copper films have also been tested and compared against those specified for the manufacture of printed circuit boards. These measurements indicate that lean electrolytes could be used for copper deposition for printed circuit boards. Overall, the study shows that additive concentration in processes for metal could be lowered. This could improve the overall environmental impact of metal plating processes.

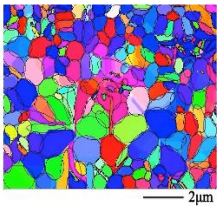

Fig.1. Electron Back Scattered Diagram of Pulse Deposited Copper from a Lean Electrolyte

Graphene oxide framework protective layer for enhancing the durability of hydrocarbon membrane in vanadium redox flow batteries

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Graphene oxide membrane with laminated structure, which features a regular interlayer spacing, possesses exceptional ion separation properties. In this regard, graphene oxide membrane is highly attractive for vanadium redox flow batteries, because it can allow the permeation of proton but block the vanadium ions, and consequently reduces vanadium crossover and membrane durability. However, an expanded laminate in water (~11.1 Å) which is larger than the hydrated dimeters of vanadium ions (> 6.0 Å) does not show the ion selectivity. In this presentation, we report an ion-selective graphene oxide framework (GOF), the interlayer spacing of which in hydrated state is tuned by cross-linking of graphene oxide nanosheets. With making use of its effective pore size (~5.9 Å), which blocks vanadium ions but allows proton conduction, the GOF membrane functions as a protective layer to address the poor chemical stability of hydrocarbon based membrane against VO_2^+ in vanadium redox flow batteries. The hybrid of GOF and hydrocarbon membrane exhibits 4.2 times lower vanadium ion permeability and five times longer durability compared with the pristine hydrocarbon membrane, which are attributed to the effective blocking of vanadium ions by the GOF membrane. Moreover, the vanadium redox flow battery with the hybrid membrane achieves an energy efficiency of 89% and a capacity retention of 88% at 400th cycle, which are better than those of Nafion 115, emphasizing the practical applicability of GOF technology for VRFB.

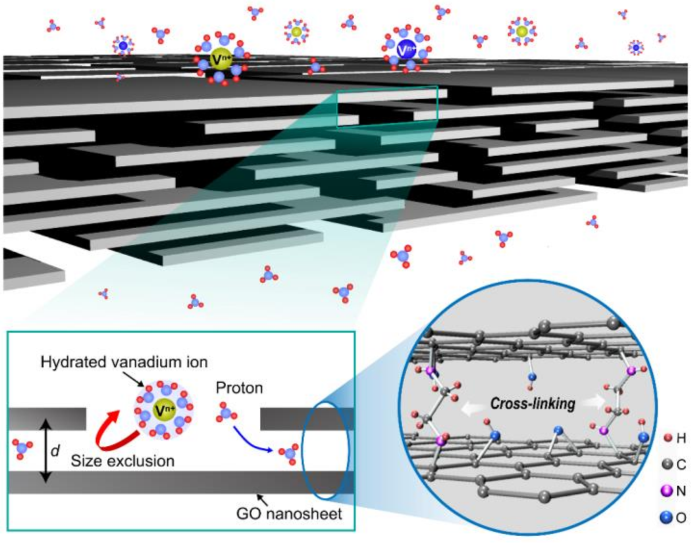

Figure 1. Schematics of the graphene oxide framework layer which provides the selective ion transfer of hydrated vanadium ions and protons. The crosslinked structure derived by ethylene diamine is sketched.

A Vitamin-Based Redox Flow Battery

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An all-organic, metal-free redox flow battery (RFB) system using a vitamin E analogue (VE_A) [1] and a vitamin K analogue (VK_A) [2] as the electron donor and acceptor, respectively, in acetonitrile containing acid was developed (Figure 1). The modified vitamin E system undergoes a fully chemically reversible one-electron oxidation process at approximately +0.5 V vs. Fc/Fc^+ to form a radical cation that is long-lived in solution and is unaffected by the presence of acid or water. The modified vitamin K system undergoes a two electron/two-proton chemically reversible reduction process to form a hydroquinone. The hydroquinone is long-lived in acidic acetonitrile solutions but the potential of reduction is greatly affected by the concentration and nature of acid. The reduction of the VK_A to the hydroquinone in the presence of acid can be represented by a series of proton-coupled electron transfer (PCET) reactions in an electrochemical square-scheme mechanism. In the absence of acid and in the presence of hydrogen bonding donors (such as water), the reduced forms of VK_A undergo strong hydrogen-bonding interactions through the negatively charged oxygen atoms, which can also be represented by the square scheme mechanism. Both protonation and hydrogen-bonding mechanisms result in a shift in reduction potential of VK_A with changing acid/H-bonding donor concentrations, which can be utilized to optimize the overall cell potential of the battery. It was found that the weak acid diethyl malonate allowed the greatest separation between the two redox couples used in the battery (~1.3 V). Controlled potential electrolysis experiments confirmed that the mixed reactant VK_A/VE_A system was long-lived in solution in both fully oxidized and fully reduced states.

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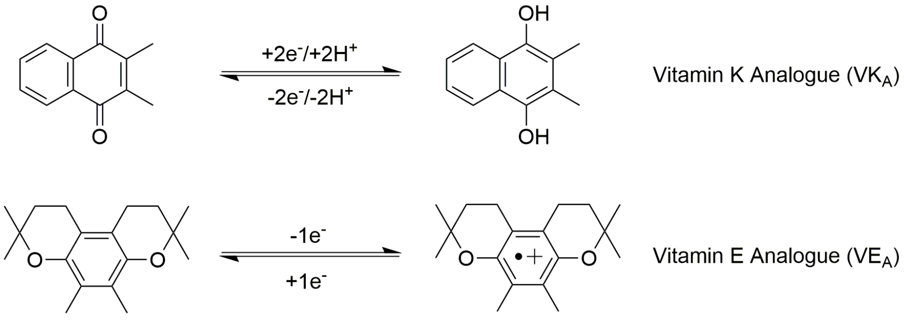

Figure 1. Redox reactions in vitamin-based battery.

Investigating an all-organic battery using polyisothianaphthene as a redox-active bipolar electrode material

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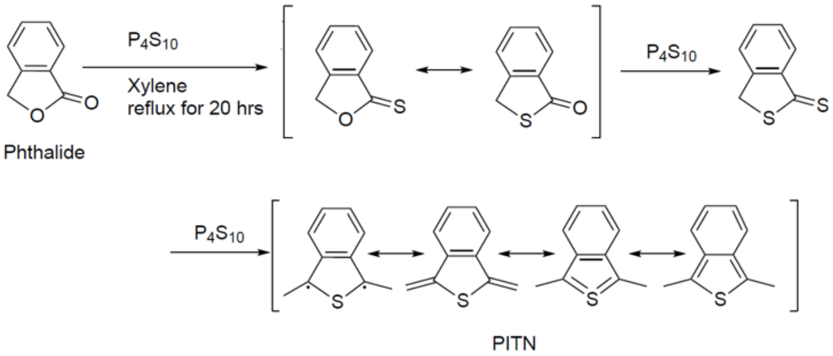
Polyisothianaphthene (PITN) has the smallest bandgap among all conjugated polymers and delivers high electrical conductivity. This study used PITN as an active material to accept both lithium ions and PF_6^- on its cyclic C–S–C bond and benzene ring during the processes of n-doping and p-doping. This study discovered that lithium polysulfide and lithium sulfide were formed during the first electrochemical reaction; however, the impedance, rate performance, and energy density of PITN cells were not affected by those side products. By contrast, an increment of superior rate (10 C) testing was significantly improved by those new sulfur-based solid electrolyte interphase formations compared with transitional anode materials, such as graphite, silicon, and other conjugate polymers. The surface characteristics of the PITN electrode were investigated through *in situ* X-ray absorption spectroscopy, *in operando* Fourier transform infrared spectroscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. Furthermore, the reaction mechanisms of n-doping and p-doping on PITN were discussed. The PITN electrode's acceptance of lithium ions exhibited a specific capacity of 730 mAh g^{-1} at the second cycle as well as of 106 mAh g^{-1} when it reacted with PF_6^-. The battery performance exhibited a capacity of approximately 92 mAh g^{-1} when operated in the bipolar mode. The low-bandgap–conjugated polymer PITN was shown to have high reversibility in terms of bipolar electrochemical reactions, which indicates that it can be a promising bipolar organic material for use in lithium ion batteries. For the first time, this study on PITN discussed and investigated its bipolar function in LIBs.

The analysis results showed that PITN can serve in both n-doping and p-doping reactions. With the unique interface reaction on the anode side, the new sulfur-based SEI was discovered, and it provided a superior rate performance (10 C) and high cycle durability (200 cycles). In addition, the energy density of PITN on the cathode side was 106 mAh g^{-1} without any decay after a few cycles. The bipolar performance of PITN confirmed the initial energy density achieved was 92 mAh g^{-1}. More studies are ongoing into the modification polymer skeletons to increase the p-doping reaction.



Scheme 1 Synthesis of polyisothianaphthene (PITN).

Development of Membrane-Free Redox Flow Batteries by using Immiscible Electrolytes

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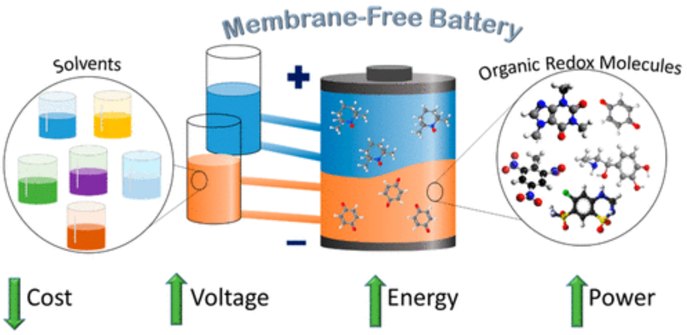
Wide-spread implementation of conventional RFBs is limited by some obstacles related to low abundance, toxicity and high cost of vanadium redox compounds, and the poor-performing and expensive ion exchange membranes. Excepting polymer-based RFB (1) where crossover can be mitigated with an inexpensive size-exclusion separator, most RFB require an ion-exchange membrane to prevent the crossover of active species.

Here, we present an innovative concept of Membrane-Free Battery which proposes to eliminate any separator or membrane by using immiscible redox electrolytes (2). These electrolytes spontaneously form a biphasic system whose interphase functions as a “natural” barrier making the use of any membrane superfluous. Moreover, the vanadium redox species are replaced by cheap and abundant organic redox molecules that can be specifically designed to exhibit high solubility, adequate redox potentials and suitable partition coefficient between the two immiscible phases. It will be demonstrated that this disruptive technology is hugely versatile with respect to the type of organic redox species as well as the nature of immiscible electrolytes forming the biphasic system. We report on the electrochemical performance of Membrane Free batteries based on aqueous/non-aqueous immiscible electrolytes (3) but also a Total Aqueous Membrane-free Battery in which the two phases are aqueous (4, which brings some advantages in terms of cost, environmental issues and battery performance. New challenges such as the inherent selfdischarge in the liquid-liquid interface and future opportunities of this innovative technology will be also discussed.



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Acknowledgments

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Compared electrochemical reactivity of hematite and iron ores for production of iron from alkaline solutions: effect of the impurities

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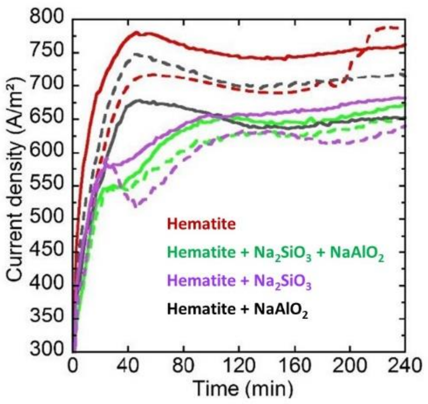
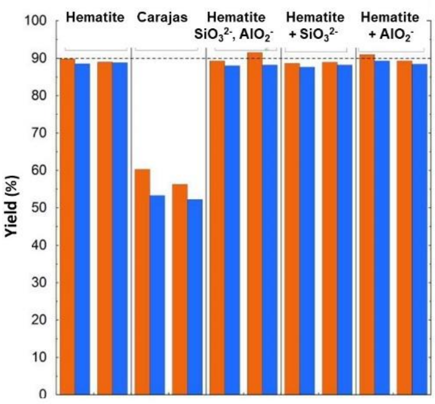
Electrochemical reduction of hematite from hematite or ores suspended in a strongly alkaline solution was shown to represent an alternative to the conventional processes with blast furnaces because of its largely reduced CO_2 emissions, the lower energy consumption induced and high current yields at current densities near 1000 A/m^2. For reduction of operating cost, cheap, abundant sources of iron oxides have to be found, but without too severe degradation of the process performance. We previously showed that among the various iron oxides, hematite was the most efficient [1], allowing both higher current density and current efficiency. The present work deals with the investigation of two abundant iron ores, namely Carajas and Tubarao, in the electrodeposition cells, in comparison with two hematite samples of different particle sizes, approx. 0.2 and 10 µm. Iron deposition has been conducted on the 10 cm^2 cylindrical cathode for 4 hour long periods at the same cell voltage and under thorough agitation of the solid liquid suspension: the solid-over liquid ratio was fixed at 10 wt.% and the liquid was a 16 M NaOH solution at 110°C. Carajas ore was in the form of 0.2 µm particles whereas Tubarao particles had a size from 1 to 30 µm; both ores had a goethite content near 14% and silica at several percents; gibbsite was also present in Carajas. The two hematite fractions exhibit slightly different behaviour, but in all cases with current yield over 80% and current density in the order of 800-1000 A/m^2. The performance of Tubarao ore in terms of current density and faradaic efficiency was approx. 20% below that of hematite, whereas Carajas allowed current density for Fe deposition near 200 A/m^2 only. Analysis of the liquid phase after the runs showed that silica and alumina were at least partly dissolved from the ore particles.

The effect of impurities on the reduction in iron deposition, was investigated by emulating the behaviour of Carajas by the finer hematite grade, with addition of soluble sodium aluminate or sodium silicate – or both of them in further deposition tests. Although visible, the presence of the two salts - at levels representative to those in Carajas, has only moderate effects on the current density at the fixed cell voltage, with nearly unaffected current yields (see figure below). The poor performance exhibited by Carajas ore is discussed in the paper, in terms of little reactive surface of the particles and efficiency of adsorption of the particles on the cathode surface, which is required in this particular deposition [2].





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Feasibility of producing electrolytic iron from red mud

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Keywords: Bauxite, iron, red mud, electrodeposition, hematite

Aluminum production by Bayer process from bauxite ore generates huge amounts of waste. This waste, commonly called red mud, contains about 50% wt. hematite (Fe_2O_3), 10 wt.% titanium dioxide (TiO_2) and about 30 wt.% aluminosilicates ($NaAlSiO_4$). About 70 million tons of red mud are produced every year in the world [1]. The management of this waste remains complex because of the amount of soda they contain ranges from 0.5 to 4% wt., and of the presence of other hazardous metals e.g. vanadium or chromium. Most research works on red mud propose to use this residue as (i) building material [2], (ii) pollutant adsorbents [3] or (iii) a source of rare metals [4].

In order to provide a real solution to the management of red mud, this study proposes to extract iron by electrochemical technique, more precisely by electrodepositing, the iron initially contained as hematite in the red mud suspended in a concentrated alkaline solution. This research work has been achieved based on experience reported in previous papers [5], [6] with hematite particles, with the following objectives: (i) reduce the waste volume, (ii) produce electrolytic iron, thus creating added value, (iii) access to other metals contained in the residues (like titanium), (iv) study the possibility of reusing the residues depleted of heavy metals for other applications such as road construction or geopolymer cement.

Therefore, iron electrodeposition tests were conducted in a double wall borosilicate glass cell (600 mL) from a suspension containing 33 wt.% red mud and 67 wt%. 12.5 M NaOH solution. The red mud fractions used in this study were first characterized by microscopic and spectroscopic techniques, in addition to granulometry. Electrolytic deposits of iron were also characterized by XRD, SEM and ICP-AES after dissolution in nitric acid. The iron deposits obtained have a purity greater than 97%, confirming the feasibility of producing electrolytic iron from red mud. On the other hand, the faradic yields, in the order of 20%, i.e. far below those from pure hematite near 85%, have to be improved. To improve these yields, several routes are explored (i) leaching of red sludge in sulfuric acid medium to eliminate aluminosilicates before electroplating of iron, (ii) reduction of hematite to magnetite by carbon monoxide followed by magnetic separation to extract the magnetite and finally electrodeposition of iron from this concentrate of magnetite. This presentation consists of two parts (i) the characterization of red mud, (ii) the electrodeposition and characterization of iron from the suspension of these residues and 12.5 M NaOH at 110 ° C.

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Electrochemical performance of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ with optimized morphology

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The layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) is a promising cathode material and represents environmentally acceptable replacement of widely used $LiCoO_2$(1). NMC is isostructural to layered $LiCoO_2$, its Co content is only 1/3 of that in $LiCoO_2$ and exhibits impressive stability upon cycling, reasonable specific capacity (150 mAh/g) and good high rate capability. The electrochemical performance of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ depends on the particle size, crystallinity, surface morphology, porosity and potential range of cycling. Due to relatively low Li^+ diffusion coefficients of the order of 10^{-10}- 10^{-15} cm^2/s (2) NMC material consisting of nanocrystals with well-developed structure represents the best candidate for stable and fast Li-ion battery.

In our study we prepared a series of nanocrystalline NMC samples by means of appropriate treatment of commercial microcrystalline NMC material. Their electrochemical performance was evaluated by cyclic voltammetry of Li insertion and galvanostatic chronopotentiometry at different charging rates. All the studied samples treated by calcination exhibited stable and reproducible electrochemical behavior. Raman analysis of the samples after galvanostatic cycling did not prove pronounced structural changes(3). Optimized samples provided charge capacity of 141 mAh/g (cyclic voltammetry) and 144 and 135 mAh/g (galvanostatic chronopotentiometry) at 1 and 10C, respectively, and the method of their preparation represents a platform for scale up during the next period of the research.

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Livestock Wastewater Treatment at a Demonstration Site

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Over the last twenty years, pig farming distribution has changed considerably all around the world. Within this period, Spain has experienced a 75% reduction of its dedicated farms, whereas the average livestock per farm has been increased by more than 500%. Regions like Aragon or Catalonia have a greater pig population density than the European average, overcoming their number of inhabitants (Eurostat (2014)). However, the centralization of the pig husbandry in some regions in detriment of others has generated new associated problems. Pig slurry, so-called swine wastewater (SW), is a mixture of urine, faeces, and wastewater that is produced massively as a result of pig farming. In 2015, Spain generated more than 61 million cubic meters of SW (Food & Water Europe (March 2017)). This huge amount cannot be managed following simple routes as in the past, since very recently, the Spanish legislation has forbidden the spread of pig manure on the ground as natural fertilizer through conventional methods (Real Decreto 980/2017, 10 November) [1]. Worth mentioning, some exceptions will be still considered. The accumulation in big reservoirs is not an ideal solution because it can give rise to hazardous leakages at mid or long term. Both have been traditional ways to get rid of this kind of wastes, but they are no longer viable since they pose different kinds of problems, such as nitrate accumulation in groundwater. SW does not contain this toxic anion, but it has a big organic nitrogen load. The natural biodegradation of nitrogenated compounds such as ammonia then causes nitrate accumulation. Therefore, improved technologies in the form of compact plant units are needed to help the farmers to treat generated wastes in situ and, possibly, creating added-value products. The big content of N, K and P in SW makes it a good candidate to produce slow-release biofertilizers. Circular economy encourages these eco-friendly solutions, being a potential way to increase the monetary income to the farms or, at least, minimize the associated costs of SW sustainable treatments.

In this work, a purpose-made pre-industrial plant, with capacity to treat up to 5 m^3 d^{-1}, has been operated in situ at a demonstration site. In particular, it was placed in a farm located in the Barcelonès area (Spain), to deal with a generation of 10 m^3 per day coming from 500 pigs. This is a compact, modular plant that can operate in continuous mode, conceived to be flexible enough so as to treat dairy, swine or olive oil mill wastewater. Advanced physicochemical units as well as electrocoagulation and electro-oxidation reactors have been included as different modules. The goals of this project are: (i) water decontamination for reuse in agricultural irrigation, and (ii) waste valorization through the generation of a biofertilizer. The physicochemical treatment used as the first step has been shown extremely effective, yielding removals of 95% of solids, 99.9% of P and > 90% of K, N and total organic carbon removal (TOC) from the liquid phase in SW. This was feasible thanks to the synergy between (electro)coagulation with iron and an advanced separation method. In addition, the enriched sludge contains less than 50% humidity.

Acknowledgements

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Electrolytic Conversion of Urea in Urine using Boron-Doped Diamond: Effect of Operational Conditions and Cell Configuration

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Conventional wastewater treatment plant processes are burdened by high influent organic nitrogen concentrations, resulting in higher costs due to increased reactor size, treatment time, and energy use. Much of the costs associated with nitrogen removal at wastewater treatment plants can be alleviated using decentralized, urine source-separation approaches. Furthermore, urea in urine is a valuable source of energy, nitrogen, and hydrogen that currently goes unused. Electrochemical cells are a promising technology for treating urea and/or recovery these products. Boron-doped diamond (BDD) has been shown to be an effective electrode for removing ammonia from stored urine, but its performance in fresh urine, where urea concentrations are high, has been sparsely reported. Herein, we demonstrate the use of a BDD anode and stainless-steel mesh cathode in 1- and 2-cell configuration for converting urea other nitrogen products. Urea removal kinetics and by-products selectivities were quantified as a function of anolyte/catholyte pH, cell figuration, applied potential, and applied current for urea only and synthetic urine solutions. Though oxidation reactions on BDD are typically more favorable in alkaline pH due to increased hydroxyl radical production, oxidation kinetics of urea were faster with decreasing pH in a 1-cell reactor, indicating the proton dependence of the reaction. Increasing potential or current resulted in typical Butler-Volmer kinetics. A minimum of 2.5 V was required to oxidize urea, confirming the pathway was due to hydroxyl radicals. Synthetic urine solutions that contained other constituents at high concentrations decreased the urea removal rate due to increased competition for oxidizing radicals. In the 1-cell configuration, urea was oxidized to nitrate at the anode and then reduced to dinitrogen at the cathode. In the 2-cell configuration, with urea in the anode chamber and water in the cathode chamber, urea was oxidized to nitrate only due to the lack of reduction from the separated cell. In summary, the results shown in this poster presentation demonstrate the efficiency of BDD as an electrode for converting urea to useful nitrogen products, the impact of operating conditions, and the importance of cell configuration for controlling the by-product.

Electrochemical degradation of trimetropim and its comparative monitoring by electrochemical sensor and HPLC

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Antibiotics represent one of the classes of drugs most consumed, this large consumption can provide a great vector of contamination of the environment and this fact requires the development of technologies to control environmental pollution. The present work aims to evaluate the degradation of trimethoprim (TMP) using H_2O_2 generated in electrochemical cell (cathode: gas diffusion electrode - GDE and anode: platinum wire) [1]. The degradation experiments (50, 75 and 100 mA cm^{-2}) were performed in K_2SO_4 0.05 mol L^{-1} pH 2 within 2 hours. For the study of trimethoprim degradation, the concentration of antibiotic (High Performance Liquid Chromatography-CLAE and electrochemical sensor) and organic load (Total Organic Carbon Analyzer-TOC) were evaluated. The electrochemical sensor was developed for quantification of TMP and was based on black carbon type Printex 6L.

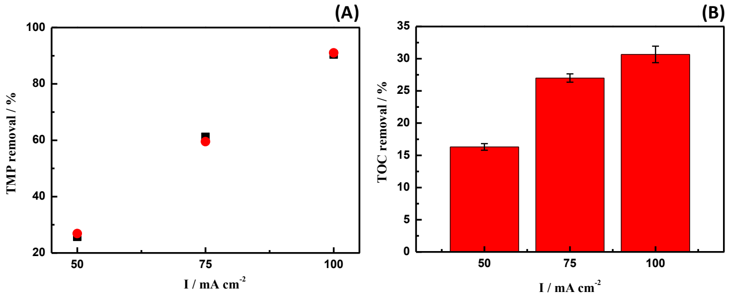

Figure 1 - (A) removal of trimethoprim (%) monitored by HPLC (■) and by electrochemical sensor (●) and (B) removal of organic load (%) in the electrochemical cell degradation experiments.

It is noted from the results shown in Figure 1A that the increase in the current density application promoted an increase in the TMP removal, reaching maximum removal of 91.0% at the end of 2 hours of experiment. Another point to be observed is the use of electrochemical sensor, the difference between the techniques of monitoring the antibiotic was only 0.66% between the two techniques, showing that the use of electrochemical sensor is efficient in the monitoring of TMP during the process of degradation by H_2O_2 electrogenerated. Removal of TMP observed in Figure 1A may be associated with the type of technique used to monitor antibiotic concentrations, minor modifications in the structure of the molecule under study may promote a decrease in its detection, however, this decrease does not necessarily represent complete degradation of the Thus, the concentrations of TOC were evaluated in the same experiments and the results are presented in Figure 1B.

TOC removal values show that the increase in applied current density promoted an increase in the organic charge removal, reaching 30.6% removal in the experiment at 100 mA cm^{-2}. Another important point to note in Figure 1B was the ratio of the current values applied and the rate of removal of the organic load, that the 50% increase in energy applied (50 mA cm^{-2} to 75 mA cm^{-2}) promoted a 39.6% increase in organic charge removal, while the 33.3% increase in energy applied (75 mA cm^{-2} to 100 mA cm^{-2}) promoted an increase of only 11.7% for removal of organic matter.

The results showed that the use of H_2O_2 electrogenerated in gas diffusion electrodes can reduce the amount of trimethoprim as well as the organic load. Another important point in the presented results was the alternative methodology of antibiotic monitoring, the use of electrochemical sensors was efficient in the quantification, presenting results very close to the classical technique, liquid chromatography.

Acknowledgments: CAPES, CNPq, FAPESP
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Evidences of the Electrochemical Production of Sulfate Radicals at Cathodically Polarized TiO_2 Nanotubes Electrodes

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Although *n*-type semiconductors, such as TiO_2, do not offer any potential electrochemical response at the anodic region (in the dark), previous studies have indicated that TiO_2 can be 'activated' by the self-doping process.[1] The cathodic polarization is the simplest method for the self-doping of TNT, able to reduce Ti^{4+} to Ti^{3+} (almost 1%) and leads to an almost metallic behavior of TiO_2 film. It was already demonstrated these electrodes can generate reactive species, such as $^{\bullet}OH$, which could mediate the generation of active chlorine.[2] Sulfate radicals are alternative oxidant species for advanced oxidation processes and have shown high efficiency in the degradation of organic contaminants, known to present comparable or even higher oxidation potential compared to $^{\bullet}OH$ (2.5–3.1 V while 1.8–2.7 V for $^{\bullet}OH$), reacts more selectively via electron transfer, acts in a wide pH range (2 – 8) and have higher half-life (30–40 µs, *vs* ~1 µs for $^{\bullet}OH$).[3] In this work, we show evidences for the feasibility of TiO_2 nanotube electrodes activated by cathodic polarization to generate sulfate radicals in sulfate-containing electrolyte in alternative to high-cost anodes (such as BDD). TiO_2 nanotubes electrodes (1 cm^2) (TNT) were prepared by electrochemical anodization in aqueous solution of 1.0 mol L^{-1} NaH_2PO_4+0.3% HF, at 20 V for 2 h, and annealed at 400 ºC for 2 h, followed by cathodic polarization in 0.1 mol L^{-1} Na_2SO_4 under −1.4 V *vs* Ag/AgCl for 10 min (CP-TNT). The electrochemical oxidation of 3.03 mg L^{-1} RNO dye (*p*-nitrosodimethylaniline) was performed under controlled current density of 7.5 mA cm^{-2} for 30 min, in 0.1 mol L^{-1} Na_2SO_4 (active) or 0.25 mol L^{-1} $NaNO_3$ (inert) supporting electrolyte. Persulfate concentration was measured by the spectrophotometric analysis of iodine. Before the cathodic polarization (Fig.1A, curve a), there is no anodic response up to 3.5 V. Nevertheless, after cathodic polarization, a remarkable anodic current arises (Fig.1A, curve b), related to the oxygen evolution reaction. Fig.1B shows the decolorization behavior of 3.0 mg L^{-1} RNO dye in 0.1 mol L^{-1} Na_2SO_4 electrolyte (curves *a*, *c*) and in 0.25 mol L^{-1} $NaNO_3$ electrolyte (curves *b*, *d*) electrolyzed during 30 min at CP-TNT electrode. The decolorization observed in NO_3^- electrolyte confirms $^{\bullet}OH$ radicals were generated. RNO decolorization was significantly improved when the electrolyte was sulfate (curve *a*), which suggests additional sulfate radicals are being generated, accelerating dye degradation. Another evidence for $SO_4^{\bullet-}$ radicals generation is the 'residual effect' of RNO decolorization in sulfate electrolyte (curve *c*) when the same samples of curve *a* were analyzed again one day after the first measurement. After 30 min electrolysis, 160 µmol L^{-1} $S_2O_8^{2-}$ (at a 5.5 µmol L^{-1} min^{-1} cm^{-2} rate).

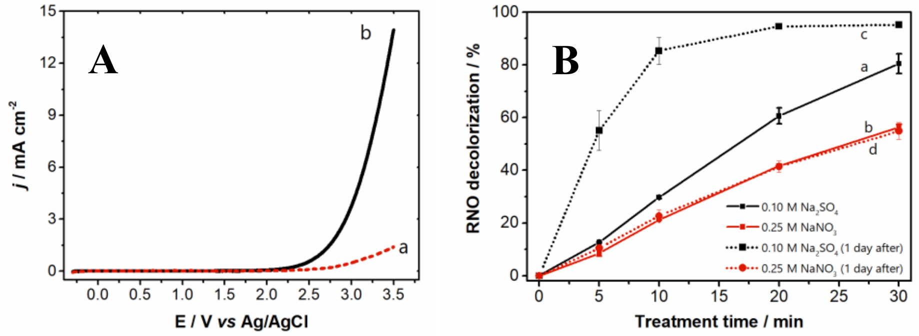

Figure 1. (A) Anodic polarization curves (LSV) for a) TNT and b) CP-TNT (0.1 mol L^{-1} Na_2SO_4 electrolyte at 50 mV s^{-1}); (B) RNO decolorization (%) in 0.1 mol L^{-1} Na_2SO_4 (curves *a*, *c*) and in 0.25 mol L^{-1} $NaNO_3$ electrolyte (curves *b*, *d*). *a* and *b* analyzed immediately; *c* and *d* (dotted lines) were analyzed one day after.

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Photoelectro-Fenton Process with Vermiculite as a Solid Catalyst for the Mineralization of Ponceau SS Diazo Dye

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Lately, heterogeneous electro-Fenton (hetero-EF) has been attracting scientific interest as an innovative approach with appealing advantages over traditional homogeneous EF (i.e., mixture of Fe^{2+} and H_2O_2). During the application of the former process, strong oxidants like hydroxyl radicals ($^\bullet$OH) are produced on the surface of the Fe-based solid catalyst. The $^\bullet$OH radical is a very active oxidizing agent ($E^o(^\bullet OH/H_2O) = 2.80$ V/SHE) capable of non-selectively react with most organic pollutants leading to their mineralization [1]. The oxidation power of hetero-EF can be enhanced by illuminating the solution with UV(A-B-C) light or sunlight, leading to the so-called heterogeneous photoelectro-Fenton (hetero-PEF) process. There exist some few works focused on the use of natural catalysts, such as magnetite, pyrite, and goethite, showing the high potential of the hetero-EF for wastewater treatment [2-4]. However, to the best of our knowledge, the iron-rich mineral vermiculite has never been tested as a hetero-PEF catalyst.

Comparative degradation trials of 0.15 mM Pounceau SS solutions were carried out by electrochemical oxidation with H_2O_2 eletrogeneration (EO-H_2O_2), hetero-EF and hetero-PEF, with BDD at $j = 33.3$ mA cm^{-2}. EO-H_2O_2 yielded 74% of color removal after 360 min. This behavior is due to the action of BDD($^\bullet$OH) species obtained from water electrolysis. This anode has a large overpotential for O_2 evolution, which allows the generation of a high amount of $^\bullet$OH weakly adsorbed at its surface, thus favoring the degradation of dye. On the other hand, the presence of 1.0 g L^{-1} of vermiculite in solution speeds up the decolorisation and mineralization of the dye. Color removal rate constants (k_{dec}) fitted well with a pseudo-first-order kinetic model. The k_{dec} values obtained for hetero-EF and hetero-PEF were 1.5- and 2.8-fold higher than that of EO-H_2O_2. These results highlight the synergistic effect of BDD($^\bullet$OH) and $^\bullet$OH electrogenerated by Fenton's reaction at the active sites of vermiculite. TOC removals were 57% and 77% for hetero-EF and hetero-PEF, respectively. Hence, UVA light radiation considerably increased the organic matter removal.

Additionally, experiments with hetero-PEF showed that the optimum concentration of vermiculite was 1.0 g L^{-1}. Above this value, a decrease in the efficiency of the process was observed. The variation of current density led to the following k_{dec} values: 0.0061 min^{-1} (R^2=0.995), 0.0127 min^{-1} (R^2=0.998) and 0.0189 min^{-1} (R^2=0.981) at 16.6, 33.3 and 66.6 mA cm^{-2}, respectively. Upon dye mineralization, short-chain linear carboxylic acids were accumulated. A final concentration of 0.45, 0.48, 1.89, 3.95, and 6.45 mg L^{-1} for acetic, malic, oxamic, oxalic, and malic acids was obtained, respectively. Vermiculite seems an interesting catalyst to be used in the hetero-EF for the treatment of dye wastewater.

Acknowledgements
The authors thank the financial support from project CTQ2016-78616-R. A.J. dos Santos acknowledges funding from CAPES (Brazil) through program "Pesquisa Pós-doutoral no Exterior" number 88881.172332/2018-01.

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Electrochemical degradation of industrial azo dyes in water using a DSA-Cl_2 anode

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Wastewater treatment can be considered one of the major threats to our environment. Textile industry, among others, uses large volumes of water in each stage of the process and therefore produces a significant volume of residual wastewater [1]. Even small amounts of dye in water interfere with the infiltration of light and may affect the aquatic life [2]. Due to the last, different technologies have been developed to treat the textile effluents. Recently, electrochemical advanced oxidation processes (EAOPs) have increased attention. The simplest and most popular process is the electrochemical oxidation (EO), is based on the electro-generation of adsorbed powerful physisorbed •OH at the anode surface M (•OH):

$$M + H_2O \rightarrow M(\bullet OH) + H^+ + e^- \qquad (1)$$

In EO process using chloride as supporting electrolyte, the oxidation of organic compounds is mainly caused by the occurrence of active chloro species such as chlorine, hypochlorous acid and hypochlorite, which are produced at the anode surface. The EO process consists in the following reactions [3]:

At the anode: $2Cl^- \rightarrow Cl_{2_{aq}} + 2e^-$ (2)

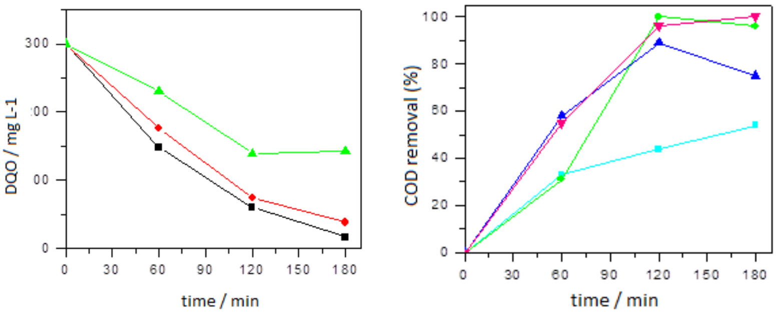
At the cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (3)

At the bulk solution: $Cl_{2_{aq}} + H_2O \rightarrow HClO_{aq} + Cl^-{}_{aq} + H^+{}_{aq}$ $\quad HClO_{aq} \rightarrow ClO^-{}_{aq} + H^+{}_{aq}$ (4) - (5)

The aim of this study was to evaluate the operating conditions (composition of the electrolyte, supporting electrolyte, current density (j) and electrode material are main factors to be considered) on dye removal efficiency in synthetic water using Acid Yellow 25 (AA25) and Acid Blue 29 (AB29) through EO with electrochemically generated active chlorine species.

The EO tests were carried out in a single open cell compartment in a batch mode. 0.1 L of dye solution was introduced into the electrolytic cell with constant stirring to ensure mass transport of the oxidant specie towards/from the anode to the bulk. A DSA-Cl_2 electrode whose composition is $Ti/Ru_{0.3}Ti_{0.7}O_2$ was used as anode and an AISI 304 stainless steel plate as cathode. The geometrical bare area of both, cathode and anode, was about 5 cm^2, having a 1.0 cm of interelectrode gap.

Figure (a) shows the effect of supporting electrolyte on dye removal 0,819 mM de AA25 in pH 7, j = 50 mA cm^{-2} and supporting electrolyte: (▲)50 mM Na_2SO_4, (●)50 mM NaCl and (■) 100 mM NaCl. Figure (b) shows the effect of applied current density on dye removal of 0,458 mM AA29 in 30 mM NaCl, pH = 7 at (■) 10 mA cm^{-2}, (●) 30 mA cm^{-2}, (▲) 50 mA cm^{-2} and (▼) 80 mA cm^{-2}.



a) b)

In the case of dye AA25, electrolysis carried out with 100 mM NaCl, reached a higher percentage of mineralization efficiency (98%) on dye removal while for the azo dye AA29, after two hours of electrolysis the electrochemical degradation reached a 100% mineralization at pH 7 with an applied current density of j = 30 mA cm^{-2}.

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Effect of pH on the Electrochemical Degradation of Methyl Orange Using Different Electrodes

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Electrochemical oxidation is an advanced oxidation technique that allows removing organic compounds from wastewater. Usually, this technique is applied when the organic pollutant is not biodegradable or when the wastewater presents certain toxicity that prevents the microorganisms to act on a biological process. Methyl orange is a non-biodegradable compound that is used, among other applications, as a dye in the textile industry; therefore, it can be present in wastewater from these facilities.

This work pretends to analyze the effect of pH on the electrochemical oxidation of methyl orange by means of using three different anodes (a BDD anode and two ceramic anodes) and three applied intensities (200, 400 and 600 mA).

In order to compare the obtained results, the evolution over time of methyl orange concentration and total organic carbon (TOC) will be analyzed; with this data the percentage of degradation and the percentage of mineralization reached will be determined.

Figure 1 shows results obtained when using a BDD anode and an applied intensity equal to 200 mA.

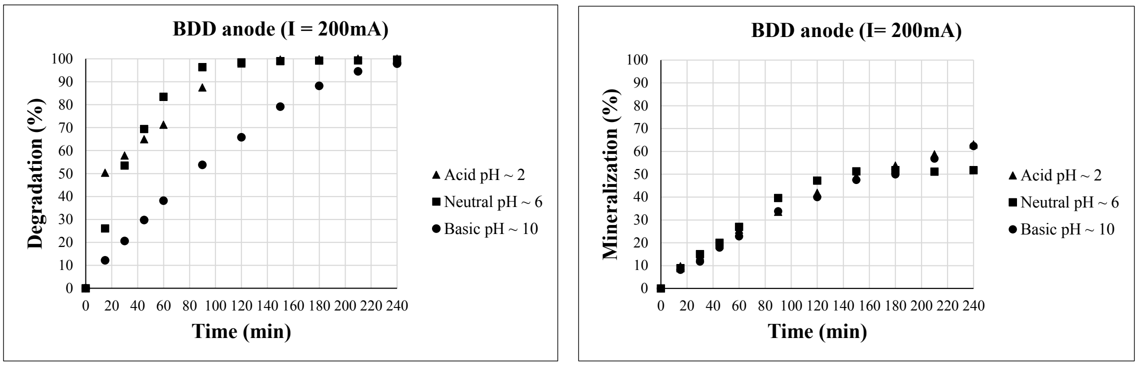

Figure 1. Percentage of methyl orange degradation (left) and mineralization (right) reached at different pH values when using a BDD anode and 200 mA.

Figure 1 shows that the percentage of methyl orange mineralization reached is lower than the percentage of degradation at all cases, that is, a complete oxidation does not take place at any pH value. On the other hand, the percentage of methyl orange degradation is similar for acid and neutral pH values; however, for a basic pH value the degradation process is slower. As applied intensity increases this difference disappear. However, observed differences for the percentage of mineralization at different pH values are small.

Acknowledgments

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Characterization of Manganese Phosphate Layers Developed on Carbon Steel

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Manganese phosphate layers have been explored for many years to improve both the wear and the corrosion properties in different metallic substrates. The phosphating method is commonly based on the immersion technique, being the immersion time and the bath temperature the most significant variables to be considered in terms of the coating performance. The most common processes operate in heavily acid solutions at 90ºC for an immersion period ranging from 30 to 60 minutes.

This work compares two different phosphating solutions, with and without $Ni(NO_3)_2$, including the influence of the ultrasonic stirring during the coating development. The coating growth could be studied by the continuous recording of the electrochemical impedance spectra at the several stages of the phosphating process. After the coating preparation, the obtained layers have been electrochemically characterized in a neutral $Na_2(SO_4)$ solution to validate the differences among the several tested conditions.

Independently on the phosphating conditions, an increase in the coating resistance was obtained as increasing the immersion time, which probes a thickening along with a reduction in the porosity as the phosphate is developed. Figure 1 compares the appearance of the Mn phosphate after 10 and 15 minutes of immersion. The further impedance analysis has allowed a complete characterization of the obtained layers and differences in terms of the coating resistivity, roughness, thickness and porosity were concluded.

This type of conversion layers could be a promising alternative for the preparation of electrodes used in Li-ion batteries, where these previous parameters play a key role in the battery performance. Thus, the careful manipulation of the phosphating procedure will assist the development of the most suitable layer for any particular circumstance.

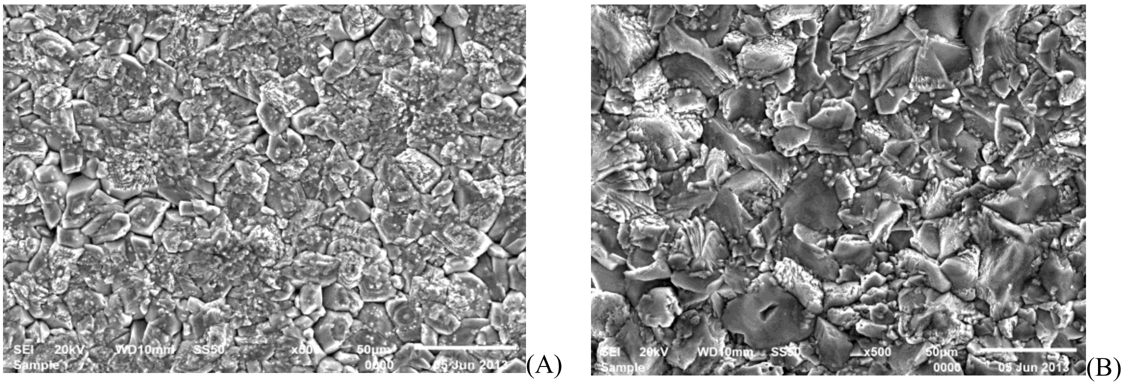

Figure 1. SEM images of the Mn phosphate obtained with ultrasonic agitation after A) 10 minutes and B) 15 minutes of immersion.

Concentration profiles within the reaction layer of a BBD anode for water electrolysis

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Boron Doped Diamond (BDD) is a fascinating electrode material known for its outstanding ability to produce hydroxyl radicals. It is the merit of Kapalka [1] that for the first time one-dimensional concentration profiles for highly-reactive hydroxyl radicals were calculated in electrochemical water splitting. This made a quantification of the resulting reaction layer thickness possible. Radical reactions in the bulk of electrolyte could be explicitly excluded, and wrong assumptions could be refuted, for instance in case of electrochemical disinfection. The analytical solutions was based on the electrochemical oxidation of water in a first step:

$$H_2O \rightarrow HO\bullet + H^+ + e^- \qquad (1).$$

The next mechanistic step assumed at the anode was the conversion to hydrogen peroxide and finally its reaction with hydroxyl radicals to oxygen:

$$H_2O_2 + 2HO\bullet \rightarrow O_2 + 2H_2O \qquad (2)$$

This mechanism represents a limiting situation because in experiments hydrogen peroxide could be clearly detected [2,3]. The fate of hydrogen is dependent on electrode potential and the presence of other reactive components.

So, another limiting case was discussed, for the first time in [4]. According to this mechanistic approach hydroxyl radicals are exclusively converted into H_2O_2:

$$2\ HO\bullet \rightarrow H_2O_2 \qquad (3)$$

This is most probably the case for very low current densities.
It can be shown that an analytical solution of reaction 4is possible for the profile of hydroxyl concentration toward the electrode.

$$D_{HO\bullet} \bullet d^2C_{HO\bullet} / dx^2 = 2k_{HO\bullet} \bullet C^2_{HO\bullet} \qquad (4)$$

Because 1 and 2 are coupled reaction, also a solution can be found for the peroxide concentration profile. Limiting conditions are discussed in detail.

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Electrochemical Incineration of the Methyl Orange Textile Dye by Photoelectro-Fenton Process

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At present, the problem of water pollution is something alarming, because it is an essential resource for life and development. Water resources are widely used in industrial processes. However, they commonly discard their effluents in bodies of water [1]. The textile industry is an important source of pollution in terms of persistent organic pollutant (POP's) that are generated in great volumes of wastewater. These effluents also include dyes of complex aromatic structures resistant to degradation in the environment The dyes most used in the textile industry are the azo type, among which we find the methyl orange (MO), that is characterized by having a chromophore group (N = N) and an aromatic structure [2]. This work presents a study on MO degradation by photoelectron-Fenton (PEF) process. The electrolyzes were performed in a laboratory flow plant containing 2 dm^3 of solution having 30 mg dm^{-3} (128ppm COD) of MO and 0.05 M Na_2SO_4 as background electrolyte at pH 3. A Ti-Ir-Sn-Sb oxide was used as anode and a graphite felt on top of carbon cloth was used as gas diffusion electrode (GDE) [3], both fitted into a filter-press reactor. In the electrolyte reservoir a UVA lamp was used. At the GDE an injection of air was applied at 3 psi of pressure. The trials were conducted at current densities of 10, 20 and 25 mA cm^{-2} at a volumetric rate (Q) of 2 dm^3 min^{-1}, Fig. 1a. The results showed a fast color removal during the first 20 min of electrolysis, which was analyzed at a maximum wavelength of 464 nm; then, at 3 hours 99.9% of color removal was achieved. This is attributed to the fact that PEF processes have higher production of $^{\bullet}$OH radicals. However, the current density did not show significantly influence on the discoloration. Fig. 1b shows a depletion of chemical oxygen demand (COD) until 90 % at 3 hours of electrolysis at current density of 10 mA cm^{-2}. While at J = 20 and 25 mA cm^{-2} a lower COD decrease was obtained. This latter is attributed to the decrease of H_2O_2 production at the cathode, at such current densities [4], which disfavor the Fenton reaction.

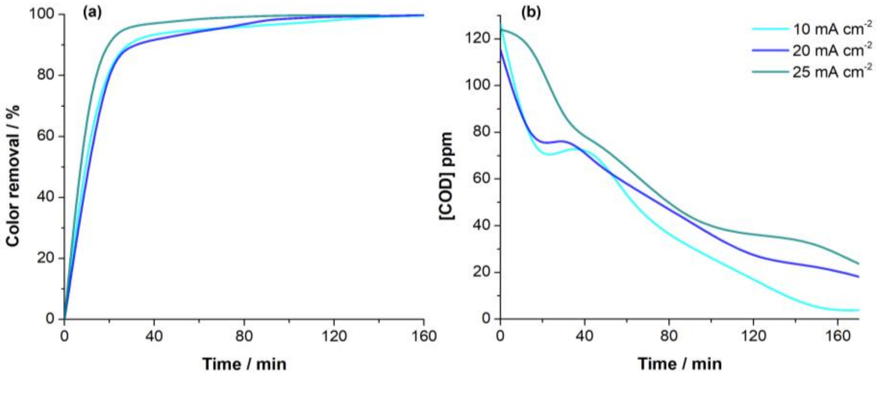

Figure 1. (a) Color removal and (b) depletion of COD during the degradation of MO dye with respect to the time by PEF process at different current densities. Electrolyte: 0.05 M Na_2SO_4, 0.5 mM Fe^{2+}, 0.178 mM MO. Electrolyte flow rate of 2 dm^3 min^{-1}, the pressure at the GDE was 3 psi. Electrode area: 24 cm^2.

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Degradation of Acid Violet 19 Dye by Electro-Peroxone Process in a Flow Plant

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The textile industry is one of the most polluting industries in terms of the volume, color and composition of its effluent discharge, which reach water bodies causing serious aesthetic and environmental damage. Therefore, several effective methods to degrade of persistent organic pollutants (POP's), such as the dyes, have been developed. In this context, the electroperoxone (E-peroxone) process has proved to be able to mineralize POP's until CO_2. This process is characterized by the *in-situ* generation of hydrogen peroxide (H_2O_2) from the cathodic reduction of oxygen (O_2) in acid medium [1], where the H_2O_2 reacts with the ozone (O_3), externally added, to produce hydroxyl radicals ($^{\bullet}OH$), Eq. 1, which are non-selective powerful oxidants [2].

$$H_2O_2 + 2O_3 \rightarrow 2\,^{\cdot}OH + 3O_2 \qquad (1)$$

The present work focuses on the degradation of the acid violet 19 (AV19) dye, which is mainly used in the staining of nylon, wool, silk, paper and leather [3], by E-peroxone process. The operation of the laboratory plant system was through an undivided filter-press reactor with an anode of Ti/IrO_2-SnO_2-Sb_2O_5 and a gas diffusion electrode (GDE) in recycle batch mode. The electrolyte volume contains 2 dm^3 of 0.05 M Na_2SO_4 solution at pH 3.0. At the GDE a continuous O_2 supply (3 psi) was feed. At the exit of the filter-press reactor the O_3 was bubbled at different flow rates to accomplish the peroxone reaction. The tests started from the characterization of the H_2O_2 electrogeneration without O_3 feed, then with an optimal H_2O_2 concentration, the influence of the current density, O_3/O_2 feed and initial AV19 concentration, were characterized in the E-peroxone process. Fig. 1a shows that the variation of O_3/O_2 flow does not show marked improvement in the discoloration of AV19, obtaining 100% of color removal after 100 minutes of electrolysis with a flow of O_3/O_2 of 1 L min^{-1}. On the other hand, the TOC removal was not improved with the increase of O_3/O_2 flow (Fig. 1b) obtaining 60% TOC removal after 8 hours, which is attributed to the poor solubility of ozone in the electrolyte. Chromatographic techniques were employed to elucidate the pathway of the degradation of AV19.

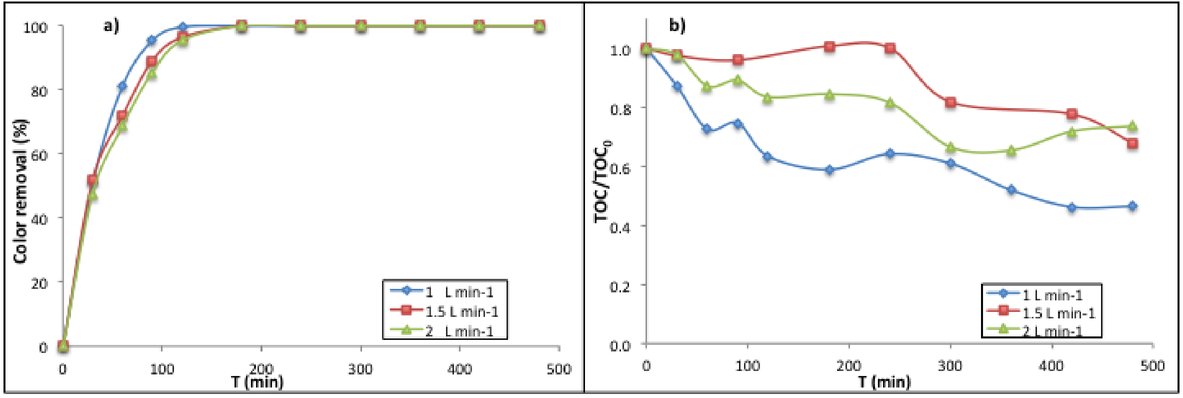

Fig. 1 Influence of the O_3/O_2 feed on: (a) Color removal, (b) mineralization of AV19 dye. Electrolyte: 2dm^3 of 0.05M Na_2SO_4 at pH 3. Air pressure of 3 psi at GDE, electrolyte flow rate 2 L min^{-1}, current density 20 mA cm^{-2}.

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Electrochemical Photocatalysis on Nanostructured TiO_2 Meshes: Degradation of Emerging Organic Pollutants in Wastewater Effluents

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A rather unexplored Advanced Oxidation Process (AOP) known as Electrochemical Photocatalysis was successfully exploited for treating, both in synthetic water and in real secondary wastewater effluent, for the degradation of carbamazepine, which is one of the main contaminants of emerging concern (CECs) in municipal wastewaters. The technique is based on the employment of photoactive TiO_2 coatings grown on titanium wire meshes by Plasma Electrolytic Oxidation (PEO) [2] and electrically biased during the wastewater treatment, leading to a synergistic effect with UV light. The process was carried out in a laboratory-scale tubular photocatalytic reactor working in semi-batch mode (Fig.1-left). Results in Fig. 1-right show that the new electrochemical photocatalytic process is effective in removing carbamazepine and leads to a faster degradation kinetics with respect to the photocatalytic process. In the real matrix, in addition to carbamazepine, the degradation of several other CECs present in the secondary effluent at concentration levels between 20 ng/L and 2 μg/L was investigated. The electrochemical photocatalysis was also compared to conventional photocatalysis on Degussa P-25 TiO_2 powders, and it showed a similar performance requiring a 50% lower UV dosage. Additional advantages of the new set-up over the conventional photocatalysis are the absence of dispersed powder TiO_2 catalyst, the suitable and easy-to-scale-up reactor design and operation costs comparable to current advanced oxidation processes, the easy production of the TiO_2 catalyst by PEO. Finally, insights were also given concerning the formation of transformation products, also in comparison with conventional photocatalysis employing suspended TiO_2.

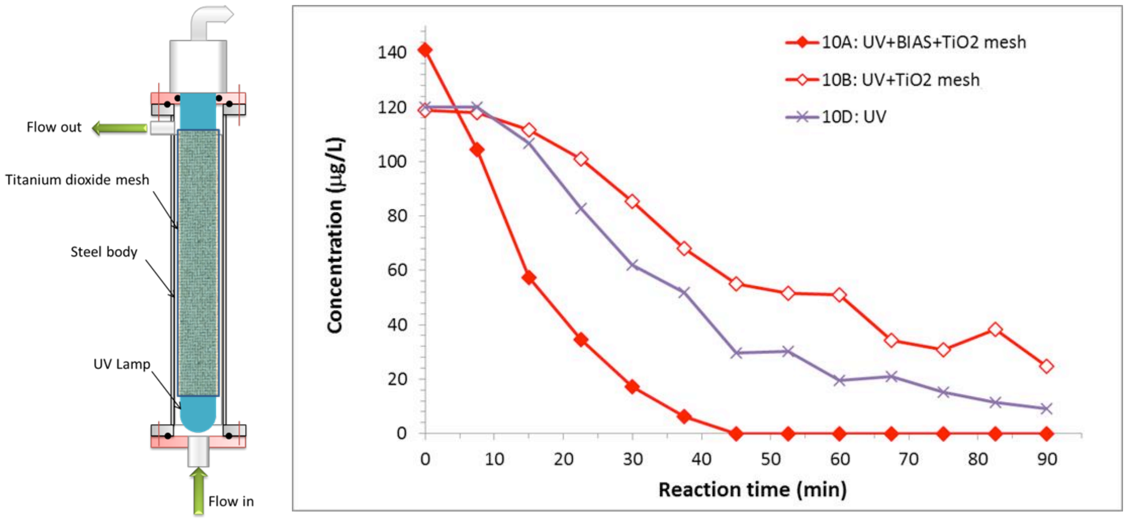

Figure 1. Laboratory-scale reactor (left); removal of carbamazepine in secondary wastewater effluent by the electrochemical photocatalytic process employing the TiO_2 mesh (right).

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The role of anode material in the selective oxidation of antibiotics in urine

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Nowadays, the presence of micropollutants in treated wastewater has significantly increased since conventional treatment processes are not able to remove these organic compounds which are presented in low concentrations: pharmaceuticals, pesticides, hormones... This problem is more worrying in the case of hospital wastewater which contain thousands of different pharmaceuticals, including high concentrations of antibiotics [1]. The presence of these pollutants in wastewater after treatment can also cause the occurrence of antibiotic-resistant bacteria and, hence, an important and hazardous problem for humans [2]. For this reason, it is necessary to develop clean and efficient technologies that allow to remove these organic micropollutants before discharge to the environment.

In this context, electrochemical advanced oxidation processes (EAOPs) can be considered as a good alternative for the treatment of hospital effluents because these technologies are based on the production of large amounts of free hydroxyl radicals as main oxidant agents for organic matter removal. Specifically, this species is mainly formed by means of water oxidation during anodic oxidation, being a clean and environmentally-friendly oxidant. Likewise, depending on the anode material and the wastewater composition, other oxidants can be produced from the oxidation of the ions contained in the effluent which also contribute to the degradation process [3]. Nonetheless, it is necessary to carefully optimize the process because anodic oxidation can favor the formation of undesirable inorganic species.

With this background, this work focuses on the removal of a model antibiotic by electrolysis with Boron Doped Diamond (BDD) and Mixed Metal Oxide (MMO) anodes in urine media. First, electrolysis in different water matrices (sulfate, chloride and urine) were carried out with diamond anodes to shed light on the contribution of mediated mechanisms. Results showed that the antibiotic was completely removed by electrolysis for electric charges below 5 Ah dm^{-3}, regardless the water matrix and the current density applied. Then, the influence of the anode material was evaluated for the degradation of antibiotic in urine media. A complete removal of the pollutant was attained, regardless anode material tested, although BDD anode was found to be more efficient than MMO, above all at the lowest current density. Results also showed that at the current charges in which the antibiotic is depleted, the removal of the other organics was much lower, and the formation of chlorates was negligible, especially operating at low current densities. Because of this selective oxidation of the pharmaceutical compound, electrolysis can be proposed to be used as a pre-treatment technology of later and cheaper biological treatment.

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Influence of the α and β phases of copper pyrovanadate on the photoelectrocatalysis of methylene blue discoloration

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Nanostructured copper vanadate is an excellent functional material due to its structural, electronic, optical and magnetic properties[1,2]. It can be organized in different structures, and the one desired in this work, copper pirovanadate, has two phases, phase α-$Cu_2V_2O_7$ (Blossite) and the phase β-$Cu_2V_2O_7$ (Zietsite). The stability of each phase is dependent on the conditions during the synthesis [3]. The method used in this work to obtain the samples was the combustion synthesis (SC), due to its operational simplicity and the intrinsic ability of the technique to alter the structure of the product as the precursors are modified. In this way, the objective of this work was to investigate the influence of the organic compounds: citric acid, glycine and urea; and to associate the products obtained in the synthesis with their respective photocatalytic responses. The products obtained were also characterized by different techniques in order to confirm the influence of the properties of the fuel in the oxide synthesis. The adjustment of the X-ray diffractograms of the samples was performed according to the Rietveld's refinement, which indicated that the phase of greatest abundance for the three samples was the phase β-$Cu_2V_2O_7$, when compared to the phase α-$Cu_2V_2O_7$ (Table 1). This can be related to factors such as the amount of gases generated and the change in the flame temperature that occurs for each type of fuel used. A study was carried out involving the thermodynamics of the reactions, considering adiabatic condition at constant pressure, where it was possible to estimate the flame temperature reached during the combustion step (Table 1). The results indicate a higher flame temperature when glycine is used as fuel, which is in agreement with the results of the X-ray diffraction, since with a higher temperature the phase α of the material is totally converted to phase β [1,2]. It was also possible to theoretically estimate the amount of gases generated in the combustion, based on the reaction of the metal precursors with the fuel (Table 1). Diffuse reflectance spectra also showed that the band gap energy value (E_{gap}) is not significantly influenced by the type of fuel used in the synthesis, and when compared to other synthetic routes, the employed in this work (SC), resulted in lower values. The photoelectrocatalytic activity was evaluated using photoelectrodes obtained from Layer by Layer (LbL) deposition on glass electrodes of type ITO and using a solution of methylene blue (0.01 mmolL^{-1}), under the application of a potential +1.1 V and visible light for electronic excitation for 150 minutes, resulting in the discolorations shown in Table 1. These results are directly related to the proportion of the α and β phases formed for each fuel, since both have an antagonistic effect when together, and the greater the proportion of the α phase to β, the smaller the photoelectrochemical response of the material. Thus, it can be stated that the type of fuel selected for the combustion synthesis influences directly the structure of the material obtained, as well as the abundance of the phases, thus demonstrating SC as a promising method when saving time, energy and materials with excellent photocatalytic responses.

Table 1. Percentage of the phases α and β, amount of gases generated, adiabatic flame temperature (T_{ad}), band gap energy (E_{gap}) and percent discoloration of the methylene blue dye for samples of copper pyrovanadate obtained using the compounds citric acid, glycine and urea.

	Fuel		
	Citric Acid	*Glycine*	*Urea*
Phases / %	α – 6.20 β – 28.70	β – 39.60	α – 4.30 β – 44.80
Gas / mol	10	13	11
T_{ad} / °C	1.115	1.507	1.188
E_{gap}	2.15	2.12	2.12
Discoloration / %	92.21	91.89	95.47

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Disinfection of urine by electrolysis: a suitable choice?

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Disinfection of urban wastewater for reuse has become an interesting topic for research, specifically in certain countries where exist problems to guarantee the water supply [1]. However, there are different types of effluents in which the concentration of bacteria can be higher such as hospital effluents pollution. Within these sanitary effluents, urine is one of the most dangerous sources of dissemination of microbiological pollution into the aquatic environment. For this reason, the development of clean and efficient technologies is necessary to attain not only a complete removal of microorganisms but also the total mineralization of urine compounds.

In this context, electrochemical oxidation with diamond anodes has become a good alternative for the removal of microbiological content in wastewater [2]. This consists mainly on the generation of disinfectant species from the electrooxidation of the ions naturally contained in wastewater. Free and combined chlorine compounds are the main disinfectant species formed during the electrolysis of wastewater containing chlorides. Nonetheless, the presence of other ions such as sulfate or phosphate leads to the generation of different peroxocompounds which can contribute to the disinfection process. In addition, hydrogen peroxide can be generated by the electrochemical reduction of oxygen over the cathode. This species presents a lower oxidation capacity than the previously commented oxidants, but it avoids the potential formation of disinfection-by-products. Hence, the production of large amounts of hydrogen peroxide could lead to an efficient and clean disinfection process for the treatment of polluted urine.

With this background, the main aim of the present work is to evaluate the application of electrolysis for the removal of microorganisms in synthetic urine media using a flow-through electrochemical reactor that improves the production of hydrogen peroxide as the main disinfectant. The influence of current density was studied, to avoid the potential formation of undesirable chlorine compounds (chlorate and perchlorate). Results show that it is possible to attain an efficient disinfection of synthetic urine for low applied electric charges, regardless the current density applied. Hydrogen peroxide and chlorine species electrogenerated (like hypochlorite and chloramines) from the reduction of oxygen and the oxidation of chlorides contained in synthetic urine are the main responsible species for the disinfection process [3].

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Acknowledgements

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Development of a Novel Electrocoagulation Reactor for Water Treatment

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During the last few decades, the electrochemical assisted coagulation process have undergone rapid development as an environmentally friendly option for a wide range of applications such as the treatment of drinking water, different types of industrial wastewater, urban wastewater and reclaimed wastewater. It is based on the action of a chemical reagent generated by electrodissolution of the anodic material (usually iron or aluminium) in an electrochemical cell and exhibits clear advantages vs. conventional chemical coagulation (Cañizares et al., 2007): specifically lower chemical dosing requirements, limited increase (or even decrease) in the ionic conductivity, better pH control and a lower operational cost.
Although there are lots of publications regarding electrocoagulation (Moussa et al., 2017), they are focused on the removal of specific pollutants and not on the development and design of new reactor approaches. Thus, the design of new approaches that help to decrease both the environmental impact of industrial activities and the cost of existing water treatment technologies is becoming a key aspect of research.
This work presents the design and evaluation of a new concept of electrocoagulation reactor. This cell has been made with PVC materials follow a cylindrical geometry equipped with two bend Mixed Metal Oxides electrodes (MMO) (Santos et al., 2019) directly connected to a power supply. The cast iron plates, which behave as bipolar electrodes, are inserted in the centre of the cylinder and just placed in slots that allow an easy replacement once they are consumed. The outlet of the dosing unit is connected to a venturi to promote the generation of iron (III) just inside the coagulation chamber. This reactor has been tested in continuous and discontinuous mode achieving a promising iron production of 20 g/h with a flowrate of 10L/h.

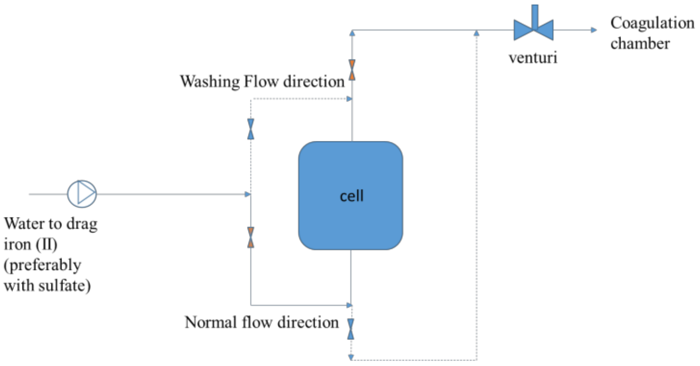

Figure 1. Scheme of the process

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Modelling and Simulation of an Electrochemical Reactor using a Flow-by Porous Electrode for the Electrosynthesis of Hydrogen Peroxide

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The presence of recalcitrant, toxic and non-biodegradable organic compounds in water bodies has been a major concern in recent years, prioritizing its elimination from wastewater. A promising way to eliminate these compounds is the use of advanced electrochemical oxidation processes (AEOP´s) that have been studied over recent years, demonstrating their efficiency in the elimination of complex organic matter [1]. The Fenton-based and electro-peroxone processes can be addressed among them where these employ hydrogen peroxide (H_2O_2) for the Fenton and peroxone reaction to yield hydroxyl radicals. Several electrode materials have been evaluated for the electrosynthesis of H_2O_2, where the carbonaceous materials are the most used, among these are the graphite felt, carbon cloth, reticulated vitreous carbon (RVC) [2], with and without dopants on its carbon matrixes. The materials are versatile and can be stacked in flow reactors, used to improve mass transport and, therefore, increasing the mineralization of the organic compounds [1]. Computational fluid dynamics (CFD) simulation is a useful tool to know the local behavior within the reactor in terms fluid dispersion, mass and heat transport, and potential and current distribution. This kind of analysis helps the design of the geometry of reactor and to characterize the optimal operational conditions (such as electrolyte flow rate, retention time, current density, initial concentrations, among others) prior to the construction of the reactor [3]. This work refers the modelling and simulation of the non-ideal flow in a reactor using RVC as a porous cathode, which will be use for the electrosynthesis of H_2O_2 occurs (via dissolved O_2 reduction in acidic medium). The transport equations employed for the numerical simulation were the Brinkman and Navier-Stokes (NS) equations. The solution of these equations was performed via finite element method using the commercial code Comsol Multiphysics®, version 5.3. Figure 1a depicts the scheme of the reactor in the *y*-*z* plane. Fig 1b shows the streamlines of 350 fluid elements, which evidence the different paths of the fluid elements within the cell. Fig 1c shows the residence time distribution (RTD) curves, at different electrolyte flow rates, where we can observe the good dispersion of the fluid and the absence of stagnant zones and recirculation. The results shown here should serve as a starting point for the simulation of mass transport and current distribution during the electrosynthesis of H_2O_2.

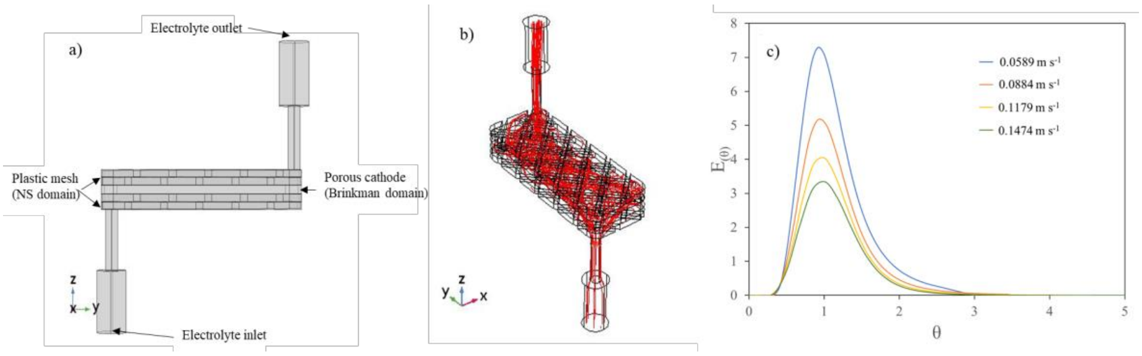

Fig. 1. a) Scheme of the reactor, b) streamlines obtained at *u* = 0.1474 m s^{-1} and c) RTD curves obtained at different mean linear velocities.

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Exploring nanoporous carbon materials as electrodes for the electro-Fenton process

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The ubiquitous presence of pharmaceutical compounds in water environments represents a potential threat to human health and aquatic life. These substances reach water bodies not only *via* direct discharge by industries or agricultural run-offs, but also through the effluents of wastewater treatment plants, which are not specifically designed to eliminate them [1, 2]. Therefore, the development of technologies to achieve an efficient removal of those pollutants is crucial. In this context, Advanced Oxidation Processes are an interesting alternative to conventional technologies. Among them, electro-Fenton (EF) process has provided promising results in the removal of several pharmaceuticals [3]. EF is based on the generation of hydroxyl radicals (capable of mineralizing a wide variety of organic compounds) by iron (II) and hydrogen peroxide (Eq. 1) under the action of an electric field. Compared with the chemical Fenton process, EF has the advantage of avoiding the use of high quantities of reagents, since the electrical current induces a continuous *in-situ* H_2O_2 generation (Eq. 2) and the regeneration of Fe^{2+} (Eq. 3) at the cathode [4].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \quad (1)$$
$$O_{2(g)} + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \quad (2)$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

However, one of the main limitations of the EF process is the cost and performance of the electrodes. Therefore, if this technology is to be implemented at large scale, it is necessary to find alternative materials to be used as efficient and cost-effective electrodes. Taking this into account, the objective of this study is to explore the use of several nanoporous carbon materials as suitable electrodes for the EF process, as they can be manufactured at relatively low cost and appropriate dimensions for pilot and industrial applications. Thus, different carbon materials of varied origin, composition and porosity were selected and characterized to evaluate their capacity for the electrochemical degradation of two pharmaceuticals (Fig. 1) present in a water matrix by an EF process.

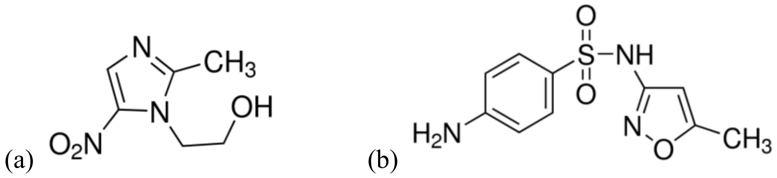

Figure 1. Structure of the pharmaceuticals employed: (a) metronidazole, (b) sulfamethoxazole

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Influence of doping level on the electrochemical oxidation of clopyralid on boron doped diamond anodes in different media

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Due to the enormous amount of pesticides used in agriculture, the contamination of soil and water by organochlorine compounds resulting from industrial and agricultural activities is a global problem. These contaminants are highly toxic and non-biodegradable. Clopyralid (3,6–dichloro-2-pyridine-carboxylic acid) is a widely used organochlorinated compound typically applied for the removal of weed in grass, that due to its high solubility in water has been detected very frequently in the environment. The use boron doped diamond (BDD) in electrochemical processes is known as a very efficient technique for the removal of several type of contaminants [1]. However, there is still a need to study the effect of diamond characteristics on performance of clopyralid degradation and its intermediates. Considering this background, the objective of the present work is to study the effect of doping level (8000, 2500, 1300, 200 and 100 ppm of boron) and the role of the electrolyte media (sulfate or chloride media) in order to optimize and analyze the degradation pathways on the performance of clopyralid degradation. For this, a fixed current of 30 mA cm^{-2} was applied. Results were compared in terms of mineralization, intermediates formation, biodegradation and toxicity. Additionally, in order to better understand the electrocatalytic behavior, all materials were characterized by cyclic voltammetry, linear voltammetry and electrochemical impedance spectroscopy tests. The results obtained indicate that the efficiency of electrochemical treatment of clopyralid depends on the quality of the BDD anode, and provide important findings that help to elucidate the electrocatalytic properties of diamonds in the oxidation of clopyralid in different treatments scenarios.

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Role of the cathode in Perfluoroctanoic acid removal by electrochemical process

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Perfluoroalkyl substances, such as perfluoroctanoic acid (PFOA), are widely used in the chemical industry due to their amphiphilicity, stability and surfactant capacity. They are employed in the synthesis of fluoropolymers and fluoroelastomers, as surfactants in fire-fighting foams, and in textile and paper production to provide water, grease, oil and/or dirt repellency surfactants. Because of its toxicity, potential for bioaccumulation, and common occurrence in water resources, PFOA has been recognized as an emerging environmental pollutant and has been included in the European Candidate List of Substances of Very High Concern (‘SVHC’). Hence, the current challenge is to develop highly efficient and cost-effective processes for the elimination of perfluoroalkyl substances, which have already been detected in natural streams, tap and bottled water all around the world.

The main challenge in PFOA degradation is to break the C-F bond, which confers a high stability and resistance to the pollutant. So far, PFOA electrooxidation has been successfully carried out in various systems, as shown in Table 1. Nonetheless, all these experiments have been conducted employing a high electrolyte concentration, which makes difficult to dispose the effluents after reaction. Furthermore, different cathodes have employed along with BDD as anode, without analyzing their influence on PFOA degradation. H_2 electro-generation by water splitting may take an important role in the hydrodefluorination of PFOA, this would explain the high defluorination obtained by Xiao et al [4], employing Pt cathode. This work aims to gain knowledge in this issue working at low electrolyte concentration (3.5 mM) and studying the influence of the cathode material in PFOA degradation, working at $[PFOA_{,0}] = 100\ mg\cdot L^{-1}$ and using BDD and Pt as cathodes.

Table 1 – PFOA electro-oxidation

$[PFOA]_0$ ($mg\cdot L^{-1}$)	Electrodes	Operating conditions	Results	Ref.
50	Anode: BDD, Cathode: BDD	Electrolyte: 1.4 g/L $NaClO_4$ (32ºC), Q= 27 kC/L	X_{PFOA}: 100% X_{F-}: 58%	[1]
50	Anode: BDD, Cathode: Pt	Electrolyte: 1.2 g/L $NaClO_4$ Q = 0.3-9 kC/L	X_{PFOA}: 85%	[2]
100	Anode: BDD, Cathode: tungsten	Electrolyte: 1.4 – 8.4 g/L $NaClO_4$, 5 g/L $NaSO_4$ (20ºC) Q = 91-363 kC/L	X_{PFOA}: 93% X_{TOC}: 95% X_{F-}: 38%	[3]
200	Anode: BDD, Cathode: Pt	Electrolyte: 7.1 g/L Na_2SO_4 (80-120ºC) Q = 6 kC/L	X_{PFOA}: 95% X_{TOC}: 90% X_{F-}: 90%	[4]

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Electrochemical Sensing Based on Molecularly Imprinted Polymers (MIP) for Monitoring Hazelnut Cor A 14 Allergen

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In the recent years, food allergies are considered a very important problem of public health, affecting a significant portion of the global population. The increasing awareness of the relevance of food allergies and the need for protecting the sensitized/allergic individuals from accidental exposures to allergenic foods has prompt the food industry and the regulatory agencies, to test and continuously monitor the presence of food allergens [1]. For this reason, it is urgent the development of novel detection and sensing systems. Smaller, faster, cheaper and smarter food sensor devices for allergen analysis are a hot topic in the emerging of advanced food monitoring systems, which are crucially dependent on innovative sensor-based strategies. Molecular imprinting polymerization (MIP) technology has been selected for this work, since it is considered one of the most suitable strategic processes to achieve highly selective polymeric materials with special molecular recognition capacity [2].

In this work, we propose to develop an electrochemical sensor by combining MIP and gold screen-printed electrodes. The electrically conducting polypyrrole film was selected as the synthetic receptor film, prepared using molecular imprinting strategies and electrochemical methods, for the specific screening of Cor a 14 allergen, which was extracted from defatted hazelnut. This allergenic protein (Cor a 14) is classified as a 2S albumin, being considered as an important molecular marker for severe and life-threatening allergic reactions to hazelnut [3].

The MIP artificial receptor for Cor a 14, as template molecule, was prepared by electrooxidative polymerization of pyrrole on a AuSPE. The several steps involved in the MIP formation, namely the protein extraction procedure and the optimization of the thickness of the polymer film were carefully tested. The binding affinity of MIP receptor film was estimated by fitting the experimental data to Freundlich isotherm and compared with the non-imprinted polymer (NIP). The incubation of the Cor a 14-MIP receptor modified electrode with increasing concentration of protein (from 1 fg mL^{-1} to 0.1 mg mL^{-1}) resulted in an increase of the hexaaminorutenium II redox current. The dynamic range for linear response was obtained from 10 fg. mL^{-1} to 1 μg. mL^{-1} determined from the calibration curves built in neutral buffer using the square wave electrochemical technique.

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Study of the Effect of Some Features of Activated Carbon on its Performance as a Cathode Material in an Electro-Fenton Process for the Discoloration of a Model Dye in Aqueous Solution

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The development of efficient and economically feasible water treatment technologies for effluents contaminated with persistent pollutants, is a serious global problem that has been continuously growing in the last decades, and is therefore one of the most important challenges being faced by several research groups around the world. In this context, Advanced Oxidation Processes represent an attractive alternative due to the strong oxidation power of the hydroxyl radical species and among these processes, the electro-Fenton approach using an activated carbon bed as a cathode is a promising technology that combines the possibility of electrochemically generating the $^{\bullet}OH$ radical on the carbon surface (by means of the reaction between H_2O_2 produced from O_2 reduction and Fe(II)), with the pollutant adsorption capabilities of the carbonaceous material.

The activated carbon particles in the packed adsorbent bed in the electro-Fenton process, is therefore a key component of the electro-Fenton processes and the understanding of its behavior as related to different characteristics of the material and to the operational factors in an electrochemical reactor, is therefore important in the scope of the development of competitive electro-Fenton water treatment technologies.

In this context, the effect of different parameters on the cathode performance of an activated carbon bed in an electro-Fenton reactor was studied and for this purpose, a design of experiments approach was employed. As can be seen in Table 1, four factors and two levels for each were considered for these experiments. The factors under study consisted in exploring two types of activated carbon and three different sizes for each one. In addition, an acid based pre-treatment of the adsorbent material was considered since the density of polar surface chemical groups has been reported to influence the electro-catalytic activity for the $2e^-$ oxygen reduction of carbon, along with the amount of Fe(II) in the reactor which is readily provided by an iron loaded resin that is washed out by the incoming contaminated effluent. The experimental response parameter for these experiments consisted on the kinetics of the electro-Fenton induced discoloration of a diluted solution of the classic Blue-1 dye.

Table 1. Identification of factor and levels.

Factor	*Low Level*	*High Level*
Activated carbon oxidation pre-treatment	No	Yes
Type of Activated Carbon	Vegetal	lignitic
Mean Particle Size (mm)	0.85, 1.0, As it is (no separation)	1.4, 2.0, As it is (no separation)
Amount of Fe loaded resin in the reactor (g)	0.25	2.5

As expected, the study revealed that the process is strongly influenced by the amount of the activated carbon surface available for pollutant adsorption and further degradation as well as by the oxidation degree of the carbonaceous surface. The type of activated carbon, i.e. lignitic or vegetal, is also an important factor which seems to be coupled with the effect of oxidation pre-treatment of the material. Iron concentration in the resin on the other hand, does not seem to have a very important effect.

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Comparative study of BDD and MMO (Ti/$Ru_{50}Ir_{50}$) in the electrooxidation of synthetic urine

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The main means of entry for pharmaceutical products into the environment is through hospital effluents where the concentration found is extremely high, especially in urine, since it can be up to 15 times more toxic than urban effluents. Disposal of hospital effluent is still poorly regulated and often treated with domestic effluent. The traditional forms of treatment (physico-chemical and biological) do not reach complete mineralization of pharmaceutical compounds. Thus, there is a need for deeper studies on the degradation of organic compounds contained in the urine [1]. The objective of the present study is to carry out urine electrooxidation in order to compare the behavior of MMO (metal mixed oxide) and BDD. Electrolyses were performed in a single compartment cell with five different electrodes MMO and four BDD (Adamant Technologies) with different levels of doped boron: 2500, 1300, 200 and 100 ppm all with 4 cm², wire platinum counter electrode and Ag/AgCl electrode reference. Results were compared in terms of mineralization, intermediates formation, biodegradation and toxicity. In addition, voltamperometric and impedance tests were carried out. Important differences were found and will be explained in terms of the anode composition, indicating the best type of anodes for different treatment scenarios.

Acknowledgements
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Electro-Fenton plus Biological Treatment, a Viable Hybrid System?

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In recent years, electrochemical advanced oxidation processes (EAOPs) have gained a great interest as alternative to traditional wastewater treatments, since they are powerful methods for the removal of recalcitrant organic pollutants. EAOPs are based on the *in situ* generation of mighty oxidants such as hydroxyl radicals ($HO^{\bullet}$). They have several advantages as their versatility, easy-handling operation and eco-friendly character [1]. However, these processes require a high energy consumption on longer electrolysis time with the consequent cost-intensive operations. Thus, in order to counter this drawback, combining systems between an EAOP and a biological treatment has been newly proposed [2].

Among all existing compounds, ionic liquids have attracted the attention of the scientific community as alternative to conventional solvents. These compounds are characterized for having a negligible vapor pressure, a high thermo-chemical stability and a low melting point [3]. Nevertheless, it has been discovered that their high solubility, low biodegradability and potential toxicity makes them potential pollutants [4]. Therefore, the objective of this study was to assess the degradation of the ionic liquid 1-butyl-1-methylpyrrolidinium chloride ([bmpyr]Cl) by coupling an EAOP with a biological treatment. In this case, the EAOP process selected was electro-Fenton (EF), since is the most popular and well-studied.

Firstly, EF experiments were carried out in an open electrolytic cell at room temperature. The operational volume and the initial concentration of [bmpyr]Cl were 230 mL and 0.15 mM, respectively. The effect of the key parameters was evaluated: iron dosage (0.1-0.2 mM), current (50-1000 mA) and ionic liquid concentration (0.075-2.5 mM). Moreover, two anode materials were tested, boron-doped diamond (BDD) and a sub-stoichiometric titanium oxide thin-film (Ti_4O_7), using carbon felt as cathode. The effectiveness of the process was evaluated as the total organic carbon (TOC) decay and the ionic liquid removal. So, based on the results, the optimal conditions selected were 0.1 mM of iron, 1000 mA and 1 mM of [bmpyr]Cl, obtaining a total removal of [bmpyr]Cl and a TOC decay of 98% within 4 hours.

Secondly, a consortium of microorganisms has been employed in the biological trials. Before the tests, biomass was washed and centrifugated. The pH of the solution was adjusted at 7 and mineral salts were added. The experiments were carried out at 30ºC and 150 rpm. In order to know the proportion of biodegradable organic compounds present in the solution and, this way, select the optimal EF treatment time, average oxidation state and carbon oxidation state were calculated. Based on the findings, 30 min of EF treatment was chosen. Then, the biological process was carried out for 8 days. A control of untreated [bmpyr]Cl with the microorganisms was performed. The evolution of the TOC and the carboxylic acid concentration was monitored along the time. When comparing both trials, we can notice that in the control with untreated [bmpyr]Cl no carboxylic acids were detected, whereas an evolution of these compounds was seen in the solution with the [bmpyr]Cl previously treated by EF process. Therefore, we can conclude that the combining process between EF and biological treatment is a plausible methodology for the degradation of ionic liquids, being necessary deeper studies.

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Differential Pulse Voltammetry as a Powerful Tool to Monitored the Electro-Fenton Process

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Currently, advanced oxidation processes (AOPs) are widely used in order to degrade the recalcitrant organic pollutants, since they have several advantages regarding the conventional treatments. Among the AOPs, the electro-Fenton (EF) process is one of the most known, in which the hydroxyl radicals ($HO^{\bullet}$) are generated by the Fenton's reaction (Eq. 1) [1].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \qquad (1)$$

Nevertheless, these methods have some drawbacks, such as the high energy consumption, which directly implies an increase in costs. To mitigate this fact, an in-depth knowledge of the process is required. To this end, it is necessary to apply analytical tools that permit elucidate partially the evolution of iron into the solution and determine the different intermediates and complexes formed during the process. One of these tools is the differential pulse voltammetry (DPV) on Screen-Printed electrodes (Figure 1) as transducer, since permits the *in situ* monitoring of the process, requires short analysis time and only 50 µL of samples is needed for the measurements [2]. Therefore, the aim of this work was to evaluate the degradation of a new kind of pollutant, the ionic liquid p-xylene-bis(N-pyridinium bromide) (DPX), by combining the EF process with the DPV technique.

Figure 1. Screen-Printed electrode.

In this study, the current intensity was evaluated since is one of the key parameters on EF process. The experiments were carried out at room temperature, in a cylindrical reactor with 230 mL of solution and 25 ppm of DPX. A range between 50 and 1000 mA was selected. The DPX removal and total organic carbon decay were followed in all the trials. Conversely, DPV technique was applied. To begin with, preliminary experiments were performed, in order to obtain information of the characteristic peaks of all species in the solution and the interaction between them. Consecutively, the EF tests were carried out to elucidate the iron behavior in the solution and the formation of complexes and intermediates along the treatment and to check the differences among all the currents studied. Moreover, bromide, nitrate and nitrite anions were monitored to confirm the data obtained throughout the DPV analysis. Based on the results, we can find differences in the degradation process of DPX in function of the current applied. Hence, this technique has demonstrated to be a powerful tool for having a better understanding of the EF process applied to the degradation of the ionic liquid DPX.

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Schiff Base Complexes as Electrocatalysts for Urea Electrooxidation

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Abstract

Finding alternative energy sources has been of prime interest over the past several decades. Hydrogen (H_2) is considered a leading candidate that is both renewable and gives zero emission. Recently, urea electrolysis has emerged as a promising new method for H_2 generation, making urea itself a potential source of sustainable clean energy. In an electrochemical cell, urea is electrochemically oxidized at the anode into N_2, CO_2, and H^+, whereas water is reduced to hydrogen at the cathode. Theoretically, water electrolysis for hydrogen production requires 1.23 V *v*s NHE, whereas urea electrolysis requires only 0.37 V, generating hydrogen in a very cost-effective way.

Different solid-state electrocatalysts have been studied extensively for urea electrooxidation, but such catalysts are inherently difficult to control, manipulate and study at the atomic level. We aim to develop molecular catalysts that can be fine-tuned relatively easily at the atomic level, and studied in detail using methods that are common for such molecular systems, such as NMR spectroscopy and single-crystal X-ray crystallography.

To the best of our knowledge, no molecular catalysts have been reported to perform the electrochemical oxidation of urea. Herein, we describe our efforts to design, synthesize and investigate nickel-based metal complexes for urea electrooxidation, utilizing imino-phenol ligands. These ligands, containing N and O donors, act as good chelators and can stabilize diverse oxidation states of metal centers. Such an imino-phenol-based complex was studied as an electrocatalyst for urea oxidation, displaying an onset potential of 0.33 V *vs* Ag/AgCl in an alkaline medium. The stability of the molecular system in alkaline media was studied using different spectroscopic methods, such as time-dependent UV-Vis, NMR and Raman spectroscopy. The electrochemical stability of the catalyst was examined using *in-situ* Raman spectroscopy and chronoamperometry. The available data indicates that the complex is the active catalyst for urea electrooxidation, and is stable both chemically and electrochemically under the studied conditions.

Comparison of Different Electrochemical Reactor Designs for the Simultaneous Production of Hydrogen Peroxide and Peroxoacetic Acid

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The production of peroxoacetic acid (PAA) is reaching an increasing industrial interest due to its properties related to disinfection, bleaching and oxidant agent. Although the in-situ production of a chemical reagent is always favorable from the viewpoint of reducing the CO_2 footprint related to its transportation [9], the in-situ production of this chemical is especially interesting due to the difficulties encountered in the handling and transport of peracetic acid (Tao et al. 2015).

The base reaction for the production of peroxoacetic acid is the equilibrium between acetic acid and hydrogen peroxide (Equation 1), which is catalyzed to the production of PAA in acidic media (Alasri et al. 1992).

$$CH_3COOH + H_2O_2 \rightarrow CH_3COOOH + H_2O \qquad (1)$$

It is thus necessary to couple the production of hydrogen peroxide and PAA to reach an efficient production process. Based on this idea, our research group recently developed an electrochemical reactor that coupled the anodic production of PAA by oxidation of the raw acetic acid on BDD anodes and the cathodic production of hydrogen peroxide from oxygen (Moraleda et al., 2016). Parallel, we also developed an electrochemical reactor for the production of hydrogen peroxide based on the use of a jet-aerator and flow-through cathode, which avoids the use of the compressor required in a typical electrochemical reactor based on gas diffusion electrodes (Pérez et al. 2016).

Based on this experience, in the present work we compare the performance of these two reactor designs in the simultaneous production of hydrogen peroxide and peroxoacetic acid. Moreover, we studied the role of the ratio between the reaction volume and the electrode area as this parameter was found to be critical in the balance of both electrochemical and chemical processes occurring simultaneously in the system. With this work, we aim to propose design rules for the efficient production of these two valuable chemicals.

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Electrochemical regeneration of spent activated carbon in 15kg batch reactor: scale-up and effect of electrolyte flow

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Adsorption in activated carbon (AC) is one of the most used technologies for the removal of pollutants from both air and water. This process has one important drawback, which is the management of spent AC. This is especially important in recent years because of the more restrictive legislation regarding pollutant concentrations in air and water streams, what results in an important increase in AC consumption in different industries. Consequently, regeneration of AC is an option which is being considered by the industries, especially drinking water industries, from an economic point of view.
Currently, the most used method at industrial scale for AC regeneration is the thermal regeneration [1]. As a promising alternative, electrochemistry was used as a method of AC regeneration due to its several advantages such as the use of the electron as reagent that can be supplied by a direct current source and that can be applied *in-situ* [2]. However, the most important disadvantage of the electrochemical method is the difficulty of reproducing it at a large scale, for example at a kilogram scale. In this work, we have developed an electrochemical batch reactor for the regeneration of 15kg of AC, which demonstrates the viability of the method. The electrochemical batch reactor has been designed, constructed and operated in agreement with the optimized conditions previously studied at 6g and 3.5kg scales [3]. The electrochemical reactor was constructed in polyvinyl chloride (PVC) with separation of compartments by a cationic membrane. Each compartment had dimensions of 85x25x60cm and a distance between electrodes of 10cm. Two commercial electrodes were used, platinized titanium as an anode and stainless steel as a cathode, 0.025A/cm^2 was set as current density and the working current was 70A, which produced a voltage between 5.7-8.2V and it was applied for 4 hours of regeneration treatment time. The spent AC from a municipal drinking water treatment is located in the cathodic compartment and 0.5M H_2SO_4 was used as electrolyte solution. To analyze the effect of the electrolyte flow, different experiments were carried out at different flow rates. To verify the regeneration treatment, porous texture analysis of the AC samples was determined by physical adsorption of gases and the electrolyte solution was analyzed by UV-VIS. After electrochemical treatment, in the same experimental conditions, the higher the electrolyte flow the higher the recovery of the porosity. A recovery of surface area of 85.3, 87.4 and 92.6% is achieved after 4 hours of treatment. In addition, by this regeneration method the pore size distribution of the spent activated carbon is recovered compared to the pristine AC. We can conclude that the electrochemical regeneration is an efficient method for the regeneration of 15kg of spent AC and, therefore, this process could be scaled at industrial level, being a real alternative to thermal methods.

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Degradation of Oxyfluorfen Herbicide by Membrane and Electrochemical Processes

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Pollution caused by human activities, such as industry and agriculture, is a major concern that requires novel technologies that might cope with the increment of persistent contaminants in soil and water (Zhang, 2009). The use of herbicides in developed countries is an essential part of agricultural production, as it is aimed to improve indirectly the crop yield by killing or inhibiting the growth of weeds that compete with the desirable main plant for nutrition, light and water. Among the herbicides most commonly used, oxyfluorfen is a hazardous organochlorinated diphenyl-ether compound that has been used to control certain annual broadleaf and grassy weeds. It is well known that the use of these chemical compounds is associated with undesirable impacts in the environment and in human health.

To deal with this problem, many technologies have been developed and tested to remove this kind of compounds from synthetic and real water effluents (López-Vizcaíno *et al.*, 2017). One of the priorities nowadays is to improve the efficiency of the different treatments including electrochemical processes, since most of the reports include concentrated effluents and generally real polluted effluents deal with more diluted herbicide concentrations. One of the solutions proposed to cope with this issue is to pre-concentrate the pollutants from water (Llanos et al., 2018). This work explores the effect of pre-concentration, through a bench-scale ceramic ultrafiltration membrane, of a low concentrated solution of oxyfluorfen to recover a concentrated sample and to improve its remediation using a subsequent electrochemical electro-oxidation process. To evaluate the performance of the combined process, a commercial solution of oxyfluorfen (Barre®) was used, which formulation includes surfactant and other minor compounds that enhance its application in agriculture. As a first step, the concentration of oxyfluorfen by a ceramic multi-channel ultrafiltration membrane at pilot-scale plant was evaluated at both total recirculation and discontinuous mode. The concentrated sample was treated afterwards using an electro-oxidation (E-O) process employing a Boron Doped Diamond (BDD) electrode as anode and a stainless-steel electrode as cathode under different current densities (from 50 to 500 A m^2) in a single compartment working in a galvanostatic mode.

Results show that ultrafiltration can concentrate the oxyfluorfen solution to almost twofold in a short time, leading the possibility to enhance the electro-oxidation process for the treatment of wastewater polluted with the non-ionic component oxyfluorfen.

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Photolysis of electrogenerated hydrogen peroxide for the treatment of theophylline as emerging contaminant

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In recent year the application of advanced oxidation process for the treatment of emerging contaminants has received increasing attention. In fact, many of these pollutants are recalcitrant to traditional removal treatments while the combination of hydrogen peroxide (H_2O_2) with UV irradiation can enhance the degradation and mineralization of compounds such as pharmaceutical and personal care products by the action of generated hydroxyl radicals (●OH).

In this work, H_2O_2-photolysis of theophylline (THPY), as model the compound, has been investigated. This alkaloid belongs to the xantine group and is included in the "Candidate Contaminant List" of EPA agency,

Degradation tests at different THPY initial concentration (20-80 mg/L) and H_2O_2 concentration, with molar ratio $R= C_{THPY}/C_{H2O2}$ ranging from 1 to 10 were performed, evaluating the effect of UV radiation intensity (4800 – 9600 $\mu W/cm^2$) and pH condition (2-12) on both degradation and mineralization of THPY.

An improvement of this technology is the in-situ production of H_2O_2 through electrochemical reduction of dissolved molecular oxygen in the presence of a carbon electrode that avoids the storage of reactive species and ensures an environmental friendly and controlled process.

Carbon based cathodes such as Carbon Felt, Grafoam ®, Sigratherm® and carbon fibers were tested as cathodic materials for the H_2O_2 production and the effect of current density (4-8 mA/cm^2) and oxygen flow source (air or pure oxygen) were evaluated on THPY removal at concentration values up to 200 mg/L.

The obtained results showed that the THPY degradation is enhanced under low-pH conditions and negatively affected by increasing current density. No differences on degradation efficiency were observed when air or pure oxygen were supplied. Among the tested materials, Carbon Felt and Sigratherm® showed the best performance. A zero-order kinetic well describes the experimental results of THPY degradation.

Electrogeneration of hypochlorous acid via chloride oxidation on Ir-Sn-Sb oxide anode in a filter-press-type reactor

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The electrochemical advanced oxidation technologies have been used for water treatment which contains persistent organic pollutants. Electro-Fenton-based process have been used to remove these pollutants due to the production of hydroxyl radicals ($^{\bullet}$OH). A new electrochemical Fenton-like process between electrogenerated hypochlorous acid (HClO) and Fe^{2+} have been reported to produce $^{\bullet}$OH [1]. In this context, this research deals with the characterization of the electrosynthesis of hypochlorous acid from the oxidation of chloride (Cl^-) on Ir-Sn-Sb oxide anode, fitted in a filter-press-type reactor, to be used in the Fenton-like process. The characterization of the electrosynthesis of active chlorine (mixture of HClO, chlorine (Cl_2), and hypochlorite (ClO^-)) was carried out in an undivided cell equipped with Ir-Sn-Sb oxide anode and stainless-steel cathode. The influence of current density on the production of active chlorine by bulk electrolysis was carried out at $5 \leq j \leq 20$ mA cm^{-2} using 6 dm^3 of electrolyte with 25 mM Na_2SO_4 + 35 mM NaCl at pH 3 in recycle batch mode of operation at volumetric flow rate of 3.2 dm^3 min^{-1}. Active chlorine concentrations of 0.44, 0.64, 1.9 and 2.2 mM were obtained at 5,10,15 and 20 mA cm^{-2}, respectively, as shown in Figure 1a. To elucidate the influence of side-reactions on the active chlorine concentration, such as the anodic formation of chlorates and perchlorates, electrolysis trials were performed using the same reactor, which included a cationic membrane between electrodes. Figure 1b shows that the active chlorine concentration decrease in the divided cell, due to the anodic oxidation of active chlorine to chlorate (ClO_3^-) and perchlorate (ClO_4^-) species [2]; however, the continuous accumulation of active chlorine, in the undivided cell showed in the same Figure, indicates that the cathodic reduction of chlorate and perchlorate to chloride favours the continuous accumulation of active chlorine. HPLC techniques were performed to elucidate on the reaction pathway of the chlorine species in the divided and undivided cell.

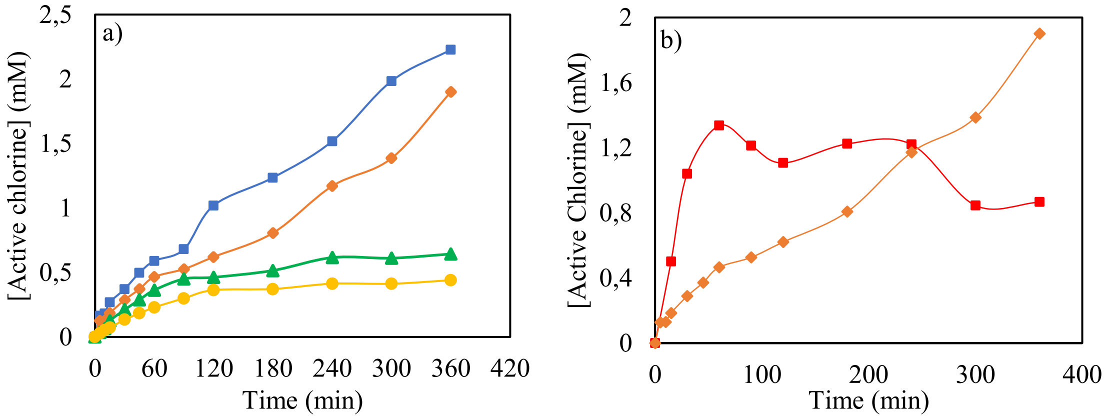

Figure 1. a) Active chlorine concentration *vs* electrolysis time for the treatment of 6 dm^3 of a solution having 35 mM NaCl+25 mM Na_2SO_4 solution at pH 3, T = 298 K, and Q = 3.2 dm^3 min^{-1} at j: (🟡) 5, (▲) 10, (🔶) 15 and 20 (🟦) mA cm^{-2}. b) Active chlorine concentration at j = 15 mA cm^{-2}: (🔶) without membrane and (🟥) with cationic membrane. The FM01-LC electrolyser with electrode area of 64 cm^2 was used.

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~~Title in Times Roman 14 point – Upper and Lower Case~~Flow injection analysis of pharmaceutical drugs in wastewater

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~~These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.~~
Paracetamol and ibuprofen are two of the drugs most widely utilized as analgesic for mild to moderate pain relief. For this reason, they are widely used in nursing homes for eldercare. However, sometimes all these active complexes are not completely assimilated by the body being excreted after the ingestion. This fact provokes the existence of pharmaceutical residues and their degradation products in senior residences wastewaters, which are very complicated to eliminate in wastewater treatment plants and they can discharged in the environment.
For this reason, the ~~D~~detection of ~~Active~~ active p~~P~~harmaceutical i~~I~~ngredients in waste water from geriatric residences is an important task in order to ~~regulating~~ regulate and ~~monitoring~~ monitory the levels of ~~pesticides~~these residues. However, ~~there is currently a clear demand in the~~the development of new and easy methodologies is necessary in order to ~~that~~ allow a quick and easy detection. In this way, a flow electrochemical system appears an interesting alternative to another methods, due to in can be used in continuous for the detection of this compounds during the discharge of the wastewaters before it arrives to the municipal plumbing system. The flow electrochemical system is based in a Thin-layer flow-cell screen-printed electrodes, which has several advantages over conventional flow cells as easier assembly, avoiding leakages. This system has been compared with a conventional flow injection analysis cell providing also good results. These two~~Both~~ drugs have been studied ~~both~~ in individual solution and in mix solution ~~with both analytes~~, being able to detect them simultaneously~~at the same time~~ in the mixture.

~~order to demonstrate the utility of electrochemical flow sistem in this field, two pesticides have been selected. Imidacloprid and permethrin are widely used for controlling different insects in agricultura and their detection is completely required. EC-SERS allows the fast and simple detection of these pesticides, opening new gates for future application in this field~~

~~The abstract **should not exceed ONE PAGE** of text, references, tables and figures. Abstracts exceeding this limit may be cut without consideration of content after the first page.~~

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This study has been financed by the SUDOE program with the project Innovec'EAU (2016-2019)/Project SOE1/P1/ F0173 Interreg Sudoe funded by FEDER (http://innovec-eau.univ-perp.fr)

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Time-Resolved Spectroelectrochemistry Study of Malachite Green

Sheila Hernandez[1], Lara Lubian-Hernando[1], Martin Perez-Estebanez[1], Juan V. Perales-Rondon[1],
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Malachite green (MG) has been used globally as a therapeutic agent in aquaculture. However it is not registered for use in food-producing animals in the European Union [1]. Some traces of MG and its metabolite, leucomalachite green (LMG), have been detected in aquaculture products, which indicate the need for controlling its contain on fish and fish products. Because of that, the monitoring or even study of the degradation of MG is of interest in the quality control programs of the fish production.

In order to understand the MG degradation, a systematic study of the oxidation-reduction during a spectroelectrochemistry experiment would be of capital interest due to the rich information about the changes of compounds on the interface as a result of the applied potential. In this sense, Raman spectroelectrochemistry (Raman-SEC) has been widely used due to the rich structural information that can be obtained. Raman-SEC provides information about the vibrational states of molecules, and therefore about their functional groups and structure, concomitantly with its electrochemical activity [2]. Additionally, the use of time resolved (TR) experiments provides the control of the applied potential with time (dynamic electrochemistry) [3], which is an advantage to follow dynamic electrochemical process at the interface. Moreover, the usefulness of TR-Raman-SEC is enhanced when SERS experiments are carried out, because of the much higher sensitivity of the technique that allows us to improve the limits of detection.

In the present work, TR-Raman-SEC has been used to study the electrochemistry oxidation-reduction of MG. Cubic gold nanoparticles (Au-NPs) enhance the Raman signal, allowing us to obtain suitable and measurable spectra during the spectroelectrochemistry experiments. As is shown in Figure 1, the spectrum of MG at different potentials demonstrates how the electrode potential modulates not only the intensity, but also changes in the Raman bands of the spectrum.

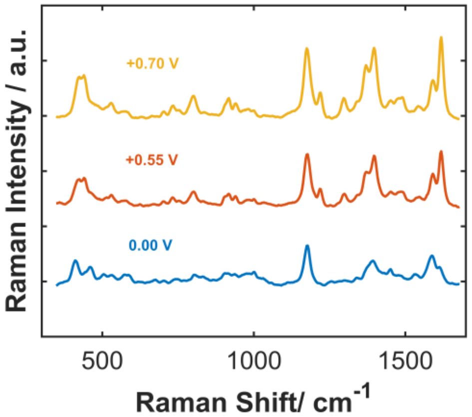

Figure 1. Comparison of SERS spectra taken during a spectroelectrochemistry experiment of the oxidation of MG 0.5 mM on cubic Au NPs placed on a carbon screen-printed electrode.

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Acknowledgements

Authors acknowledge the financial support from Ministerio de Economía y Competitividad (Grant CTQ2017-83935-R-AEI/FEDERUE) and Junta de Castilla y León (Grant BU297P18).

Bioinspired W/WO_3 electrodes applied in the improvement of quality of hemodialysis dialysate contaminated by *C. parapsilosis*

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The photoelectrocatalysis constitutes a successful alternative method for the inactivation of microorganisms based in oxidative advanced process since it can promote inactivation in a short time and no formation of undesirable by-products and harmful to the people [1]. Among several semicondutors, WO_3 is a n-type semiconductor with small band gap energy (2.4 - 2.8 eV) photoexcited in the ultraviolet and visible region with high application in photoelectrocatalytic process [2]. In addition, the materials constructed by biomodelling is one of the fields that has attracted great attention for create new morphologies, such as biofilms produced by microorganisms with great potential on design of new materials with high superficial area and controlled roughness [3]. This work reports the preparation of W/WO_3 bioinspired films of fungi grown onto tungsten substrate by electrodeposition. This electrode was applied in the photoelectrocatalytic disinfection of dialysate sample contaminated by fungus *C. parapsilosis*. The bioinspired electrode was characterized by scanning electron microscopy and showed high porosity and organization, respectively. The presence of W and O was confirmed by EDS and the monoclinic form by X-ray diffraction. The PEC reactor is based on W/WO_3 film acting as photoanode, Pt grid as counter electrode and Ag/AgCl as reference electrode.

A dialysate solution donated by the Center of Hemodialysis of Araraquara was tested as supporting electrolyte (pH 7.3). High pressure Hg lamp (125W) was used as a source of electromagnetic radiation and the applied and optimized potential was 1.5V. In order to evaluate the method efficiency it was investigated the microbial death, dissolved total organic carbon, active chlorine and organochlorides generation during degradation. Therefore, aliquots were removed during 120 min of treatment and analyzed for microbial count, total organic carbon removal, gas chromatography and spectrophotometric measurements, respectively. The best condition for treatment was investigated and after only 1 min of the photoelectrochemical treatment *Candida sp* was inactivated under UV and visible light irradiation and 65 % of the organic matter mineralization. Spectrophotometric measurement confirms the low active chlorine formation at pH 7, which is higher at lower pH. Gas chromatographic test indicates the no occurrence of organochlorides formation. These results show that despite chloride ion be present in the dialysate is contributing to secondary reactions or death the fungus that occurs preferentially due cell wall rupture by hydroxyl radicals generated in the process. The obtained results indicated that photoelectrocatalysis is a promising method for fungi degradation and disinfection of water and hemodialysis water under UV and visible light irradiation.

Acknowledgments: The authors thank CAPES and FAPESP for financial support.

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Preparation and electrochemical behaviors of reduced graphene oxide composite electrodes containing iron oxides

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Reduced graphene oxide (rGO), one-atom-thick of sp2-bonded carbon, are promising materials due to their high surface area, excellent electronic conductivity and good mechanical flexibility. rGO is an ideal carbon electrode material for supercapacitor because of their high surface area that is capable of storing high capacitance on the surface [1-3]. However, rGO tends to aggregate when obtained by chemical reduction method because of intersheets van der Waals interaction. It results not only a lower specific capacitance because of the decrease of effective surface area but also poor stability and electrical conductivity. So it is very important to prevent the aggregation of rGO for improving the electrochemical performance of supercapacitor.

To improve the energy density and to avoid aggregation of rGO, metal oxide nanoparticles (MNPs) are considered as the best candidate because of their availability of the variable oxidation states for the charge storage mechanisms. The open edges of rGO hold the MNPs with the help of functional group for the final formation of rGO/MNPs hybrids, which can efficiently prevent them from agglomerating and restacking and hence enhancing the active surface for electrochemical reactions. MNPs tightly adjusted into the rGO interconnected network. Filling of rGO interconnect network by MNPs, facilitates the electron transport between MNPs and rGO. The existence of such network formation by MNPs and rGO may be advantageous for fast diffusion and easy accessibility of the related ion species. This study deals with the capacitance analysis of rGO composite electrodes containing iron oxides.

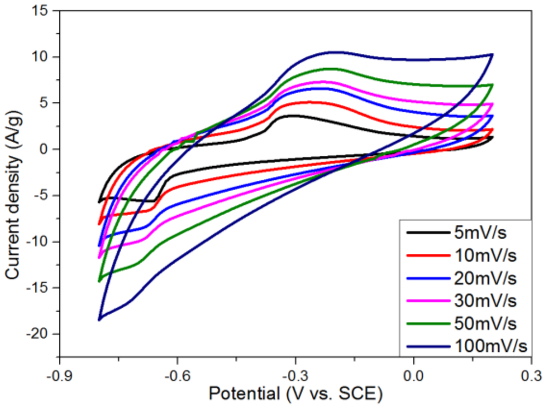

Figure 1 CV curves of the Fe_3O_4/rGO composite at various scan rates

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OER/ORR properties of MoS_2/Ni_3S_2 on nickel foam

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The oxygen electrode is the most important part in lithium air batteries for oxygen reduction and evolution reaction (ORR/OER) in order to get closer to the theoretical energy density of 11,238 Wh/kg, which is the best among the batteries ever developed. Many carbon materials have been researched as candidate oxygen electrodes for lithium air batteries such as a carbon black, CNTs and 2D graphene. Compared to the many research results, there are still many controversies on optimum oxygen electrode for lithium air batteries. Besides that, carbon and binder have been known to deteriorate OER/ORR properties for Lithium air batteries by generating Li_2CO_3 and other bi product.

MoS_2/Ni_3S_2 has been studying on HER and OER as electrodes for water splitting electrolyzer. HER and OER performances were better than commercial HER and OER catalysts (worse than Pt/C though). To my best knowledge, there's no report on Lithium-air battery cathode for example, like ORR. Therefore, in order to research ORR properties of MoS_2/Ni_3S_2, MoS_2/Ni_3S_2 has been synthesized on Nickel foam as well as Nickel powder and SEM, TEM, coin cell and RRDE (Ring Rotating Disk Electrode) analysis have been conducted for a cathode material for Lithium air batteries.

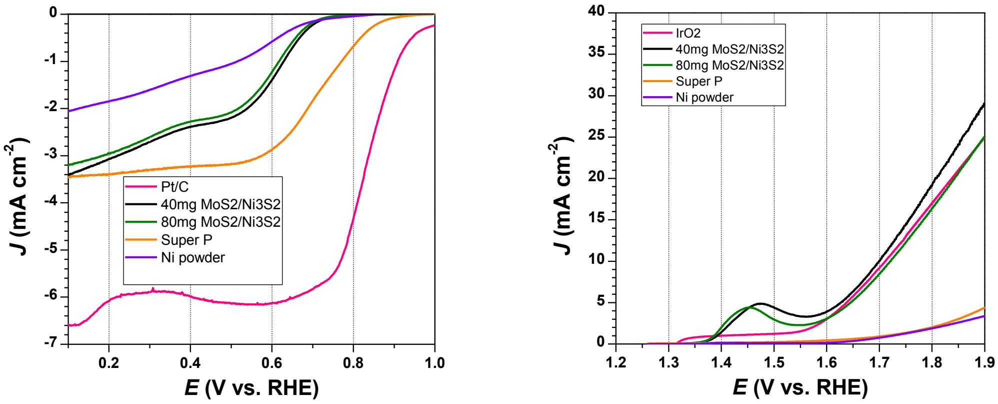

Figure 1. ORR(left) and OER(right) of MoS_2/Ni_3S_2 Ni-powder and their comparison with Super P, As-received Ni powder and Pt/C

Novel process of making lithium impregnated anode of thermally activated batteries using a screw type mixer system

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Recently, a thermally activated battery is widely used military power source, especially guided missile system because it has long shelf and reliability. For the development of thermally activated batteries, an anode of a battery is quite important because it is closely related to the performance (a potential, a capacity, etc) of thermally activated batteries.

This paper describes novel process of making lithium impregnated anode of thermally activated batteries using a screw type mixer system. We use this screw type mixer to mix lithium and iron powder for homogeneous state of an anode. This paper also describes mixing method and process to make an anode of thermally activated batteries. so we achieve better electrochemical performance of thermally activated battery cells using this novel process. And we also perform electrochemical analysis including EIS(Electrochemical Impedance Spectroscopy)and discuss results of experiments and electrochemical analysis.

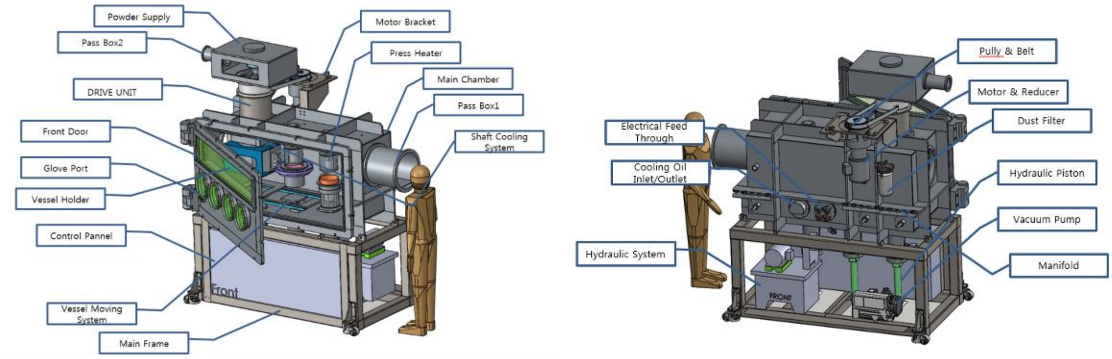

Figure 1. A screw type mixer system for making anode of thermally activated batteries

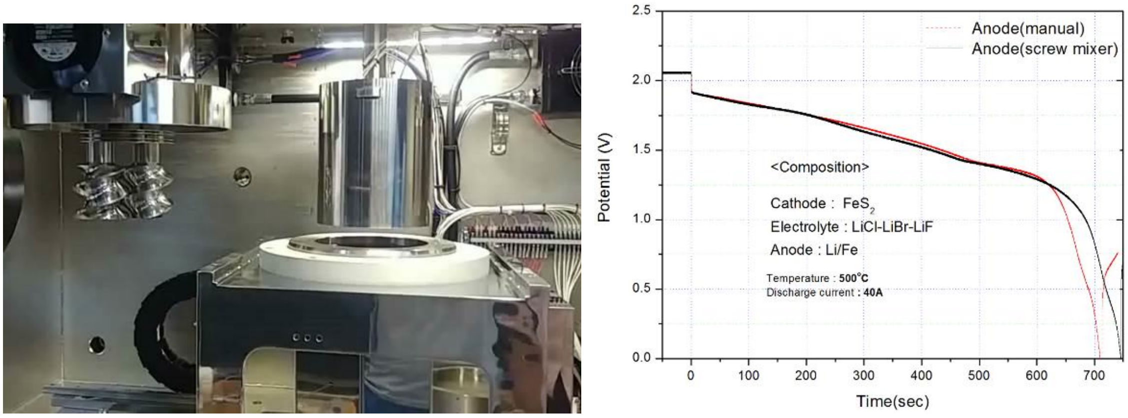

Figure 2. A picture of screw type mixer and Comparison of discharge curves with experimental results

Theoretical analysis of mass transfer during anodic dissolution of metal with the formation of stable complex with anion of solution

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The nature of the interaction of electrolyte anions with the anode surface during the electrochemical dissolution of metals is an important problem. In many cases, complex ions of dissolving metal with anions of electrolyte form the primary product, which is involved in the elementary act of ionization of metal atoms. The anodic dissolution of tungsten, molybdenum, rhenium and other refractory metals in the alkaline solutions proceeds according this mechanism. It forms the basis for electrochemical polishing and electrochemical machining of metals, electrochemical sharpening of a wire for fabrication of scanning probe microscope tips and tools for electrochemical micro/nanomachining.

In [1, 2] the rate of mass transfer in the anodic dissolution of metal with the formation of stable cationic and anionic complexes were calculated within the approximation of Nernst diffusion layer. In these works, the conditions for the absence of the limiting current associated with slow delivery of solution anions were determined, and approximate analytical equations for the limiting current were obtained. These equations give a semi-quantitative estimate of the mass transfer rate, because they ignore the presence of ions of other types in the solution and do not take into account the presence of several diffusion layers, which are associated with different diffusion coefficients of ions.

This work is devoted to the theoretical analysis of mass transfer during anodic dissolution of metal with the formation of a stable complex with the anion of solution without using the approximation of Nernst diffusion layer and taking into account the presence of background electrolyte. The Nernst-Planck equations and the electroneutrality condition, which take into account the electro-diffusive and convective transfer of ions, are used as the mathematical model. The numerical solution is performed using the finite element method. The results of modeling anodic dissolution of rotating disk electrode with the formation of stable cationic and anionic complexes are presented. The dependences of the limiting current on the composition and concentration of solution and the transport properties of ions are obtained.

The study was funded by Russian Foundation for Basic Research and Tula region according to the research project № 19-48-710008.

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Effect of migration on homogeneous redox electrocatalysis at rotating disk electrode

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Electrocatalysis is important to many applications in the electrochemistry. A large number of works have been devoted to the experimental and theoretical study of homogeneous redox electrocatalysis. The theory of catalytic currents can be illustrated by the reduction of hydrogen peroxide in the presence of ferric ions [1]. In this system iron, changing its valence, seems to be the transfer agent for electrons from the electrode to hydrogen peroxide. The slow stage of the process is the reaction between H_2O_2 and Fe^{2+}, and therefore the height of the catalytic wave is governed by the rate of this reaction. The current increases due to hydrogen peroxide, which by itself is not reduced electrolytically until much more negative potentials are reached, although chemically it is a more powerful oxidizing agent than ferric iron [2]. The theory of homogeneous electrocatalysis is most well-developed for polarography; however, in some works, variously shaped electrodes and chemical reactions of various orders were considered. In all works devoted to the theoretical study of homogeneous redox electrocatalysis, the ionic migration was ignored. In many cases, the supporting electrolyte is present in the solution, which almost completely suppresses the migration of electroactive ions. However, in some cases, the concentration of supporting electrolyte can be rather low or it is absent at all [3]. In this case, the migration transfer of all types of ions, which are present in the solution, should be taken into account.

This work is devoted to the theoretical study of the effect of migration on homogeneous redox electrocatalysis of electrochemical reactions at the rotating disk electrode. The mathematical model involves the Nernst-Planck equations that take into account diffusion, migration, convection, homogeneous chemical reactions, and electroneutrality condition. For the convenience of solving and analyzing the results, the mathematical model was reduced to the dimensionless form. The numerical solution was performed by the finite volume method on the nonuniform grid. Based on the results of computational experiments, for the electrocatalytic reduction of hydrogen peroxide in the presence of ferric ions, three zones were observed in the plane of concentrations of H_2O_2 – H_2SO_4. These zones differ in the nature of the limiting current: for H+ ions, Fe^{+2} ions, and hydrogen peroxide H_2O_2. The dependences of the limiting current on the concentrations of H_2SO_4 and H_2O_2 were determined with and without consideration of the ionic migration. It was found that the ionic migration may be ignored only in the cases that the concentration of H_2SO_4 is significantly higher than that of H_2O_2. It was shown that the strongest effect of ionic migration is reached on the boundaries between zones that differ in the nature of the limiting current.

The study was funded by Russian Foundation for Basic Research and Tula region according to the research project № 19-48-710008.

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A Shape Controllable ZIF-67-derived 3D Hollow Cobalt–Molybdenum Nitride for Oxygen Evolution Reaction

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Oxygen evolution reaction (OER) is an essential process for the water electrolysis to realizing the renewable energy sources scalably. Recently, transition metal nitride have been exhibited excellent OER electrocatalytic activities [1,2]. In this work, a 3D hollow Cobalt-Molybdenum nitride compound was prepared by ZIF-67 template. Three different kinds of morphologies with large specific surface areas were controlled by changing the contents of water and 2-methylimidazole. The electronic structure can be adjusted to regulate electron density of Co and Mo by introduce of N. These binary metal features offer a feasible way for electronic transfer between the different components. The as-resulted compound was used as an electrocatalyst and exhibited a high catalytic activity and long-term cyclic stability for OER with the overpotential (η_{10}) of only 294 mV [3].

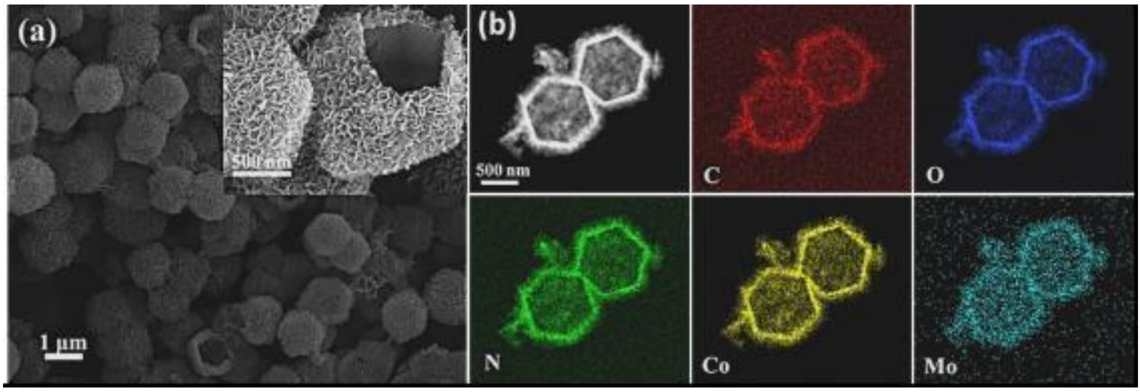

Figure 1 (a) SEM images of ZIF-67-derived 3D hollow Cobalt–Molybdenum Nitride. (b) TEM image and elemental mappings of 3D hollow Cobalt–Molybdenum Nitride.

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On the electrochemical behavior of non-steroidal anti-inflammatory drugs, using 2D and 3D carbon electrodes modified with RGO and platinum.

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The presence of pharmaceuticals in surface natural waters is considered an emerging environmental problem due to its potential toxicological risk on living organisms, even at low concentration. The low efficiency of conventional treatment plants in the elimination of this waste requires the development of more efficient technologies. Advanced oxidation processes have been shown to be able to efficiently oxidize most organic pollutants. In the present work, we study the implementation of two-dimensional (fabrics) and three-dimensional (foams) carbon materials as electrodes in order to perform the study of the electrochemical degradation of these products. The use of fabrics (2D electrodes) allows the exploitation of properties such as its high ratio between the surface area and the total mass or volume, or its dimensional versatility. In this way, with a smaller size electrolysis cell, it is possible to handle larger volumes of effluent. The carbon foam materials (3D electrodes), with a high surface-to-volume ratio, were manufactured using pressure infiltration techniques. We have initially selected non-steroidal anti-inflammatory drugs, such as ibuprofen and naproxen, due to their high consumption as anti-inflammatory and analgesic, and because they are drugs that appear more frequently in wastewater analysis.

The carbon materials used in the present work were modified by coating their surface with reduced graphene oxide (RGO) and Pt nanoparticles. Reduced graphene oxide (RGO) was synthesized on 2D and 3D electrode surfaces by means of potentiodynamic method. The resulting coating was characterized, among other techniques, by means of cyclic voltammetry (CV) and EIS (Electrochemical Impedance Spectroscopy). Pt nanoparticles were synthesized on C-RGO electrodes by means of potentiostatic, potentiodynamic and alternate current methods. The samples obtained by the last method demonstrated to be an efficient alternative to traditional potentiostatic or potentiodynamic methods, because more electroactive coatings with less effective synthesis time are achieved. Field Emission Scanning Electron Microscopy (FESEM) was also employed to observe the morphology of the coatings.

Cyclic Voltammetry (CV) was used to study the electrochemical characterization of the pharmaceutical compounds using 2D and 3D modified carbon materials as working electrodes. It was observed stable oxidation products blocking the surface of the electrodes. These products, which modified the voltammetric profile of the successive CV cycles, were partially removed by reduction. This behavior was taking into account in the electrolysis assays, in which alternate current experiences were developed, among others, with different electrolysis cell configuration. Different analytical methods were employed to monitoring the evolution of the electrochemically treated solution: HPLC, GC-Mass chromatography, UV-vis and ATR-FTIR spectroscopies, TOC and DQO.

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Electrochemical Degradation of Phenol and Chlorophenol using Boron Doped Diamond and Composite of Fe_3O_4 Nanoparticles + Chitosan

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Phenol, o-, m- and p-chlorophenol were electrochemically degraded using a boron doped diamond (BDD) electrode and a composite of Fe_3O_4 nanoparticles (NPs, Figure 1A and 1B) and chitosan (CS). Results showed that it was possible to remove more than 95 % of entrained phenol, o-, m- and p-chlorophenol were electrochemically removed from an industrial sample (Figure 1C) using the arrangement of electrodes BDD │ Fe_3O_4 NPs + CS │ Ti in acid conditions during treatment test covering 240 min while applying 2.3 V (Figure 1D). This destruction was enabled by the generation of $^{\bullet}OH$ radicals at the electrodes an only limited direct sorption of the effect of phenolic compounds (only 4 %) by this Fe_3O_4 NPs + CS composite. This study, demonstrated another application of Fe_3O_4 NPs + CS composite in the presence of BDD, as an attractive technique to treat industrial wastewater effluents polluted with phenolic compounds.

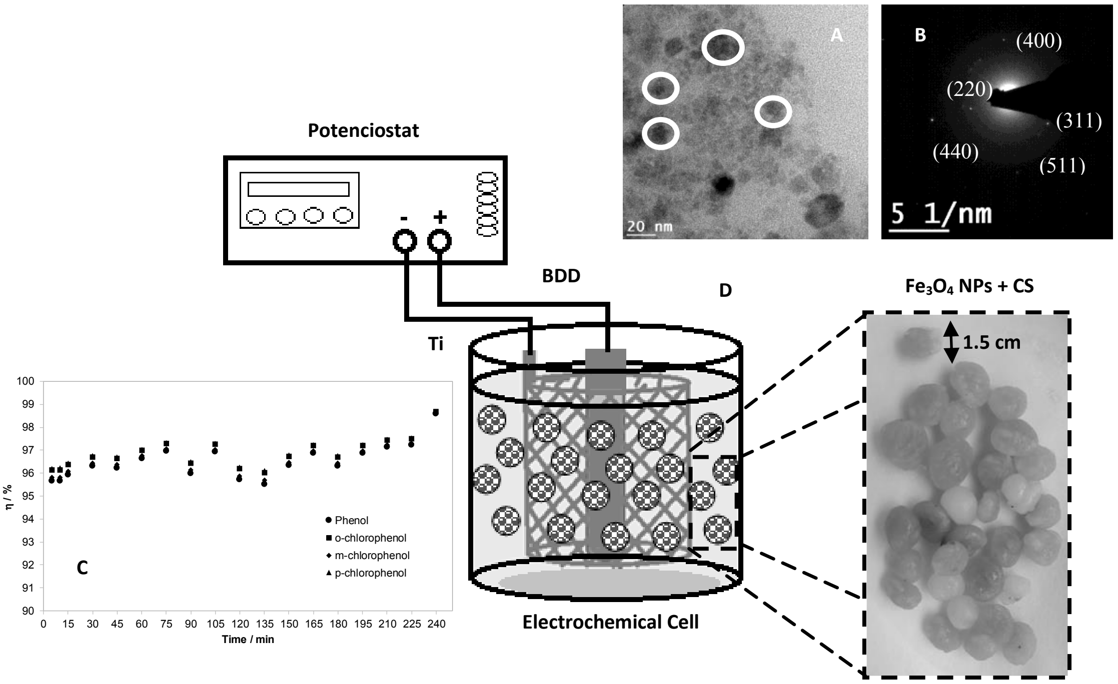

Figure 1. TEM image of Fe_3O_4 NPs (20 nm) shows some agglomerations (A). EDX analysis with the Miller index related with the magnetite (B). Removal efficiency (η) in aqueous 0.5 M H_2SO_4 support electrolyte during an electrolysis test cycle operated for 240 min with a 2.3 V DC electric field on the removal of phenol, o-, m- and p-chlorophenol in the industrial sample (C). Experimental setup for the electrochemical degradation of phenolic compounds in 0.5 M H_2SO_4 using as central anode, a BDD plate (+), and a Ti mesh coated in the composite Fe_3O_4 NPs + CS as cathode (-); both electrodes are connected to a potentiostat contained in an electrochemical cell (D).

Activation of Copper(I) Oxide Photocathodes for Enhanced Solar Water Splitting

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Though the field of photoelectrochemical (PEC) solar fuel production focuses on a broad variety of materials, metal oxides are probably the most commonly employed materials in state-of-the-art photoelectrodes. There are, however, enormous challenges to be overcome to obtain sufficient solar water-splitting efficiency, such as over-potential losses due to fast recombination rates of charge carriers, electrode photo-degradation, limited light-harvesting capacities, to name a few. In this work, we report an extensive study on Cu_2O based photocathode for hydrogen evolution reaction (HER) in terms of enhancing its solar-to-hydrogen (STH) conversion efficiency, while using low-cost fabrication methods. We have addressed the inefficiency of Cu_2O which mainly arises due to incompatible light absorption and charge carrier diffusion lengths, by fabricating highly reproducible Cu_2O-nanowire arrays on Cu substrate. Recently, to replace the expansive noble metals in electrocatalyst, transition metals with low cost and comparable performances are chosen as substitutes. Among transition metals, iron, which is one of the most abundant metal in the earth crust, is relatively out of the attention as an electrocatalyst. To enjoy the strong cost competitiveness of the iron, the poor catalytic property of the iron based electrocatalysts, particularly its low current density should be enhanced. According to several studies, it is known that certain phase, iron oxyhydroxide, can have much higher current density than existing iron-based electrocatalysts. Especially, iron oxihydroxide (FeOOH) belongs to thermodynamically stable form among iron oxides and presented to have enhanced catalytic property by experiments. Though, there are not enough theoretical investigations on its catalytic activity. Herein, Cu_2O/FeOOH core-shell nanowires (NWs) were synthesized with a simple wet-chemical process as shown in Figure 1. The uniform coverages of the FeOOH shell at thickness a few nm and core diameter ~100 nm of Cu_2O NW were confirmed with SEM and TEM. With XRD and XPS we analyzed the structural and composition features of the core-shell NWs. This heterojunction structure would significantly cause a further negative shift of the flat-band potential and increase the surface band bending, relative to a bare electrode. These characteristics resulted in a doubling of photocurrent and a greater PEC stability at a less positive potential for the decomposition of water in a practical application. Our experiments improve our understanding of the heterojunction effect on PEC activity and provide a blueprint for the design of materials in the application of solar hydrogen.

Keywords:：photoelectrochemical, solar hydroge, water splitting, cuprous oxide, Iron oxide-hydroxide.

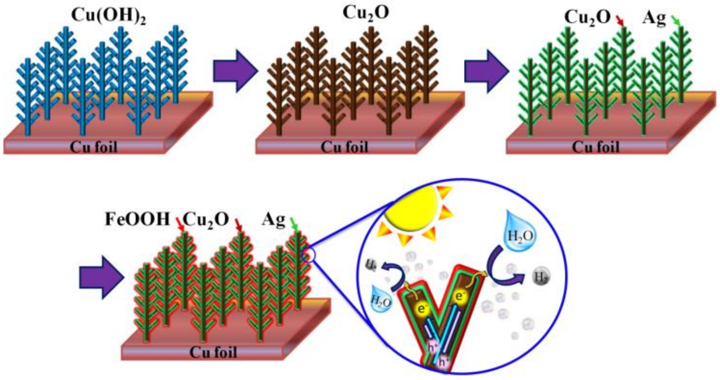

Figure 1. Schematic diagram of synthesis of core-shell nanowires as photoelectrode.

Development of a Membrane for Elevated Temperature PEM Water electrolysis (I)

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Hydrogen is expecting as an abundant energy element for the next generation which is a smart grid society. Hydrogen does not exist in nature, and it is important to develop a process to produce hydrogen with less energy. The hydrocarbon reforming reaction is most promising as a method for producing hydrogen but is required high energy. Water electrolysis is a hydrogen production method which has many features such as high hydrogen production rate, the synthesis of high purity hydrogen without containing CO_2 and CO, compact, and easy scale up. In particular, the polymer electrolyte membrane (PEM) water electrolysis has high energy efficiency for hydrogen production, and when natural energy such as wind power generation and solar power generation is used as electric power. It is possible to synthesize hydrogen with accumulation of natural energy and without CO_2 release. [1,2] Therefore, the main point of the hydrogen production is to the cost, and to decrease the energy consumption. One of the methods is improving the efficiency of the electrolysis. To do that, there is to increase the operating temperature for proton exchange membrane (PEM) electrolyzer. The energy efficiency should be significantly improved because of the decreased thermodynamic energy requirement, enhanced electrode kinetics, enhanced membrane conductivity, decreased resistivity in the interface of membrane electrode assembly, and the possible integration of heat recovery. It is hot issue to develop and/or improve the materials such as anode and cathode catalysts, temperature tolerant membranes, gas diffusion layers, bipolar plates and high temperature electrolyzer system. [2,3]

We are constructing a single cell MEA and electrolyzer which have an operation at the elevated temperature of 120 ^{o}C under pressurized condition. As a first step, in this presentation, a high temperature water electrolysis using a perfluorosulfonic acid (PFSA) polymer electrolyte membranes will be introduced in the conference.

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Assessment of a PBI based SO_2 depolarized electrolysis cell

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Hydrogen can be produced from a broad range of renewable energy sources acting as a unique energy core providing low or zero emission energy to all energy consuming sectors. On the way to "hydrogen economy" [1], and to a "Green hydrogen" the ideal raw material is obviously water. However, due to its unfavourable thermodynamics, the single step thermal dissociation of water to hydrogen and oxygen is one of the most challenging processes to produce hydrogen in practice [2]. Among the different routes to produce hydrogen with low environmental impact, the thermochemical cycles using a high temperature thermal source have been proposed as one of the most promising technologies for massive hydrogen production [3]. One of the leading thermochemical cycles to produce hydrogen with a high sustainability is the hybrid Sulphur cycle, also known as Westinghouse cycle. It is a hybrid electrochemical-thermochemical cycle. It was originally proposed in 1975 [4] and developed by Westinghouse electric corporation. The process is labelled "hybrid" because of the substitution of one thermochemical reaction by the electrochemical oxidation of SO_2 with water to yield sulphuric acid and hydrogen [2]. The SO_2 is electrochemically oxidized at the anode to form sulphuric acid, protons and electrons (E^0 = 0.158 V vs SHE). The protons are conducted across a proton exchange membrane (PEM) that acts as a separator to the cathode where they recombine with the electrons to form hydrogen according to equations 1 and 2 [3].

$$SO_2(aq) + 2\,H_2O \rightarrow H_2SO_4(aq) + 2H^+ + 2\,e^- \qquad (1)$$

$$2H^+ + 2\,e^- \rightarrow H_2(g) \qquad (2)$$

The typical PEM used in the electrolysis cell is a Nafion membrane. However, Nafion based membranes show several limitations, including the inability to operate at elevated temperatures and the decreased performance observed when exposed to high acid concentrations [5].

This work is focused on the study of the SO_2 depolarized electrolysis at high temperature (100-200 °C) using a phosphoric acid doped PBI membrane as PEM. The tests are performed in a 25 cm^2 SO_2 depolarized electrolysis cell using a commercial PBI membrane (DAPAZOL, supplied by DPS, Denmark) doped in 85 wt% H_3PO_4. 0.9 mg Pt/cm^2 were deposited on both electrodes (anode and cathode) using 40 % Pt/Vulcan caborn XC72 as catalyst. Different operation conditions are evaluated such as temperature, SO_2 flow and the SO_2/H_2O molar ratio. Polarization curves and impedance spectroscopy analysis are carried out to evaluate the performance of the cell and the ohmic and charge transfer resistances. A preliminary stability test will be performed to assess the stability of the different components of the cell (membrane and electrodes).

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Influence of the anode composition on performance of Reversible Chlorine PEM cells

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Reversible Chlorine cells are a promising type of devices for the regulation of the energy produced by wind turbines and solar PV panels. In the electrolytic mode, this type of cell transforms hydrochloric acid into hydrogen and chlorine, which can be stored helping to regulate the exceeding energy. In fuel cell mode the reversible reactions occur, and hydrochloric acid is regenerated. Integration of the both modes of operation into the same cell is an important handicap which has been faced in this work, using different Mixed Metal Oxides anodes in order to determine the most efficient formulation, different proton exchange membranes and operation conditions. This work reports some of the most interesting results obtained in this promising technology.

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Evaluation of CO_2RR to methanol catalysts and stable OER catalysts for a 2 kW methanol demonstrator plant

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As the energy landscape changes due to the introduction of renewable energy, new opportunities arise for power to fuels which enable the carbon cycle loop to be closed. One such process is converting CO_2 to methanol using electrolyser technology. Methanol is advantageous as an energy vector as it can be stored/transported in the liquid form and has a high energy density.

Within the framework of the EU H2020 project LOTER.CO_2M "CRM-free Low Temperature Electrochemical Reduction of CO_2 to Methanol", we aim to produce a 2kW demonstrator with ambitions goals of >60% conversion rate of CO_2 and a >90% selectivity towards methanol at the cathode and a critical raw material (CRM) free anode for oxygen evolution capable of 50 A g^{-1} while only losing 1% activity over 1000 hours operation.

Electrochemical conversions of CO_2 to methanol and other alcohols have up till now suffered from low selectivity (~40%) or low turnover frequencies ($r = \sim 10\ \mu mol\ m^{-2}\ s^{-1}$ or $\sim 1\ mA\ cm^{-2}_{Geo}$), Figure 1. Here we introduce the project and present recent results on material development and electrochemical testing procedures for both CO_2RR and OER catalysts to be used in the demonstrator.

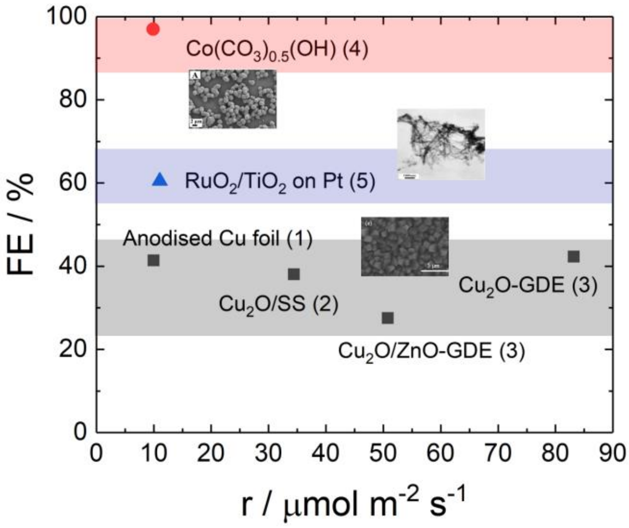

Figure 1. Literature comparison of current catalysts used for CO_2RR to methanol showing the Faradaic efficiency and the geometric rate. Typical conditions include neutral pH and close to standard pressure and temperature.

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Low-Cost Perovskite-Type Oxides as Efficient Electrocatalysts for Oxygen Evolution in Alkaline Media

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The consumption of finite reserves of carbon-based fossil fuels and world's concern over greenhouse gas emission have triggered many studies on safe, clean and sustainable sources of energy. Several electrochemical energy conversion and storage systems, such as metal-air batteries, fuel cells, or alkaline water electrolyzers, have been in the center of spotlight as attractive solutions for notable reduction of human dependency on fossil fuels. Electrochemical water splitting involves oxygen evolution reaction (OER) at the anode and hydrogen evolution reaction (HER) at the cathode, with the former being the most kinetically sluggish. Thus, OER as a four electron-transfer process requires high overpotentials for overcoming kinetics barrier and it is seen as the bottleneck of water splitting. Hence, in order to making water splitting a feasible energy technology, development of stable, cost-effective catalysts with high activity for OER are needed [1,2].

Within this scenario, considerable efforts have been devoted to investigating the intrinsic OER activity of metal oxide catalysts containing transition metals, and among them perovskite-type oxides (ABO_3). Perovskites have been revealed to exhibit extraordinary good intrinsic electroactivity towards OER [3]. Besides economic benefits of using transition-metal based perovskite-type oxides, important advantage is flexibility in their compositions and structures that can result in completely tunable physicochemical properties and OER performances.

Herein, to the authors' best knowledge, the electrocatalytic activity of various samples of perovskite oxides and Ruddlesden-Popper oxide phases was investigated for OER in alkaline media for the first time. Samples were synthesized in both powder ($BaSmMn_2O_5$, $BaSrMoCoO_6$ and La_2CoO_4) and disk forms ($Sr_2Fe_{1.6}Mo_{0.4}O_6$, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ and La_2CuO_4). In order to prepare working electrodes, 5 mg of each powder sample was dissolved in 125 μL of polyvinylidene fluoride (PVDF) solution and after 30 minutes homogenization in the ultrasonic bath, 10 μL of the ink was deposited onto glassy carbon electrode and dried overnight at temperature of 85 ºC. Working electrodes from disks were fabricated using silver paint to glue each disk with a copper wire protected by a thin glass tube. The samples were then mounted in an epoxy resin. Subsequently, in order to obtain smooth surfaces, electrodes were polished using SiC papers of decreasing grit sizes.

Electrochemical measurements were performed in 8 M KOH electrolyte in typical three-electrode cell. The samples activity for OER were examined by means of linear scan voltammetry. From obtained data, kinetic parameters such as Tafel slope and exchange current density were evaluated. Polarization curves for each sample were recorded in the 25 - 85 ºC temperature range in order to calculate the OER activation energy. To get insight into materials' stability, chronoamperometric measurements were carried out. Electrochemical impedance spectroscopy analysis were performed at different potentials and temperatures.

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Electrochemical Impedance Study of the Oxygen Reduction Reaction on $La_{0.8}Sr_{0.2}Co_xFe_{1-x}O_{3-\delta}$/C Electrocatalysts in Alkaline Medium

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The major advantages of alkaline over acidic medium concerning oxygen reduction reaction (ORR) are the faster ORR kinetics and the less corrosive environment, which allow the use of a wider range of electrocatalysts, including mainly carbon-transition metal hybrids, nonmetal-doped nanocarbons and transition metal oxides [1], such as perovskite oxides [1-3].

In the present work a series of $La_{0.8}Sr_{0.2}Co_xFe_{1-x}O_{3-\delta}$ perovskite oxides [denoted as LSCF 82x(1-x)], including $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (LSC) and $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ (LSF), were synthesized via a combustion method and, mixed with carbon black in 3 to 1 mass ratio, were studied towards their ORR activity in O_2 saturated 0.1 M KOH solution at room temperature, using electrochemical impedance spectroscopy. The experiments were carried out in a typical three-electrode cell with each tested electrocatalyst (working electrode) being deposited on a glassy carbon rotating disk electrode (RDE) in the form of a thin film (74 μg_{oxide} cm^{-2}_{disk}) [2]. A Pt foil and a Ag/AgCl (3 M KCl) electrode were used as counter and reference electrodes, respectively. Impedance spectroscopy data were collected at different RDE rotation rates and different applied potentials, in the frequency range 100 kHz – 10 mHz.

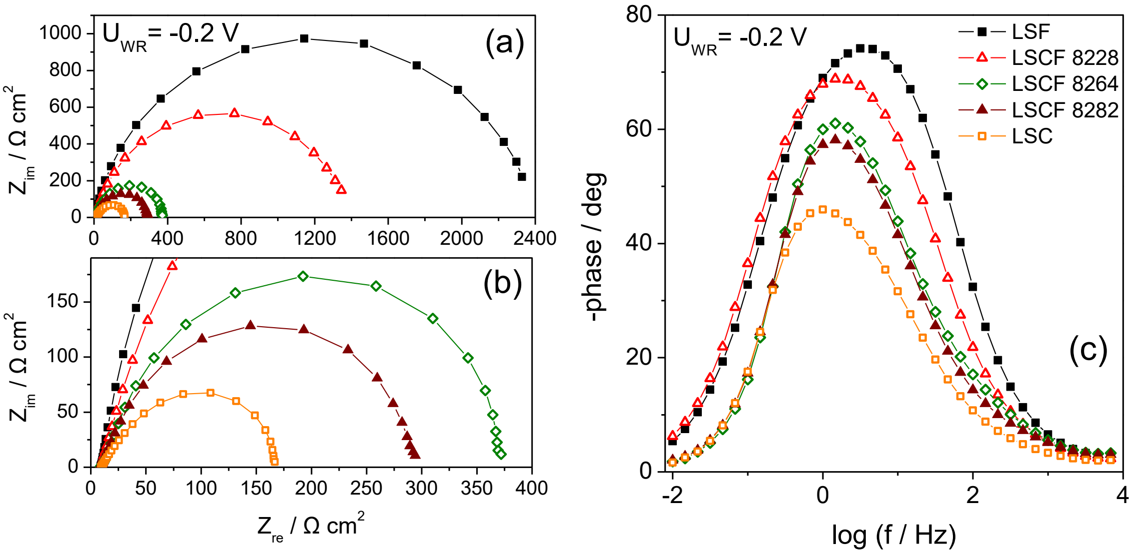

Fig. 1 Comparison of the impedance characteristics of the tested $La_{0.8}Sr_{0.2}Co_xFe_{1-x}O_{3-\delta}$/C electrocatalysts at -0.2 V vs. Ag/AgCl, in the form of Nyquist (a, b) and Bode (c) plots; 0.1 M KOH; room temperature; RDE rotation rate: 3000 rpm.

In Fig. 1 are shown, in the form of Nyquist (Figs. 1a and b) and Bode (Fig. 1c) plots, impedance data obtained with the tested electrocatalysts at 3000 rpm RDE rotation rate and at an applied potential of -0.2 V vs. Ag/AgCl. The latter corresponds to the kinetic control region, as confirmed by the absence of change in the impedance spectra when changing RDE rotation rate. As shown in the figure, increasing substitution of Fe by Co results in decrease of the polarization resistance (Figs. 1a and b), indicating an increase in ORR activity, as well as in a less pronounced capacitive behavior (Fig. 1c). The observed increase in ORR activity of the perovskite/C electrocatalysts upon gradual substitution of Fe by Co can be associated with induced changes in the surface B-sites electronic structure [2, 3] and in surface oxygen vacancy formation [2].

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Graphene-Supported Pt Cathode Materials for Polymeric Exchange Membrane Fuel Cells

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Graphene-based materials (GMs) have attracted considerable attention as catalyst support for Polymer Exchange Membrane Fuel Cells (PEMFCs) due to their high conductivity, surface area and mechanical strength [1]. They also improve the dispersion and distribution of metallic nanoparticles, and therefore, an enhancement of the catalytic performance toward several reactions is usually reported [2].

In the current work, graphenic materials (GMs) were obtained by chemical reduction of graphene oxide (GO) employing sodium citrate (rGO) and dimethylsulfoxide (S-rGO) as reducing and doping agents. Pt nanoparticles were supported on rGO (Pt/rGO), S-rGO (Pt/S-rGO) and carbon back (Pt/C) considering a nominal metallic loading of 20 wt% by the formic acid method.

Physicochemical characterization was conducted by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and Raman spectroscopy. Meanwhile, the electrochemical performance of the catalysts toward the oxygen reduction reaction (ORR) was evaluated on a PEMFC test station. In all the performed studies, the anode catalyst was prepared with a commercial 20 wt % Pt/C (ETEK), pure hydrogen and oxygen were supplied to the anode and cathode and working temperatures of 30, 60 and 90 ºC were employed.

Main results indicate an enhancement of the catalytic activity by GMs-based materials in comparison to carbon black-based catalyst. Furthermore, S-doping greatly increases the overall PEMFC performance, indicating the importance of sulfur insertion into the graphene network.

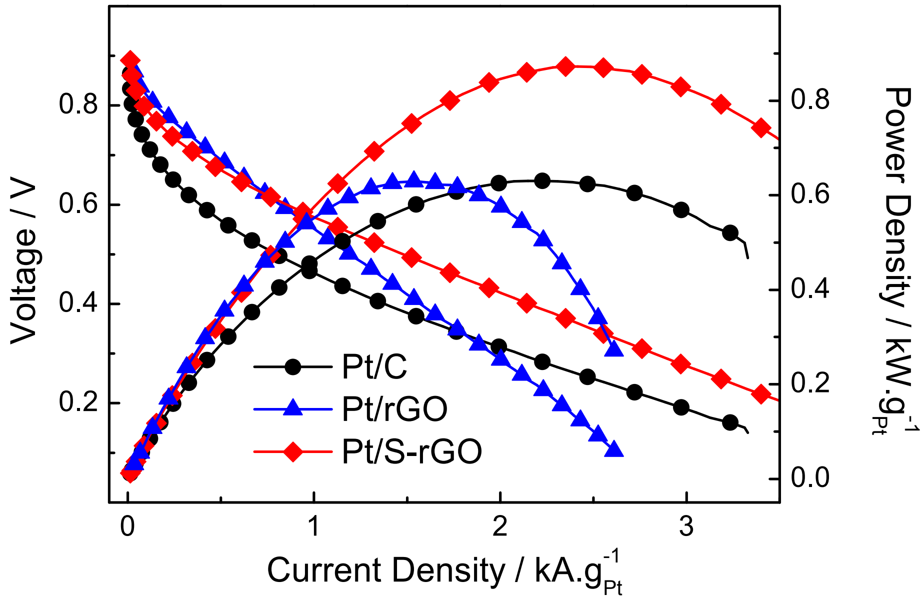

Figure 1. Polarization and power density curves of acidic PEMFC devices comprising Pt/C, Pt/rGO and Pt/S-rGO as cathode catalyst layer. Commercial Pt/C (ETEK) was used for the anode catalysts layer. Operation conditions: H_2/O_2 anode/cathode gas flow, 30 °C cell temperature and zero back pressure.

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Ionic Liquids with Dicyanamide Anion as Potential Electrolyte Additives for Alkaline Water Electrolysis

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Alkaline water electrolysis presents the most promising, environmentally friendly method for hydrogen production. Water splitting occurs through two half-reactions, i.e., hydrogen evolution reaction (HER) proceeding at the cathode and oxygen evolution reaction (OER) proceeding at the anode with OER generally requiring higher overpotentials. There is a wide search for novel electrode materials that would lead to a decrease in the required overpotential and, consequently, to a reduction in the energy consumption and overall electrolyzer cost. Another possible way to increase the efficiency of the water electrolysis process is through electrolyte engineering [1].

Room temperature ionic liquids (RTILs) are gaining more and more attention for electrolyte applications, i.e., as additives to electrolytes in alkaline water electrolyzers due to their exceptional properties such as wide electrochemical potential window and low vapor pressure [2]. Furthermore, they can be used with no supporting electrolyte (due to the abundance of charge-carrying ions), they are more eco-friendly than volatile organic solvents (due to their near-zero volatility) and they are thermally and chemically stable (due to ions chemical robustness). Recently studied as additives to electrolytes for HER, RTILs were shown to improve electrolyte's properties and efficiency of the process at room temperature [3]. Properties of RTILs such as viscosity, density, conductivity, melting and decomposition temperatures, as well as hydrophobicity/hydrophilicity are determined by the choice of cation and anion where there is an endless number of the cation/anion combinations. Electrochemical window is determined by the reduction and oxidation potential of the cationic and anionic components, respectively.

Within the present study, five different RTILs were prepared and subsequently investigated as additives to alkaline aqueous solutions for OER. These RTILS were: 1-butyl-3-ethylimidazolium dicyanamide, 1,3-dibutylimidazolium dicyanamide, 1-butyl-3-hexylimidazolium dicyanamide, 1-butyl-3-octylimidazolium dicyanamide and 1,3-diethylimidazolium dicyanamide.

The OER studies were performed using Pt working electrode in 8 M KOH using linear scan voltammetry from the open circuit potential up to 1.8 V vs. RHE. The obtained current densities were compared to those recorded in 8 M KOH with no RTILs added. Reaction parameters, including Tafel slope and exchange current density were determined, enabling further evaluation and comparison of RTILs-containing electrolyte systems. Moreover, influence of temperature on the OER efficiency of the system with mixed RTIL-KOH electrolyte was studied. Voltammetric measurements were complemented with electrochemical impedance spectroscopy measurements. Finally, stability of the systems was explored by chronoamperometry at a constant potential for 1 h and by cycling polarization measurements.

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Lanthanum-Based Perovskite Oxides for Efficient Electrolytic Oxygen Evolution in Alkaline Media

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Hydrogen economy is forecast as the most likely scenario to partially replace the prevailing fossil fuel-based energy systems. Among the different methods used for large-scale production of hydrogen (mostly based on fossil fuels), alkaline water electrolysis is seen as the most eco-friendly process [1,2]. However, the efficiency of water electrolysis is limited by the large overpotentials necessary for hydrogen evolution reaction (HER) to proceed at the cathode and oxygen evolution reaction (OER) at the anode. Furthermore, the high energy consumption necessary to split water molecules leads to the high price of the electrolysis process and, consequently, to the high price of the hydrogen produced. OER kinetics are rather sluggish due to unfavorable removal of four electrons to form oxygen–oxygen double bond [3,4]. Thus, creating anode materials highly active for OER in alkaline media is essential for increasing the efficiency of the water electrolysis process and lowering the price of the hydrogen product.

Herein, seven lanthanum-based perovskite and Ruddlesden-Popper oxide phases (2 ABO_3 + 5 A_2BO_4) were prepared in order to evaluate their activity for OER in alkaline media. Namely, $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_3$ (LSFC), $La_{0.7}Sr_{0.3}MnO_3$ (LSM), $La_{1.9}Pr_{0.1}CuO_4$ (LP1C), La_2NiO_4 (LNO), $La_{1.9}Pr_{0.1}NiO_4$ (LP1N), $La_{1.8}Pr_{0.2}NiO_4$ (LP2N) and $La_{1.9}Sr_{0.1}NiO_4$ (LS1N) were prepared by high−energy milling and high−temperature treatment of oxide mixtures. Dependent on the cations in A and B sites, as well as stoichiometry, different performances for the OER are anticipated. The prepared materials were characterized using several physicochemical techniques. The electrodes were made by gluing each ceramic disk to a copper wire using silver paint, with a thin glass tube shielding the wire. The disks were then mounted in an epoxy resin and polished using SiC abrasive papers to obtain smooth surfaces. As the aim of this study was to examine the intrinsic electrocatalytic activity of lanthanum-based perovskite oxides for the OER, carbon was not added to increase conductivity.

OER studies were carried out in 8 M KOH electrolyte solution by recording linear scan voltammograms (LSV) from the open circuit potential up to 2.3 V vs. RHE at a scan rate of 0.05 V s^{-1}. LSM, LNO, LS1N and LSFC exhibited activity for the OER with current densities increasing in the following order LSM (10 mA cm^{-2}) < LNO (75 mA cm^{-2}) < LS1N (115 mA cm^{-2}) < LSFC (180 mA cm^{-2}). On the other hand, LP1C, LP1N and LP2N exhibited poor activity for OER with much lower current densities. Furthermore, reaction parameters including Tafel slope and exchange current density were evaluated from the LSV data. The highest exchange current density of 0.37 mA cm^{-2} and low Tafel slope of 32 mV dec^{-1} were determined for OER at LSFC. Moreover, influence of the electrolyte solution temperature on the OER at lanthanum-based perovskites oxides was investigated in the 25 - 65 ºC temperature range. OER activation energy of LSFC was evaluated to be 62 kJ mol^{-1} using the LSV data at different temperatures.

LSFC exhibited the best activity for OER in terms of the highest current density and the highest exchange current density and, as such, it is proposed as a potential anode material for alkaline water electrolyzers.

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A High-Performance Direct Alkaline Formate Fuel Cell using Functionless Cation Ionomer

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Fuel cells have been paid attention as sustainable energy conversion systems, substituting for existing energy conversion systems using fossil fuels. Amongst varying types of fuel cells (e.g. hydrogen, methanol), direct formate fuel cells (DFFCs) in alkaline media have advantages such as high theoretical cell potential of 1.45V and the oxidation of formate ($HCOO^-$) without the production of carbon monoxide (CO) on palladium, causing poison effect to electrocatalysts. Recently, although there have been some improved and optimized studies for cell performance in DFFCs field [1-3], the research on optimization for electrode structure is still necessary. In this study, we focused on function of cation ionomer in electrode structures in alkaline DFFC systems. From our experimental results, the cation ionomer seemed to be functionless because it was contributed as binding catalyst. Nevertheless, the cell performance using cation ionomer was competitive with that of anion ionomer. As a result, we not only investigated the role of cation ionomer in catalyst layers, but also demonstrated high cell performance using functionless cation ionomer.

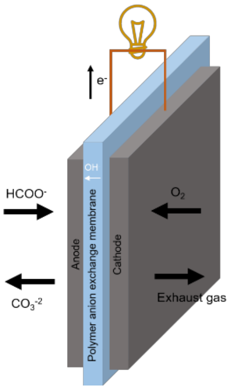

Figure 1. The scheme of reaction process for DFFC.

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The Effect of Morphology and Hydride Incorporation on the Activity of Pd/C Catalysts for HCOO- Oxidation in Alkaline Medium

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The formate ($HCOO^-$) as a fuel have attracted due to its higher performance, having faster oxidation kinetics compared with other direct liquid fuel cells (DLFCs) in alkaline media. In addition, direct formate fuel cell (DFFC) system has higher theoretical potential of $HCOO^-$ of 1.45 V than that of other DLFCs such as 1.23 V for methanol and 1.14 V for ethanol. [1] The oxidation of $HCOO^-$ on palladium (Pd) in alkaline media had been investigated since 1969, some researches were reported for DFFC and showed remarkable power performance through not only optimization of DFFC conditions such as a loading amounts, concentration of fuel and cell temperature but also a modification of Pd catalyst by using metal alloy and heteroatoms. [1-4] From the mechanistic study, chemisorption strength of the adsorbed hydrogen (H_{ads}) should be reduced for enhancing catalytic activity of the oxidation of $HCOO^-$ on Pd because H_{ads} is site-occupying species when the oxidation of $HCOO^-$ on Pd occurs, so that it acts to the rate-determining step. [5] In this study, we have investigated not only the correlation of morphological effect for Pd-H catalyst synthesized in accordance with temperatures, but also the electronic effect of Pd-H compared with commercial Pd/C catalyst. [6]

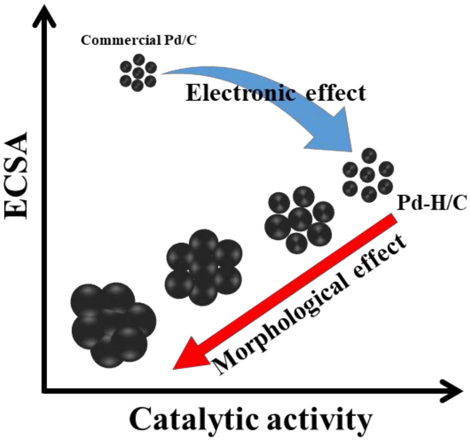

Figure 1. The effect of morphology and electronic effect on Pd/Cs for HCOO- oxidation.

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Hybridization of small electric van powered by PEM fuel cell

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Electromobility is back on the stage after 100 years break. At the beginning of 20th century Ni-Fe accumulator was used to supply electrically powered cars by energy. Later on, in 1962, first vehicle powered by fuel cell was constructed by Alise Chalmers. At this time, however, such innovative technology could not compete with the well established combustion engines. During current reincarnation of the electrically powered cars, lithium ions, lead, or Ni-MH accumulators are most commonly used as energy carriers. Main disadvantage of vehicles based on this approach represents range limitation and long time necessary for recharging. Alternative source of energy for the car propulsion and for accumulators on their board represent fuel cells. They have a number of advantages, like high energy conversion efficiency, flexibility and absence of toxic product. Absence of moving parts is main reason, why fuel cells are significantly more silent than combustion engines. Important aspect represents also the fact, that the hydrogen, i.e. fuel, reservoir can be reloaded within few units of minutes. All these advantages support application of fuel cell technology in mass automotive production.

Unfortunately, PEM fuel cells reach highest efficiency close to the thermodynamic one just under low current load. Here impact of all irreversible contribution is limited. In the car propulsion system, however, the problem is broader and energy consumption of all its parts has to be included into the consideration. Hence, the operation at low current density does not represent an optimum, as the consumption of the peripheries represents an important portion of the energy produced. Additionally, a car propulsion represents typical dynamic load. This is another characteristics limiting application of fuel cell as an exclusive power source. All this, together with a number of additional aspects, like economy of the process, energy for the fuel cell start and shut down etc., calls for hybridization of the system and integration with a suitable technology for storage of limited amount of electrical energy. It can be most efficiently done using accumulators, supercapacitors, or their combination.

Improvement in supercapacitor technology in last decade leads to the production of capacitors with capacity as high as 3600 F and more. They offer many advantages, like ability to operate with high currents, typically 1000-3000 A, long lifetime, rapid switching between charging and discharging mode and no memory effect. But they have although some disadvantages, like relatively low storage capacity or relatively fast selfdischarging. On the other hand, accumulators are able to store much larger amount of energy. But their capacity strongly depends on the temperature. This is problem, which can lead to damage of accumulators by a sudden decrease of temperature. Other problems are shorter lifetime of accumulators, lower operation currents and slow switching between charging and discharging mode. These facts decrease efficiency of energy recuperation during braking. Therefore, hybridization of fuel cell by accumulators and supercapacitors seems to be technologically optimal solution. Accumulators store energy necessary for starting of whole system and long term driving under excessive energy consumption. Supercapacitors then store energy from braking for fast acceleration. Design of all three parts for small electrovan with fuel cell is subject of this contribution.

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Platinum Photo-Deposited on SnO_2-C Nanocomposite: An Active and Durable Catalyst for the Electrochemical Reduction of Oxygen

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Degradation of the supported Pt nanoparticles (NP) used as cathode catalyst for the oxygen reduction reaction (ORR) in low-temperature fuel cells such as proton-exchange membrane fuel cell, is one of the main barrier in the industrial development of the fuel cell technology. Metal-support interaction is known to play a key role in the durability of such electrocatalysts [1]. It has been reported earlier that metal oxide-carbon composite support increases lifetime of the Pt electrocatalysts because of the strong metal-support interaction [2]. In the present work, Pt NPs are photo-deposited onto SnO_2-C nanocomposites using a UV-Vis Xe-lamp (159 W). Different loadings of the metal oxide were used in the support to evaluate its role in the stability of the catalytic centres. Surface morphology, structure and composition of the prepared catalysts were examined by SEM, TEM, XRD and XPS analysis. Electrochemical characterization is carried out by cyclic voltammetry (CV) and CO stripping experiments performed in 0.1 M $HClO_4$ solution. CO stripping profile of the Pt/SnO_2-C catalyst confirmed metal support interaction at the interface (Figure a). The ORR electrocatalytic activity and durability of the prepared catalysts is compared to that of the Pt/C catalyst (Figure b). It is revealed that Pt photo-deposited onto SnO_2-C nanocomposites is more durable than Pt/C because of the strong anchoring mechanism of the Pt NPs to the metal oxide induced by photons of appropriate wavelength.

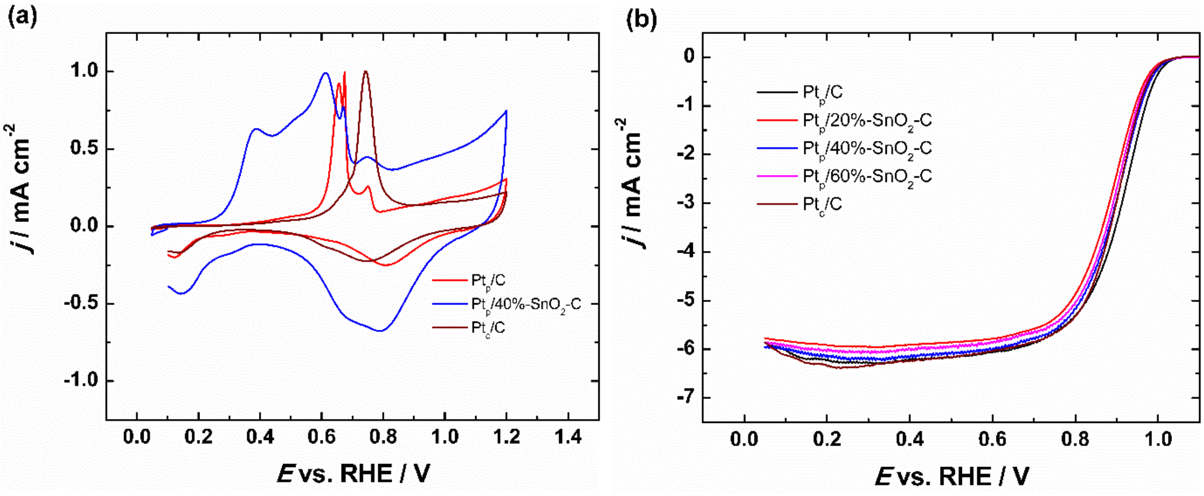

Figure. CO-oxidation profiles of Pt-SnO_2-C catalyst in comparison to Pt/C (a) and RDE polarization curves for ORR measured at 1600 rpm in oxygen-saturated 0.1 M $HClO_4$ solution (b).

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Gas Flow in PEM Fuel Cell System – Process of Model Simplification for Large Scale Unit Modelling

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Nowadays polymer electrolyte membrane fuel cells (PEM FCs) are near to commercialization, but there is still space for further development and optimization. Many research groups pay attention to reduce of amount of Pt catalyst by improving its form. However, for instance degree of its utilization also represents an important aspect to be considered. In this case, the uniform distribution of reactants over the electrode represents prerequisite. It can be influenced mainly by (*i*) design of a flow filed and (*ii*) properties of gas diffusion layer (GDL). Here, mathematical modelling seems to be very powerful tool for study of gas flow inside the system on a local scale.

Description of the gas flow through individual PEM FC components can be accomplished on different levels: from microstructure modelling to simplified models neglecting the detailed structure of the large-scale system. The microstructure modelling allows to describe flow in pores of gas diffusion electrodes; however, it is extremely computational demanding. Thus, only small part of the system can be described. On the other hand, the simplified models can consider entire fuel cell. They can, however, loose some important information on its complex structure, which can significantly influence the flow distribution inside the system.

In the present study, detailed model of gas flow through distribution channels of the flow field and through adjacent GDL is reported. It considers full resolution of the flow-field geometry (single serpentine) and considered also an adjacent GDL as a porous medium. The Navier-Stokes equation was used to describe gas flow dynamics in this system. In case of GDL, the Navier-Stokes equation was extended by a term based on Darcy's law. The model was solved by finite element method implemented in commercial software Comsol Multiphysics. Besides, the single serpentine system with adjacent GDL was studied experimentally to obtain data for validation.

The above-mentioned model was used as a stepping-stone for modelling of entire flow-field. Since a detailed model of the flow field geometry is not suitable for description of an industrial scale system, the process of simplification was initiated. It is designed to maintain information about local direction of gas flow, but also to decrease the number of elements of discretization mesh. The proposed approach based on volume-averaged method, so-called macrohomogeneous approach, enabled simulation industrial-scale flow fields.

Mathematical modelling of gas flow inside fuel cell systems is crucial for optimization of the fuel cells. The proposed approach enables to perform simulation even operating of the industrial-scale PEM FC stack (100 cells) with reasonably high computational power [1, 2].

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Ionic Liquid-Derived Carbon-Supported Metal Electrocatalysts for Direct Borohydride Fuel Cells

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Current changes in the energy production field encompass the usage of environmentally friendly processes that demand low-cost fuels and more efficient technology. Within the latter, fuel cells are an alternative to a carbon-based economy, not only because they can be easily conveyed, but also because they provide high current and power densities [1]. Direct borohydride fuel cells (DBFCs) are amongst the most suitable cells operated at ambient temperature conditions, in which the oxidation of a stable compound (e.g., sodium borohydride, $NaBH_4$) dissolved in strongly alkaline media generates electrical energy [2].

$NaBH_4$ as a fuel has many advantages, such as high gravimetric and volumetric densities (7100 Wh kg^{-1} and 7314 Wh L^{-1}, respectively) and produces water-soluble products when oxidized, which can be recycled at the end of the process [3]. Still, DBFC's power output can be further increased by using a metal-based electrocatalyst for borohydride oxidation reaction (BOR), such as Au and Pt electrocatalysts.

Herein, carbon-supported metal nanoparticle electrocatalysts were prepared by a novel approach, i.e., starting from two newly synthetized ionic liquids (ILs). Namely, [Hmim][$AuCl_4$] and $[Hmim]_2[PtCl_4]$ were prepared and subsequently carbonized by heating up to 400 ºC for 1 h and then up to 800 ºC for another hour (under nitrogen atmosphere), resulting in Au/c-IL and Pt/c-IL, respectively.

Electrocatalysts' performance for was studied for BOR by electrochemical techniques in a conventional three-electrode cell. A glassy carbon rod covered with catalytic ink (0.945 cm^2) was used as the working electrode. Cyclic voltammetry (CV) was used to determine the charge transfer coefficients in 0.03 M $NaBH_4$ + 2 M NaOH solution using scan rates between 5 and 250 mV s^{-1}. Activation energy and order of reaction were also obtained from CV measurements at temperatures ranging from 25 ºC to 65 ºC and $NaBH_4$ concentrations from 0.01 M to 0.12 M, respectively. Both electrocatalysts showed activity for BOR and borohydride hydrolysis. To quantify the hydrolysis, linear scan voltammetry with rotating ring disc electrode (RRDE) experiments were performed using rotation rates up to 2400 rpm and ring potentials between -1 V and -0.8 V. Chronoamperometry was used to perform stability tests of the electrocatalysts for a total time of 2 hours.

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The Influence of the Reduced Graphene Oxide Layer Deposited on Nickel Sheet on Formation of Nickel Hydride Layer

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The increasing energy demand and stronger stress on the sustainability and independence on dwindling fossil fuels represent essential challenging issues. They generate a push on development of the alternative renewable energy source and efficient designing of energy storage devices. However, renewable sources like solar and wind are unstable in time from their nature. Energy conversion devices are thus necessary in order to store surplus electricity and deliver it when needed. Among the other technologies of the energy conversion, the electrochemical water splitting represents a promising approach for generating hydrogen (H_2) considered as a clean energy vector. During electrochemical water splitting two electrochemical reactions take place. These are hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) at the cathode and anode, respectively. Efficient water splitting can be achieved by utilizing active electrocatalysts. These are nowadays mostly based on platinum (Pt) or platinum group metals (Ru, Ir). These state-of-art catalysts can be used as efficient electrocatalysts for water splitting with low overpotential but their high cost and scarcity restrict their broad usage. Development of the efficient, stable, operating at low overpotential, cheap, and earth-abundant HER and OER electro-catalysts for water splitting is vitally important to attain economically competitive and efficient hydrogen generation.

Ni-based catalysts represent low-cost electrode materials for electrolytic hydrogen generation by alkaline water electrolysis, which is a well-established technology of producing H_2 as fuel and/or industrial feedstock. However, Ni cathodes show a significant decrease in their HER activity after several hours of operation. This is attributed to formation of the Ni-hydride layer exhibiting high overpotential for HER.

As it was shown in our previous work [1] the rGO deposited on the Ni foam can decrease the overpotential of HER and prevent the formation of the Ni-hydride layer due to the spillover effect. The aim of this work is to experimentally verify the role of the rGO deposited on the Ni surface as well as optimize the synthesis of the GO and conditions of its deposition. The graphite oxide (GrO) is prepared electrochemically from graphite rod connected as anode and immersed in the solution of the ammonium sulfate. The counter electrode is represented by Ni sheet. GrO is filtrated and washed with ethanol and demineralized water. The dispersion of GrO is ultra-sonicated in order to exfoliate the GrO into the GO. Reduction of GO and deposition of the rGO layer on the Ni sheet is carried out in one step by electrophoretic deposition at different voltages and times from dispersion of GO in demineralized water (concentration GO 4 mg cm^{-3}). Working electrode (electrode for deposition) of dimensions 1 x 1 cm^2 is connected as the anode. The counter electrode is again Ni sheet (3 x 4 cm^2). Deposited layers are investigated by Raman spectroscopy, XPS, scanning electron microscopy and optical microscopy to characterize the purity and composition of the deposited layers as well as their homogeneity. Electrochemical characterization is accomplished by cyclic voltammetry, linear sweep voltammetry and electrochemical impedance spectroscopy in 10 wt.% potassium hydroxide (KOH) at temperature 24 °C. The common 3-electrode arrangement is used with prepared electrodes connected as working electrode, Ni wire as counter and mercuric sulfate electrode (0.6125 V vs. SHE at 25 °C) as reference electrode. The samples of modified and unmodified Ni electrodes are treated at -1.9 V in the range of 0-16 hours prior to electrochemical characterization to investigate the influence of the rGO layer on the electrochemical properties of the electrode and possibility to prevent the formation of the Ni-hydride layer. The results show that Ni-hydride layer can be observed by CV after 10 minutes of the cathodic polarization on pure Ni sheet. The presence of the rGO layer is not only able to reduce or even prevent its formation but it has positive effect on the HER overpotential as well.

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Pt(Cu) Core-Shell Nanoparticles Supported on Advanced Carbonaceous Materials as Electrocatalysts for Low-Temperature PEM Fuel Cells

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The low-temperature polymer electrolyte membrane fuel cells (PEMFC) can undoubtedly contribute to the mitigation of the climate change. However, one of the main problems is that the best catalyst for the hydrogen oxidation reaction and the oxygen reduction reaction is Pt. Regarding the former reaction, this expensive and scarce catalyst is easily poisoned by impurities contained in H_2 fuel of industrial grade, namely, carbon monoxide, causing a loss of performance of the PEMFC. Considering the amount of CO present in the anode feed, several strategies have been developed to overcome this issue, like the utilization of "air bleeding" procedures or alternative Pt-Ru bimetallic electrocatalysts in the anode [1].

An alternative strategy would be to synthesize nanoparticles with a core-shell structure, where the cores are made from a sacrificial metal that is covered by a Pt shell. It is proven that nanoparticles with a Cu core produce an electronic effect on the Pt shell, thus improving its CO tolerance apart from reducing the total amount of Pt used. Carbon supported Pt(Cu) nanoparticles have been previously and satisfactorily synthesized by electrochemical deposition of Cu [2]. A further step would be to obtain Pt(Cu)/C catalyst in powder form, allowing the improvement of the electrode manufacturing. For this, carbon black is the most commonly used Pt support, because of its good balance between properties, availability and cost. However, it has some drawbacks, like the presence of a large amount of micropores, organo-sulfur impurities and thermochemical instability. Ordered mesoporous carbons, with improved textural properties among others, can offer a solution to these disadvantages [3].

In this work, Pt(Cu) core-shell nanoparticles have been synthesized and supported on different carbonaceous materials by electroless deposition of Cu, followed by a partial galvanic exchange with Pt. Ordered mesoporous carbons and conventional carbon black have been used as catalyst support. Physicochemical characterization, as well as electrochemical characterization in a three-electrode cell using cyclic voltammetry and the rotating disk electrode techniques, has been carried out. The results obtained showed that supported Pt(Cu) core-shell nanoparticles with suitable dispersion and particle size can be satisfactorily synthesized, thus reducing the amount of required Pt by about 50%.

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Bi-functional Pt-free catalysts for the oxygen evolution and reduction reactions

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The growing energy worldwide requirements need of suitable facilities developments that allow the clean energy production through effective ways [1]. In this sense, electrochemical devices, such as metal-air batteries, electrolyzers, polymeric fuel cells and regenerative fuel cells, appear as the real option to solve these energetic issues. However, the searching of active and stable oxygen electrodes toward oxygen evolution (OER) and oxygen reduction reactions (ORR) become an important challenge in performance enhancement terms. In addition, the use of noble metals like Pt, Ir and/or Ru represents a great barrier for their insertion to the market [2].

In this study, graphenic materials (GMs) obtained from graphene oxide reduction using hydrazine (H-rGO) or thiourea (SN-rGO) as reducing agents, as well as carbonaceous materials including carbon nanofibers (HC-CNF) and mesoporous carbon (g-CMK3) were synthesized, characterized and tested toward OER/ORR and compared to commercial carbon black (Vulcan) and graphite. Physicochemical characterization was conducted by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), elemental analysis and Raman spectroscopy. Besides, the catalytic performance toward ORR and OER in alkaline medium (0.1 M NaOH) was carried out by the rotating ring-disk electrode (RRDE) technique.

Figure 1 indicates a profound impact of the carbonaceous structure on OER and catalyst stability. Graphenic materials mainly suffer corrosion at higher potentials than 1.0 V vs. RHE, while graphitic structures promote the oxygen evolution in basic media. Nevertheless, a possible influence of remaining metal impurities from the HC-CNF synthesis must be considered in these results.

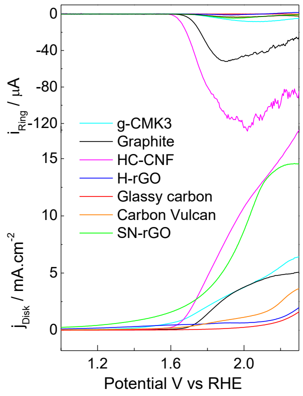

Figure 1. Polarization curves of g-CMK3, Graphite, HC-CNF, H-rGO, Glassy carbon, Carbon Vulcan and SN-rGO in 0.1 M NaOH at a scan rate of 10 mV s^{-1} and rotating speed of 1600 rpm. E_{ring} = 0.40 V vs RHE.

Acknowledgment

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Graphene catalysts nanomaterials for the Oxygen reduction reaction

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Fuel cells (FC) have been attracting a lot of attention since they can convert chemical energy stored in fuels directly into electrical energy through electrochemical reactions with high power density. Furthermore, the overall fuel-conversion efficiency is not limited by Carnot cycle law. However, the performance of these devices is limited due to the sluggish kinetic of the oxygen reduction reaction that occurs at the cathode. Although it has been recently demonstrated that ORR kinetic is substantially improved when the device operates in alkaline medium, it's still necessary the use of catalyst in order to speed up the rate of the ORR[1]. There are several proposed catalysts materials that allow a kinetic improvement of the ORR, being platinum-based catalyst those that offer a better performance. However, these materials present a series of drawbacks such as their susceptibility to CO poisoning and the high cost of platinum which rise the fabrication costs of FCs. Several carbon materials such as carbon nanotubes, graphene or mesoporous carbon have demonstrated electrocatalytic activity towards ORR[2].

In this work, different doped reduced graphene oxide (rGO) materials were synthetized and studied. These materials were characterized by several physicochemical techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and elemental analysis. The electrocatalytic activity was also evaluated by cyclic and linear sweep voltammetry using a rotatory ring-disk electrode. Furthermore, sulfur and nitrogen co-doped reduced graphene oxide with Co_3O_4 nanoparticles (CoSN-rGO) was tested as ORR catalyst in a single alkaline direct ethanol fuel cell (DEFC), obtaining promising results compared to a platinum-based commercial catalyst.

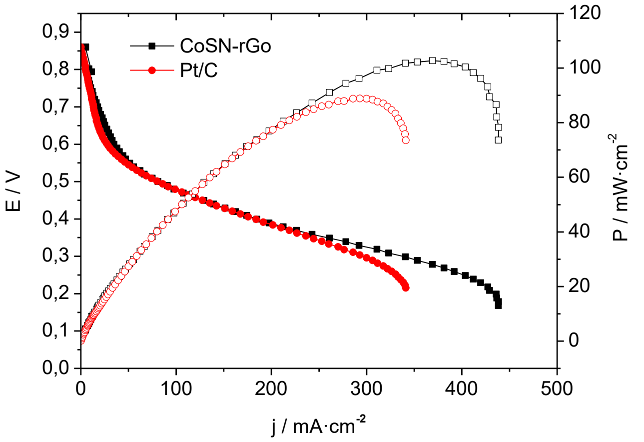

Figure 1. Polarization and power density curves at 90 ºC for alkaline DEFC prepared using CoSN-rGO (black) and a Pt/C commercial material (red) as cathodic catalyst. Flow rate of ethanol/KOH 1 ml/min and 0.2 ml/min O_2.

Acknowledgments
The Spanish Ministry of Science, Innovation and University (MICINN) has supported this work under project ENE2017-83976 -C2-2-R (co-funded by FEDER). Authors thank SEGAI for the physicochemical analysis.

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A DEMS Study of Hydrogen Evolution on Ionic Liquid – Transition Metal Carbide Composites in Basic Media

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Hydrogen is one of the most important fuels for primary energy source in a new consumption model. However, some requirements as efficiency and high purity production proves challenging. Pt is currently the best catalytic material for the HER, but its low Earth-abundance and high capital cost affects negatively to the mass implementation in H_2 production market. The improvement of new cathodic materials for hydrogen evolution reaction (HER) has been related to different properties of the employed catalysts, such as its composition or electronic configuration [1]. Thus, the study and design of new low-cost catalytic materials with high efficiency and durability are expected to have positive effects on water-electrolyzer industry. Potential alternative electrocatalysts are transition metal carbides (TMCs). The great interest of these materials resides in their similar electronic structure near Fermi's level of the Pt-group metals [2]. On the other hand, ionic liquids (ILs) are green solvents and emerge as good alternatives for electrode modification due to their mechanical strength and high electrical conductivity [3].

In the current work, composite materials (TMCs + ILs) were synthesized and their catalytic activity toward the HER in basic media was studied. To this end, N-octylpyridinium hexafluorophosphate (IL) was synthesized through a simple method, which is free of organic solvents [4]. Then, the IL was physically mixed with commercial TMCs to obtain composite catalysts. The physicochemical characterization was accomplished by XRD, XPS and TEM techniques. Meanwhile, the catalytic performance toward the HER was carried out by linear sweep voltammetry (LSV) and differential electrochemical mass spectrometry (DEMS).

Main results indicate an enhancement of the catalytic performance of the HER on composites in comparison to TMCs, i.e. a synergism effect between IL and TMCs improves the overall HER. On the other hand, DEMS appears as an excellent tool to study kinetic and mechanistic aspects for non-noble materials due to it can easily discriminate the hydrogen current from other currents that may take place on the catalytic surface (e.g. electroreduction of oxide species), which cannot be assessed by classical faradaic currents (Figure 1).

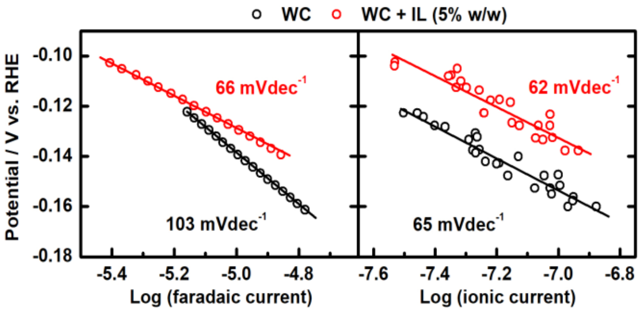

Figure 1. Tafel plots from faradaic (left panel) and ionic (right panel) currents for commercial WC and commercial WC + 5% w/w IL. The experiment was recorded in 0.1 M NaOH at 1 mVs^{-1}.

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Post iron doping of activated carbon supports as Fe-N-C catalyst for ORR in PEMFC

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Proton exchange membrane fuel cells (PEMFCs) are the alternative for the replacement of gasoline internal-combustion engines in automotive sector. However, the scale-up of these devices is hindered by the high cost of components. According to a U.S. DOE estimation, PGM catalyst in PEMFC systems account for about 50 % of total cost [1]. Research on non-precious metal catalysts (non-PGMCs) as an alternative to Pt-catalyst has been developed over several decades. Relevant studies on this perspective have validated that the carbon-based electrocatalysts especially with iron-nitrogen active sites could be the better replacements for the state-of-the-art Pt based systems. In such Fe-N-C materials, two kinds of active sites, namely Fe-N_x coordinated sites and N-functional groups are considered to be responsible for their high catalytic activity [2]. Another property that has to be taken into account is microporosity, which influences the formation of Fe-N_x sites [3]. However, the general synthesis of Fe-N-C catalyst involves complex pyrolysis reactions, which not allow to tune and optimize the pore structure[4]. Generally, these catalysts are synthetized by heat treatment of mixed precursors containing nitrogen sources, carbon sources and iron precursor and they demonstrate low porosity and poor surface area. Therefore, various activation treatments have been adopted to improve structural properties, but at the same time they breach active sites, reducing ORR activity [4].

In this paper we evaluated different carbon sources (commercial and homemade) (Fig1) with specific micro- and mesopore ratio, in order to find the best structural properties for the exposition of Fe-N_x sites on the surface. The final materials were fully characterized by RRDE technique for understanding the activity and selectivity toward ORR. Special attention was put in the correlation between catalytic performances and the density of active sites through XPS analysis.

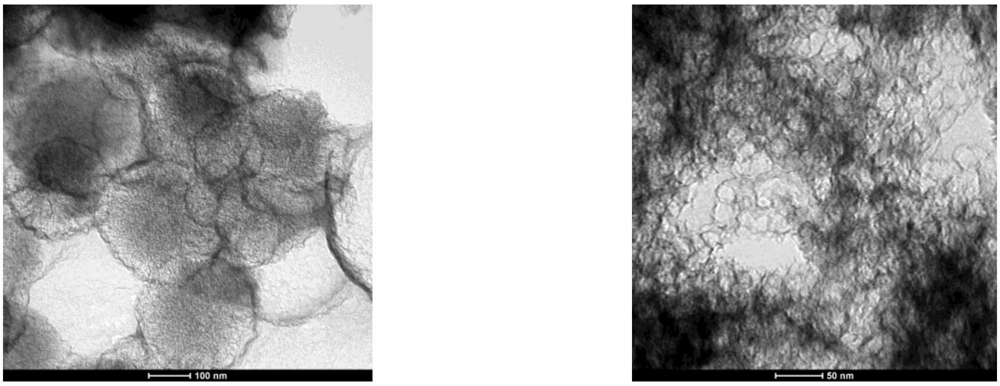

Figure 1: Carbon support obtained from hard template synthesis and after a gas reactive treatment.

Acknowledgements
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Synthesis of perovskites $LaMn_{1-x}Co_xO_3$ and their application in oxygen reduction reaction

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The development of materials for oxygen reduction reaction (ORR) is highly important to substitute the commercial noble metals that are scarce and expensive. Materials based on non-precious metals present advantages related to the abundancy and cost of the catalyst[1]. Perovskite-based oxides with a general ABO_3 formula are promising catalysts for ORR due to the flexibility of tuning their physicochemical properties and as a result their catalytic properties[2]. The A-site cation that presents the best performance for ORR is the lanthanum due to its cation size and the highest electrical conductivity of the perovskite [3]. The B-site cation, normally a transition metal, has an important role in the mechanism of ORR, so it is interesting to combine different cations in order to obtain a better performance. In this investigation, we propose perovskite materials based on the formula $LaMn_{1-x}Co_xO_3$ ($0 \leq x \leq 1$) synthesized by different methods such as sol-gel and hydrothermal methods for ORR. The perovskites have been characterized using different techniques like XPS, XRD, TEM, etc. Then, the structure, morphology and surface composition of the perovskites are characterized and the catalytic activity towards ORR is performed by the rotating ring-disk electrode (RRDE) in alkaline conditions. The results show that the progressive introduction of cobalt in the $LaMnO_3$ perovskite has an impact on the particle size and changes the crystal structure from a cubic to rhombohedral hexagonal structure. The introduction of Co^{3+}, that has a smaller atomic radius than Mn^{3+}, decreases the lattice parameters, what is especially clear for the rhombohedral hexagonal structure. By XPS it has been observed the presence of a mixture of the different oxidation states of manganese (Mn^{4+} and Mn^{3+}) and cobalt (Co^{3+} and Co^{2+}) that play an important role in ORR activity and depending on the degree of substitution the performance in this reaction is different. In addition, the capacitance of these oxides measured by cyclic voltammetry is affected by the incorporation of cobalt. The $LaMn_{1-x}Co_xO_3$ perovskites show an acceptable activity towards the ORR in alkaline conditions by a pathway much closer to the ideal 4-electron pathway to water. Therefore, the $LaMn_{1-x}Co_xO_3$ perovskites are promising materials that can be studied as an alternative to the commercial electrocatalysts for cathodes in fuel cells and metal-air batteries.

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Characterisation of LSM/YSZ Interface in SOC Electrochemical Reactors

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With increasing production of electric energy from renewable sources, the energy storage technologies are necessary to keep stability of electric network. This problem can be solved by conversion of electric energy to chemical energy of a bond between hydrogen and oxygen. Currently, low temperature processes as alkaline water electrolysis and PEM water electrolysis are widely studied and primarily used for electrochemical production of hydrogen from water. However, the high temperature process is preferred from thermodynamic and mainly kinetic point of view.

The high-temperature water electrolysis with a solid oxide electrolyte, the so called solid oxide cells (SOCs), offers significant advantages for storage of excess energy over the competitive technologies. This is mainly the consequence of high operating temperature (700 – 900 °C), which leads to fast electrodes kinetics without expensive electrocatalysts. Significant benefit represents also the possibility to operate in reversible modes (electrolysis – EC or fuel cell – FC) within single cell and possibility to operate in co-electrolysis mode to convert CO_2 to the valuable products. However, the high operating temperature also enhances degradation processes. Insufficient lifetime is the main barrier for wide application of SOC technology.

The critical parts of SOC systems are the interface contacts electrode/electrolyte. Reduction of the three phase contact or formation of insulating interlayer causes performance decrease. LSM/YSZ-interface in oxygen electrodes is one of these interfaces. Moreover, the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), depending on operation mode, is mostly responsible for the cell activation losses. Thus, for proper SOC operation it is important to minimise activation and ohmic losses of the oxygen electrode. Therefore, a thorough understanding of the electrochemical reaction kinetics and structural characteristics of the oxygen electrode-electrolyte interface is necessary.

In current work $La_{1-x}Sr_xMnO_3$ (LSM), ZrO_2 – 8 mol.% Y_2O_3 (YSZ) and Ni were used as most common materials in SOC. Hence, series of button cell YSZ electrolytes with screen printed LSM electrodes were prepared with Ni or LSM counter electrode. Thus, standard cells in electrolysis and fuel cell mode as well as symmetric cell in oxygen pump mode were studied. To investigate initial SOCs systems stability, each LSM-YSZ-Ni cell was tested at first in FC and then in EC mode for 300 h in potentiostatic regime. After several days in either mode a degradation of cell was observed. The degradation was faster in fuel cell mode in comparison to electrolysis. In the next step, symmetrical LSM-YSZ-LSM cells were prepared to examine degradation mechanisms and kinetics of OER and ORR under different O2 partial pressures. Each cell was examined by electrochemical methods (CV, EIS, PP). To obtain information on kinetic parameters values, the polarisation curves were fitted by Butler-Volmer equation. The structural changes at the interface were examined by post-mortem SEM analysis and spectrometric analyses. During an operation at 700 °C only a slight increase in polarization and ohmic losses was observed; however, at 800 °C the ohmic losses increased rapidly. SEM analysis suggested negligible morphological changes at the interface. On the other hand XRD analysis identifies formation of new resistive phase in long operating cells.

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Titanium Oxi-nitrate as a New High Surface Area Support for Ir-Catalyst for Oxygen Evolution Reaction in Acidic Media.

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The always growing world demands for energy along with the problems due to fossil fuels such as global warming and limited resources have encouraged the research and use of renewable energies. However, solar or wind sources are intermittent and efficient conversion and storage systems need to be developed. Hydrogen is believed to be a viable solution due to its high storage capacity and clean conversion process. Taking advantages of the oxygen evolution reaction (OER), water electrolyzers (WE) can produce hydrogen and oxygen from water through the supply of electric energy. Unfortunately, the state-of-the-art catalyst used in WE, IrO_2, suffers from high prices and scarcity of material which hinder the global commercialization of this technology. One possible approach to improve Ir-based catalysts and decrease the price of WE is to increase the active surface area of the catalyst. In the same way as for Pt-catalysts used for the oxygen reduction in fuel cell, the introduction of a support looks like an effective strategy to reach that goal. A good support would help to reduce the amount of noble metal needed and could also help to improve the stability of the active nanoparticles. The usual requirements for catalyst supports are high surface area, high electrical conductivity, long-term stability under operational conditions, etc. Unfortunately, carbon materials usually used as support for Pt in fuel cell are not suitable here due to severe degradation at high potential (during OER) and strong acidic environment. Thus, a new stable support needs to be developed for Ir-based catalysts during OER. This approach is not new and many different supports have been proposed for OER. The most investigated ones are semi-conducting metal oxides as SnO_2 or TiO_2, non-stoichiometric oxide (Ti_4O_7, $Nb_{0.05}Ti_{0.95}O_2$), carbides (TiC, SiC) or nitride (TiN).[1] Usually, these supports lack one of the requirements previously mentioned (stability, conductivity, high surface area) and thus none of them has taken the lead in Ir-supported research.

Here, we propose a home-made $TiON_x$ support as it shows good electronic conductivity due to the TiN and good stability in corrosive environment due to TiO_2. Moreover, the synthesis was adjusted so as to allow a high surface area of TION and uniformly dispersed Ir nanoparticles. (Fig.1a) The results indicate that Ir-TiON is a promising, efficient and stable catalyst for OER in acidic media. The home-made catalyst is also compared to a commercial pure Ir catalyst and to an Ir-$TiON_x$ made from Degussa P25 (commercial TiO_2). (Fig1b.)

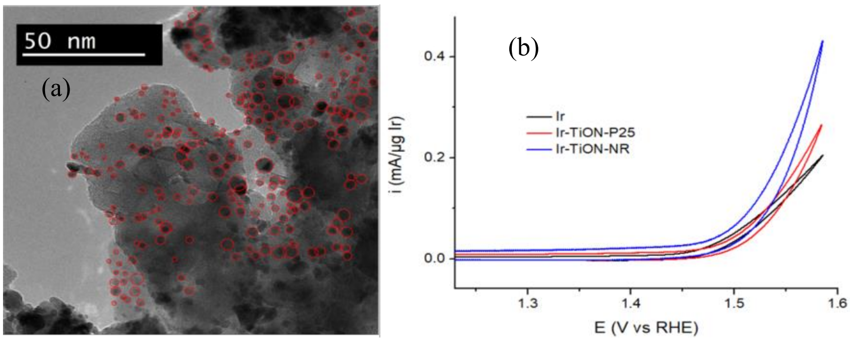

Figure 1 : a) TEM micrographs of Ir-TiON-NR sample, Ir nanoparticles are circle in red. b) Average activity of prepared samples.

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Anion exchange membrane water electrolysis with ultra-thin film electrodes prepared by magnetron sputtering

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Hydrogen production by water electrolysis is a sustainable and environmentally friendly alternative energy process. Alkaline and proton exchange membrane are traditional and most used types of water electrolysis. Nevertheless, less used anion exchange membrane (AEM) water electrolysis solves the associate problems with these two technologies and allows the possibility of using water without potassium or non-noble catalysts. This study reports the performance of several copper-cobalt mixed oxides and nickel electrodes prepared by magnetron sputtering at oblique angle as shows Figure 1.a) incorporated to a AEM cells. This thin film growth technology increases the electrode performance and decreases the amount of required material electrode, two critical points in the water electrolysis devices. In addition, this fabrication technique produces highly mesoporous thin films, a very suited characteristic to use in water electrolysis.

The electrocatalytic performance of the thin film electrodes were tested in a 3-electrode glass half-cell. Thus, the influence of the Co/Cu ratio, the crystallization temperature, the load and stability were investigated. Figure 1.b) shows the cyclic voltammetry curves of a nickel electrode used as anode under 1.0 mol dm^{-3} KOH solution prepared with deionized water at room temperature. In addition, a thorough structural and chemical characterization of these porous thin film electrodes by SEM, XPS or IR, before and after being used, were carried out to complete these half-cell studies. Finally, the optimal electrodes were tested in a Membrane Electrode Assembly configuration water electrolysis cell using an anion exchange membrane (Figure 1.c)). In this step, the global stability of the cell, the influences of several membranes or the assembly conditions were studied. Moreover, several electrolyte solutions as deionized water, tap water and multiple KOH solutions were used. A great stability and an outstanding current density (close to 100 mA cm^{-2}) in relation to the amount of catalyst were obtained.

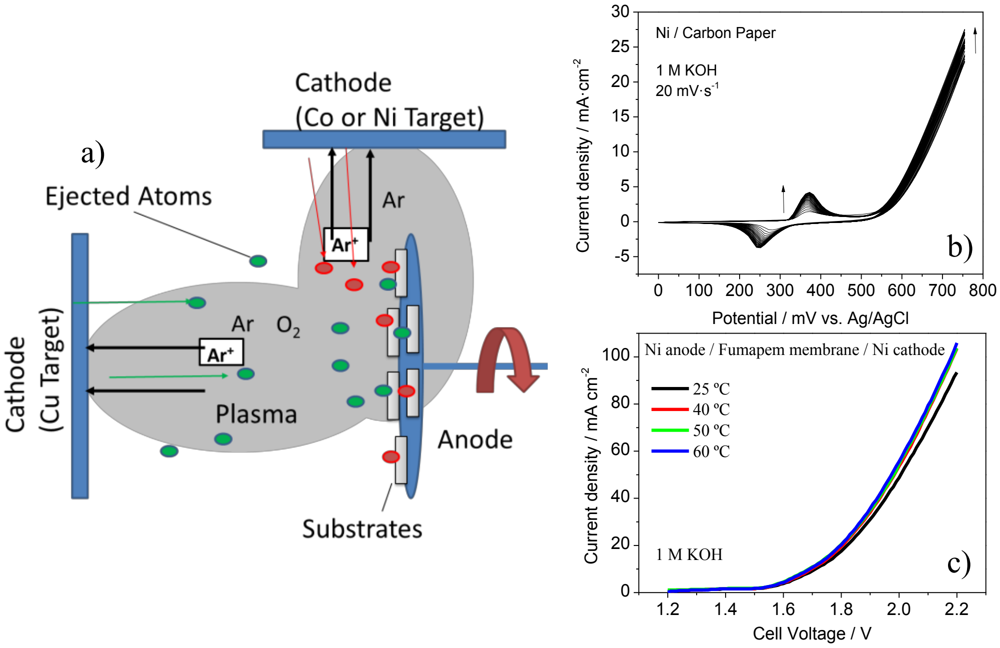

Figure 1. a) Diagram of the Magnetron Sputtering Process; b) Half cell cyclic Voltammetry of Ni catalyst deposited on carbon paper support used as anode; c) Influence of the temperature on the polarization curves of the MEA configuration.

Electrophoretic Deposition of Catalytic Nanomaterials to Modify Cathode Structure in Electrochemical Energy Storage Systems

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Abstract

The growing demand for developing efficient and cost-effective electrochemical energy storage systems entails the application of proper catalysts to enhance the re-dox reactions on both cathodic and anodic side. These processes, which vary from the sluggish oxygen reduction/evolution reactions (ORR/OER) in fuel cells to the slow formation/decomposition of Li_2O_2 and Li_2S_2/Li_2S in Li-air and Li-S batteries (LSBs), respectively, have been widely improved by incorporating metallic and nonmetal catalysts [1]. Conventionally, different binder-based strategies including tape casting (Doctor Blade) and powder spraying have been adopted to apply these catalysts on the electrode surface [2]. In the present study, metal oxide (MO) nanoparticles were applied as PS immobilizers on a 3-D network of carbon fibers in LSBs owing to their polar structure compared with the non-polar nature of carbonaceous materials [3]. For this purpose, the electrophoretic deposition (EPD) method was successfully applied as a binder-free approach to deposit MO nanoparticles with homogeneous distribution on carbon fiber paper (CFP) for being used as cathode in Li-S cells. According to the charge-discharge tests, the initial specific discharge capacity of CFP/MO/S increased from 560.9 to 1348.7 mAh g^{-1} as the MO loading was increased from 1.2 mg to 11.8 mg, respectively. Also, the columbic efficiencies (CE%) higher than 98% percent were achieved in the presence of the MO film, revealing the effective role of the EPD-MO layer in modifying the performance of CFP by adsorbing long-chain soluble PSs. Increasing the MO loading was also observed to improve the rate performance of the Li-S cells, delivering a specific capacity of 842.5 mAh g^{-1} at 1C for the EPD-MO (8.5 mg) sample. In spite of the significant improvement of the specific capacity, the capacity retention deteriorated as the MO loading increased, being attributed to the formation of cracks across the MO film at higher loadings (thicknesses), as clearly demonstrated by scanning electron microscope (SEM) images. Furthermore, the microscopic study of the CFP/MO/S surface at the end of the charging step revealed the formation of flake-shaped chains of sulfur with preferred growth directions.

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Facile Synthesis of Non-precious Metal Catalysts with Highly Porous Structures by using Salt-Templating Approach

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The development of inexpensive non-precious metal catalysts for the oxygen reduction reaction (ORR) is one of the key research topics for polymer electrolyte fuel cell (PEFC) technology. Among various types of non-noble metal catalysts reported so far, one promising class is metal-nitrogen-carbon (Me/NC) type materials in which transition metals, particularly Fe and Co, are bound to nitrogen doped carbon (NC).[1,2] The surface chemistry and morphological properties of carbon matrix strongly affect the the electrocatalytic activity and stability levels of the final catalyst. These include the concentration and nature of N-sites anchored in the carbon framework, the electrical conductivity, (electro)chemical stability and the porosity. It is widely accepted that the ideal active sites in Fe/NC catalysts should consist of Fe (or other transition metals) directly coordinated to nitrogen atoms to form MeN_x centers, a porphyrin-like structure.

The synthesis procedures for preparing such Fe/NC catalysts are quite different ranging from direct carbonization of iron containing macromolecules e.g. porphyrins or phthalocyanines to complex multistep procedures where separate precursors for carbon, nitrogen, and iron are mixed and pyrolyzed at high temperatures. The high-temperature pyrolysis generally leads to the formation of undesired metallic species such as iron oxides, nitrides, and carbides, which can potenitally lead to low catalytic performance and/or poor stability. In addition, generally employed synthesis methods include multiple heat-treatment steps followed by acid leaching step(s) and/or NH_3 treatment steps to get rid of undesirable Fe species and enhance the basicity (and porosity), respectively. For most of the reported non-precious catalysts, decent ORR activity levels are achieved only after multistep treatment procedures.[3,4]

In this presentation, we have explored a simplified synthesis route for the Fe/NC catalysts employing the salt-templating method. The salt-templated carbon structure is characterized by large hierarchical porosity giving advantageous mass-transport properties, which are important for catalytic performance and the salt metal cations act as Lewis-acidic and facilitate formation of FeN_x sites.[5,6] This unique synthetic approach provides various advantages over previously reported methods: 1) simplified synthesis route involving only 3 steps (precursors' mixing, pyrolysis, and washing), 2) highly porous structure of Fe/NC catalysts that is desired for better mass transport of species, and 3) facile control over adjusting and manipulating the catalyst morphology to optimize ORR performance. The optimized catalyst shows quite high ORR activity levels in both alkaline ($E_{1/2} > 0.9$ V) and acidic ($E_{1/2} > 0.75$ V) media. We will present and discuss the detailed structure and ORR activity of the synthesized Fe/NC electrocatalyst with respect to the synthesis conditions by utilizing various characterization tools including N_2-physisorption, XPS, TEM, and EXAFS etc. in the meeting.

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PtCu/C catalysts doped with various amounts of gold for oxygen electroreduction and methanol electrooxidation reactions

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Carbon-supported platinum-based catalysts are currently the most important component of the various types of low-temperature fuel cells. To reduce the cost of power, produced by low temperature fuel cells, it is necessary significantly reduce the noble metal loading in the catalyst layer, without reducing the catalyst's specific characteristics and durability [1-3].

The aim of this work is to obtained trimetallic PtCuAu nanoparticles with the different content of gold deposited on a highly disperse carbon carrier as highly efficient materials for low-temperature fuel cells. Trimetallic PtCuAu nanoparticles were synthesized by galvanic replacement of Cu to Au in PtCu/C material obtained early [1]. The characterization of prepared PtCuAu/C materials was performed by HRTEM, XRD, CV, LSV and Pt, Au L3- and Cu K-edge extended X-ray absorption fine structure (EXAFS).

Among the studied materials the highest activity in oxygen reduction reaction (ORR) and methanol electrooxidation reaction (MOR) was demonstrated a material containing 5% Au (fig1.). We assume that this amount of gold is optimal for high catalytic activity of materials.

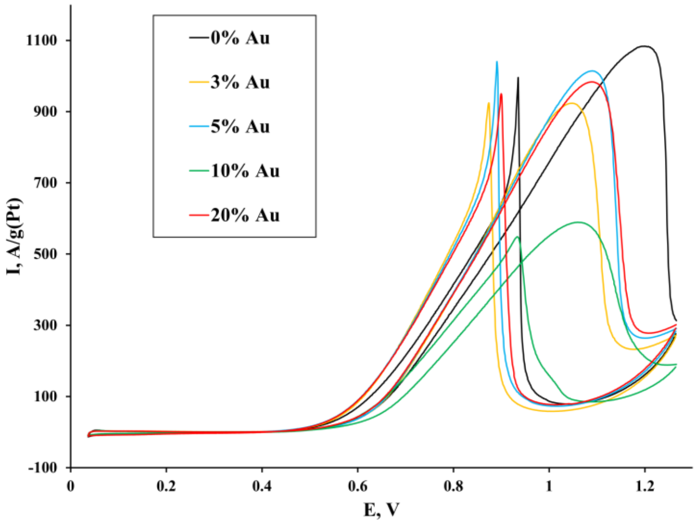

Figure 1. CV curves for PtCuAu catalysts with the different content of gold in 0.5 M CH_3OH + 0.1 M $HClO_4$, sweep rate 20 mV/s.

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Comparison of different composite graphites for PEM fuel cell bipolar plates

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Electromobility is the most expansion area of automotive. Energy used for car propulsion can be stored in accumulators, or in hydrogen. In the latter case, fuel cells with polymer electrolyte (PEM FC) are used for efficient conversion of chemical energy carried by hydrogen into electrical energy. They possess several important advantages, such as high efficiency, high flexibility, silent operation, nontoxic reaction products (pure water) or absence of moving parts. Old generation of electric car used motors with operation voltage of 48 to 76 V. It was a reason, why maximum speed of these cars was 90 km per hour. Modern electric cars operate typically with voltage in a range of 300 to 400 V. Hydrogen fuel cell provides maximum voltage of 1.223 V under open circuit conditions. When loaded, the voltage further decreases due to the irreversible losses. It is clearly insufficient for desired applications. Using of voltage convertor to increase this value is possible. Nevertheless, such a high difference between original and target voltage decrease efficiency of conversion and increases complexity of converter. Fuel cells are therefore arranged into stacks to increase resulting operation voltage and to simplify the voltage conversion. Bipolar plates represent one of the vital components in such fuel cell stack.

Bipolar plates material has to possess high chemical resistance, high electronic conductivity, high mechanical strength and low permeability to reactants. Chemical resistance is necessary, because corrosion of the cell would poison the cell. Low permeability of the material is necessary due the safety reasons (prevents mixing of hydrogen and oxygen). High electronic conductivity is essential to maintain the ohmic losses low. High mechanical strength of the material is necessary to minimize thickenss of the plate and thus to reduce weight of the stack.

Both sides of bipolar plate are provided by gas distribution channels. They ensure homogeneous distribution of fuel and oxidation across the electrodes surface. Construction of bipolar electrode have to allow sealing and insulation of individual electrodes in the stack. Bipolar plates are currently produced mainly from the carbon-based materials or from metals. Carbon based materials used in the fuel cells industry can be divided into two groups. First group represent high-density microcrystalline graphite with density in range 1.9 – 2.1 g cm^{-3}. Second group represents composite material based on carbon black particles blended with suitable polymer binder. Second group is characterized by a lower density, lower permeability for gases, better machinability and mechanical properties. Negative aspect represents higher ohmic resistance of this composite in comparison with high densities graphite.

Good mechanical properties are important parameters for mass production. Graphite materials have to be easy to machine, of formed into final form by pressing or extrusion. The target of this contribution is to provide an overview of the commercially available bipolar plates together with their main characteristics.

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Graphene/MoS_2 Nanocomposite Flexible Paper Negative Electrodes as High Capacity Anode Material for Li-Ion Batteries

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Due to widespread of electric vehicles and hybrid vehicles, development of lithium ion batteries (LIBs) with higher energy density, better rate capability, and longer cycling life is highly demanded [1]. In order to increase the energy density of the commercial LIBs, commercial graphite anode (theorotical capacity is 372 mAh/g replacing the) need to be replaced with alternative high capacity anode materials with lithium metal alloys (Si, Sn, etc.) metal oxides (Fe_2O_3, TiO_2, SnO_2, etc.) [2]. Recently, researchers have been reported Graphene like 2D materials such as MoS_2 as an alternative anode materials, which has specific capacity up to 1000 mAh/g for LIBs However, the cyclic stability and rate capability of the most MoS_2-based electrodes are still unsatisfactory due to the intrinsically poor electrical conductivity of the MoS_2. To overcome this issue, the main strategy is to prepare composites with carbonaceous materials [3].

Here we reported high capacity and long cycle life Graphene/MoS_2 flexible composite paper anodes for LIBs. For preparation of the composite anode, 1T phase MoS_2 was exfoliated with electrochemical exfoliation process. In this process MoS_2 pellet was prepared and used as working electrode, platinum electrode was used as counter electrode and silver wire was used as reference electrode, and 1M $LiClO_4$ dissolved in TEGDME used as electrolyte. After exfoliation process multi-layer MoS_2 nano-sheets were obtained. Graphene oxide was synthesized with Hummors method. Selected amount of Graphene oxide and MoS_2 sheets were dispersed in DI water and homogeneously mixed with ultrasonication process. The mixture were vacuum filtrated and form GO/MoS_2 paper on PVDF membrane. After then GO/MoS_2 composite was reduced in tube oven under Ar gas flow at 500^{o}C and Graphene/MoS_2 nanocomposite paper electrodes were obtained. The surface morphology of the electrodes were characterized using scanning electron microscopy (SEM), phase structure of the composite electrodes were studied using Raman spectroscopy and X-ray diffraction. Produced composite electrodes were tested in CR2032 test cell between 0.01 V and 3.0V at the constant current of 200 mA/g. For further electrochemical characterization were performed using cyclic voltammetry and EIS measurements.

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Model Electrodes to Evaluate Catalyst Materials for AEMFC

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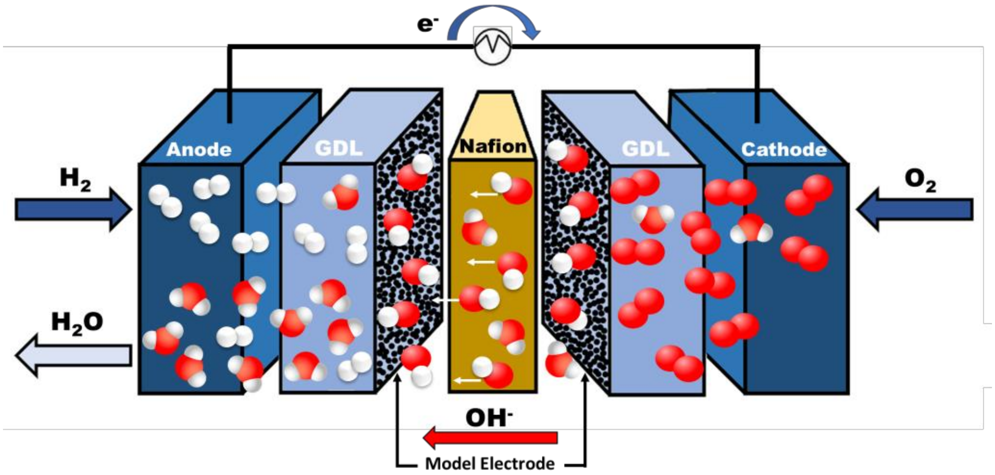
The widespread use of low-temperature fuel cells in automotive vehicles is impeded by the high cost associated with the large amount of platinum needed to compensate for the sluggish oxygen reduction reaction (ORR). The current leading low temperature fuel cell is the Polymer Electrolyte Membrane Fuel Cell (PEMFC), operating in acidic media, where Pt-based catalysts are among the few materials with high enough stability and activity for the ORR. In contrast to acidic media, the alkaline conditions of the Alkaline Electrolyte Membrane Fuel Cell (AEMFC) allow the use of non-noble metals, which open up new possibilities of finding less expensive catalyst materials without compromising the power density of the fuel cell[1,2]. One approach to study catalyst materials for AEMFC is to use model electrodes that can measure the catalysts materials under realistic AEMFC conditions. As the conditions in liquid half-cell measurements are markedly different compared to those in an operating fuel cell, we believe it is important to evaluate catalyst materials under realistic conditions. The model electrode should ideally be capable of isolating the catalyst contribution. We have previously developed model electrodes with very low loadings (0.1-0.4 $\mathrm{mg_{Pt}\ cm^{-2}}$), which result in low concentration gradients in the electrode layer and low iR losses. A model electrode should also ensure a high degree of reproducibility and maximized mass activity in order to provide a reliable comparison between different catalyst materials[3,4]. Therefore, fabrication techniques assuring minimal structural variation between samples are preferred. In this work we use physical deposition techniques, such as sputtering and evaporation in vacuum to prepare thin-film model electrodes on conventional gas diffusion layers (GDLs) which are evaluated in single cell AEMFC measurements. This poster will show the fabrication of these model electrodes and the results from evaluation under real AEMFC conditions. We will show the model electrode concept applied to both the hydrogen oxidation reaction (HOR) on the anode side and the ORR on the cathode side.



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CO-assisted *Ex-situ* Chemical Activation of Pt-Cu/C Oxygen Reduction Reaction Electrocatalyst

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In future, low-temperature proton exchange membrane fuel cells (PEMFC), together with batteries, are expected to compete and eventually replace conventional combustion engines in the automotive industry. Currently, the most promising strategy towards cost-effective and highly-active oxygen reduction reaction (ORR) catalysts seems to be alloying of Pt with less expensive and less noble 3d transition metals (Cu, Co and Ni,…). Besides being less expensive, such alloys can also substantially enhance ORR performance by a combination of a ligand and/or strain effect. A crucial issue to be resolved in the near future is, however, to bridge the gap between the remarkable activities measured on the laboratory scale with thin film rotating disk electrode (TF-RDE) and the industrial membrane electrode assembly (MEA). In the case of Pt-Cu alloy, one of the major reasons for this difficulty is inadequate removal of unstable Cu or in other words, improper 'activation'. Inadequately removed Cu can act as an impurity by poisoning the Pt surface via the well-known underpotential deposition (UPD) interaction, resulting in the inhibition of ORR performance. In order to *in-situ* electrochemically activate (*in-situ* EA) a Pt-Cu/C catalyst, a small amount of catalyst (~20 µg) is usually potentiodynamically cycled (e.g. 200 cycles, 0.05 – 1.2 V_{RHE}, 300 mV s^{-1}). The *in-situ* EA results in dealloying of any unstable Cu that is being highly diluted in a large volume of the electrolyte (usually ~100 mL). In addition, one can exchange the electrolyte prior to the evaluation of the ORR performance and removing Cu impurities in the process, preventing its redeposition and poisoning of the Pt surface. Due to highly favourable experimental conditions, *in-situ* EA in TF-RDE setup thus masks many of the issues one experiences when trying to do the same *ex-situ*. When *ex-situ* chemically activating (*ex-situ* CA) grams of Pt-Cu/C catalyst, the concentrations of dissolved metals are several orders of magnitude higher as well as potentiodynamic cycling (applying external potential control) is not possible. Thus, matching the ORR performance obtained after *in-situ* EA with *ex-situ* CA in the case of Pt-Cu system has so far not been shown.

Based on a deeper understanding of *in-situ* EA of our in-house designed Pt-Cu/C catalyst we here demonstrate development of carbon monoxide (CO) assisted *ex-situ* CA method (Figure 1).[1] By using this gram scale *ex-situ* CA method, we for the first time show that a Pt-Cu system can achieve very high ORR performances without any need for the use of *in-situ* EA.

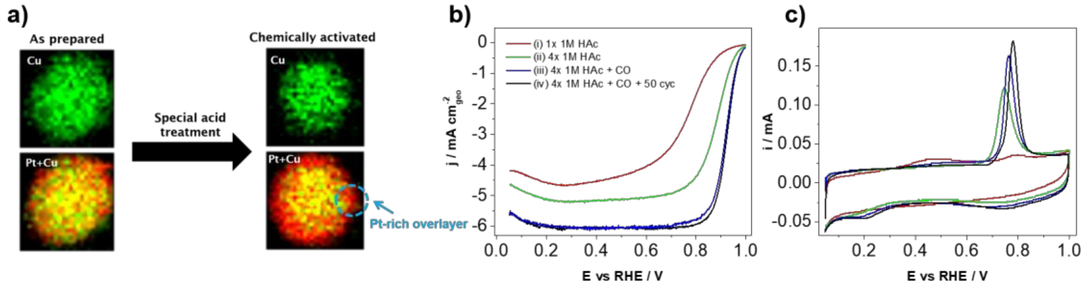

Figure 1: (a) Chemical mapping using a transmission electron microscope of a representative as-prepared Pt-Cu nanoparticle and another nanoparticle after *ex-situ* CA. Comparison of **(b)** ORR polarisation curves and **(c)** CO stripping for analogues that were activated via *ex-situ* CA protocols (i) – (iii) as well as (iv) after additional potentiodynamic cycles of *in-situ* EA.

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New sulfonated pentablock copolymer membranes and modified gas diffusion layers for the improvement of Ir free water splitting processes.

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Polymer electrolyte membrane (PEM) water electrolysis is one of the most promising technologies for hydrogen production due to its relatively high compactness, simple system, low operating temperature and high efficiency [1]. The durability and costs of PEM electrolysers are still the two main barriers for their commercialization. The aim of this work is to evaluate the possible use of Nexar™ polymer [2], a sulfonated pentablock copolymer (s-PBC), whose structure is formed by tert-butyl styrene, hydrogenated isoprene, sulfonated styrene, hydrogenated isoprene, tert-butyl styrene (tBS-HI-SS-HI-tBS), as a more economical and efficient alternative to the most used membrane for PEM (proton exchange membrane) cells, i.e. Nafion® [3]. Furthermore, we have studied the modification of Gas Diffusion Layers (GDL), by depositing the catalysts and a polymeric protective layer on their surface, allowing the improvement of the contact with the membrane. Morphological, structural and electrical characterization were performed on the Nexar™ membrane and on the modified GDLs. s-PBC and s-PBC nanocomposite films, prepared by dispersing titania and graphene oxide nanoparticles in the commercial solution changing the solvent, have been tested in a home-made water splitting cell and their performance was compared with Nafion (Figure 1). The results in terms of water uptake, electrical properties and current generated during water electrolysis show that Nexar™ is an efficient and cheaper alternative to Nafion® as proton exchange membrane in water splitting applications.

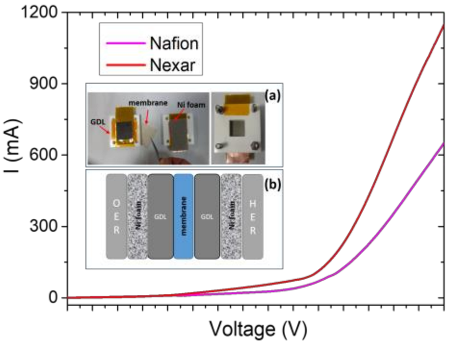

Figure 1: I-V curves for the water splitting tests comparing Nafion and Nexar in a cell configurtion as ahown in the inset of the figure.

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PdCo@Ni$_{foam}$ and PdCoP@Ni$_{foam}$ Catalysts for Intermediate Temperature Electro-Reforming (ITER)

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The electro-oxidation of alcohols at intermediate temperatures (100-250°C) in devices like Direct Alcohol Fuel Cells (DAFCs) and Alcohol Electro-Reformers (ER) is an essentially unexplored field. ER and DAFCs are more efficient devices using strong alkaline environments due to faster alcohol oxidation kinetics and lower corrosion of the cell components, anyway the partial oxidation of alcohols to carboxylates at high pH limits their energy efficiency. We have set up an electrochemical autoclave to study, for the first time, the electrooxidation of alcohols in 2m aqueous KOH at $T < 180°C$. We have synthesized nanostructured palladium-based catalysts supported on nickel foam. The 3D structure of these catalysts guarantees fast mass transport of the alcohol fuel in the liquid phase and enhances gas permeability. These catalysts are electrochemically characterized both in half-cells and in a complete Intermediate Temperature ER. The Pd catalysts are used as anodes and are coupled with a commercial Pt(40%)/C cathode for the hydrogen evolution reaction. Alcohol electroreforming at temperatures over 100°C in a pressurized vessel, couples the advantages of increased catalyst's activity and selectivity with the production of pure and safe pressurized hydrogen.

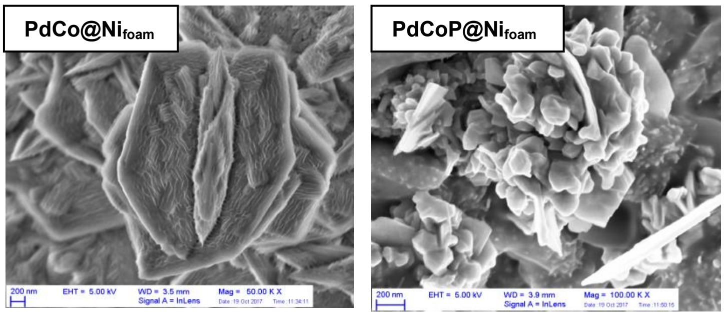

Figure 1. SEM image of PdCo@Ni$_{foam}$ and PdCoP@Ni$_{foam}$

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Healing Chemistry for Disorder-engineered Photoanodes to Achieve Highly Efficient Solar Water Oxidation

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Introducing a disordered layer around a crystalline metal oxide (e.g., black TiO_2) can provide a promising pathway to suppress charge recombination and boost hole transfer, which in turn tremendously improve photoelectrochemical (PEC) water oxidation efficiency. However, the uneven oxygen vacancy distribution in few-nm-thick disordered layers gives rise to unsatisfactory PEC performances. Here, we present on a "healing" chemistry technique to eliminate predictable charge trapping sites located in the outermost part of disordered layers via using chemical interactions between the oxygen-deficient disordered layer (DL) and oxygen-rich carbon nitride quantum dots (CNQDs). The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) results provide clear evidence for DL healing by CNQDs. As a result, a WO_3 nanoparticle film with a ~3-nm-thick DL healed by CNQDs (DL-WO_3/CNQDs) has a 1.5-fold enhancement in its PEC performance and a cathodic shift in the onset potential of 100 mV compared to the pre-optimized DL-WO_3 photoanode. DL-WO_3/CNQDs can facilitate charge transfer to the electrolyte, impressively enhances the efficiency from 60% for DL-WO_3 to 87% and improves the charge separation efficiency to above 80% at 1.23 V vs RHE. Density function theory (DFT) calculations reveal that DL-WO_3/CNQDs produces a stepped valance band alignment, which, together with the removal of charge trapping sites, is capable of overcoming the hole transfer limit at the photoanode/electrolyte interface.

Catalyst Development for the Selective Electrochemical Conversion of CO_2 to CO

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Electrochemical conversion allows the production of added-value chemicals by direct use of electricity. If the electrical energy is provided by renewables, electrosynthesis will offer a unique opportunity to harvest surplus renewable energy and to store it in the form of chemical energy, i.e. in the form of chemical bonds.[1]

These processes will become highly appealing, if the cost for this production of chemicals is comparable to that of conventional synthesis methods. To achieve that, it is essential to develop catalysts which can carry out the reactions of interest with minimal energy losses and with high selectivity, i.e. with limited formation of less valuable by-products.

One important feedstock chemical is carbon monoxide (CO) which can be produced by the electroreduction of carbon dioxide (CO_2). The most prominent representatives of catalysts for the selective conversion of CO_2 to CO are gold, silver and zinc.[2]

Hence, we envisage the exploitation of new catalysts for the selective electrochemical reduction of CO_2 to CO, aiming to find materials that catalyze the reaction at lower overpotential compared to silver. Here, we present results on alternative catalysts, obtained by using our 3D printed three-electrode, two-compartment cell coupled to an online gas chromatograph. The analysis of liquid reaction products is performed offline via GC/MS and ion chromatography.

Several characterization techniques, including XPS and SEM, are used to identify changes in the composition or morphology of the samples before and after electrolysis.

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Bi-enzyme Catalysts Modified Anode Electrodes for Self-Pumping Glucose Oxidase Fuel Cells

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This research purpose is to fabricate a new biocatalyst composited by Polyethyleneimine (PEI) combined with Terephthalaldehyde (TPA) for co-immobilized enzymes of glucose oxidase (GOx) and horseradish peroxidase (HRP) on the anodic electrode namely [TPA(HRP/GOx)] PEI/CNT for self-pumping GOx fuel cell performance improvement. By using cyclic voltammetry (CV) measurement, the electrochemical properties of the [TPA(HRP/GOx)] PEI/CNT biocatalyst with various GOx/HRP enzyme ratios can be optimized and achieved the maximum biocatalyst activity when the enzyme ratio is 1:2 (GOx:HRP). In addition, the microchemical structures of the new biocatalyst coated on carbon cloth (CC) electrode ([TPA(HRP/GOx)]PEI/CNT-CC(1:2)) and on carbon paper (CP) electrode ([TPA(HRP/GOx)]PEI/CNT-CP(1:2)) were tested by scanning electron microscope (SEM) and Fourier transform infrared (FTIR) analysis. Finally, the performance comparison between the self-pumping GOx fuel cell with [TPA(HRP/GOx)]PEI/CNT-CC(1:2) and [TPA(HRP/GOx)]PEI/CNT-CP(1:2) modified anodic electrode can be evaluated. The maximum power density of the self-pumping GEFCwith[TPA(HRP/GOx)] PEI/CNT-CC(1:2) is 1.68mW cm^{-2} which is higher than that of the cell with [TPA(HRP/GOx)] PEI/CNT-CP(1:2) (1.31mWcm^{-2}) and 86.66% improvement compared to the [TPA/GOx] PEI/CNT biocatalyst without adding the HRP(0.90mWcm^{-2}). The [TPA(HRP/GOx)] PEI/CNT-CC(1:2) biocatalyst stability can be maintained at least 48% for 60 days.

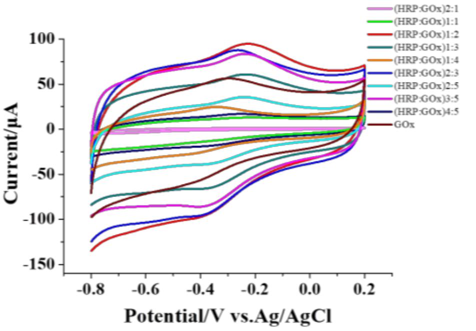

Fig. 1. CV of the [TPA(HRP/GOx)] PEI/CNT coated on Glassy carbon electrode with different HRP/GOx mass ratios.

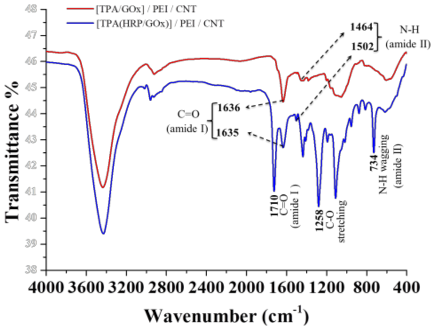

Fig. 2. The FTIR analysis of [TPA(HRP/GOx)]PEI/CNT and [TPA/GOx] PEI/CNT.

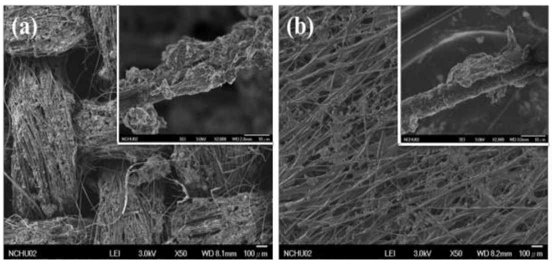

Fig. 3. The SEM images of (a) [TPA(HRP/GOx)] PEI/CNT-CC(1:2) and (b) [TPA(HRP/GOx)] PEI/CNT-CP(1:2). The insets are at high magnification images.

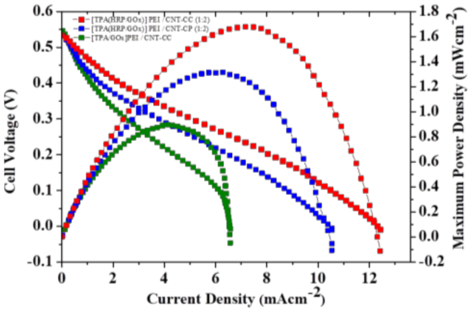

Fig. 4. The performance of the self-pumping GEFC with [TPA(HRP/GOx)]PEI/CNT-CC(1:2) and [TPA(HRP/GOx)]PEI/CNT-CP(1:2).

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Electrochemical Fabrication of CoMo Cathode for Proton Exchange Membrane Water Electrolyzer

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Hydrogen has been recognized as a sustainable future energy source to replace fossil fuels, which are getting depleted. Among the hydrogen production methods, water electrolysis has been received attention because it is an eco-friendly process that generates only pure hydrogen and oxygen. Platinum catalyst is most effective catalyst for hydrogen evolution reaction (HER), which is typically combined with gas diffusion layer to fabricate cathode for water electrolysis. However, scarcity and expensive cost is difficult to commercialization. To solve this problem, a transition metal-based alloys and compounds have been investigated as HER catalysts for cathode.

In this study, CoMo catalysts were fabricated on carbon paper by electrodeposition method with an electrolyte containing $CoSO_4$ and MoO_4. Since, previous studies have shown that transition metal-based catalysts for HER have degradation problem for acidic condition. To solve this problem, a leaching process was conducted on CoMo catalysts by applying constant potential. Catalytic activity measurements were performed at three electrodes cell system with Ar-purged 0.5 M H_2SO_4 electrolyte. Leached CoMo catalysts have high and stable performance for acidic HER.

Furthermore, leached CoMo catalysts was applied as a gas diffusion electrode (GDE) for the cathode of proton exchange membrane working electrolyzer (PEMWE). The single cell test depending on compressibility of CoMo GDE were investigated.

Morphology-dependent Electrocatalytic Activity of Rhodium Phosphide for Hydrogen Evolution Reaction

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Hydrogen production via water electrolysis system connected with renewable energies is a promising method owing to the high-purity of hydrogen, zero emission of pollutants, and moderate operating condition. Although tremendous efforts have been made on development of transition metal based electrocatalysts, noble metals in platinum group metal (PGM) are still known as highly active electrocatalyst, especially in platinum for hydrogen evolution reaction (HER). However, the expensive cost and scarcity of platinum limit commercial use of the catalyst in the water electrolysis system. To solve the problems, PGM based core-shell or alloy electrocatalyst with transition metals and compounds with non-metals have been investigated to improve catalytic performance as well as to reduce the noble metal loading.

In this work, we have fabricated the rhodium phosphide catalyst using electrodeposition method. The morphology of catalyst was controlled by varying electrolyte configuration such as metal/phosphorus precursors and additives. In 0.5 M H_2SO_4 electrolyte, HER catalytic activity was examined based on the geometric and electrochemical surface area. Then, the relationship between the material property and HER activity of rhodium phosphide catalyst has been investigated.

Scroll-like Ag coated paper electrode for electrochemical reduction of CO_2 to CO

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As the global warming is getting serious, interest in renewable energy which can replace the fossil fuel is arisen. Connected with the electricity from the renewable energy, the CO_2 conversion to various chemical fuels becomes entirely clean process. The CO_2 can be electrochemically reduced to C1 fuels such as HCOOH, CO, CH_4 or CH_3OH. Among them, the CO is known as the most cost-effective product. For the reduction, the Au and Ag are known as highly selective catalysts due to the suitable *COOH binding energy. Although many approaches have been conducted to develop Au and Ag-based catalysts, their activities are still low for commercialization.

In this study, 3D structured, rollable, and scroll-like Ag coated paper was fabricated by colloidal Au nanoparticles deposition and subsequent Ag enhancement process. As a first step, Au nanoparticles are synthesized on a paper substrate using a typical hydrothermal method. Then, Ag shells are formed by the following Ag enhancement, packing each fiber of paper. The composition and thickness were controlled by varying the Ag enhancement process. Finally, post-treatment was conducted in NaCl solution to increase the electrical conductivity. The material properties of Ag paper were examined using various microscopic and spectroscopic techniques. The Ag coated paper was used as electrode by rolling up at fixed diameter. Varying the length of paper enables to control the surface area per unit volume. The CO Faradaic efficiency on scroll-like Ag coated paper electrode was measured by the gas chromatography analysis. Then, the catalytic performance depending on the surface area per unit volume was investigated.

Enhanced Electrocatalytic Activitiy of Ultrathin Pt Film on Nanostructured Au for Formic Acid Oxidation Reaction

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Direct formic acid fuel cell (DFAFC) has been considered as a reliable energy device owing to the low toxicity, the small fuel crossover, and the storage convenience. In order to achieve reasonable performance of DFAFC, development of an efficient electrode is essential. For the anode, the multi-component Au-Pt catalyst has been proved to be highly active in the formic acid oxidation reaction (FAOR) because of the synergy effect between Au and Pt atoms. However, the high cost of noble metal has constrained its practical application. Since an effective strategy is to maximize activity per catalyst mass, various methods have been conducted to investigate the optimal composition of Au-Pt catalyst, minimizing the catalyst loading mass.

In this study, Pt self-terminating electrodeposition was applied to roughened Au surface to improve the performance of FAOR. The Au was electrodeposited on carbon paper with an electrolyte containing Au precursor by controlling the deposition potential and time to have large electrochemical surface area. The Pt coverage on Au surface was controlled by deposition potential, time, and number of pulses in Pt self-terminating electrodeposition, thereby improving the performance of FAOR. In cyclic voltammetry, the direct path way of FAOR was improved due to the rearrangement of Au and Pt surface where ensemble, ligand, and strain effect exist.

New Pt/C Electrocatalysts with Excellent Properties

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Most commercially produced H_2/Air fuel cells with a polymer proton-exchanged membrane use nanostructured Pt/C materials as an electrocatalyst. The actual problem of such catalysts - reducing the content of precious platinum while maintaining high activity and stability, is solved both by selecting the optimal carbon carrier and by controlling the size, shape, size and spatial distribution of platinum nanoparticles.

In this paper, a comparative study of the structural and functional characteristics of the original Pt/C electrocatalysts developed by PROMETHEUS R&D Ltd. (Russia) with commercial Pt/C catalysts on the world market was conducted. It was established that the electrocatalysts of the PM_X series (where X = 20 - 60 and corresponds to Pt-loading, % wt.) demonstrate the highest ORR activity among the Pt/C materials studied.

Figure 1a shows a PEM photograph of a fragment of the PM40 electrocatalyst surface, indicating a small size (2.8 ± 0.2 nm) of Pt NPs. Due to the strong anchoring and small size of NPs, the PM series catalysts exhibit higher electrochemically active surface area (ESA) during accelerated voltammetric stress testing (Fig. 1 b) and, as a result, higher durability and mass activity in ORR compared to other studied catalysts.

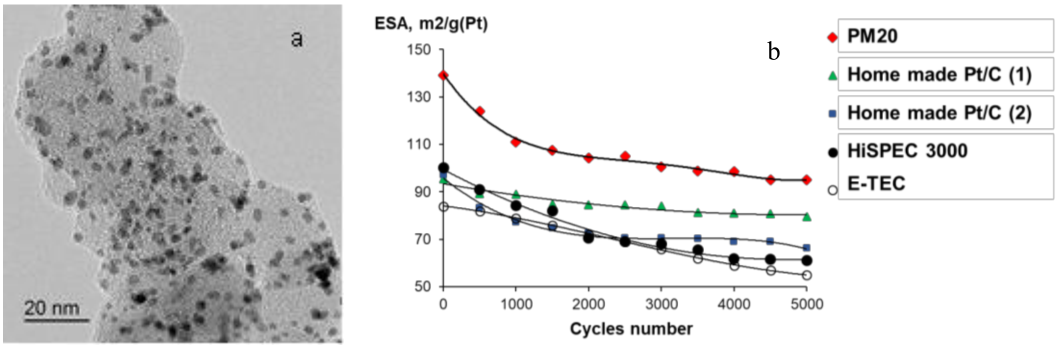

Figure 1. (a) PEM photograph of the PM40 electrocatalyst surface fragment and (b) the change of ESA of electrocatalysts during CV stress testing (potential range 0.6–1.0 V; 0.1 M $HClO_4$; Ar).

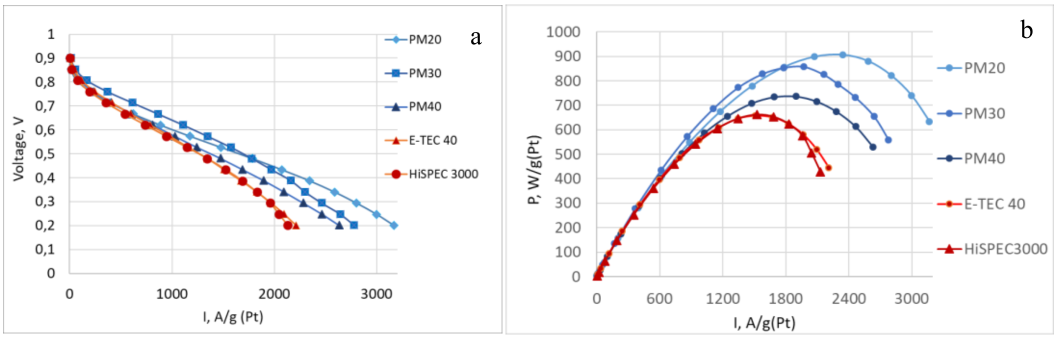

Figure 2. (a) Polarization and (b) power density curves for MEAs with studied Pt/C electrocatalysts. H_2/O_2, p = 10^5 Pa, 25 °C, wettability = 100%, 0.4 mg(Pt)/cm^2.

Pd-Ni Nanoparticles Attached onto Carbon Supports as Anode Catalysts for Anion Exchange Membrane Fuel Cells

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Anion exchange membrane fuel cells (AEMFCs) have recently attracted enormous attention due to their possibility of using non-Pt catalysts. In the present work, bimetallic Pd-Ni nanoparticles supported on Vulcan XC72R carbon black (Pd-Ni/C) using a wet impregnation method applied for AEMFC anode electrodes were developed. The Pd-Ni/C electro catalysts containing similar metal contents (40 wt.%) and various Pd:Ni ratios were synthesized and evaluated. The X-ray diffraction (XRD)spectrum confirmed that the Pd-Ni/C electro catalysts were successfully prepared and Pd and Ni crystallite sizes were less than 8 and 11 nm, respectively. In addition, the surface electronic states of Pd and Ni were determined by X-ray photoelectron spectroscopy (XPS) and the results revealed that the co-existence of Pd-Ni was observed by inhabitation of Pd oxidation in the catalyst samples. The H_2/O_2 AEMFC using the bimetallic Pd-Ni/C anode catalyst and the commercial Pt/C cathode catalyst showed a highest peak power density of about 300 mWcm^{-2} for the Pd:Ni weight ratio of 50:50. This result is consistent with the cyclic voltammetry measurements where the Pd-Ni/C electro catalyst with the Pd:Ni weight ratio of 50:50 exhibited the largest electrochemically active surface area (EASA). The experimental results showed the implementation of non-Pt catalysts for AMEFCs.

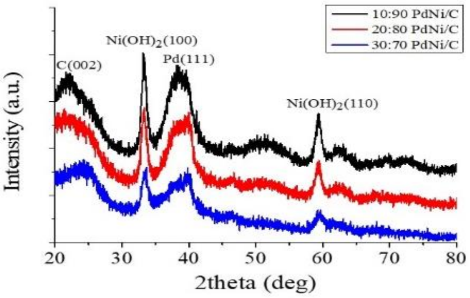

Fig. 1. XRD patterns of the Pd-Ni/C electro catalysts with various Pd:Ni wt.% ratios.

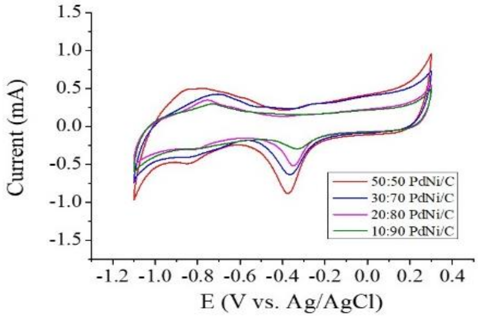

Fig. 2. CVs of the Pd-Ni/C electrocatalysts in 1M KOH solution, scan rate: 20mV s^{-1}.

Table 1. Parameters involved in the EASA of Pd-Ni catalysts using PdO reduction

Pd:Ni wt.% ratio	Conversion factor (μC cm^{-2})	Integral coulomb (μC)	Metal loading (mg cm^{-2})	EASA (m^2 g^{-1})
50:50	424	8740	0.1	20.6
30:70	424	6285	0.1	14.8
20:80	424	4400	0.1	10.4
10:90	424	2500	0.1	5.9

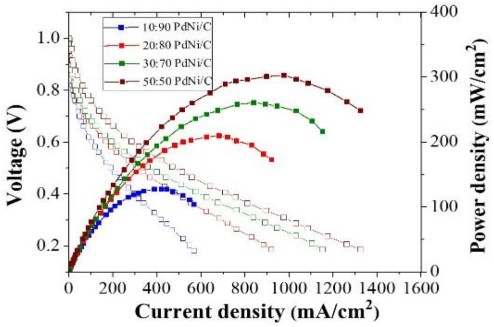

Fig. 3.AEMFC performance of Pd-Ni/C catalysts with various Pd:Ni wt.% ratios.

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Production of syngas by electrochemical CO_2 reduction in water at carbon cloth electrodes functionalized with a fac-Mn(apbpy)$(CO)_3$Br complex

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The electroreduction reaction of carbon dioxide represents one of the most challenging strategies for excess renewable energy storage into carbon-neutral high-energy-density forms such as CO, CH_4 and liquid fuels (ethanol, methanol, formic acid). Particular interest is aroused by the production of carbon monoxide, as it is a fundamental building block for many industrial processes including Fisher-Thropsch and hydroformilation of olefines. An innovative approach is to use organometallic complexes as electrocatalyst allows, in principle, a higher metal utilization efficiency (i.e. lower metal loading needed), compared to metal-nanoparticle-based electrocatalyst. In addition this strategy opens the the possibility to fine tune the selectivity by varying the electronic properties and the coordination geometry of the complex. In addition, anchoring the complex on electro-conductive supports helps to overcome the mass transport limitations of the electroactive species from the bulk to the electrode surface and allows a much higher electrocatalyst stability. Among many types of electro-conductive supports, carbon cloth (selected as support for this study) represent an excellent material for the fabrication of electrodes, both as gas diffusion layers and in immersion in the electrolyte, with high structural strength and high conductivity. Herein we describe the use of a manganese-tricarbonil-bipyridin Lehn-analogue complex (fac-Mn(apbpy)$(CO)_3$Br) grafted on carbon cloth support by diazonium salt reduction, used as electrocatalyst in aqueous media for the reduction of CO_2 to CO. The electrocatalyst, supported in carbon cloth (0.45µgMn cm^{-2}) in aqueous media was able to convert CO_2 into syngas (CO+H_2) as the only product with a CO-faradaic efficiency higher than 50% at -1.3V vs Ag|AgCl|KCl_{sat} at a productivity rate higher than 870Nl h^{-1} gMn^{-1}, attaining turnover numbers up to 33000 in 10h of operation with negligible electrocatalyst degradation.

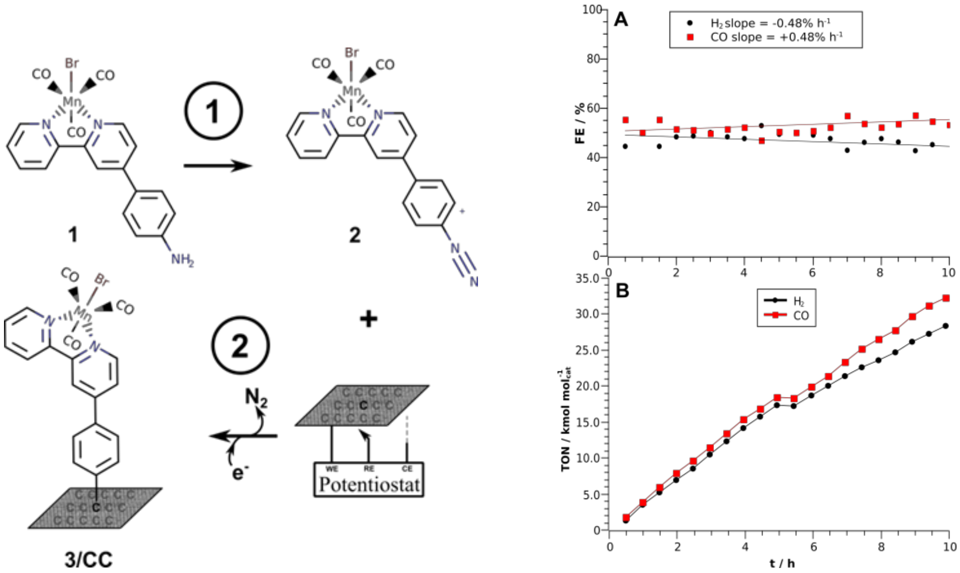

Figure: left) fac-Mn(apbpy)(CO)3Br grafting process on carbon cloth; right) CO-faradaic efficiency and electrocatalyst turnover number (TON) time profiles

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Electrocatalytic Activity of Pt and bimetallic PtPd Nanostructures on Au Nanoparticles in Oxygen Reduction Reaction

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One of the main obstacles for the commercialization of direct methanol fuel cells (DMFCs) is methanol crossover from the anode to the cathode through the polymer electrolyte during cell operation. This problem could be solved by the modification of the structure and composition of the electrocatalyst, which are major features in determining the adsorption/desorption of reactants and catalytic properties in an electrochemical reaction. In our previous studies, carbon-supported Au nanoparticles (NPs) were decorated with Pt, Pd and PtRu by a successive reduction process, and these NPs exhibited high reactivity in methanol and formic acid oxidations, due to their high utilization and the modified intrinsic properties of the active elements by the Au NPs. However, the Pt-decorated Au nanoparticles showed lower area-specific current densities at 0.6 V vs. NHE than Pt/C in methanol electro-oxidation, indicating its low intrinsic electrochemical activities. This result is likely due to the strengthened Pt–CO bonding or the weakened ensemble effect. In line with our ongoing effort to investigate the reactivity of surface-modified Au NPs, we have attempted to synthesize bimetallic PtPd-modified Au NPs and characterize their reactivity for oxygen reduction reaction in solutions with and without CH_3OH. In conference, we will report the electrochemical evidences which represent the synergistic effect of Au-PtPd NPs in their electro-catalytic reactivity.

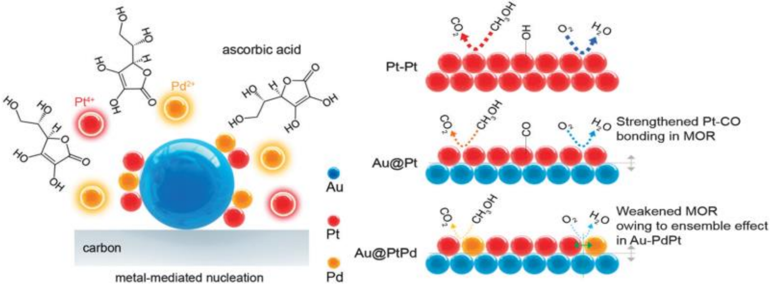

Fig. 1. Schematic diagram of the fabrication process for Au-PtPd NPs and a conceptual diagram of the Pt, Au-Pt and Au-PtPd during methanol oxidation and oxygen reduction.

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Mechanistic Investigation of Platinum Decorated Iron-Based Electrocatalysts for the Oxygen Reduction Reaction

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Finding cost-effective alternative electrocatalysts for the oxygen reduction reaction (ORR) is considered as one of the most important challenges in the development of electrochemical technologies such as fuel cells and metal-air batteries. Although significant progress has been made in developing non-precious metal based ORR catalysts such as Fe- and Co-N-C, they still lack sufficient performance in H_2-Air fuel cell rather than Pt as well as a limited stability under typical operating conditions.[1–4] In terms of activity, even though it is still necessary to optimize cell configuration and operating condition, it is usually accepted that higher loading of electrocatalysts can compensate for their lower activity because of their low cost and high abundance. In order to improve the stability, there are several approaches to achieve the still necessary improvements.[5–7] One of them is to load ultra-low amounts of Pt onto/into a well-characterized Fe-N-C material, which shows increased performance.[6,7] However, the mechanistic investigation of the Pt loaded Fe-N-C electrocatalyst is still necessary for a better understanding of the underlying processes.

Here, we prepared ultra-low amount Pt decorated Fe-N-C electrocatalyst and investigate the mechanistic origin of improved activity and stability. Based on the detailed physicochemical analysis, we show that the hydrogen peroxide production rate varies with the addition of Pt, which might be related to the enhanced activity and stability. This mechanistic understanding can contribute to the rational development of further non-precious metal based ORR electrocatalysts to improve their performance as economically feasible fuel cell catalysts.

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Nitrogen-Doped Carbon Supported with Gold Nanoparticles as an Efficient Catalyst for Glucose Electro-Oxidation and Oxygen Electro-Reduction

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This study is focused on the preparation of gold nanoparticles (AuNPs) supported carbon (C) and nitrogen-doped activated carbon (N-doped C) nanocomposites and their application for the electro-oxidation of glucose and oxygen electro-reduction. The AuNPs/N-doped C nanocomposite was prepared by two-step process. At first, activated wood-based carbon was prepared from alder charcoal and doped with nitrogen by pyrolising samples at a temperature of 800 °C in the presence of dicyandiamide (DCDA). Further, the AuNPs were deposited on the obtained N-doped activated carbon material or carbon using glucose and ascorbic acid as reducing agents. The prepared nanocomposites were characterized by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), X-ray powder diffraction (XRD), Raman and X-ray photoelectron spectroscopy (XPS). The electrocatalytic activity of the nanocomposites for oxygen electro-reduction and glucose electro-oxidation was investigated using the cyclic voltammetry and rotating disk electrode (RDE) methods.

It has been determined that the AuNPs/N-doped C and AuNPs/C nanocomposites had a higher catalytic activity for the electro-oxidation of glucose than the pure Au or carbon and N-doped carbon alone, indicating the synergistic effect of AuNPs and N-doped carbon or carbon. Moreover, the highest activity shows the AuNPs supported N-doped carbon as compared with that of AuNPs supported carbon.

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Study of the heating method on the electrochemical properties of Ti/Ru$_{0,70}$Sb$_a$Ir$_b$O$_x$ electrodes

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Metal mixed oxide (MOMs) have been highly investigated for electrochemical degradation of organic compounds. In general, MOMs are prepared by thermal decomposition in which films of metallic oxides are deposited on metallic support, often titanium [1]. However, to make feasible the scale up of the oxidation electrochemical process as a more efficient alternative to treat effluents containing persistent pollutants, it is still required to developed cheap electrodes whit high catalytic activity and long-life time. Therefore, the study proposes an alternative heat treatment technique to produce the MOMs, that is simple, fast and able to produce electrodes with high surface area, high catalytic activity, and long life using the microwaves irradiation instead of the conventional heating using electric furnace. Different electrodes were produced with composition of Ti/Ru$_{0,70}$Sb$_a$Ir$_b$O$_x$ (a = 0,20 or 0,25 and b = 0,1 or 0,05, respectively) by two heating method, one at microwave by irradiation and other by conventional heating at electric furnace. The precursor solutions were synthesized by the Pechini method and the calcination temperature was 500ºC. The anodes were characterized by scanning electron microscopy, cyclic voltammetry, linear sweep voltammetry, morphology factor, electrochemical impedance spectroscopy and accelerated lifetime. The composition of the MOMs and the heating method play an important role in the electrochemical proprieties of the anodes. The comparative study of the physical and electrochemical characteristics of MOMs produced shows that the heating using irradiation microwave required lower time to synthesis the anodes and they presented better electrochemical characteristics (higher voltammetry charge, lower current transfer resistance and longer test live) than the anodes synthesized by conventional heating. Therefore, the irradiation microwave heating appears to be a promising technique to produce MOMs and the MOMs produced by irradiation microwave shows more suitable to be applied as anode in electrochemical process to degrade organic compounds.

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Petroleum removal in the presence of anionic surfactant during electrokinetic remediation

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Soil pollution with petroleum is a worldwide environmental concern, due to industrial activities during the exploration and production. Brazil was estimated petroleum production at about 3363 thousand barrels per day during 2017. In this context, the soil and aquifers contamination by hydrocarbons, due to leaks in underground tanks, has been the most frequent environmental event in the world. In this context, Electrokinetic (EK) remediation is one technique that can be employed for the decontamination of polluted sites from various organic (pesticides, polycyclicaromatic hydrocarbons, TPH) and inorganic (toxic metals) pollutants. However, in recent years, much attention has been devoted to the coupling of technology suitable for the remediation of environmental contaminants from soil. Among the different technologies investigated the electrokinetic soil flushing has been in investigated to the soil remediation. López-Vizcaíno and coworkers investigated the electrokinetic soil flushing remediation of kaolin soil polluted with phenanthrene (PHE), comparing three different scales, lab, bench and pilot scale plants. They described the removal of PHE from soil using sodium dodecyl sulfate (SDS) as a flushing-fluids, in order to improve the decreasing the interfacial tension and breaking up PHE into the hydrophobic cores of surfactant micelles. In this work, we investigated the concentration of SDS during the electrokinetic soil flushing remediation real soil polluted with petroleum. The soil used in this work was collected in the Natal, Brazil, and it consists mainly of thin and medium granite quartz sandstones. The bench setup used in this work was constructed from transparent methacrylate and divided in to five compartments (see Fig. 1). The soil was air-dried and 4000 g of soil was polluted with 40 g of petroleum until an initial pollutant concentration 10000 mg kg^{-1}. The experiments were performed of 1.0 V cm^{-1} during 20 days. Graphite electrodes were used as anode and cathode. The anodic compartments were filled with water while cathodic compartments were SDS (0, 2, 5 and 7 mM). In this case of SDS, it was used to promote the mobility of TPH and HPA into the soil.

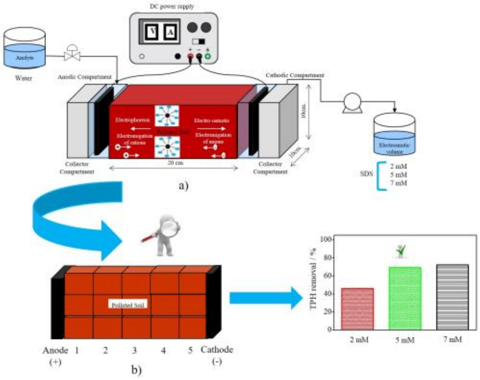

Figure 1. Scheme of soil remediation

From this work about petroleum removal by enhancing the efficiency of electrokinetic soil flushing, the important conclusions have been summarized as follows:

- TPH and HPAs removal was lower for electrokinetic without surfactant. Conversely, when EK remediation was coupled to addition of surfactant, its efficacy was improved, achieving high TPH and HPAs removal. However, HPAs removal efficiency was lower due to high-molecular weight polycyclic aromatic hydrocarbons.

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Study of the Interaction Between the Pesticide Malathion and the Cu (II) Metal Ion by Electroanalytical Methods

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Due to the indiscriminate use of pesticides and the incorrect disposal of heavy metals, these species have been commonly found in the environment. Pesticides are usually organic molecules that contains functional groups capable of interacting with metal ions. Such interactions alter the properties of both pesticides and metal ions. In this way it is important to make an evaluation of the interaction of these species in solution. Malathion (O, O-dimethyl S-(1,2-dicarbethoxyethyl) dithiophosphate) is an aliphatic organophosphorus insecticide used in agricultural, domestic and commercial purposes. It has sulfur and oxygen atoms that contains pairs of free electrons capable of binding to metallic ions. The metal ion copper is present naturally in the environment, so the purpose of this work was to evaluate the interaction between the pesticide malathion and Cu (II) metal ion using electroanalytical methods.

The electrochemical measurements were performed on a potentiostat/galvanostat in a conventional 3-electrode cell. Gold working electrode, Ag/AgCl reference electrode and platinum electrode. As support electrolyte was used KCl 0.1 mol L^{-1}.

Initially a study of the electrochemical responses of the two species in 0.1 mol L^{-1} KCl under a gold electrode was carried out, where Malathion presented a reduction peak at -0.360 V with irreversible process characteristics. The Cu (II) ion presented characteristics of a quasi-reversible process, with a reduction peak at 0,174V and an oxidation peak at 0,350 V. The analyzes are made by electrochemical measurements, evaluating changes in the voltammetric profile of the species when in presence of the other one. After that, an evaluation of the interaction between copper (II) and malathion was made, first analyzing the electrochemical response of copper when added pesticide to the medium. The voltammograms for metal ion Cu (II), 5.0 x 10^{-5} mol L^{-1}, with additions of aliquots of pesticide solution in different proportions showed that when adding the pesticide in a 1: 0.5 Metal:Ligand stoichiometry, we have the displacement of the redox process to more positive potentials. This tendency is maintained up to the ratio 1:2 Cu: Malathion, with a displacement of 287 mV, indicating that up to this ratio, the metal center divides the electronic density with the ligands, making the metal center deficient in electrons, which consequently makes it more difficult to oxidize and easier to reduce. When added to a ratio of 1: 3, it is observed that the excess of ligand in the coordinating sphere of the metal makes it richer in electrons, and thus we have a displacement of 144 mV to more negative potentials. To evaluate the electrochemical behavior of Malathion when in the presence of copper, the same procedure described above was carried out, however aliquots of copper solution in 5.0 x 10^{-5} mol L^{-1} malathion solution was added. It could be observed that the peak of reduction attributed to malathion does not suffer great variations. According to the literature, the reduction of malathion occurs by the interaction of the sulfur atom of the molecule under a gold electrode, by the transfer of two electrons. This little variation suggests that the complexation must occur by the oxygen atoms of the carbon chain, not the phosphate group.

Studies have shown that the formation of a complex between the pesticide malathion and copper metal ion occurs. The cyclic voltammetry technique proved to be efficient in the detection of this new species in solution and could be used to monitor the formation of the new species in natural matrices.

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Hydrodynamics and Current Distribution Analysis of Flow Field Designs for Vanadium Redox Flow Batteries

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Over 70% of Colombia electricity comes directly from hydroelectric power, which are generated by the operation of water dams in hydroelectric power plants. Larger hydroelectric power plants face many difficulties to escalate and keep a constant electricity supply. To address these problems the development of energy storage systems is a priority to guarantee a continuous electrical supply. All-vanadium redox flow batteries (VRBs) are a favorable solution for their capacity to grid-level store energy allowing commercially competitive systems. Many investigations have been carried out on the design optimization of VRB batteries through performance tests, distributed current measurements and flow visualization[1-4]. The cell performance of RFBs, including the charge-discharge performance in a single cycle and the cycling performance in the long-term, is heavily dependent upon the transport processes such as charge transport and mass transport of active species. In order to obtain an efficient VRB we must minimize them. However, is a difficult task to simultaneously achieve these goals, as these transport processes are linked, contradicted each other, and strongly coupled with electrochemical reactions [1, 3, 5, 6].

For VRB systems, it is important to evaluate concentration overpotential, pump losses, flow rate optimization, and electrolyte flow patterns to achieve high system efficiencies. Predominantly, concentration overpotential and pressure losses are related to mass transport of active species being influenced by the flow field design and the volumetric flow rates [1, 5, 7]. Mass transport of active species has been studied for the common electrode configurations, porous flow-through (FT) carbon electrodes or flow-by electrodes. The FT structure works as forced-convective flow throughout the electrode, mass transport of the reactants within the electrodes is excellent. However, the FT cell design requires relatively thick electrodes to minimize pressure drop, especially in a cell with large geometrical area. In contrast to the FT structure, the flow-by structure enables the use of thin electrodes and has been configured to different types of flow fields, i.e., parallel, serpentine or interdigitated with better performance than the FT ones [1, 3, 5, 6, 8].

Flow field designs can affect the cell performance in two ways: i) by modifying the overall mass transport coefficients; and ii) by improving the pump work. For instance, a parallel flow field enables a low pressure drop but there is virtually no force convection through the electrode, resulting in poor cell performance. In comparison to the parallel flow field, the serpentine flow field exhibits a much stronger under rib convection, resulting in a higher performance. The interdigitated flow field design outperforms serpentine design at low flow rates while serpentine design performs as well as interdigitated design with thicker electrodes [3, 5]. This research focuses on the search for the optimal design of the flow field of an all-vanadium redox flow battery that allows to increase the energetic efficiency of the system by improving performance and reducing pressure drop. To enhance better mass transport of active species and battery performance, the key design parameters are: the channel size, the rib size, and open ratio.

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Study of the Lead-Acid Battery Lifetime by Combining Electrochemical and Electrical Models

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Energy generation with renewable sources demands energy storage coupling to maintain power quality in the electrical generation and supply for smart grids. Electrochemical energy storage has become the option due to compactivity, easy arrangement, economic factors, and because it delivers nearly instant response both to input and output from the battery to the network. Among storage technologies, lead batteries offer a reliable, cost-effective solution adaptable to different types of energy generation systems (1-4). Predicting the lifetime of lead-acid batteries represents a challenge due to the irregularity of the cycling regime with charging and discharging intercepting each other constantly. To achieve better accuracy in the lifetime description, it is desirable to combine performance and lifetime models. However, this is a complex task due to the phenomena affecting the lifetime of the battery such as corrosion, acid stratification, gassing, sulfation and sulfate crystal growth, and degradation of the active material (1, 3, 5-7) .

The most representative model is presented by Schiffer and collaborators (7), it is based on the concept of 'weighted Ah throughput' with a weighting factor to understand the full charge and partial SOC cycling and its changes due to acid stratification, gassing, and high temperature. Corrosion effects are calculated based on battery voltage and temperature. Other electrical models are based on equivalent circuit analysis such as: *a)* Thevenin, Impedance and Run-time based electrical models (8, 9), which uses a series resistor and an RC parallel network to predict battery response to transient load events at an specific SOC, by assuming constant open-circuit voltage (9). *b)* The impedance model employs electrochemical impedance spectroscopy to obtain the AC-equivalent impedance model. However, the fitting process is difficult and only work for a fixed SOC and temperature setting. *c)* Runtime-based models use a complex circuit network to simulate battery runtime and DC voltage response for a constant discharge current. They cannot predict neither runtime nor voltage response for varying load currents accurately (9).

Most of these models are adjusted or obtaining from experimental data sets and are highly dependent on the parametrical adjustment to accurately describe the lifetime process. Moreover, phenomelogical description of process such as corrosion, gassing or sulfation are not quite understood under extreme temperature and operation conditions. The aim of this study is to combine electrochemical and electrical equations to describe the performance of lead-acid batteries. By combining Schiffer's approach with Butler-Volmer type description of phenomena such as load current, corrosion processes and gassing, as function of temperature, we will gain insight and better description of ageing phenomena. Our propose methodology can be summarized as: i) overpotential calculation based on experimental data, ii) load current calculation by using experimental overpotentials and Butler-Volmer equations as a function of temperature, iii) overpotential calculations such as corrosion and gassing with electrochemical models.

Acknowledgements

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In situ Surface-Enhanced Infrared Absorption Spectroscopy and Electrochemistry Study of Cytosine Adsorption on Gold Electrodes as a function of pH

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The adsorption of DNA bases on solid substrates has important practical implications in the manufacturing of biosensors for DNA sequencing recognition, in targeted drug delivery or in molecular electronic nanotechnologies[1,2]. Cytosine is one of the DNA bases that undergoes two acid/base equilibria (pK_a values 4.5 and 12.2) and can present several tautomeric forms in aqueous solutions[3,4]. The tautomeric equilibria seem to affect the bases pairing in the replication process[5].

In this communication the facilities provided by the in situ Surface-Enhanced Infrared Absorption Spectroscopy in the Attenuated Total Reflection mode (ATR-SEIRAS) are exploited for the characterization of cytosine adsorption on gold thin-film electrodes from solutions of three pH values (below the second pK_a) using H_2O and D_2O as solvents, in order to determine the adsorption behavior of the different forms that are connected to acid-base or tautomeric equilibria. The results are compared with the spectra in solution. The spectra are interpreted based on DFT calculated spectra of the different acid-base and tautomeric forms in solution and in the adsorbed state on clusters of 19 gold atoms. Previous electrochemical and spectro-electrochemical studies[6,7] have distinguished different potential regions starting from negative potentials at which cytosine forms a disordered phase of weakly adsorbed molecules (physical adsorption) to the most positive potentials at which a chemically bounded cytosine adlayer is formed. However, the determination of the molecular orientation and sites of interaction with the metal are still controversial.

It is found that the deprotonated cytosine species is adsorbed, even at pH values bellow the first pK_a. The preponderance of the canonical keto-amino tautomer in solution, with some contribution of the keto-imino tautomer is concluded but the equilibrium between these two forms is inverted upon adsorption, depending on the pH value and the electrical potential applied to the electrode. The tautomeric equilibrium is shifted to the keto-amino form at potentials of the physical adsorption region and to the keto-imino tautomer in the chemical adsorption potential region.

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Promotion of Oxygen Evolution Selectivity in Acidic Chloride Solution Using a MnO_x/IrO_x Buried Interface

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The oxygen evolution reaction (OER) and chlorine evolution reaction (CER) both play central roles in electricity-to-chemical conversion on a large scale. The OER represents the desired anodic reaction in water electrolysis, which allows the capture and storage of electrical energy in the form of H_2 as a chemical fuel. The CER on the other hand is the core reaction in the chlor-alkali process that produces chlorine and caustic soda, bulk chemicals which are required in large amounts throughout the chemical industry. Both OER and CER are thus are highly important regarding the electrification of the world energy infrastructure.

Control over selectivity between OER and CER can be a serious challenge and is a central topic in the utilization of these reactions. Although the two reactions seem like very different reactions at first glance, it is well established that they tend to occur simultaneously on many catalytic materials, which can be described as a scaling relationship. Such a relationship implies that the two are fundamentally linked, perhaps in the form of a common intermediate surface species and/or a shared active site. Attempts to electrolyze acidic chloride solutions may therefore result in the formation of a mixture of O_2 and Cl_2 at the anode, which is unlikely ever a desired outcome.

With regard to OER, an oxygen-selective anode would allow the direct splitting of saline water without the costly need of removing chloride from the system, making direct seawater electrolysis possible. Unfortunately, increasing the selectivity towards OER is by far the most demanding, since CER has inherently faster kinetics than OER. It may be exceedingly difficult, if not impossible, to promote selective OER on the basis of kinetic considerations alone, such as by finding a catalyst with 'an appropriate active site'. Despite this, anodes using manganese oxide (MnO_x) have shown extremely high selectivities towards OER, often reaching nearly 100%.

In this work, we explore the origin of the remarkable performance (in terms of selectivity towards OER) on MnO_x-based anodes, by depositing thin layers of MnO_x of varying thicknesses on iridium oxide (IrO_x) with the use of rotating ring-disk electrode and on-line electrochemical mass spectrometry studies. We argue that the thin MnO_x films are in fact not catalytically active, but form a physical barrier that hinders the transport of Cl^- ions to the buried interface of the IrO_x catalyst. We will also explore the synthesis and performance of other metal oxide-based deposits in enhancing OER selectivity. The use of thin, porous overlayers to selectively disfavor the transport of a reactant may be a promising approach towards controlling selectivity in OER versus CER, and may be extendable to other electrocatalysis fields as well.

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Layered Double Hydroxides for oxygen evolution reaction: a noble metal-free unconventional system

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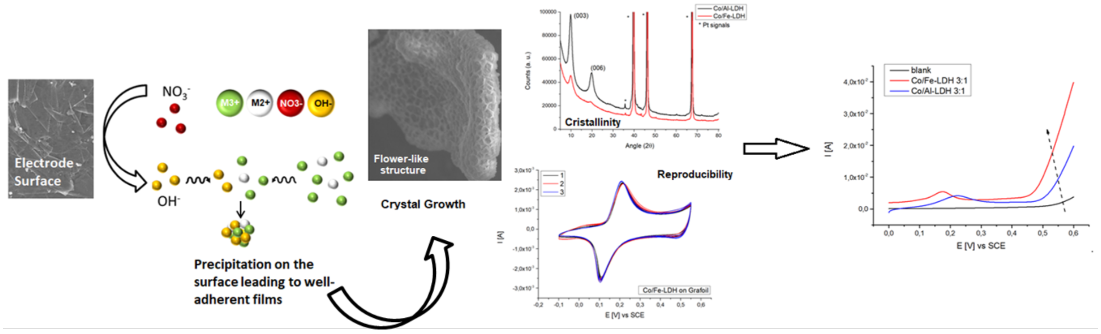
The global energy demand grows and renewable resources are the only possible tools to rely on for the future. The most relevant problem is that they tend to be intermittent and unpredictable. [1] As a result, there will be an increasing need to store this energy for when the sun is not shining, and the wind is not blowing. Water electrolysis has drawn a lot of attention to store energy from renewables. In this scenario, layered double hydroxides (LDHs) containing redox active metals are promising materials due to their versatility, tunable properties, wide range of compositions and low cost. [2][3]

Cobalt based LDHs catalysts with iron and aluminum in different molar ratios, ranging from 1:1 until 4:1, were synthesized by a newly developed electrochemical potentiodynamic method. [4] The obtained catalysts were characterized by a comprehensive combination of techniques and were firstly evaluated for the oxygen evolution reaction (OER) with classically used rotating disk electrodes. In all cases investigated, an optimal Fe and Al content was highlighted. Moreover, the performances were estimated in an all-noble metal-free unconventional stationary system, based on a graphite sheet. The performance resulted highly reproducible and the electrodes showed very good stability for at least 24 h, when tested at a current density of 10 mA cm^{-2} in 1M NaOH (at a potential of approximately 0.5 V *vs* SCE).



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Selective and Efficient CO_2 Electroreduction at Atomic Level Interface

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CO_2 electrocatalytic reduction is a promising method to tackle the global warming problem.[1] Up to now, a wealth of catalysts have been investigated in CO_2 electrorduction.[2] Among them, single atom catalysts (SACs) with high atom utilization efficiency and high reaction selectivity, have aroused great interest.[3-5] In terms of the CO_2 electroreduction to CO, the formation of intermediate *COOH is the rate-determining step in the reaction.[6] This proton coupled electron transfer process accompanies with the activation of both CO_2 and H_2O molecules simultaneously. Only catalysts with dual catalytic sites can realize the process. Namely, one catalytic site adsorbs CO_2 and the other adsorbs H_2O. Therefore, SACs with single component catalytic site can not meet the requirement. It is essential to develop novel atomically dispersed electrocatalysts with diverse catalytic sites to promote the CO_2 activation.

Herein, we constructed the electrocatalysts with dual catalytic sites by anchoring Cu atom-pair on the $Pd_{10}Te_3$ nanowires. The K-edge XANES of Cu reveals that the valence of Cu is between 0 and +2, and both Cu-Cu bond and Cu-O bond can be found in the catalysts. The EDS-mapping data shows that a number of O atoms are found to be accompanying the Cu atoms, confirming the existence of $Cu^{\delta+}$-Cu^0 in the Cu atom-pair. The density functional theory calculations (DFT) further predict that the atomic interface between $Cu^{\delta+}$-Cu^0 can activate CO_2 efficiently. The Cu^0 site adsorbs CO_2 and the adjacent $Cu^{\delta+}$ site adsorbs H_2O, which facilitates the proton coupling with CO_2. The CO_2 electroreduction measurements confirmed this theoretical deduction. The $Cu^{\delta+}$-Cu^0 atom pair on $Pd_{10}Te_3$ nanowires show higher CO current density and CO selectivity than pure $Pd_{10}Te_3$ nanowires. The CO faradaic efficiency (FEco) of $Cu^{\delta+}$-Cu^0 catalytic sites is 92% at the potential of -0.78V vs. RHE, which is much higher than that of pure $Pd_{10}Te_3$ (14%). Moreover, the H_2 faradaic efficiency on $Cu^{\delta+}$-Cu^0 is only 3%, indicating that the hydrogen evolution reaction is inhibited utterly on this atomic interface. The stability of $Cu^{\delta+}$-Cu^0 is further confirmed by the long-term durability tests with no obvious decay in total current density and FEco.

In our work, the CO_2 activation of electrocatalysts are promoted via a "bi-atomic activating bi-molecular" mechanism. The $Cu^{\delta+}$-Cu^0 atomic interface on $Pd_{10}Te_3$ nanowires can adsorbs the H_2O and CO_2 simultaneously, resulting in the high efficient CO_2 conversion. The concept of atom pair catalyst we proposed is an effective supplement to single atom catalysts, and will provide important guidance for designing novel atomically dispersed catalysts.

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Quantification of Phenolic Compounds by Flow Injection System Using TiO_2 Under the UV Light

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A voltammetric method for quantification of phenolic compounds was proposed using titanium dioxide (TiO_2) under the UV light illumination by flow injection system (FIA). Phenolic compounds are a class of molecules which are widely used in the manufacture of several products (plastic, pesticide, dye, detergent, etc). Due to its high estrogenic and carcinogenic potential and high stability in aqueous matrix, the phenolic compounds are harmful to the environment [1]. Thus, the concern with public health needs accurate knowledge, in real time, of the water contamination level, as well as soil and food, with these phenolic molecules. In recent years photoelectrochemical analysis has been explored, increasingly, for the analysis of molecules of interest. In this technique, a semiconductor material, such as TiO_2, is used to harvest the energy from UV or visible light and transform it into the electron/hole pair [2]. The holes and electrons can react with the available molecules adsorbed on TiO_2 surface, like OH^- and H_2O and generate reactive oxygen species (ROS). ROS can oxidize the phenolic compounds allowing the quantification of these molecules. A flow injection system was used for the amperometric measurements of phenolic compounds, using a peristaltic pump (Perkin-Elmer, France) with 1 mL/min of flow rate and manual injection valve with 50 µL of volume. Electrochemical measurements were carried out using a PalmSens (Utrecht, The Netherlands) controlled by PSTrace software (version 5.3). A screen-printed electrode of graphite (DropSens, Spain, SPCE model DRP-110) modified with 5 µL of TiO_2 suspension (HEPES + Nafion®) was used as work electrode. Pt and Ag were used as counter and reference electrodes, respectively. The system optimization was conducted by studies of effects of channel thickness from flow cell, of potential, and pH. At the optimum conditions it was possible to quantify 8 different phenolic compounds. Linear calibration curves were obtained on the range 0.0125 – 1.0 µM, with LOD = 31 $nmolL^{-1}$ and sensitivity = 0.2 A M^{-1} cm^{-2} for Hydroquinone, using it as a model molecule, and LOD = 18 $nmolL^{-1}$ and sensitivity = 0.5 A M^{-1} cm^{-2} for 4-Aminophenol (Fig. 1). A simple analytical methodology was used and a sensitive low cost photosensor was developed with possibility of application "in situ" and in real-time for the quantification of phenolic compounds.

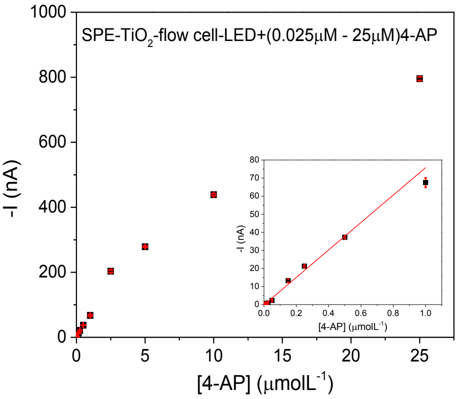

Figure 1. Calibration curve for 4-AP. Inset: linear range.

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Isotope-Labeling Studies in Water Oxidation Electrocatalysis

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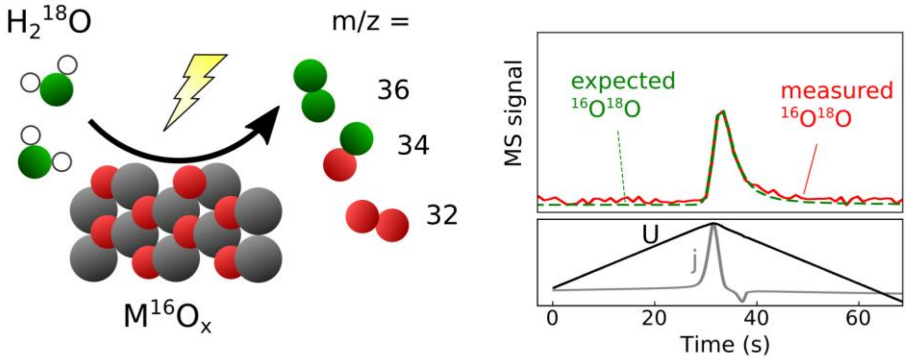
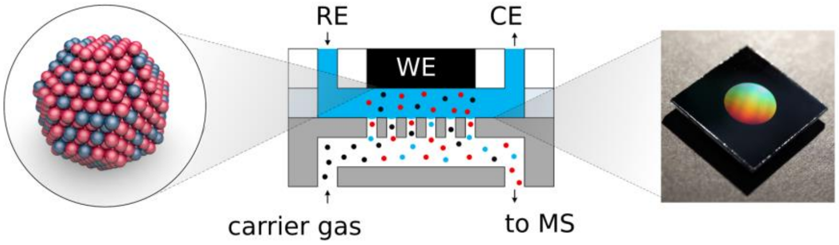
Improving understanding of the electrocatalytic mechanisms for the oxygen evolution reaction (OER) will help in designing electrode materials with lower catalytic overpotential and greater stability, increasing the efficiency and economic viability of electrolysis. Isotope-labeling can be a powerful tool for elucidating catalytic mechanisms, including in electrocatalysis. Herein, we apply 18-O labeling, utilizing a fully quantitative electrochemistry - mass spectrometry method with unprecedented sensitivity[1] and post-characterization by low-energy ion scattering spectrometry, to investigate the electrocatalytic mechanism of oxygen evolution.

Nickel-iron based electrodes are used in industrial alkaline water electrolysis, but questions remain about the intrinsic activity and electrocatalytic mechanism. By performing a series of isotope-labeling experiments on a model system of mass-selected Ni-Fe nanoparticles, we show that oxygen evolution does not proceed via lattice oxygen exchange and that only the surface of the nanoparticles are active[2]. This allows us to estimate the turn-over frequency of the active sites, 6 O2 molecules per site per second, which is higher than previous estimates. We also quantify lattice oxygen exchange in IrO2 and RuO2 thin films during oxygen evolution in acidic electrolyte as a function of electrochemical roughening, and perform oxygen stripping experiments to probe OER intermediates. This talk will describe these findings and further explore the potential of isotope labeling studies in electrocatalysis.





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Modeling of Electrodialytic Treatment of Lithium-Ion Batteries

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Lithium-ion batteries are currently present in most portable electronic devices and their use is rapidly growing in the field of electric vehicles and renewable energy storage. Many components in lithium-ion batteries are toxic and/or environmentally hazardous. Furthermore, some of them are expensive and listed as critical materials in terms of supply-chain risk. Therefore, the need to improve the recycling techniques for lithium-ion batteries is becoming a priority.

Herein, we describe and present a model for the electrodialytic treatment of disposed lithium-ion batteries. Electrodialysis is a separation process based on the use of electric fields and ion-selective membranes. The electrodialytic cell can be designed in different configurations, to enhance the selective extraction of the target products. In a standard electrodialytic cell, the treated matrix is separated from the anode and the cathode compartments by means of anion- and cation-exchange membranes respectively. However, depending on the ionic charge and the specific chemistry of the matrix, different cell designs can be used.

In the present work, different possible configurations are explored for the optimization of the extraction of key valuable components from spent lithium-ion batteries, taking into account the chemical properties of the system depending on the chosen extracting agent and cell configuration. The model presented here is based on a set of differential and algebraic equations consisting of a Nernst-Planck based continuity equations for each of the chemical species involved in the process, coupled with the electroneutrality and the local chemical equilibrium conditions.

The numerical solution is performed using COMSOL Multiphysics, and the simulation results are compared with experimental data for model validation.

Acknowledgements:
The authors acknowledge the financial support from the University of Malaga, project: PPIT.UMA.B5.2018/17 and the e.THROUGH (H2020-MSCA-RISE-2017-778045), financed by the European Commission. Villen-Guzman acknowledges the funding from the University of Malaga for the postdoctoral fellowship PPIT.UMA.A.3.2.2018.

Evaluation of New Electrode Materials for the Lignin Electrorecovery from Kraft Black Liquor

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Lignin is an aromatic polymer that can be used as raw material for different applications, namely as a phenol substitute in phenolic resins, as a complementary crosslinker in epoxies, as an additive for biodegradable plastic and even as binding agent [1,2]. Lignin is a component of wood, being the second most abundant natural polymer in the world after cellulose [3]. An important source of lignin is the black liquor, a by-product of the papermaking process. Different ways to recover the lignin from black liquor have been studied in the last few years, such as membrane processing, acidification and electrolysis [2,3].

Finding an industrially feasible process for lignin recovery from black liquor is still challenging. The electrolytic method is a promising technology since it is a low-cost process of simple operation. Moreover, the known properties of the Kraft black liquor, such as high ionic conductivity, alkaline pH and considerable lignin concentration, makes the electrochemical process a potential method to be implemented in industrial pulp mills [2,3]. It has been reported that the lignin recovery can be carried out by anodic electrodeposition, which involves an oxidation process of black liquor [2,4]. However, few materials have been studied for the electrorecovery of black liquor's lignin; among them are platinum, nickel and AISI 304 stainless steel [2–4].

Considering that, in this work, low cost materials, such as iron, zinc, copper, cadmium, tin and lead are evaluated as potential materials for the lignin electrorecovery from a *Eucalyptus globulus* black liquor sample provided from a Kraft pulp mill. Firstly, the black liquor samples are physicochemically characterised regarding the dry solids content, organic/inorganic ratio, pH, conductivity, viscosity and lignin concentration. Then, the catalytic activity of the potential materials is analysed by cyclic voltammetry at different scan rates (5 – 1000 mV s^{-1}) in the 25 – 75 ºC temperature range. Charge transfer coefficient and number of exchanged electrons is calculated for all materials tested and compared with the results previously obtained for nickel, platinum and AISI 304 stainless steel. Chronoamperometry technique is also used to verify the stability of the materials in black liquor solution.

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Energy Efficient, Highly Selective Anodes for the Chlorate Process

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Chlorate is produced by electrolysis of a concentrated salt solution of sodium chloride and sodium chlorate in an undivided cell, using Dimensionally Stable Anodes (DSA) and low carbon steel or titanium cathodes. The primary products of this process are chlorine on the anode and hydrogen on the cathode. Chlorine forms chlorate in a series of chemical reactions in the electrolyte.

Oxygen is a byproduct that can be formed in several reactions, electrochemical as well as chemical.[1] Since the oxygen formation decreases the current efficiency, highly selective anodes should be developed to minimize the parasitic reactions. By suppressing the anodic oxygen evolution reaction (OER) the efficiency of the chlorate process will increase and it also reduces the risk of explosion. Therefore suppressing OER kinetics is advantageous for safety control of the chlorate process.

In this study we investigated new anode materials with reduced amounts of noble metals. We produced anodes with initial composition of metals, in molar ratios, as follows: Ti:Ru:Sn:Sb = 34:30:30:6. This material was compared to traditionally used DSA, with the following composition: Ti:Ru = 70:30. The electrodes were characterized by cyclic voltammetry, polarization curves, scanning electron microscopy, X-ray fluorescence and Raman spectroscopy.

The chlorine evolution selectivity was evaluated by means of operando electrochemical mass spectrometry, which allowed us to detect the gaseous products generated during galvanostatic electrolysis. The newly synthesized electrode showed enhanced selectivity towards chlorine, which translated in less oxygen formed.

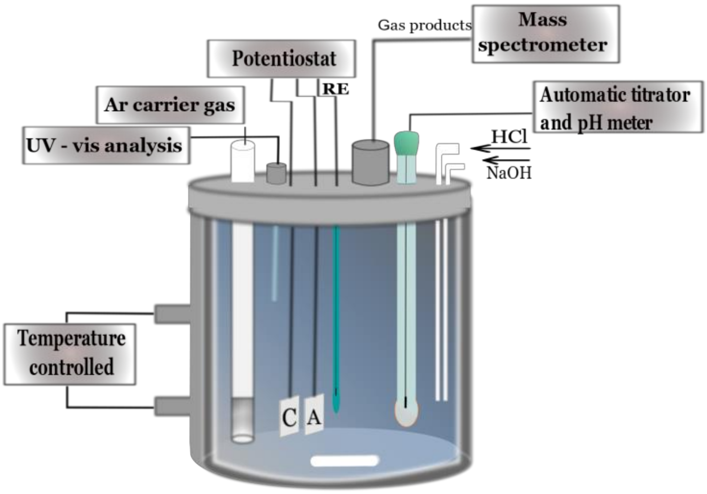

Figure 1. Shematic presentation of experimental setup

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H_3PO_3 Adsorption at Pt Electrode in Concentrated H_3PO_4 Solutions

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Interaction of phosphorus oxoacids with Pt-based catalyst in high-temperature fuel cells with proton exchange membrane (HT PEM FC), where the membrane is doped with phosphoric acid and operates in temperature range between 120 and 180 °C, largely influences behaviour of this type of fuel cell. Despite the fact that this interaction is of primary importance for the performance of the system, it is far from being well understood. It is known that H_3PO_4 adsorbs at the Pt surface and negatively influences the kinetics of, especially, oxygen reduction reaction. Recently it was confirmed that H_3PO_4 is, under conditions of HT PEM FC operation, reduced by H_2 at the surface of anode Pt catalyst yielding compounds such as H_3PO_3. In this context, we previously investigated behaviour of H_3PO_3 in diluted acidic solutions at ambient temperatures and found that it strongly adsorbs at the Pt surface and that extent of the adsorption increases with increasing temperature. It was also confirmed that H_3PO_3 can, at potentials present at the HT PEM FC cathode Pt catalyst surface, easily reoxidise to H_3PO_4 [1, 2].

Aim of the present work was to extend our degree of understanding of H_3PO_3-H_3PO_4-Pt system behaviour in more concentrated H_3PO_4 solutions. This is more relevant for the HT PEM FC operation. In particular, we have investigated concentration and temperature range of 0.5-10 M H_3PO_4 and 25-75 °C, respectively. A combination of cyclic voltammetry and electrochemical impedance spectroscopy was used during the experiments. These results suggest that there is competition between H_3PO_4 and H_3PO_3 for Pt surface. The system is very complex and novel approaches has to be utilised in order to elucidate it into more details.

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Cubes, Spheres and Octahedrons of Cu_2O Deposited on TiO_2NT/PDA Electrodes: Influence of Morphology on the Conversion of CO_2 to Methanol by Photoelectrocatalysis

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The production of solar fuels is the most efficient way to use, storage and transport the solar energy, with high energy density and cost-effectiveness [1,2]. CO_2 recycling via artificial photosynthesis enables the efficient introduction of this renewable energy in the production chain, which in a long term can become a key element of sustainable carbon-resource management, thus helping to slowly lessen our consumption of fossil fuels [1]. With remarkable advances in the last decades, photoelectrocatalysis techniques have proven to be viable alternatives for CO_2 conversion to formic acid, methane, methanol [3] and ethanol [4]. To increase the conversion yield of CO_2 to methanol is imperative: i) the generation of sufficient electron–hole pairs, ii) with efficiently separation of charges, and iii) active catalytic sites in semiconductor, as well as iv) to increase the absorption ability of semiconductor in the solar spectrum [5]. Thus, the comprehension of the morphological properties of catalyst and co-catalyst onto to the semiconductor materials can ensure its effective application. This paper presents a study concerning the influence of morphology on reactivity of Cu_2O nanoparticles (cube, NcCu_2O; sphere, NsCu_2O and octahedron, NoCu_2O) applied for the photoelectrocatalytic conversion of CO_2, in TiO_2NT electrodes functionalized with polydopamine (PDA). The photoelectrocatalytic experiments were performed in low bias potential (+0.2 V), using 0.1 mol L^{-1} of Na_2SO_2 electrolyte saturated with CO_2 (pH 4.5) in closed system (1 kgf cm^{-2}) for 2 h. The system was irradiated by either UV-Vis irradiation or solar simulator. The characterization of the electrodes, performed by MEV-FEG, Infra-Red, Diffuse Reflectance Spectroscopy and XRD techniques, demonstrated that: PDA promotes a good adhesion of nanostructures with improved CO_2 adsorption, and the Cu_2O nanostructures deposited on the NtTiO_2/PDA led to different values of band gap energy: 2.50 eV (NcCu_2O), 2.55 eV (NeCu_2O) and 2.60 eV (NoCu_2O). In addition, besides a good photocurrent response, all the modified electrodes also presented good reproducibility. In photoelectrocatalytic experiments it was observed that the electrodes presented a significant performance in the conversion of CO_2 to methanol: 10 ppm (NcCu_2O), 6.0 ppm (NcCu_2O) and 5.4 ppm (NsCu_2O) under UV-Vis radiation, and 3.8 ppm (NcCu_2O), 1.7 ppm (NcCu_2O) and 1.3 ppm (NsCu_2O) under solar simulator. Therefore, the following order of reactivity could be established during the photoelectrocatalytic process: NsCu_2O <NoCu_2O <NcCu_2O. The results obtained showed that both the optical properties and the photocatalytic performance of these nanostructures are facet-dependent, that is, they are closely related to the morphological properties. Therefore, the synthesis of particles with controlled morphology is an extremely important issue for the effective application of these materials as photocatalysts. It is important to highlight that the use of PDA is a good strategy to obtain p-n heterojunction semiconductors without affecting the morphological properties of the nanoparticles deposited, besides promoting the improvement of its response in visible light region. The photoelectrocatalysis technique performed with TiO_2NT/PDA electrodes modified with Cu_2O nanoparticles is a promising alternative for converting CO_2 into value-added compounds.

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New Perspectives for Electrodialytic Remediation

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Electrodialytic remediation has been widely used for the recovery of different contaminants from numerous matrices, such as, for example, polluted soils, wastewater sludge, fly ash, mine tailing or harbour sediments. The electrodialytic remediation is an enhancement of the electrokinetic remediation technique, and it consists of the use of ion-exchange membranes for the control of the acid and the alkaline fronts generated in the electrochemical processes. While the standard electrodialytic cell is usually built with three-compartment configuration, it has been shown that for the remediation of matrices that require acid environment, a two compartment cell has given satisfactory removal efficiencies with reduced energy costs.

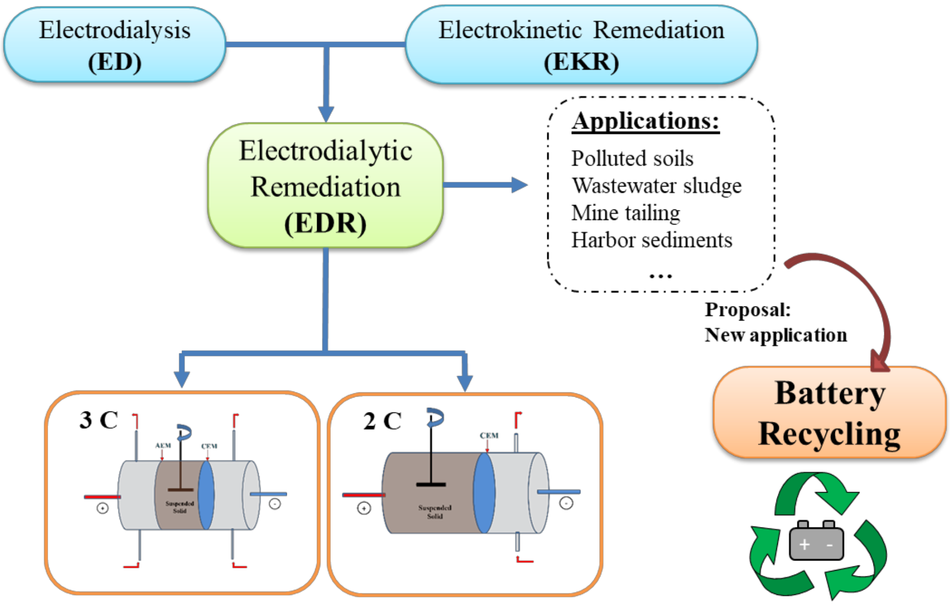

Figure: Overview of electrodialytic treatments and battery recycling perspectives.

Recycling secondary batteries, with growing demand, has an increasing economic and environmental interest. This work focusses on the proposal of the electrodialytic remediation technique as a possible application for the recycling of lithium-ion cells and other secondary batteries. The recovery of valuable components, such as lithium, manganese, cobalt of phosphorous, based on current recycling processes and the characterization of solid waste is addressed.

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Influence of Preparation Procedure and Activation Protocol on the Performance of Catalyst Coated Membrane Fuel Cell Assembly

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Low-temperature fuel cell with proton-exchange membrane (LT PEM FC) is a leading type of hydrogen-operating FC family. Moderate operating temperature, high specific current densities and reasonable lifetime of unit are key advantages that make this fuel cell type viable for widespread implementation in the fields of transportation and delocalised electricity supply. It utilizes Pt nanoparticle catalyst on both electrodes and perfluorinated sulfonated membranes as PEM.

One of the challenges before large-scale production of LT PEM FC is deposition of catalytic layer on gas-diffusion support/membrane interface. Homogeneity of Pt nanoparticle distribution in catalytic layer and, mainly, three-phase contact between Pt, carbon support and proton-exchange medium are critical for fuel cell performance. Easily scaled, reproducible method of membrane-electrode assembly preparation leading to viable fuel cell performance is therefore of utmost importance.

In principal, two main methods of membrane-electrode assembly preparation are possible: (*i*) preparation of gas-diffusion electrodes and subsequent (hot) pressing of electrodes to membrane (CCE) or (*ii*) direct deposition of catalytic layer onto the membrane (CCM).

Principal advantage of CCE is well defined loading of catalyst and significantly lower stress on membrane during membrane-electrode assembly fabrication in comparison with CCM. However, contact of catalytic layer on gas-diffusion electrodes with membrane is, in the best case, not ideal. That can be partly solved by hot pressing, though membrane can undergo irreversible changes during the process, including perforation. CCM, on the other hand, provides very good contact of catalytic layer with membrane. Still, preparation of CCM is far from standardization and faces many challenges, connected mainly with repeated drying and humidification of membrane. During catalyst layer deposition, membrane has to be heated and its drying takes place. After deposition, humidification during membrane-electrode assembly activation can lead to changes in membrane morphology and subsequently, to defects in catalytic layer.

The goal of this work is to optimize preparation of CCM in terms of temperature of catalytic layer deposition and catalytic ink composition. Deposition was performed using catalytic ink, consisting of commercial catalyst, solvents and ion-exchange binder, by ultrasonic sputtering in combination with fully automatized CNC unit. In-house prepared CCM membrane-electrode assemblies were fabricated and tested in LT PEM FC single cell. Activation of membrane-electrode assemblies was performed either inside the fuel cell or by immersing of CCM in hot water and these two approaches were compared. Performance of experimental FCs was investigated by means of U-I curves and electrochemical impedance spectroscopy. Evaluation of results enabled optimization of CCM preparation method, resulting in reasonable reproducibility of catalyst layer deposition and FC performance.

The work was supported from European Regional Development Fund-Project "Fuel Cells with Low Platinum Content" (No. CZ.02.1.01/0.0/0.0/16_025/0007414).

Influence of anodization time on the formation of iron oxide nanostructures

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Today, most of the electrical demand in the entire world is supplied by fossil fuels. However, fossil fuels are limited sources and they are detrimental for the environment, contributing to the global climate change. In this way, renewable energy sources are investigated as an alternative to fossil fuels. In particular, the production of hydrogen by photoelectrochemical water splitting using solar energy is one of the most attractive options. Different metal oxides in its nanostructured form have been studied to be used in the photoelectrochemical process as photoanodes. Among them, iron oxide is one of the best options since its band gap (2.1 eV) absorbs in the visible region of the solar spectrum, which means that its theoretical solar-to-energy efficiency is about 15 %. Furthermore, it is a non toxic, abundant, environmentally friendly and chemically stable material.

In this work, electrochemical anodization of iron at different times (5, 10, 15, 30 and 60 min) was performed in order to study its influence on the nanostructures properties. Nanostructures were characterized by different structural techniques such as Field Emission Scanning Electron Microscopy and Laser Confocal Microscopy with Raman Spectroscopy, to see its morphological and crystallinity evolution with the different anodization times. Also electrochemical and photoelectrochemical characterization was performed by means of Mott-Schottky analysis and Electrochemical Impedance Spectroscopy. Finally, nanostructures were tested in water splitting experiments to check its viability as photocatalysts for the production of hydrogen. Results revealed that samples anodized for 10 min and with an electrode rotation speed of 1000 rpm were the most suitable for photoelectrochemical water splitting.

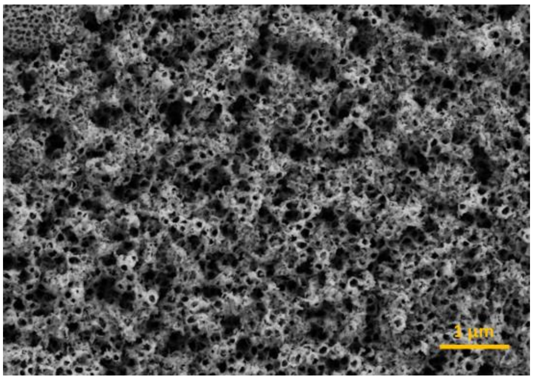

Figure 1. Field Emission Scanning Electron Microscopy image of the nanostructure synthesized by electrochemical anodization for 10 min under hydrodynamic conditions.

Acknowledgements
The authors would like to express their gratitude for the financial support granted by the Ministerio de Economía y Competitividad (Reference: BES-2014-068713 and Project CTQ2016-79203-R), for its help in the Laser Raman Microscope acquisition (UPOV08-3E-012) and for the co-finance by the European Social Fund.

Photodegradation of the antibiotic sulfamethazine for animal use present in water using WO_3 nanostructures anodized under hydrodynamic conditions

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1. Introduction. Tungsten trioxide (WO_3) can be used as a photocatalyst in environmental applications because it is an n-type semiconductor with a band gap of 2.6-2.8 eV and an appropriate band position. The aim of the present work was the decontamination of antibiotic sulfamethazine (SMT) for animal use present in water by WO_3 nanostructures in the presence of radiation. It was studied the influence of the pH in the SMT solution and the combined influence of the temperature and the doping with nitrogen during the annealing of the WO_3 nanostructures.

2. Experimental procedure. The anodization of W was performed in a 2-electrode cell with a rotating disk electrode (RDE) configuration. W was anodized in a 1.5 M sulfuric acid (H_2SO_4) + 0.1 M sodium fluoride (NaF) solution at 20 V for 4 h under hydrodynamic conditions of 375 rpm. The as-formed WO_3 layers were annealed in a furnace for 3 h at 400 ºC and 600 ºC in air atmosphere and at 600 ºC in N_2 gas atmosphere. The photodegradation tests were performed in a 3-electrode cell with the WO_3 nanostructure as working electrode using an electromagnetic radiation of 420 nm. Antibiotic SMT was used as organic pollutant, with an initial concentration of 30 mg/L at neutral pH and pH 3. The degradation of SMT was controlled by the ultraviolet-visible molecular absorption spectrophotometer, taking measurements of absorbance during the time of the test.

3. Results and Discussion. Figure 1 shows the effect of the pH on the degradation of SMT. It is remarkable that an increase of the degradation is associated to a decrease of the pH in the SMT solution. Figure 2 shows the effect of the annealing temperature and the doping with nitrogen of the WO_3 nanostructures on the degradation of SMT at pH 3. It is observed that an increase of the annealing temperature enhances the degradation of SMT. On the other hand the doping with nitrogen of the WO_3 nanostructures produces higher degradation of SMT.

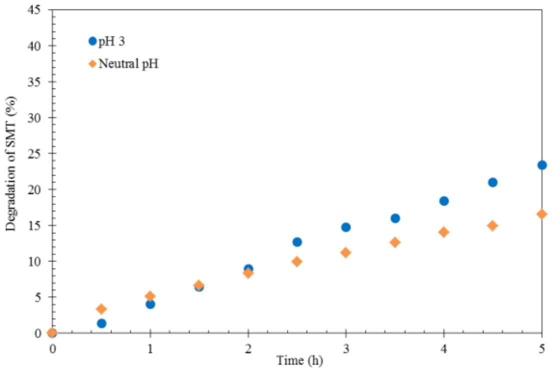

Figure 1. Effect of the pH on the degradation of 30 mg/L SMT with WO_3 nanostructures anodized at 375 rpm and annealing at 400 ºC in air atmosphere.

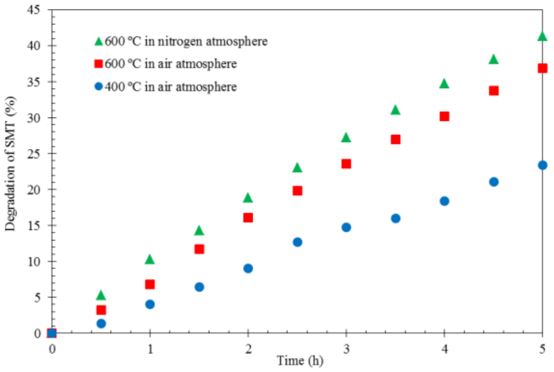

Figure 2. Effect of the annealing temperature and the doping with nitrogen on the degradation of 30 mg/L SMT at pH 3 with WO_3 nanostructures anodized at 375 rpm.

4. Conclusions. The decrease of the pH in the SMT solution enhances the degradation of SMT. The increase of the temperature and the doping with nitrogen during the annealing of the WO_3 nanostructures implies higher degradation of SMT.

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BIOELECTROCHEMICAL SYSTEMS FOR THE DECHLORINATION OF 2,4-DCP

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The use of organochlorinated pesticides and herbicides to enhance the production of crops may produce soil and groundwater pollution, some of them with bio-refractory properties. 2,4-dichlorophenol (2,4-DCP) is one of these compounds mainly used as precursor of 2,4-dichlorophenoxyacetic acid (2,4-D), a commercial and widely used herbicide. Several techniques have been investigated to eliminate these hazardous compounds, either chemical, biological, electrochemical or bioelectrochemical. The previous dechlorination of chlorophenols has the advantage that the resultant by-products are less toxic and less bio-refractory, so a conventional biodegradation process may be set after the dehalogenation process, in order to mineralize entirely the resultant organics. In this work, it is studied an alternative treatment of 2,4-DCP in bioelectrochemical systems (Wen et al., 2013) (both by Microbial Fuel Cell and Microbial Electrolysis Cell systems) dehalogenating such molecule at the abiotic cathode of bioelectrochemical systems (Figure 1).

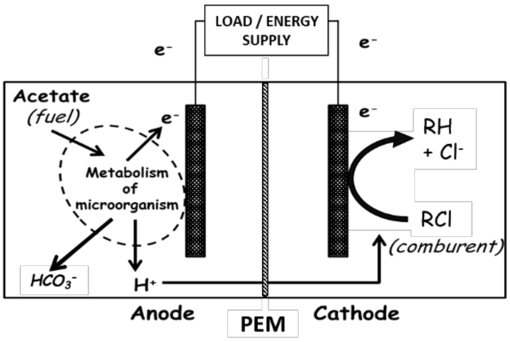

Figure 1. Conceptual description of the BES for R-Cl dechlorination.

The enrichment procedure and isolation of the electrogenic consortium in the anode was started with activated sludge from the wastewater treatment plant of Ciudad Real, Spain, with 1 g/L of sodium acetate. The catholyte contained 300 ppm of 2,4-DCP and supporting electrolyte. The anode electrode was carbon felt and the cathode was carbon cloth.

Various conditions and variables were set in order to optimize the dechlorination of the molecule. It was operated at two different pHs at the catholyte: pH 5 and pH 7. Moreover, it was studied the effect of the catalyst load (Pt) at the cathode and the operation of the BESs.

Our preliminary results indicate that the catalyst decrease the cathodic overpotential for the dechlorination of 2,4-DCP improving the efficiency. Moreover, a lower pH has been proven to favor the dehalogenation of the aromatic ring regarding the cathodic half-reaction.

The dechlorination process in our BESs is expected to be thermodynamically more favorable and more environmentally friendly compared to pure electrochemical dehalogenation systems.

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Design of doped TiO_2 nanotubes for photoelectrochemical water splitting

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Nowadays, there is an urgent need to stop using fossil fuels since they are not renewable and they are responsible for the global warming. For this reason, new renewable energy sources should be used such as solar, wind and hydro power. In this way, hydrogen is a fuel which can be formed by photoelectrochemical water splitting with solar light using a photocatalyst. Among all transition metal oxides, TiO_2 is one of the most widely used photocatalyst due to its high stability and semiconductor abilities capable of generating charge by absorbing energy. In order to achieve a high surface area and consequently, to enhance the photocatalytic activity, TiO_2 is synthesized in the form of nanotube structures. Electrochemical anodization under hydrodynamic conditions allows creating new and tailored nanostrcutures which are formed directly back-contact to the titanium substrate. On the other hand, the efficiency of TiO_2 nanotubes is limited by its wide intrinsic band gap of ≈ 3.2 eV for TiO_2 in anatase phase. Therefore, the usable fraction of the solar spectrum which can be exploited is only 5%. This is the reason why the process of inserting impurities (doping) in the TiO_2 nanotubes is becoming more and more used for the purpose of modulating their electrical properties, in order to increase their efficiency.

To overcome these drawbacks, this study is focused on TiO_2 nanotubes doped with argon and nitrogen. TiO_2 nanotubes were synthetized by electrochemical anodization at different hydrodynamic conditions (0, 2500 and 5000 rpm) in ethylene glycol based electrolytes imposing a potential difference of 55V. Field Emission Scanning Electron Microscope (FE-SEM) and Raman Confocal Laser Microscopy were used to characterize the nanostructures. Additionally electrochemical techniques such as Incident Photon to Current Efficiency (IPCE) and photoelectrochemical water splitting tests for hydrogen production have been also used.

The results show that TiO_2 nanostructures doped with argon and nitrogen present better response in terms of photoelectrochemical water splitting for hydrogen production.

Acknowledgements: Authors thank to the financial support to the Ministerio de Economía y Competitividad (project code: CTQ2016-79203-R), for the co-finance by the European Social Fund and for its help in the Laser Raman Confocal Microscope acquisition (UPOV08-3E-012).

A membrane-less electrolyzer for H_2 production: towards a new concept of alcohol electrochemical reforming

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The increasing demand of worldwide energy joint to the environmental problems encourages the development of clean and renewable energy such as hydrogen. Water electrolysis is the most stablished technology to produce pure and free carbonaceous hydrogen in a single step, although it requires high cell voltages which mean high energy consumption [1]. In the latest years, alcohol electrochemical reforming has become an attractive alternative due to the high energy contained in these fuels.

The conventional electrochemical reforming studies typically include a membrane electrode assembly (MEA) configuration which separates the anodic compartment from the cathodic one [2]. The membrane is the critical component of the electrochemical reformer limiting the cell life-time and also attaining its high cost. Drying, cracking and other mechanical problems are the most common early life failures [3]. In order to contribute for the practical application of this technology, in this work a new concept of alcohol electrochemical reforming was developed, using a membrane-less electrolyzer configuration, i.e., where the anode and the cathode are in a single chamber configuration.

In this study, Pd supported on carbon Vulcan and Pt on carbon black (20% Pd/C, 20% Pt/C; Alfa Aesar) were used as the anodic and cathodic catalysts respectively. Both catalysts were mixed with a Nafion and isopropanol solution and were sprayed on Carbon Paper (Fuel Cell Earth). The metal loading was 1 $mg\cdot cm^{-2}$ for each electrode. A wide variety of experimental tests were carried out in an electrolysis cell (Figure 1 a)) in order to study the viability of the new system (Figure 1 b) is shown as an example).

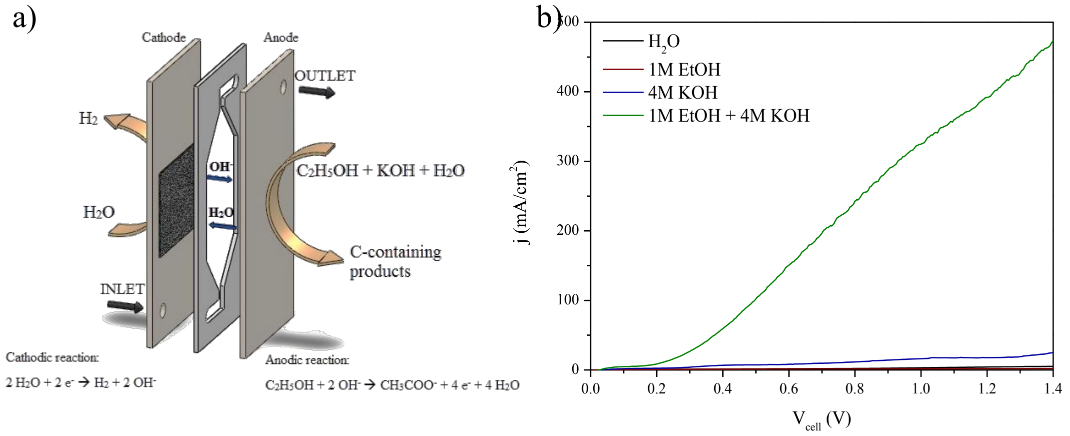

Figure 1. a) Membrane-less system scheme, b) Polarization curves. Scan rate = 5 $mV\cdot s^{-1}$. T = 85 ºC.

Linear sweep voltammetry measurements in a 0-1.4 V range proved that current densities obtained with a 1 M ethanol + 4 M KOH solution were due to the alcohol electrochemical reforming since no current was detected when water, ethanol solution or KOH solution were fed to the cell. Separate GC-gas analysis demonstrated that pure hydrogen were obtained under all explored reaction conditions on the simplified membrane-less configuration. These results corroborated that alcohol electro-oxidation occurred at cell potentials lower than water electrolysis reducing the energy consumption to values below 25 $kWh\cdot kg_{H2}^{-1}$, showing the interest of this technology.

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Algorithm for Assessing the Convergence of a Cyclic Voltammetry to its Limit Cycle

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Keywords: Algorithm, Automated measurements, Convergence assessment, Cyclic voltammetry, Limit Cycle.

Cyclic voltammetry is one of today's standard electrochemical measurement techniques. It has been, and continues to be, extensively used in a broad range of different fields. As in other voltammetric methods, in cyclic potentiostatic voltammetry a time-dependent potential is applied to a working electrode, while the current flowing through the electrochemical cell is monitored. In general, in this kind of measurements, the system tends to a stationary state, which is known as limit cycle. The common practice for assessing the voltammogram convergence is to perform a multicycle cyclic voltammetry, and visually compare the sequential cycles in order to see if there are significant changes from one cycle to the following one. The main limitation of visual comparison is its limited accuracy and its dependence on the analyst's subjectivity. In this work, an algorithm for quantitatively assessing the convergence of experimental cyclic voltammograms (CVs) was developed.

Two types of cyclic voltammetries can be identified:

- Type I CV: The list of applied potentials is the same from cycle to cycle.
- Type II CV: The list of applied potentials changes from cycle to cycle.

The developed algorithm is based in two convergence indicators: a cycle-to-cycle convergence indicator and a long term convergence indicator. The algorithm was successfully validated experimentally using two systems, one that generated type I CVs and the other one that generated type II CVs. Both systems consisted in a conventional 3-electrode thermostatted electrochemical cell, with a commercial Pt ring electrode as counter-electrode, and a commercial Ag/AgCl (3M KCl) electrode as reference electrode. In the first system, the working electrode was a mirror polished Pt electrode; whereas in the second system, the working electrode was a Sb-doped SnO_2 ceramic electrode. The particularity of these ceramic electrodes, from a cyclic voltammetry perspective, is that they cannot withstand cathodic polarization, since this type of polarization would irreversibly reduce the tin oxide, producing permanent electrode damage. In both cases, the algorithm was able to determine whether the CV converged to its limit cycle, and when (i.e. at which cycle) it converged. Moreover, the algorithm is able to quantify the measurement noise (i.e. how much the CV changes just because of the measurement error).

The first advantage of using the developed algorithm with respect to the visual inspection method, is that the algorithm is an objective and quantitative method, whereas visual inspection is subjective: the algorithm allows to determine at which cycle convergence has been achieved according to a certain numeric convergence criterion, while this is much more difficult using the visual inspection method. However, this is only a minor advantage. The definitive advantage of the algorithm over the visual inspection method arises from its low computational cost. The execution time of the algorithm is low enough in order to execute it in real time during the cyclic voltammetry measurement. In this way, it can be used in order to decide when to stop cycling: rather than selecting the number of cycles as in traditional cyclic voltammetry, convergence criteria would be selected. Some of these criteria could be: limit in the convergence indicators and number of cycles below the limit, maximum number of cycles, etc…. Then, the measurement software would cycle until the convergence criteria are met. In this way, the measurement could be completely automated, and would not require the intervention of the operator at any point. This could be extremely useful in some cases, as overnight measurements.

Acknowledgments
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A Hierarchical Porous Carbon Structure with Ru Catalysis as Multifunctional Cathode for Li-O_2 Battery

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Because of their extraordinary theoretical energy density, lithium oxygen (Li-O_2) battery is attractive for next generation battery system which is able to substitute natural resource. However, they have several critical problems which are poor rate capability, low energy efficiency and poor cycle life. To overcome these drawback, we synthesized unique porous carbon structure for oxygen electrode called triple hierarchical porous carbon sphere (THPC). Unlike common porous carbon material, THPC containing all types pore has multifunctional advantage like (i) micro pore can provide channels for oxygen without interruption by accumulated discharge product (Li_2O_2), (ii) meso pore can control the size of the discharge product, (iii) macro pore can facilitate transporting the electrolyte. Therefore, THPC exhibit superior electrochemical results compared to a typical carbon black cathode. In addition, to further promote Li2O2 formation/decomposition, THPC was decorated by Ru nanoparticle by hydrothermal method. The synergic effect of Ru-THPC from the THPC structure and Ru catalytic property increases the capacity and rate capability with lower over-potential. The effectiveness of the Ru was evidently observed by the formation of uniformly sized toroidal-shaped discharge product (Li2O2) which has positive influence on charge performance.

Investigation of Oxygen Reduction Reaction on Platinized Platinum Electrodes

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Rotating disk electrode (RDE) and cyclic voltammetric measurements were carried out over various Pt/Pt electrodes in 0.5 mol dm^{-3} H_2SO_4 electrolytes to investigate the effect of the parameters of platinum deposition on the electrocatalytic activity of the deposit in oxygen reduction reaction (ORR). Different galvanostatic platinization methods were achieved by using chloroplatinic acid solution with different Pt, Cl ions concentrations, current densities [1] or adding a few percent of Pb^{2+} ions to the platinization solution. Electrooxidation behavior of deposited hydrogen in cyclic voltammetry over various Pt/Pt electrodes, as a surface sensitive method, has been used to find a correlation between surface properties and ORR activities. Additionally, the ratio of electrooxidation peaks attributable to the amount of hydrogen adsorbed over different Pt facets (P1/P2) has been calculated as well. These variables have been correlated with Oxygen reduction activity. ORR activity was characterized by acquiring the kinetic data like kinetic currents, Tafel slopes and overpotential values of the different Pt/Pt electrodes. It was found that changing the parameters of the platinum deposition methods has an influence on the electrocatalytic activity of the deposit for ORR. Yet, the presence of Pb^{2+} ions in the platinizing solution has a significant effect on the electrocatalytic activity in ORR of the Pt deposit. It is demonstrated by Fig(1) that Pt/Pt electrode with R^* = 20 prepared from lead-containing solution is more active (smaller overpotential) comparing to a four-fold larger one (R = 88) deposited from the same solution but without lead.

*R: Roughness factor has the usual meaning: R = electrochemical active surface area (calculated from the hydrogen adsorption capacity)/ geometric surface area.

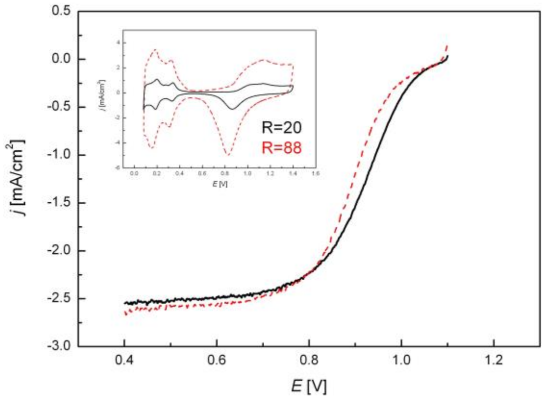

Fig. 1. Effect of Pb^{2+} ion content of platinizing solution on the electrocatalytic activity in the ORR of the Pt deposit. ORR of Pt/Pt electrodes from Pb^{2+} containing (—) and Pb^{2+} free (----) platinization solution at 5mV/s with 625 rpm in 0.5 mol dm^{-3} H_2SO_4; Inserted: cyclic voltammetry of the corresponding electrodes in oxygen-free 0.5 mol dm^{-3} H_2SO_4 at 50 mV/s.

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Electrochemical Promotion of Propylene Combustion over Ag Nanoparticles

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Electrochemical Promotion of Catalysis (EPOC) is an innovative concept for boosting catalytic processes in a reversible and controlled manner [1]. The EPOC phenomenon takes place in fuel-cell type reactors where the catalytic coating is an electrode supported on a dense ionically conducting ceramic material (solid electrolyte). The main technological issue of EPOC is related with the use of continuous metallic coatings deposited on dense solid electrolyte supports. On account of that, the metallic dispersion of the catalyst-electrodes, and therefore their catalytic activity, is usually far lower than that of commercial dispersed catalysts. During the last years, some studies were focused on the quest of electropromoted nanoparticles (NPs). For instance, we found that under small positive polarizations (few µW cm^{-2}), O^{2-} ions supplied from the electrolyte can strongly improve the catalytic performance of Pt and Pd NPs dispersed in a Mixed Electronic and Ionic Conducting (MIEC) porous layer for propane and methane deep oxidation, respectively [2-4]. This study reports, for the first time, the possibility to electropromote Ag NPs dispersed in a MIEC electrode. Ag is an abundant and cheaper metal compared with Platinum Group Metals. The electrochemical promotion of propylene combustion has been carried out on Ag-LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$)/YSZ catalysts for various Ag loadings and microstructures of the LSCF layers (thickness, porosity).

A perovskite powder of LSCF, a MIEC oxide, was prepared by the Pechini method. This powder was spin-coated on Yttria-Stabilized Zirconia (YSZ) dense membranes to achieve porous and 5 – 15 µm thick coatings. The microstructure of LSCF deposited layers were modified by changing heat treatment protocol and suspension recipe. A solution of silver nitrate was then infiltrated and reduced in H_2 at 300°C to obtain different loadings (1 - 5 wt.%) of metallic Ag NPs into the porosity of the LSCF layers. Catalytic and electrochemical properties of these Ag-LSCF/YSZ catalysts were investigated at 300°C in both stoichiometric and oxidizing conditions. A typical transient curve is depicted on Figure 1. Small positive currents slightly increase the catalytic performances of Ag NPs with apparent Faradaic efficiency up to 12. We observed a two-step enhancement of the alkene conversion with time : a first small rapid increase when the current is applied that may correspond to the electrochemical promotion of Ag NPs at the YSZ/LSCF interface and a much more pronounced second one after around 1 h. These two waves EPOC behavior has been already observed with Pt nanoparticles dispersed in a LSCF/GDC layer [2] upon positive currents and were attributed to the low ionic conductivity of LSCF at 300°C and then to the slow diffusion of oxygen ionic species through the LSCF layer. Cyclic voltammetry was used to investigate the redox and electrochemical properties of the different Ag-LSCF/YSZ catalysts. The LSCF layer microstructure clearly acts on the rate-determining step of the oxygen electrode reaction and then on the EPOC magnitude. This study demonstrates that the electrochemical promotion of propylene oxidation is possible at low temperature using Ag NPs dispersed in a MIEC porous electrode.

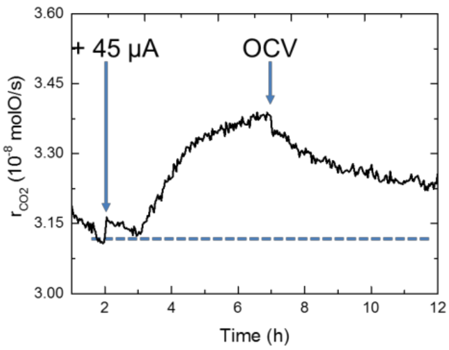

Figure 1 : Impact of a positive current of + 45 µA on the CO_2 production rate at 305°C. 2 wt.% Ag. C_3H_6/O_2 : 1000 ppm / 5000 ppm.

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Anodic Oxidation of Benzotriazole: Effects of Sulphate on Chlorinated Byproducts Formation on Chloride Electrolyte

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Abstract: In recent years Benzotriazole (BTA, $C_6H_5N_3$) has been detected in European waterbodies with a high concentration which raises the awareness to develop removal methods [1]. Within various technologies, electrochemical oxidation (EO) could be an effective BTA removal technology since the BTA is hard to degrade biologically[2]. This study investigated the anodic oxidation of BTA using a boron-doped diamond (BDD) anode in NaCl, Na_2SO_4, and (NaCl+Na_2SO_4) mixed electrolytes in a single compartment flat cell in batch recirculation mode. Initially, BTA degradation efficiency and energy consumption in the different electrolytes were investigated. The roles of important oxidants such as hydroxyl radicals, sulphate radicals and active chlorine species in the system were studied. In addition, the BTA degradation intermediates were analyzed by LC-MS.

Experimental results show that BTA degradation efficiency was much higher in Na_2SO_4 and mixed electrolytes than in pure NaCl electrolytes. For instance, in Na_2SO_4 electrolytes and in mixed medium degradation efficiency reach >99% within 60 minutes of oxidation whereas in NaCl electrolytes it was only 60%. In the sulphate containing electrolytes, BTA degradation was dominated by hydroxyl and sulphate radicals whereas in chloride medium the reaction was chlorine species (ClO^-) dominated. The sulphate radicals have higher oxidation capability compared with hypochlorite, therefore, BTA degradation was faster in sulphate medium. The energy consumption was 0.8 kWh/g BTA in the Na_2SO_4 system which was nearly 10 times lower than in the chloride medium (7.93 kWh/g). LC-MS analysis indicated that a number of chlorinated intermediates were formed during BTA oxidation in NaCl electrolytes. For instance, mono chloro-benzotriazole, and dichloro-benzotriazole was detected in pure NaCl medium. The study shows that the number of chlorinated intermediates increased with increasing of the NaCl/Na_2SO_4 ratio. This phenomenon indicates that in presence of Na_2SO_4 medium most of the BTA was quickly oxidized and less exposed to the hypochlorite. For example in pure NaCl, 2:1 and 10:1 molar mixture of Na_2SO_4 and NaCl medium six, four and zero chlorinated compounds were detected respectively.

Considering higher degradation efficiency, low energy consumption and less chlorinated intermediates in the system, a sulphate rich electrolyte is suitable for anodic oxidation of Benzotriazole (BTA).

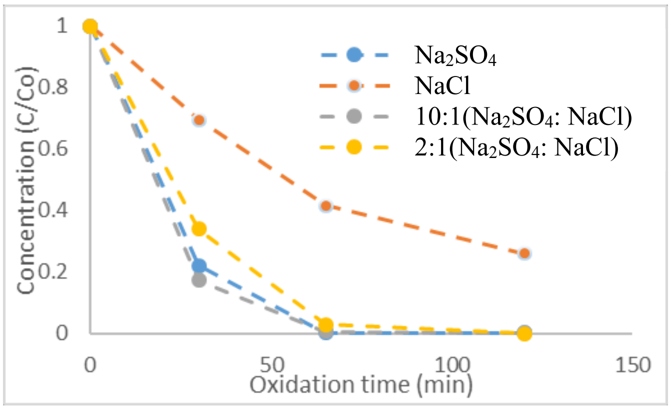

Figure: BTA oxidation on BDD anode in 0.1M NaCl; 64mM Na_2SO_4, mixed 10:1 (60mM Na_2SO_4 + 6mM NaCl) and mixed 2:1 (48mM Na_2SO_4 + 24mM NaCl) electrolytes (in all condition conductivity was 10mS/cm) at 4.3V (potential vs. Ag/AgCl) for 120 min, initial pH 5.6, [BTA]=10mg/L.

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Iron Fluorides Grown on Carbon Steel for Li-ion Battery Applications

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The Li-ion batteries sector plays one of the most important roles in the field of energy storage. The reaction mechanism in both electrodes, the anode and the cathode; involves insertion reactions. The cathode material and the electrical contact between active material and the current collector still represent the main limitation for the cell capacity increasing. Directly grown layers of the active material on the current collector decreases ohmic resistance and increases the available charge. This guarantees good electrical contact and, if the active material is able to work under conversion reactions, it is possible to increase the nominal capacitance respect to insertion reactions. The electrode material will reach all its entire range of oxidation states. Transition metal fluorides, such as FeF_3 are good candidates to the conversion reactions with lithium ions due to their high nominal capacity [1,2].

Direct formation of a fluoride based layer has been achieved by anodizing iron strips in ethylene glycol and NH_4F as electrolyte, resulting a highly nanoporous layer of a mixture of iron oxyhidroxifluorides [3]. Nevertheless, those fluoride layers were of poor electronic conductivity, which limits their performance as electroactive material. Recently, it was also demonstrated that using mild steel instead of iron as substrate material increases the electronic conductivity of these layers [4].

So, the present work focuses on developing a FeF_3 conversion layer on cheap carbon steel with the aim of decreasing costs and improving the electronic conductivity of the layers synthesized as in [3]. The results show that the carbon of the metallic matric incorporates to the conversion layer increasing its conductivity and improving its electrochemical properties.

Keywords: Li-ion batteries, electronic conductivity, iron fluorides

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Mechanism of the Electro-oxidation of Methyl Paraben on Mixed Metal Oxides Anode for Cl_2 Evolution

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Parabens are preservatives widely used in the pharmaceutical and cosmetic industries and their characteristics of endocrine disruption may be the cause of adverse effects on the environment and human health. These compounds are not completely removed from wastewater by the most common treatments and thus, they contribute to environmental contamination[1]. In this context, the electrochemical processes stand out due to their effectiveness in the treatment of many types of effluents. However, a better kinetic and mechanistic understanding as well as of the energetic parameters of the applied processes is important, in order to establish the characteristics of electro-oxidation systems of wastewater that lead to the expansion of its applications. Thus, this work focuses on the study and mechanistic proposal of the degradation of methyl paraben (MeP) by electrolysis on a mixed metal oxides anode. For that, a commercial $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode was used as anode and a Ti plate as cathode (both with 54.4 cm^2) in a recirculation batch system, for the treatment of 1.7 L of MeP solution (100 ppm) in 0.15 mol L^{-1} of NaCl. MeP was determined by HPLC (C18 column; mobile phase: ACN/H_2O 40/60) with a UV detector and total organic carbon (TOC) was quantified in a carbon analyzer. Intermediates were analyzed by liquid chromatography coupled to mass spectrometry (quadrupole/TOF). The variation of the applied current density (j_{app}), from 1.0 to 15 mA cm^{-2}, showed that MeP elimination follows *pseudo*-first order kinetics, removing 30% of MeP in the lowest j_{app} (after 2 hours) and 100% after 40 min with 15 mA cm^{-2}. However, only 30% of TOC was removed even at the highest j_{app}, probably due to the formation of intermediates more recalcitrant than the MeP. After 2 h of treatment, the initial clear solutions were turned into turbid solutions due to the presence of a yellow suspended solid, which was produced at the cathodic region. This solid was analyzed by infrared spectroscopy, showing characteristic transmittance bands of aromatic and aliphatic organochlorine compounds. Moreover, cyclic voltammetry of the cathode was carried out after different times of electrolysis, indicating that an oxidation product of MeP is reduced on the cathode. The presence of phenolic compounds and their oxidized forms in the same solution may result in their polimerization[2]. Thus, under the applied conditions, it seems that the yellow solid is a polymerization (or oligomerization) product, which justifies the low mineralization efficiency of the electrochemical process. In order to investigate the intermediates formed, electrolysis with 15 mA cm^{-2} was carried out during 4 h, in which 36% of mineralization was achieved. By the end of the process, no aromatic compounds were detected, which means that the remaining TOC is attributed only to aliphatic compounds. It was possible to identify 6 aromatic compounds, for which a mechanistic proposal for the oxidation of MeP is based on. Initially, MeP is hydrolyzed to its precursor *p*-hydroxybenzoic acid (P1). P1 can follow $^{\bullet}OH$ addition or chlorination, resulting in the products named as P2 and P3, respectively. Different from the expected[3,4], those intermediates are combined through oxidative coupling at the *ortho* position, producing compounds with higher molecular weight. Thus, at this point, three main pathways may take place, by the recombination of P1 with P2, P2 with P2, and P3 with P2 (organochlorine route). Next, the coupling products follow steps of decarboxylation, hydrolysis and aromatic ring rupture, resulting in the aromatic products identified by mass spectrometry. After this point, as mentioned, the remaining organic matter is ascribed to aliphatic compounds, thus it is expected that the rupture of benzenic rings takes place, producing several aliphatic carboxylic acids until partial mineralization is reached[3–5]. This oligomerization pathway was not expected, considering the oxidation routes of MeP reported for BDD anodes[3,4]. However, it explains the low mineralization efficiency of the process and agrees with the formation of the solid product observed. These results remark the importance of the anode selection and account for possible unwanted outcomes when the electrochemical process is applied for wastewater treatment.

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Influence of the support of Pd anodic catalyst for the electrochemical reforming of ethanol in alkaline media

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In the last years, hydrogen could be considered as one of the most promising energetic carrier to provide a clean, reliable and sustainable energy. Nowadays, the electrochemical reforming of water-alcohols mixtures (or electrolysis) is a very interesting method for hydrogen production, since it allows a production of pure hydrogen in a single reaction/separation step, using an anionic exchange membrane (AEM) electrochemical cell. This technique needs lower energy requirements in comparison with conventional water electrolysis, since an organic molecule provides part of the energy [1, 2].

In this work, different anodic catalysts were synthesized based on Pd 20% of total metal loading, supported on different carbonaceous supports such as functionalized low-density nanofibers, graphene flakes and commercial non-functionalized low-density nanofibers. Physicochemical and electrochemical characterization of the synthetized catalyst was performed by means of N_2 adsorption/desorption, XRD, electrochemical active surface area (ECSA) and ethanol electro-oxidation activity.

Pd supported on non-functionalized low-density nanofibers (CNF LS) showed the highest electro-catalytic activity, which was attributed to the combination of different properties such as a high BET specific surface area and ECSA values. Thus, this anodic catalyst was chosen for the development of a different Membrane Electrode Assembly (MEA) using two anionic exchange membrane: Tokuyama and PBI membrane, in order to determine the viability of this kind of membranes in the electrochemical reforming of ethanol in alkaline media. Figure 1 shows the influence of the temperature in the MEA systems, integrated by Pd/CNF LS and Pt/C (anodic and cathodic catalyst, respectively) and Tokuyama (left) or PBI (right) membranes. As shown, the system with Tokuyama membrane provides a higher electro-catalytic activity in comparison with PBI membrane system, leading to energy consumption values below 30 $kWh\cdot kg_{H2}^{-1}$. In addition, in view of its practical application for the renewable hydrogen production from electrochemical reforming of ethanol in alkaline media, studies of the stability of the system in mild-term performance and impedances tests (not shown here) were also performed. The obtained results show the potential of using Carbon Nanofibers as anodic catalyst supports with a Tokuyama membrane as an alternative to commercial materials.

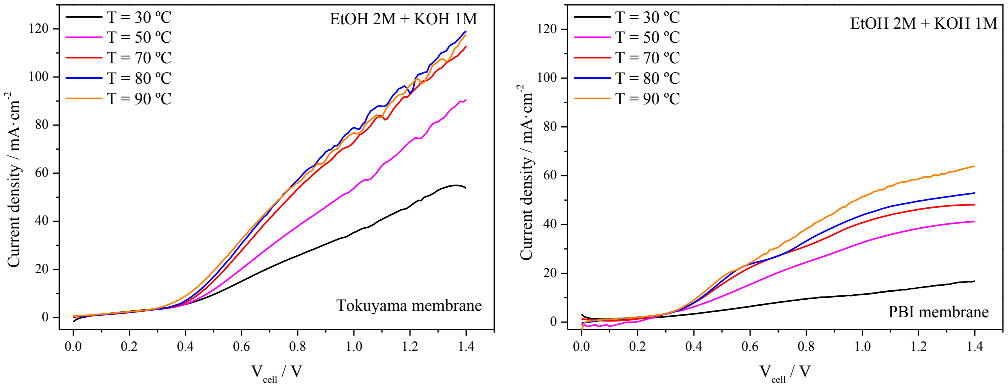

Figure 1. Influence of the temperature on the polarization curves for Pd/CNF LS and Pt/C, as anodic and cathodic catalysts respectively, and Tokuyama (Left) or PBI (Right) membrane. Conditions: Anode chamber (2 mol·L^{-1} ethanol and 1 mol·L^{-1} KOH) and cathode chamber (1 mol·L^{-1} KOH). Scan rate 5 mV·s^{-1}.

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Detection of pesticides by Electrochemical Surface-Enhanced Raman Spectroscopy (EC-SERS).

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Over the last years, the development of new procedures has allowed the improvement of Raman spectroelectrochemical features. An interesting methodology consists of the combination of electrochemistry and Surface-Enhanced Raman Scattering (SERS) effect. Enhancement of the Raman signal displayed by Electrochemical Surface-Enhanced Raman Scattering (EC-SERS) is associated with two phenomena: (1) the interaction of the species with the electrode surface is potential-dependent and certain potentials increase the analyte adsorption on the electrode surface, and (2) the in-situ generation of fresh nanofeatures with SERS properties in presence of analyte.

Detection of pesticides in food is an essential safety issue for protecting human health. Currently, there is a clear demand in the development of new and easy methodologies for quick and sensitive detection of pesticides residues. The utility of EC-SERS in this field has been demonstrated by the detection of different pesticides as for example imidacloprid (Figure 1) by EC-SERS. In this case, the employed procedure consists of the in-situ generation of metal nanoparticles and pesticide detection in a unique experiment. Hence, EC-SERS allows the fast and simple detection of pesticides, opening new gates for future application in this field.

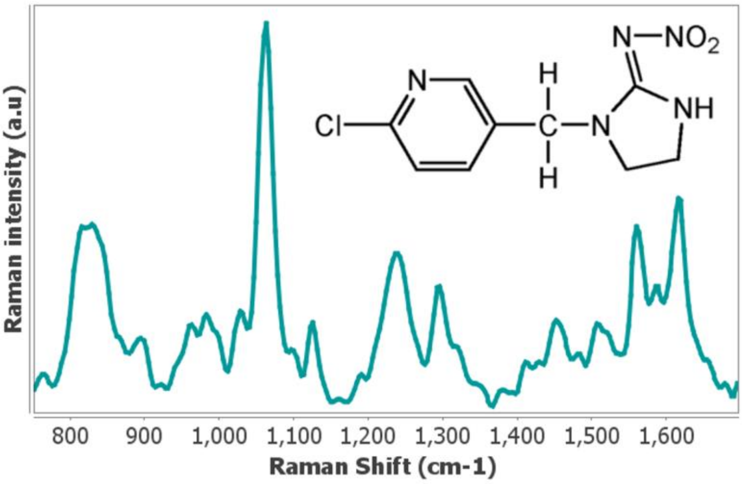

Figure 1. Raman spectrum of imidacloprid obtained by EC-SERS.

Fabrication of porous nickel photocathodes by selective corrosion of copper in Cu/Ni electrodeposits

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Highly porous metals have attracted considerable interest in wide range of applications such as catalysis, fuel cells and electrochemical capacitors, thanks to their large specific surface area and light weight. Porous nickel is a potentially low-cost alternative to precious-metal catalysts: Ni-based materials have been studied for its application in electrochemical capacitors, photovoltaic devices and water splitting, owing to their excellent properties, such as chemical stability, earth abundance and excellent electrochemical properties.

In this work nickel (Ni) nanoporous photocathodes have been prepared by selective electrochemical dissolution of copper (Cu) from Ni-Cu deposits. The anodic dissolution of Cu was carried out in aqueous solutions containing boric acid (0.5M) using pulsed voltage waveforms. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) showed that porous nickel foams have been obtained under the operative conditions adopted, with average pores diameters from 100 to 300 nm.
After the anodic etching, the samples were submitted to thermal treatment in air atmosphere for 30 min at 500 C°, after ramping the temperature at 5 °C min^{-1}, in order to convert $Ni(OH)_2$ and NiOOH groups in NiO p-type semiconductor. The electrodes have been characterized by linear sweep voltammetry, electrochemical impedance spectroscopy and cyclic voltammetries both in dark conditions and under irradiation with a 300 W Xe lamp equipped with AM0 optical filter. Photoelectrochemical reduction of CO_2 in aqueous solutions has been performed to test the photocatalytic activity of the samples. The results demonstrated that NiO porous electrodes show improved photoelectrochemical activity with respect to smooth Nickel electrodes mainly due to the larger specific area. Moreover, the electrodes shown catalytic activity towards the reduction of CO_2.

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Entropy Change during H-UPD and HER on Platinum

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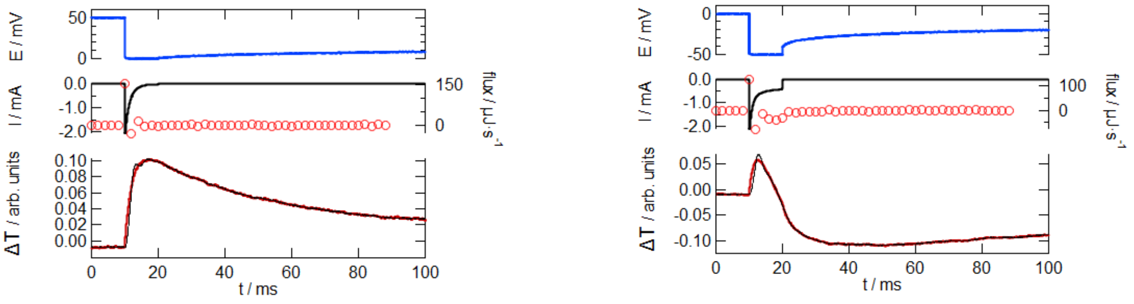
The Hydrogen Evolution Reaction (HER) is one of the most important electrocatalytic reactions for fuel cells or electrolysers. Even though the topic has been investigated for more than 100 years there are still unsolved issues, e.g. the physical state of the reactive hydrogen species [1].

We want to obtain additional information on the EC reaction mechanism by time–resolved electrochemical microcalorimetry. We measure the heat evolution after pulsed hydrogen underpotential deposition and pulsed H_2-evolution (10-100 ms) on Pt-foil or in-situ deposited Pt-films in H_2SO_4. The measured heat is directly correlated to the reaction entropy of the half-cell reaction [2].

The heat evolution differs significantly between the H-UPD and HER region (Fig.1 **a** and **b**). Since the heat flux during H-UPD (red dots, Fig. 1**a**) follows the current flow (black), the heat evolution can be interpreted by a single reaction step, i.e. the ion transfer reaction of the H^+ to the surface. On the contrary, during the HER one can clearly distinguish between two reaction steps, with first positive and afterwards negative heat input.

For further interpretation, we want to disentangle the two reaction steps by a simulation employing a network formalism [3], which is currently in progress.



(a) **(b)**

Fig.1: Potential (blue), current (black) and temperaturechange (red) during an 10 ms, -50 mV potential pulse in the H-UPD-region **(a)** and the HER-region **(b)**. The red dots show the heat flux derived from a fit of the temperature transient (black) considering the thermal response function of the calorimeter .

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Development of a carbon paste electrode chemically modified with Cu (II) trans 3-MeO salcn complex for cocaine detection: environmental and forensic approach

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ABSTRACT – A growing literature on the development of electrochemical sensors using chemically modified electrodes with Schiff base complexes for environmental and forensic application is observed [1-3]. This work shows a study of the electrochemical activity of cocaine in carbon paste electrode chemically modified with Cu (II) trans 3-MeO complex. Square-wave voltammetry was performed on 0.1 mol.L^{-1} KCl supporting electrolyte using an electrochemical cell composed of three electrodes: One Metrohm® reference electrode - Ag /AgCl electrode (filled KCl 3 mol.L^{-1}), and two working different electrodes: a platinum spiral electrode and a carbon paste electrode chemically modified with Cu (II) trans 3-MeO complex. Two forms of cocaine were analyzed: (i) Cocaine hydrochloride (pH 3), with an anodic peak at 0.8 V (Fig. 1a), which showed a linearity range too between 2 and 20 µmol.L^{-1}, and had LOD and LOQ of 7.92 and 2.41×10-5 mol.L^{-1}, respectively. (ii) Cocaine in free base form (pH 8), with an anodic peak at -0.4 V (Fig. 1b), which provided a linearity range between 2 and 20 µmol.L^{-1}, and had LOD and LOQ of 2.24 and 6.82x10^{-5} mol.L^{-1}, respectively. The study also proved that cocaine is adsorbed on the surface of the working electrode through an irreversible process since only anode peaks are observed. It can be understood as the cocaine oxidation, which occurs in the hydrophilic region due the loss of two electrons. The mechanism of this reaction was confirmed by *ab-initio* quantum mechanics calculation using B3LYP/631G** method. To the best of our knowledge, these results attend the minimum parameters for cocaine detection in seized samples and sewer aliquots for environmental purpose [4].

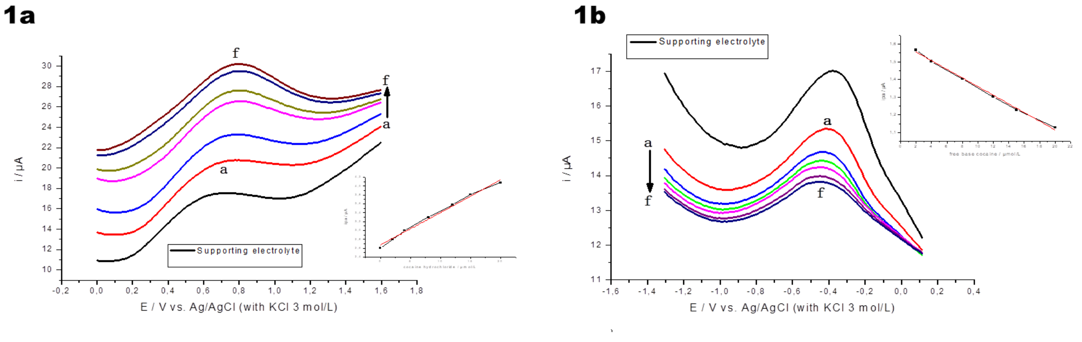

Figure 1 – Cyclic voltammograms obtained at 100 mV.s^{-1} for the modified carbon paste electrode with Cu (II) trans salcn in 0,1 mol.L^{-1} KCl solution containing different cocaine concentrations (a = 2, b = 4, c = 8, d = 10, e = 12, f = 15 and g = 20 µmol.L^{-1}).

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Electrochemical Real-Time Mass Spectrometry Resolving Transients in Carbon Dioxide Reduction Experiments

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Electrochemical carbon dioxide (CO_2) reduction is of general interest to meet the rising demand for sustainable energy and resources of an ever-growing modern society. Building on the pioneering discovery of copper as a suitable catalyst for the activation of CO_2 and transformation to diverse value-added chemicals such as formic acid, methane or ethylene (C_2H_4)[1], recent findings were in the direction of controlling the selectivity of the catalytic reaction towards C_2 and C_3 products[2-4]. In benchmarking the chemical product spectrum of potential catalysts, long-term electrochemical measurements and ex situ analytical techniques such as online gas chromatography, or nuclear magnetic resonance are commonly employed[5]. The advantage of these techniques is their quantifiability on an experimental time scale of minutes. Yet, these techniques lack in adequate temporal resolution to detect transient behavior in time-dependent electrochemical experiments.

Herein, we present a novel method of coupling real-time analytical instruments based on mass spectrometry to an electrolytic cell. Changes in the production rate of selected gases and liquids are resolved down to a time interval of a few seconds. Thereby, we resolve the time-dependent evolution of selected products between differently pretreated copper electrode surfaces during the first seconds of CO_2 reduction. The impact of copper pre-oxidation and (partial) oxide reduction on the time evolution of products, particularly C_2H_4, will be discussed.

Acknowledgements
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Simple Environmentally-Friendly Reduction of 4-Nitrophenol

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4-Nitrophenol (**4NP** in Fig. 1) is an organic phenolic compound which is widely used in a diversity of industrial processes including the production of drugs, medicines, pesticides, dyes and explosives. As a consequence, 4NP can be found usually in industrial waste. For this reason, and in contrast to its *ortho* and *meta* isomers, 4NP has been listed, according to the US Environmental Protection Agency, as a common toxic and hazardous organic pollutant. In this context, the realization of novel protocols to degrade 4NP, efficiently and cleanly, is of the essence.

Several strategies have been reported for this purpose heretofore. One possibility is its thermal decomposition; however, even more toxic nitrogen oxides are produced. Other proposed methodologies involve the chemical reduction of 4NP to 4-aminophenol (**4AP** in Fig. 1). This method is particularly attractive since 4AP is not only less toxic than 4NP but also it can also be exploited as a starting material in a wide variety of industrial processes. Several reducing agents ($LiAlH_4$, $NaBH_4$, H_2 or $SnCl_2$) can be used for this task. Nevertheless, in some cases, the reduction step does not yield the expected amine or it requires the assistance of heavy transition metals as active catalysts; in all instances, either the excess of the reductant or the used catalyst remains always in the final reaction mixture.

Figure 1. Reduction of 4-nitrophenol (**4NP**) to 4-aminophenol (**4AP**).

In this work, we have focused on the electrochemical reduction of 4NP. Literature findings reveal that the electrochemical reduction of 4NP to 4AP can be achieved with suitable noble metals either in ionic liquids or through electrocatalytic hydrogenation in aqueous media.[1,] This protocol generally requires the use of complex materials (metallic nanoparticles, bimetallic active catalysts or graphene-modified structures) that ensure a high surface/volume ratio, which is crucial for an effective reduction to be achieved.[2,3] The main aim of this work is to electrochemically-degrade 4NP to 4AP in water by means of a simple, inexpensive and environmentally-friendly method. With this in mind, we have investigated the electrochemical reduction of 4NP to 4AP under different experimental conditions (distinct metallic substrata (glassy carbon, Ag, Au, Pt, Ni and Co), applied voltages and temperatures). The reduction reaction has been monitored by means of different techniques such as HPLC-MS and UV-Vis spectroscopy. The structural identity of the reduction products has been confirmed by means of ^{1}H NMR spectroscopy.

Acknowledgements

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New Exploration on A Well-defined Pd Monolayer Deposited on Pt(111) Single Crystal: H/OH adsorption and Formic Acid Oxidation Mechanism

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The structure and composition of the complex electrode-electrolyte interface can affect the rate and mechanism of electrocatalytic reactions. The sharp features on Pt surfaces located at low potential region were previously believed to be solely due to hydrogen adsorption on step sites[1], and exhibit an anomalous non-Nernstian dependence on pH[2]. Using density functional theory and experimentally measured voltammograms, we have supported recent arguments that these features actually correspond to the competitive adsorption of hydrogen and hydroxide on to Pt step sites[3,4].

Palladium surfaces show higher activity towards formic acid oxidation and the remarkable difference with Pt is the absence of CO poisoning. However, the most fundamental aspects of the well-characterized Pd surfaces, the hydrogen and hydroxide adsorption behavior, are still not fully clarified[5,6]. In the current work, we first combine cyclic voltammetry and density functional theory (DFT) based calculations to investigate the nature of the species adsorbed when a Pd monolayer deposited on Pt(111) single crystal substrate in contact with a perchloric acid solution. The understanding of "hydrogen region" of the well-characterized $Pd_{ML}Pt(111)$ surface has been improved considerably: the "first hydrogen peak" H_{I} at 0.246 V_{RHE} in the cyclic voltammogram actually involves the replacement of hydrogen by hydroxyl similar to what happens on Pt, and the "second hydrogen peak" H_{II} at 0.306 V_{RHE} appears to be the sequential hydroxyl adsorption, which is coverage dependent. The CO-charge displacement experiment has been used to determine the coverage of the adsorbed hydrogen and hydroxyl in the potential region where adsorption of both species takes place.

Further, to fully understand the high activity and CO poison free path of formic acid oxidation on Pd surfaces, which involves an adsorbed bidentate formate as intermediate, we will present our most recent work examining the role of the adsorbed bidentate formate and the absence of CO poisoing on Pd surfaces.

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All Solid State Thin Film Battery with $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$(NCA)/LiPON/$TiO_2$ by DC/RF Sputtering

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Lithium secondary batteries are widely used various electronic devices such as mobile phones, camera, smart watch and so on. However, several problems with the safety, performance, and cost of these batteries remain to be solved, in particular, the safety problem presented by the flammable liquid electrolytes that are conventionally used. All solid state Li-ion batteries are the next generation secondary batteries to replace safety problems, which is the biggest problem of organic liquid electrolyte batteries. Also, as modern device becomes smaller and flexible, wearable, batteries must also be changed accordingly. One of the ways to make this possible is the all solid state thin film battery. In order to make thin film battery, there are some various methods such as sputter, molecular beam epitaxy (MBE), plasma laser deposition (PLD), E-beam evaporator and so on. Among these methods, sputtering is able to deposit a thin film of relatively high quality.

In this study, we fabricate thin film battery by using direct current (DC), radio current (RF) sputtering for all solid state Li-ion battery. Ti and Cu/Ti thin films were deposited by DC sputtering for cathode and anode current collector, respectively. $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ (NCA) cathode, lithium phosphorous oxynitride (LiPON) electrolyte, and TiO_2 anode were deposited by RF sputtering. NCA cathode with (100~200)nm, LiPON electrolyte with 1500nm thickness, were deposited, respectively. Cathode, electrolyte and anode grown by sputtering were almost amorphous compared to target materials which are crystalline. Thickness of cathode and anode current collector were 100nm and 100nm/100nm, respectively. Morphologies and cross sectional view of thin films were examined by field emission scanning electron microscopy (FE-SEM). The x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) used to investigate for binding energies and compositions of thin films, respectively. Ionic conductivity of LiPON electrolyte was 1.04 x 10^{-6} S/cm which is matched with reference value. Electrochemical properties of thin-film batteries were also characterized galvanostatic system.

Thin-Films Grown by DC/RF Sputtering for All-Solid-State Thin-Film Lithium Ion Battery.

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Due to the rapid development of micro-processing technology, the technology of micro-devices such as semiconductors, MEMS, and micro-mechanical parts has been accelerated. The problem with this trend is the development of energy sources for device operation. Therefore, it is essential to develop a high-performance thin-film battery to realize a more complete micro system. Thin-film batteries usually have a thickness of less than 1μm and have very low weight, which is advantageous for use in micro device or very small devices. In order to fabricate the thin-film batteries, there are various available technics such as E-beam evaporator, PLD(plasma laser deposition), MBE(molecular beam epitaxy), sputter and so on. Among them, sputtering has the advantage that the filming speed is constant. The adhesion of thin-film is also good. Especially, RF sputtering is possible even when the target material is an insulator. It is also possible that the target material is an oxide or a nitride. In this case, an oxide or nitride thin-film could be deposited by using O_2 or N_2 gas.

In this study, we prepared and characterized of thin-films by direct current(DC), radio frequency(RF) sputtering for all-solid-state lithium ion batteries. Ti and Cu/Ti thin-films were deposited by DC sputtering for cathode and anode current collector, respectively. $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$, lithium phosphorous oxynitride(LiPON) were deposited by RF sputtering for cathode and electrolyte, respectively. While the target materials are crystalline, all thin films became amorphous or partially crystalline. For the reason, when ionized materials by plasma deposited on the substrate, it might be quenching effect. A lithium metal, an anode material, was deposited by thermal evaporation.

The surface morphologies and cross sectional view of thin-films were characterized by field-emission scanning electron microscopy(FESEM). The structural properties of thin films were evaluated by X-ray diffraction(XRD). The binding energies and compositions of thin films were characterized by X-ray photoelectron spectroscopy(XPS). Thickness of Ti and Cu/Ti current collector deposited by DC sputtering were 100nm and 100nm/100nm, respectively. $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$ cathode with 200nm thickness, LiPON electrolyte with 1500nm thickness, were deposited.

Ionic conductivity of LiPON electrolyte was 1.04×10^{-6} S/cm which is matched with reference value. Electrochemical test shows reasonable capacity compare to those of bulk Li-ion batteries using NCM cathode. Electrochemical properties of thin-film batteries were also evaluated by galvanostatic system.

Blood-based Catalysts for Reversible and Sustainable Li-CO_2 Batteries

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Carbon dioxide (CO_2) as a representative greenhouse gas should be reduced to relieve sudden increase in atmosphere temperature, resulting in climate change issue. Effective ways to deduct evolved CO_2 gases have been introduced by development of diverse chemical and electrochemical conversion systems such as CO_2 capture, photo-induced CO_2 conversion and batteries.[1] Li-CO_2 batteries as next generation rechargeable batteries have recently received great attentions because of (i) their high energy density, (ii) environmental benign, (iii) reversible solidification and evolution enabling CO_2 capture and storage.[2] However, the Li-CO_2 batteries often suffer from large overpotential problem induced from insulating carbonate products, thereby degrading cell performance. Therefore, it is needed to develop efficient catalysts for realization of eco-friendly and promising Li-CO_2 batteries.

Environmentally-friendly and economic production of the catalyst materials is an important factor to be used for future Li-CO_2 batteries. In this regard, direct utilization of blood proteins obtained from blood bio-waste (i.e. slaughter, food industry, and medical waste) has been considered for developing catalyst alternative in Li-O_2 cell.[3, 4] Hemoglobin as a core-protein in blood transports both oxygen and carbon dioxide for breath and it has a lot of organic based atomic species (such as iron, carbon, oxygen and so on) that can be a source of catalyst elements. Furthermore, reversible redox properties of Fe center in hemoglobin can facilitate battery performance (i.e. higher capacity, reduced overpotential, and long cycle performance).

In this work, we first report co-use of hemoglobin as catalyst precursor and catalyst itself for efficient and sustainable Li-CO_2 batteries. We examine the morphological and structural features of the hemoglobin-based catalyst materials. We achieve improved electrochemical performance of Li-CO_2 cell employing the hemoglobin-based catalyst, compared to reference cell without the catalyst.

Free-standing TiC-fiber cathode as effective cathode for Li-O_2 batteries

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The large theoretical energy density makes the aprotic lithium-oxygen (Li-O_2) batteries one of the most attractive technology for the next-generation electrochemical energy storage. A cathode of the Li-O_2 batteries hosts the reversible reduction of oxygen to form discharge product such as lithium peroxide (L_2O_2). One of the key issues which severely restricts the performance of the Li-O_2 batteries is cathode passivation due to the thick deposition of discharge product. Here we show that TiC nanofiber array coating is the efficient way to minimize this cathode passivation issue. A free-standing TiC nanofiber array was grown onto a carbonized T-shirt (C-fiber) and fully covered exposed surface of C-fiber and SEM, TEM, XRD, Raman and N_2 gas adsorption-desorption isothermal experiments validate the successful coating of TiC nanowires on C-fiber (called TiC-fiber). TiC-fiber composite electrodes show enhanced oxygen reduction/evolution activity and cyclability compared to the TiC nanoparticles when evaluated as cathodes of Li-O_2 batteries. With the aid of surface analysis techniques, the role of the vertical TiC nanowire for stable cycling is demonstrated. In addition, this study highlights that the discharge product can be efficiently decomposed due to catalytic effect of TiC even though there is deposition of side products such as lithium carbonate and acetate on the vertical TiC nanowire. The presented results are a further step toward a wise design of stable cathodes for Li–O_2 batteries.

A self-buffering effect of a hierarchical structure for application in high-performance sodium-ion batteries

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Abstract

Sodium ion batteries (SIBs) have been received significant attention as a promising alternative to lithium ion batteries (LIBs) due to an abundance of sodium element. The sulfides show high specific capacity than the oxides especially iron sulfides have been considered promising electrode candidate for SIBs due to their high theoretical capacities, natural abundance, relatively low price, and low toxicity. However, the promising materials suffer from large volumetric change during charge/discharge due to its reaction mechanism with sodium ions of conversion and/or alloying reaction. The repeated volumetric changes during cycling could induce the pulverization of the active material, which leads to the fast degradation of the cycle performance. Here, we report hierarchical nano/micro structure constructed by Fe_7S_8 nanoplates for SIBs. Our unique design enables the self-buffer effect on the relaxation of the stress associated with the volume change of sulfide materials, which significantly enhances the cycling stability (515 mAh g^{-1} after 200 cycles at 1C) and excellent rate performance (380 mAh g^{-1} at 40C). In addition, the Fe_7S_8 as a whole did not show any apparent volume changes during cycling. The self-buffering structure is expected to be effective in accommodating volume changes in real batteries.

Carboxymethyl Cellulose Lithium via Weak Acid Treatment for High Energy Density Graphite Anode in Li-Ion Batteries

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Carboxymethyl cellulose lithium (CMC-Li) has been studied as a promising aqueous binder for Li-ion batteries due to its enhanced Li^+ ion conductivity compared to carboxymethyl cellulose sodium (CMC-Na). CMC-Li has been generally prepared by CMC acid form (CMC-H) as an intermediate product using a strong acid, which could induce the severe degradation of CMC. Here, we report a synthesis method of CMC-Li through the use of a weak acid (acetic acid) and its application for the graphite anode with a high energy-density. CMC-Li prepared with an acetic acid (CMC-Li (A)) exhibits enhanced physicochemical properties including an appropriate viscosity of ～3000 mPa·s at a shear rate of 4 s^{-1}, good slurry stability, and strong adhesion force of 1.4 gf/mm compared to those of CMC-Li synthesized by hydrochloric acid. The high energy-density graphite anode prepared with CMC-Li (A) shows higher charge/discharge capacities and capacity retentions in various rates of 0.05−2 C than those of the electrode prepared with CMC-Na.

Electricity generation by means of membraneless H_2O_2 fuel cells fed with solar-driven generated aqueous H_2O_2 from low-cost photocatalytic nanoporous TiO_2/C films immersed in O_2-saturated pH 2 buffer solutions

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In this work, we present the preparation of nanoporous TiO_2/C films utilizing electrophoretic deposition of colloidal suspensions containing low-cost nanoparticulate TiO_2 and Cabot XC-72R carbon powder on conductive glass plates, their employment as photocatalytic surfaces able for promoting the solar-driven generation of aqueous hydrogen peroxide (H_2O_2) from O_2-saturated pH 2 phosphates buffer solutions, as well as the successfully operation of membraneless H_2O_2 fuel cells which were fed with these solar-driven produced H_2O_2 solutions. In this sense, the nanoparticulate TiO_2 utilized for preparing photoactive TiO_2/C films were obtained by electrochemical dissolution of remelted titanium components [1]. For comparison purposes, commercial Degussa P25 TiO_2 powder was utilized for preparing photocatalytic P25-TiO_2/C films in order to have a reference source of photochemically prepared aqueous H_2O_2 to feed the mentioned fuel cells [2]. Particularly, the membraneless H_2O_2 fuel cells here employed were designed ex professo to contain a Prussian Blue-modified glassy carbon cathode and a polycrystalline gold anode, which together promote the efficient generation of electricity via the spontaneous decomposition of aqueous H_2O_2.

Our experimental results demonstrated on one hand that the photocatalytic production of aqueous H_2O_2 from TiO_2/C films (0.147mM maximum) was equally efficient than from P25-TiO_2/C films, under the same conditions of simulated solar illumination (80 mW/cm^2 for 250 min). On the other hand, a comparison between those performance parameters (Table 1) estimated from discharge curves associated to the operation of membraneless H_2O_2 fuel cells which were fed with aqueous H_2O_2 solutions photogenerated from TiO_2/C or P25-TiO_2/C films, revealed that both sets of parameters reached the same values. These interestingly results confirmed that the low-cost nanoparticulate TiO_2 here reported can be employed instead the commercial Degussa P25 TiO_2 to produce aqueous H_2O_2 solutions which are able to be fed in membraneless H_2O_2 fuel cells.

Table 1. Performance parameters estimated from H_2O_2 fuel cells fed with aqueous H_2O_2 solutions photochemically produced from TiO_2/C or P25-TiO_2/C films immersed in pH 2 phosphates buffer solution, where: E_{oc}, j_{sc}, and P_{max} are open-circuit potential, short-circuit current and maximum power, respectively.

photocatalytic film [H_2O_2]=0.147mM	**performance parameters for H_2O_2 fuel cells**		
	E_{oc} (V)	**j_{sc} ($\mu A/cm^2$)**	**P_{max} ($\mu W/cm^2$)**
TiO_2/C	0.42	2.58	0.48
P25-TiO_2/C	0.41	2.63	0.47

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On the Stability of Iridium during Electrochemical Water Splitting

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Iridium is the state-of-the-art oxygen evolution reaction (OER) catalyst in the proton exchange membrane water electrolysis (PEMEL). Its low natural abundance, however, is considered as a serious limiting factor preventing the widespread commercialization of the PEMEL technology. Indeed, in order to play any significant role in the renewable energy-powered hydrogen production, one to two orders of magnitude decrease in the catalyst loading is required [1]. Most widely pursued strategies to decrease electrocatalyst loading in electrocatalysis include: (a) high level of catalyst dispersion, e.g. small nanoparticles and aerogels; (b) use of catalyst supports; (c) use of alloys/mixtures. While it has been proven that any of these strategies can be successful in decreasing loading and maintaining high catalytic activity, studies on the stability of such alternative catalysts are still limited [2].

This work aims at clarifying the interplay between iridium catalyst structure, activity, and stability (structure-performance correlations) in common Ir-based OER catalysts. For this, dissolution stability of Ir in the form of metallic Ir, amorphous hydrous Ir oxide (IrO_x), and rutile Ir oxide (IrO_2) is evaluated first. Both, bulk and nanocrystalline supported and unsupported materials are considered. It is shown that while having the highest activity, stability of IrO_x is probably too low to be considered in the real application [3]. On the other hand, stabilization of metallic Ir during the electrochemical oxidation makes this material a promising alternative to extremely stable IrO_2 [4, 5]. Next, stability of supported Ir catalysts is evaluated. It is shown that, due to the selective leaching of the common dopant elements such as In and Sb [6], the overall catalyst layer stability is questionable in this case. Finally, we take a look at the Ir-based mixtures. Particularly, dissolution stability of Ir single and double perovskites is quantified and compared to those of IrO_2 using a new stability metric, the so-called stability S-number [7]. It is concluded, that having several orders of magnitude lower S-number, studied Ir perovskites are unlikely candidates to replace pure Ir in PEMEL. As a summary, as an outcome of the results presented above, we present a new strategy to decrease catalyst loading while still maintaining relatively high catalytic activity and stability.

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Strong, persistent superficial oxidation-assisted chemical bonding of black phosphorus with multiwall carbon nanotube for high-capacity ultradurable storage of lithium and sodium

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We report a new composite of black phosphorus and multiwall carbon nanotube (BP-CNT) prepared via a surface oxidation-assisted chemical bonding procedure.[1] The controlled air exposure successfully changed the naturally hydrophobic BP powder to the desired hydrophilicity, which was found indispensable to stable bond formation between the BP and the functionalized CNTs during ball milling. The BP-CNT composites were further fabricated into anodes for both Li- and Na-ion batteries, using a sodium carboxyl methyl cellulose-poly(acrylic acid) (NaCMC-PAA) binary polymeric binder. The hydrophilicity of BP also played a very important role in forming strong bonds with the hydroxyl groups of NaCMC and the carboxylic acid groups of PAA. The plausible mechanisms of stable bond formation were comprehensively examined, and the results revealed two types of strong connections: P-O-C bonds and dehydration cross links. Consequently, the material delivered outstanding electrochemical performance in the anode, with a high discharge capacity of 1681 mAh g-1 after 400 cycles at a current density of 0.2C (1C = 2596 mA g-1) for Li-ion batteries. It also successfully delivered a first discharge capacity of 2073 and 850 mAh g-1 at 0.2C and 2C for Na-ion batteries, respectively, with excellent capacity retentions at both rates after 200 cycles. These salient results, which originated from the modified hydrophilic BP, will give further impetus to explore BP-based composites for use as high-performance materials for advanced energy storage applications.

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Graphane@RuO_2 Composite as a High-Performance Free Standing Cathode Catalyst for Rechargeable Li–O_2 Batteries

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In the development of rechargeable battery-based electric vehicles for a cleaner future, one of the biggest hurdles has been the limited energy density of current lithium-ion batteries (LIBs), which has prevented sufficient driving range from being achieved. For this reason, the development of battery systems surpassing the performance of current LIBs, such as Li-sulfur, multivalent ion and metal-air batteries, has been an area of active research. Among these candidates, Li-air batteries represent a promising Li-based energy storage system, which achieve a higher energy density (about 3.5 kWh kg^{-1}) compared with existing Li-ion batteries (about 500 Wh kg–1) [1,2]. Furthermore, even when reactions related to Li_2O_2 are facilitated, the formation of byproducts such as Li_2CO_3 and LiOH is unavoidable in many cases, owing to side reactions,[3,4,5] and the poor chargeability of such byproducts has been theoretically and experimentally demonstrated.[6,7] The accumulation of these byproducts causes deterioration of reversibility of operation during cycling, especially under high rates.

In this work, we have targeted to produce Graphene@RuO_2 free-standing composite cathodes to enhance reversible reaction of Li_2O_2 with preventing irreversible side reaction compounds such as Li_2CO_3, LiOH and Li_2O. To produce Graphene@RuO_2 composite electrode, we first synthesize the Graphene Oxide (GO) by Hummors method and then 20 mg GO dispersed in DI water and were mixed with different concentration of $RuCl_3$ (1, 3, 5 and 8 mg). NaOH was added the obtained GO/$RuCl_3$ suspension to transform structure into GO/RuOH and filtered by vacuum filtration to form free-standing paper on filter membrane. The GO/RuOH was heat treated at 200^{o}C under Ar-H_2 gas flow using quartz tube furnace to acquire Graphene/RuO_2 composite structure. In this composite, content of RuO_2 was altered using different concentration $RuCl_3$ to investigate effect of RuO_2 content on the oxygen evaluation (OER) and oxygen reduction reaction reactions (ORR). The produced composite paper was used as cathode, lithium foil was used as anode and 1M $LiClO_4$ salt dissolved in TEGDME solvent was used as electrolyte and assembled in ECC-Air test cell into Ar-filled glove-box. EIS results of the cell were measured at the frequency range from 1000kHz to 0.01Hz. Cyclic voltammetry test of the cell were performed between 2.2V to 4.5V at the scan rate of 0.2 mV/s. Charge-discharge profile of the cells were performed between 2.2V and 4.5V at the current density of 0.1 mA/cm^2.

Acknowledgments
The authors thank the TUBITAK for supporting this work under the contract number 315M461.

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Application of Scanning Kelvin Probe to study the effects of Strain and Hydrogen on the passivity of stainless steel AISI 304.

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The interplay between mechanical stresses and electrochemical reactions may lead to stress corrosion cracking or hydrogen embrittlement for many materials. In this work, the effects of the tensile stress and hydrogen charging on the passivity breakdown and repassivation of AISI 304 stainless steel was studied using Scanning Kelvin Probe (SKP). The SKP potential monitoring in air was compared with transients of open circuit potential in inert aqueous electrolyte.

A constant load cell was used to stress the tensile sample to different levels. The electrochemical properties of the material were measured *in situ* under the load or at the rest conditions. The surface topography was also determined as function of the stress level. X-ray photoelectron spectroscopy was used to characterize the oxide films in locations with residual stress.

SKP measurements show that plastic strain created dislocations and dislocation pile-ups that emerged to the surface and decreased the potential of steel by 250 mV. This is related to the formation of new active surfaces and it is accompanied by an increase of the surface roughness. At yielding 5 to 15% the potential decreased proportionally to the elongation and at higher strain (e.g. in the range 20-30%) the potential decreased and reached a plateau value.

After the application of plastic stress, the Volta potential of steel surface increased due to passivation of new-born surfaces either under the load or in load free conditions. The potential during passivation depends on time according to: $E= A \ln (t) +B$, corresponding to Field Assisted Ion Migration mechanism of oxide growth.

Hydrogen is strong reducing agent activating the steel surface. Effect of cathodic hydrogenation on the potential of the steel electrode with local residual stress was studied. It was shown that combination of the stress and hydrogen creates most negative locations on the electrode surface where the hydrogen can be trapped by the field of dislocations. Thus, combination of stress and hydrogen creates most active locations where hydrogen-induced failure is possible.

Development of Carbon-Free Metal Oxide Cathode Materials For High Reversible Li-O_2 Batteries

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Lithium-oxygen (Li-O_2) batteries are attracted for large-scale energy storage applications due to its high theoretical energy densities. However, it suffers from low energy efficiency, cycle life, and power capability [1]. Although several studies reported that the low energy efficiency take place due to the instability of the carbon-based air electrodes, which mainly cause the formation of undesired Li_2CO_3 [1,2], carbon has still the most widely used air breathing electrode in Li–O_2 batteries [1]. But Li_2CO_3 formation and the other irreversible side reactions, occur due to the carbon based electrode, which leads to cover the surface of electrode, clogging the porous and prevent the oxygen flow whole of the cathode volume and result in poor cyclability [1,2].

Here, we aimed to develop an alternative metal oxide carbon-free electrode material to improve the stability, reversibility and cycle life of Li-O_2 battery. Metal oxide air electrodes such as TiO_2, Fe_3O_4 and MnO_2 have been synthesized using wet chemical reduction process as nanopowder form and prepared as a cathode material for li-air batteries in order to investigate oxygen reduction (ORR) and oxygen evaluation reaction (OER) potentials of TiO_2, MnO_2 and Fe_3O_4 electrodes. To prepare the electrode, a slurry mixture containing 85 wt.% metal oxide nanopowder, 10 wt.%. CMC binder and 5 wt.% carbon black cast on nickel foam and coated with doctor blade and then dried in oven at 80ºC. Produced metal-oxides were physically characterized using scanning electron microscopy (SEM), X-ray diffraction pattern (XRD) and Raman spectroscopy. The electrodes were tested using ECC-air test cell at 1 atm pressure and 8 ml/min pure O_2 flow. For electrochemical characterization of the produced electrodes, we have performed cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge discharge test from 2.2V up to 4.5V at 0.05 mA/cm^2.

Acknowledgments

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Behaviour of Electrokinetic Soil Remediation under Mineral Precipitation/Dissolution processes

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ElectroKinetic Remediation (EKR) is a technology employed for the polluted-soil treatment, it focused on the application of an electrical potential gradient between electrodes located in a soil. This electrical potential gradient activates several of electrokinetic transport mechanisms such as: (i) electroosmosis, capable of mobilising water, (ii) electromigration, involves transport of ionic species and (iii) electrophoresis, based on the movement of charged particles. Moreover, other electrochemical processes take place in the EKR treatment, e.g. redox reactions on the electrode surface. The electrolysis of water is the most usual redox process in EKR treatment, where simultaneously high concentrations of protons (H^+) and hydroxyl ions (OH^-) are generated in anodic and cathodic reactions respectively. The transport of these ions through the soil produces a mobile acid and alkaline pH fronts that directly influences in the chemical speciation of the substances present in the soil and in porewater and, consequently, it can determine the primary mechanism of transport of chemical species in the soil. In addition, an external factor influencing the pH is the buffering capacity of the soil, mainly determined by the dissolution-precipitation of minerals.

In this context, in order to have an overall understanding of the pH behaviour in an EKR process, it is necessary to have a better knowledge of the interactions achieved between electrokinetic transport phenomena and the physical, chemical and electrochemical processes that take place in an EKR treatment. For this reason, the main objective of this study is to evaluate the influence of changes in soil buffering capacity produced by mineral precipitation/dissolution processes on the performance of an EKR process. To do this, a numerical inspection of an EKR treatment of a polluted soil with an organochlorine acid herbicide (2,4-dichlorophenoxyacetic acid) was carried out. The numerical tool used for this analysis was the Multiphysics for EKR (M4EKR) module (López-Vizcaíno et al., 2017), programmed by the authors on the COMSOL Multiphysics platform. A detailed analysis of the pH, the distribution of the species that have a significant influence on the buffering capacity of the soil (mineral species) and the pollutant, has been conducted. In this way, the kinetics of the dissolution-precipitation processes have been analysed to determine the pH of the porewaters and, therefore, how it affects the efficacy of the treatment.

In conclusion, this study provides useful information on the influence of soil buffer capacity on the general performance of an EKR process applied to the decontamination of a soil with acidic contaminants.

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Pickling process of flat carbon steels: reaction mechanisms and surface morphology

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In the industrial process of flat carbon steel production after hot rolling step the steel strip is covered by an oxide layer of a few µm thick (scale) which is further removed by pickling operation to obtain satisfactory surface quality for following cold rolling process step. Therefore, the control of the pickling process is crucial to avoid significant productivity losses and limited quality [1, 2]. The essential difficulty for such control is the evaluation of the optimal pickling state. Indeed, it is evident that high strip quality requires complete elimination of the oxide at the strip surface – the under-pickling cannot be tolerated. What is less obvious is that over-pickling i.e. attack of the iron by the pickling solution can also represent a serious problem in terms of quality and productivity losses.

For classical steels the scale is mainly composed of wüstite (FeO) which is covered on its top surface by thin layers of magnetite (Fe_3O_4) and hematite (Fe_2O_3). Scale removal mechanisms during pickling in HCl medium at about 80°C consist in acid infiltration through cracks network and following FeO dissolution by the reaction $FeO + 2HCl \rightarrow FeCl_2 + H_2O$ [3]. Our recent study with the help of electrochemical cell coupled to ICP-OES chemical analysis demonstrated that dissolution of hematite is mainly of chemical nature, whereas the dissolution of magnetite and wüstite is both chemical and electrochemical [4, 5]. Initially, chemical dissolution of the scale dominated. The electrochemical reactions included oxidation of magnetite and wüstite and reduction of ferric ions formed by chemical dissolution. After the electrolyte reached the steel substrate, electrochemical dissolution of the iron is the main reaction (over-pickling step). This reaction leads to the production of hydrogen gas and should be avoided. For this purpose, a corrosion inhibitor is introduced into the pickling bath. It allows steel surface protection against dissolution and limits by this way the iron losses during the process [6].

If the pickling operation is now well managed for low alloyed carbon steels, adjustments are still necessary for high strength steel grades alloyed with elements like silicon, manganese and aluminum. These elements lead to the formation at hot rolling of their oxides at steel/scale interface and, therefore, to a different behavior in pickling baths and variable surface morphologies after pickling.

This study is focused on experimental simulation of pickling process for low alloyed and Si-alloyed grades at different conditions (scale cracking, bath hydrodynamics, presence of the corrosion inhibitor...) in order to understand the influence of steel alloying on the rate of scale dissolution and steel surface morphology. The interest of catalyst additives for pickling process improvement is also discussed.

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Anion Exchange: an Effective Approach to Prepare Co-Fe Bimetallic Disulfide for Electrochemical Hydrogen Evolution Reaction

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The development of highly efficient and earth-abundant electrocatalysts for hydrogen evolution reaction (HER) remains urgent. The bimetallic catalysts have drawn extensive attention because of their high catalytic performance. It is anticipated that bimetallic disulfide catalysts can combine the favorable features of both metallic disulfide and also improve their overall performance as a result of possible synergistic interaction on the molecular level. At present, the preparation strategies of bimetallic disulfide catalysts mainly includes electrodeposition, mechanical mixing, and metal smelting. Among them, electrodeposition has been widely applied. The electrocatalytical activity of the sample is not only affected by the deposition potential but also by the temperature, pH, and other environmental factors. Additionally, the compact structure of the electrodeposited product is found to hinder the electrocatalytic activity. For the other two methods, the huge energy consumption seriously limits their widespread application. Therefore, developing a facial, effective and controllable approach to prepare bimetallic disulfide with high HER activities is desirable.

Here, we report a fast anion exchange approach to prepare a Co-Fe bimetallic disulfide catalyst. Firstly, cobalt carbonate with uniformly spiny structure is grown on carbon cloth (CC) by a low temperature hydrothermal method. Afterwards, ferricyanide anion are employed to replace part of the carbonate ions to form cobalt ferricyanide. The Co-Fe bimetallic disulfide with abundant lattice defects is subsequently generated by annealing in H_2S. The composition of biometallic disulfide can be easily controlled by anion-exchange time. The resultant Co-Fe bimetallic disulfide exhibits excellent HER performance with an overpotential of 205 mV to obtain current densities of 100 mA cm^{-2} and the value of Tafel slope is only 57 mV dec^{-1} in acidic solution. This work provides an effective strategy in the synthesis of bimetallic sulfide catalyst for electrochemical hydrogen evolution reaction.

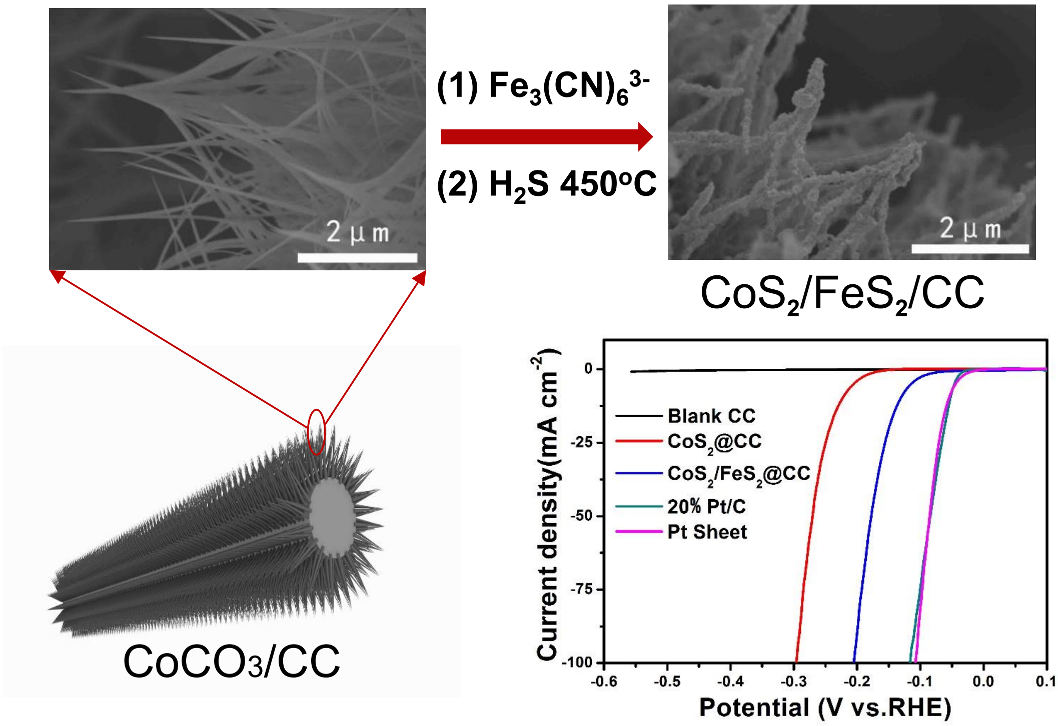

Figure 1. Schematic illustration of the preparation of Co-Fe bimetallic disulfide by anion exchange reaction and the related HER activities.

Biomimetic ZnO@ZnS micro/nanostructures for Pollutant Remediation

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Ensuring sustainable management and availability of water has become a prominent societal issue. Since conventional water-treatment technologies are currently insufficient to eliminate certain persistent organic pollutants, the development of advanced oxidation processes is a challenge. Photochemistry is a highly promising approach, as it uses solar light – a renewable, abundant, and clean energy source. New green and sustainable nano/micromaterials have been investigated for implementation in photocatalysis; among these, semiconducting materials have been proposed as powerful and efficient photocatalysts.

ZnO is one of the most fascinating semiconductors for this purpose, due to its physicochemical properties, low toxicity, antibacterial activity, and high production of reactive oxygen species (ROS). However, it has a wide band gap (3.36 eV), which needs to be modulated by doping ZnO with other elements, in order to extend the light response to visible domain and to minimize the recombination rate of photogenerated species. In this communication, the influence of S in ZnO microstructures for sunlight photocatalytic applications is presented.

Apart from the electronic properties, the shape and architecture of the photocatalysts have also been demonstrated as determinant factors that control photocatalytic activity, due to the active surface to trap light and pollutants. Among the different possible architectures, biomimetic structures are well-known as extremely efficient platforms for reaction processes. This work is devoted to studying the enhancement of photocatalytic properties by the formation of fern-like microleaves of ZnO@ZnS. These core@shell structures have been fabricated by electrochemical deposition of branched-ZnO nanorods arrays, subsequent sulfidation in an aqueous solution, and annealing in argon atmosphere. After verifying the formation of ZnS shell along the microfern by *ex-situ* characterization techniques, the efficiency of the bioinspired structures was tested by analyzing the degradation kinetics for methylene blue (MB), 4-nitrophenol (4-NP), and rhodamine-B (Rh-B) persistent organic pollutants under UV, simulated and natural UV-filtered sunlight irradiation. The ZnO@ZnS microferns present excellent photocatalytic activity using sunlight, with a performance comparable to, or better than, that of benchmark materials reported in the literature. These results, combined with the exceptional photo-stability and photo-corrosion resistance observed in these materials, greatly facilitates their recyclability and hence enhances their potential as optimal photocatalysts for "green" photocatalytic water-remediation purposes using sunlight.

Acknowledgements

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Identification of Electro-Hydraulic Parameters in Soil Electrokinetic Remediation Processes. PAR4EKR project

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The growing world population and the increase in the number of potentially contaminant activities have caused an upward trend in the number of soil-contaminated sites. To guarantee that these places do not imply an unacceptable risk to human health or the environment, a remediation process must be conducted. Among the technological alternatives available, ElectroKinetic Remediation (EKR) is one of the most promising options in soils with low permeability. Many physical, chemical, and electrochemical processes that occur simultaneously during the EKR process. The coupling of all these processes and the interaction between them results in a complex study of EKR treatment. For this reason, the development of numerical models is necessary to improve the knowledge of EKR treatments. The reliability of the results obtained by EKR numerical models is determined by the quality of the parameters that define the electro-hydraulic behavior (among others). However, the electro-hydraulic characterization is a complicated task since it requires a complex experimental test developed in highly specialized devices, hardly found in commercial laboratories of environmental characterization of soils. The project PAR4EKR, aims at solving this limitation.

This project proposes the definition of a methodology (See Fig.1) for estimating the characteristic electro-hydraulic flow parameters. To do this, a simple experimental device has been designed where the EKR reactor is the soil sample extractor. In this way, device allows a precise control of the boundaries and the initial conditions of EKR test, in order to simulate this process with the numerical tool, M4EKR (López-Vizcaíno et al., 2017) implemented in Comsol Multiphysics. The resolution of inverse problem from EKR tests conducted in the designed device allows the estimation of hydraulic and electroosmotic conductivities and the water retention curve of the soil without the need to use more expensive and complex experimental techniques. The methodology proposed has been applied to Kaolin, low permeability material extensively studied in the EKR literature. This material has been selected in order to evaluate the plausibility of the parameter estimates made and the feasibility of the methodological proposal itself.

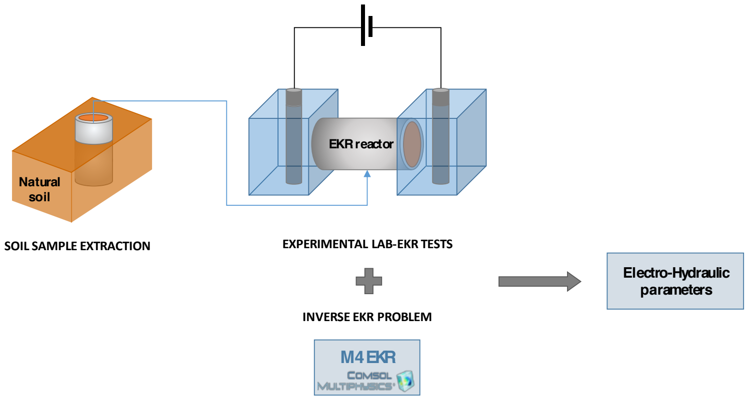

Figure 1. PAR4EKR methodology.

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High selectivity of the reduction of Carbon Dioxide on copper nanoparticles electrocatalysis

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Fossil Fuels dependence from human has increased the atmospheric concentration of CO_2, generating the phenomenon called global warming. The reduction of CO_2 emissions worldwide is currently a subject of great concern. This has stimulated the development of electrochemical systems capable of generating useful products by reducing CO_2. It has been shown that nanostructured surfaces improve the activity and selectivity of many catalysts. In addition, a preferred crystallographic orientation increases the catalytic activity and together the formation of a specific reaction product for CO_2 reduction [1-2].

Copper nanostructures are prepared *in situ* on polycrystalline Cu surface. These are wire type which grow vertically and horizontally on the surface, measure between 50 and 100 nm. Both families of structures have a preferred crystallographic orientation (111) and (200) respectively, which depends clearly on the purity of the Cu surface. For the $RRCO_2$ on these electrodes, performed in $KHCO_3$ buffer at pH 6.8, electrolysis at controlled potential was carried out -1.9 V *vs* Ag / AgCl. The analysis of the catholyte by ^{1}H-NMR showed a high selectivity for formate ($HCOO^-$) and gas chromatography (GC) for methane (CH_4), in contrast to the polycrystalline surface in which formate, methanol (CH_3OH) was obtained, ethanol (CH_3CH_2OH) and acetone ($CH_3C{=}OCH_3$) and by GC methane and ethylene (C_2H_4). Therefore, the selectivity is directly related to the crystallographic orientation of the copper nanostructures on the surface.

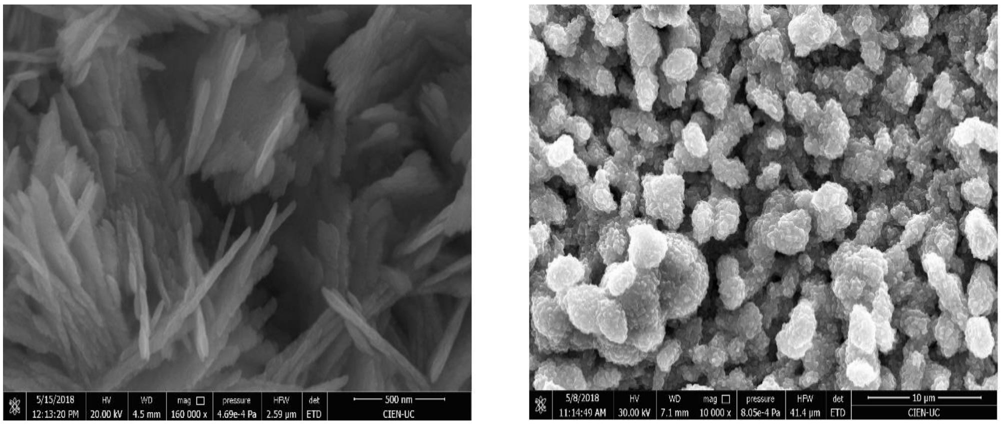

Fig. 1. SEM imagen of Cu 99.998% purity a) CuNWa electrode; b) CuNWb electrode.

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Anatase TiO_2 Mesocrystals as Anode Materials for Na-ion Batteries. In Operando Synchrotron Measurement of Na^+-Storage Mechanism

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Electrical power generation from renewable sources is considered one of the most powerful strategies to overcome climate change and the high dependency on fossil fuels. Among the different electric energy storage systems, rechargeable batteries are one of the most competitive devices because of their high conversion efficiency and low environmental impact. Nowadays, Na-ion batteries (SIBs), based on inexpensive, sustainable, and widely available sodium feedstocks, are considered one of the most promising technology for the long-size stationary batteries required for renewable energies. As an emerging technology, search and study of new active electrode materials is one of the key research line in SIBs. Recent researches have shown that metal oxides can reversibly storage Na^+ ions at low potential with good electrochemical properties. Among them, TiO_2-based anodes are very promising because they are abundant, low cost, chemically stable and environmentally safe [1].

To improve the electrochemical performance of Ti-based electrodes, we developed an original synthetic procedure that combines thermally-driven self-assembly of nanomicelles with seeded assisted chemistry which allowed us to prepare sophisticate TiO_2 anatase nanostructures [1]. In this communication, we will show several of the most relevant results dealing with the study of the electrochemical properties of an optimized mesoporous TiO_2 anatase mesocrystal as anode material for SIBs. Particular attention will be paid to our in-operando synchrotron measurement of the Na-ion storage mechanism in TiO_2 [2], as it is still not completely understood. Fig. 1a show as the primary particle size (d_1) remain constant throughout the first discharge/charge at the low current of C/12 (28 mA/g). Moreover, the mean secondary NP center-to-center distance (D_2) increased following a sigmoidal temporal profile (Fig. 1b), which is consistent with either aggregation of the TiO_2 nanostructures and/or electrode swelling. These results show as in-operando SAXS is a powerful tool to address nanoscale phenomena in Metal-ion batteries.

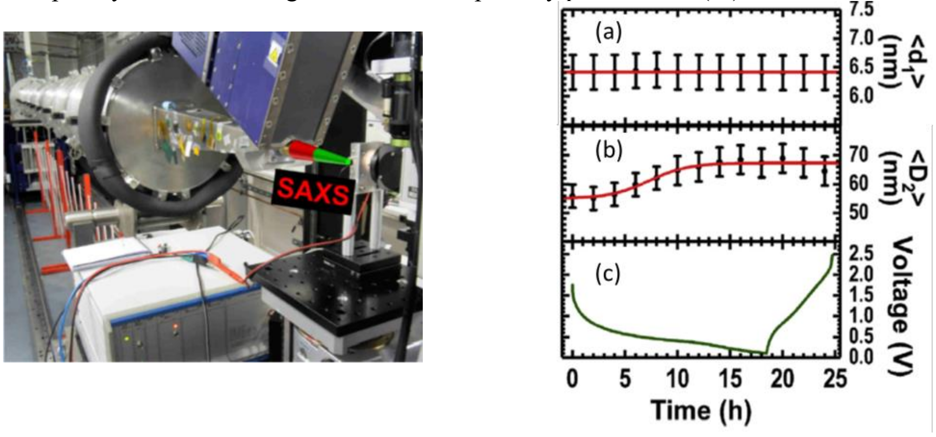

Figure 1: Experimental setup at NCD beamline of ALBA synchrotron (Cerdanyola del Vallès, Barcelona, Spain) (left). (a) Primary particle mean diameter, (b) mean NP center-to-center distance as extracted from the fitting of the SAXS profiles, and (d) first discharge-charge voltage profile at C/12 rate (right).

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Geminal Pyrrolidinium and Piperidinium Dicationic Ionic Liquid Electrolytes. Synthesis, Characterization and Cell Performance in $LiMn_2O_4$ Rechargeable Lithium Batteries

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Rechargeable lithium-ion batteries are excellent candidates for the next generation power sources because of their high gravimetric and volumetric energy compared to other battery chemistries. Conventional LIBs, based on organic carbonate liquid electrolytes, suffer from potential thermal and chemical threats associated with the thermal runaway hazard, low thermal stability, low flash points, toxicity, high volatility and flammability. Aprotic ionic liquids represent a safe alternative to organic carbonates due to their negligible vapor pressure, non-flammability, wide liquid range, high thermal stability, high ionic conductivity and wide electrochemical stability window. However, problems associated to their high viscosity, especially when lithium salts have been added, low stability of the solid electrolyte interphase (SEI), and high cost need to be solved.

In this contribution, we report on the synthesis and characterization of a series of novel room temperature dicationic ionic liquid electrolytes based on pyrrolidinium and piperidinium cation moieties linked by short oligo(ethylene glycol) chains. Electrochemical performance of Li-half cells assembled using $LiMn_2O_4$ spinel as cathode material and 1M LiTFSI doped dicationic ionic liquid electrolytes have been tested. Results obtained indicate that the length of the oligo(ethylene glycol) chain has a crucial role in the properties of the ionic liquids. In fact, both pyrrolidinium and piperidinium ionic liquids linked by short chains are crystalline solids, while increasing the spacer chain lead to liquid samples. Regarding electrolytes, the highest ionic conductivity ($\approx 10^{-4}$ S cm^{-1} at room temperature) was obtained for the pyrrolidinium-based ionic liquid electrolyte with the intermediate length chain length spacer. It has to be pointed out that all electrolytes have a high potential electrochemical stability. Another noticeable result is that cell performance is not only controlled by electrolyte ionic conductivity, but other magnitudes, such as interactions taking place between the ionic species of the electrolyte, modify the Li^+ ion diffusion and so the kinetics of the Li^+ de-insertion/insertion process, in good agreement with previous data [1].

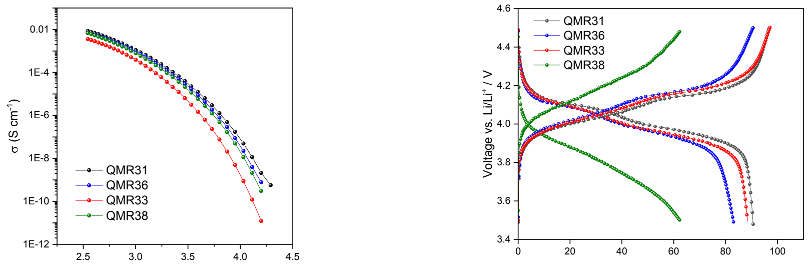

Figure 1. Temperature dependence of ionic conductivity for geminal pyrrolidinium and piperidinium 1M LiTFSI doped dicationic liquid electrolytes (left) and charge/discharge curves recorded at 0.2C rates for $LiMn_2O_4$ half-cells at 60ºC (1C= 148 mA g^{-1}) (right).

Acknowledgements
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Ionic transport study of PVA-KOH Hydrogels to be applied in Zn/air batteries.

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Different pure PVA and PVA-KOH membranes have been obtained by a solution cast method [1] and they have been analyzed by several experimental techniques, such as XRD, XPS, ATR-FTIR and TGA. The ATR-FTIR analysis evidences of H-bond network formation, where the PVA OH groups, OH^- anions from KOH and the H_2O molecules included inside the polymer will participate.

Besides, when these membranes are swollen in 12 M KOH aqueous solution a higher quantity of KOH and H_2O molecules are incorporated into the membrane, enhancing the polymer structure changes.
This improves ionic conductivity and energy activation values. On the other hand, when the PVA-KOH gel immersed in KOH 12M was used in a Zn/PVA-KOH/air battery larger capacity values resulted.

Rise of KOH and H_2O molecules inside the membranes improve the ionic transport due to the increase of the PVA inter-chains canals, a higher degree of amorphousity in the host polymer and the formation of a H-bond network.

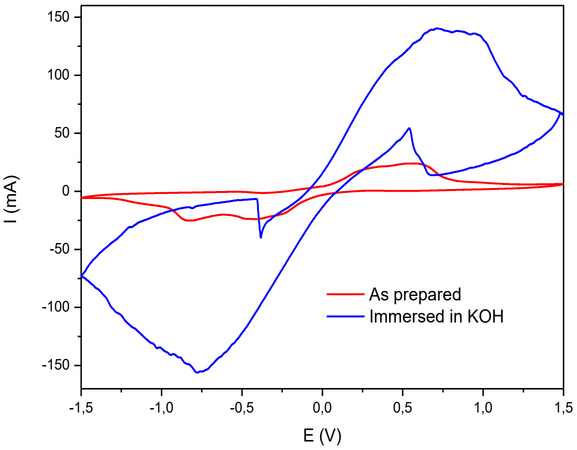

Figure 1. Cyclic Voltammograms of PVA-KOH and PVA-KOH swollen membranes.

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SYNCHROTRON XRD IN OPERANDO STUDY OF Zn/PVA/AIR BATTERY

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Nowadays, metal-air batteries are considered as ones of the most interesting energy storage systems. Although several research groups are focused in the development of batteries including Li, Al, Mg or Na as negative electrodes, Zn-air batteries are up to date the only ones with a real commercial application.

In this work, we have carried out an in operando study of a Zn/PVA/air battery by synchrotron XRD technique to analyze the restructuration of Zn electrode produced during discharging and recharging processes[1]. Synchrotron radiation allows us to obtain well defined peaks in X-Ray patterns though the X-ray bean have to pass through a wide gel electrolyte layer[1, 2], as it is shown in the Figure 1.

Besides, the goniometer allows us to move the sample in Z axis and thus we can examine the PVA gel region close to the air electrode. In this way, we have found the formation of a K_2CO_3 structure inside the PVA gel, indicating the entrance of CO_2 together with O_2 in the battery during the discharge process. These results will be discussed in the communication.

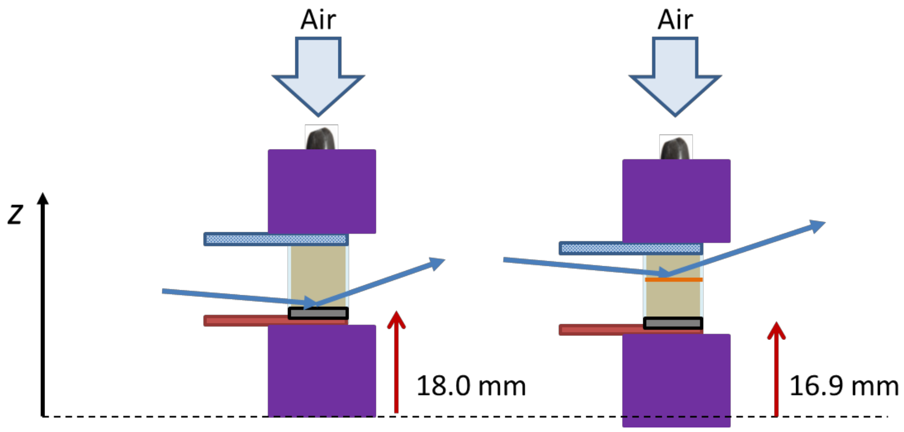

Figure 1. Scheme of the XRD Synchrotron measurements changing the Z axis of the goniometer

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Electrochemical Behaviors of Molybdenum Current Collector in Rechargeable Aluminum-ion Batteries

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Rechargeable secondary battery has been utilized as an energy storage technology for portable devices and transportations for decades. Lithium-ion battery is one of the most widely used systems. However, in recent years, with the rapid expansion of electric vehicles and the portable device market, lithium is unable to accommodate to the demand, owing to the increasing cost and the lack of reserves. The aluminum metal as the anode material is a promising candidate for the next-generation energy system motivated by the high theoretical capacity, low cost, abundant reserves, and safety.[1]

In this work, we report the electrochemical and chemical reactivities of current collectors, such as nickel (Ni), molybdenum (Mo), and tungsten (W), in aluminum-ion batteries with an acidic ionic liquid produced by mixing 1-ethyl-3methylimidazolium chloride ([EMIM]Cl) and aluminum chloride ($AlCl_3$) as the electrolyte. We developed a new suitable current collector for rechargeable Al-ion batteries owing to the undesired reactions of the most-used nickel current collector. The Ni current collector is electrochemically and chemically unstable because of the continuative galvanic corrosion in the acidic ionic liquid. Therefore, an Al-Ni alloy is formed on the separator and electrode in the expanded operating potential window of 0.0–2.5V, leading to the interruption of the movement and reaction of chloroaluminate anions, and cell failure. In contrast, the Mo current collector is extremely stable and sustainable without any side reaction and effect against chloroaluminate anions in both the electrochemical and chemical experiments, which can expand the available potential window. The cell performance shows a higher specific capacity and tremendous cyclability with high Coulombic efficiency compared with other results in the common potential range. Furthermore, Al metal anode showed an electrochemical reactivity when it is exposed to electrolyte, which would limit the shelf-life of Al-ion battery.[2] Mo current collector can suggest a new approach to overcome the Al corrosion problem by removing Al anode in battery construction. Aluminum anode can be fabricated on stable Mo current collector by electroplating just before the use of battery.

A high-purity Al metal (99.99 %, Toyo Aluminum K.K., Japan) was treated with the electrochemical polishing to remove the thick and irregular oxide layer on the aluminum surface. The as-prepared Al metal surface exhibited an extremely thin and uniform oxide layer. The ionic liquid electrolyte was prepared by mixing 1-ethyl-3-methylimidazolium ([EMIM]Cl, granules, TCI) with $AlCl_3$ (99.99 %, powder, Sigma Aldrich) to a molecular ratio of 1:1.3 in the Ar-filled glove box (O_2 ppm <1.0) to obtain homogeneous and transparent yellow liquid. The cathode was made with synthetic graphite powder (<20 mm, Sigma-Aldrich) and polyvinylidene fluoride (PVDF, Sigma Aldrich) in 9 :1 mass ratio. The surface morphology and chemical composition of current collector and electrode surface were observed using field-emission scanning electron microscopy (FE-SEM, 4300S, Hitachi) equipped with an energy-dispersive X-ray (EDX) spectrometer. X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220i-XL spectrometer, Fisons), using an Al Ka X-ray source, was performed to demonstrate the detailed chemical composition of the specimens.

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Organic electrolytes for redox flow battery – electrochemical properties on glassy carbon and graphite felt electrodes

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Redox flow battery is a promising technology for the stationary energy storage for large-scale applications. The main advantage of the flow concept, when compared to standard Li-ion batteries, is the decoupled power to capacity, non-flammability and simplified heat removal, which ensure safe and durable battery operation. The systems based on inorganic (especially vanadium) chemistry are being installed worldwide in MWh scales[1]. The increased price of vanadium and its limited energy density stimulate the development of alternative electrolytes. The organic redox-couples are potential candidates for the application[2-3] as their properties can be tuned by their chemical structure and they can be cheaply produced e.g., from oil residues.

In our contribution we present electrochemical properties of the selected compounds based on quinone and viologen derivatives. The kinetic parameters of electrochemical reaction and diffusion coefficients were evaluated from voltammetric experiments using glassy carbon rotating disc electrode at different pH of electrolyte. The selected molecules were tested in a flow half-cell using carbon felt electrodes and the effect of electrode surface functionalization on the reversibility was investigated. Finally, the mid-term electrochemical stability of the most promising candidates was assessed using repetitive constant current charge-discharge cycles. The chemical structure of the redox molecules before and after the cycling is evaluated by NMR analysis of the electrolyte.

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Sulfur Doped $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) Ceramic Membrane for Solid State Li-Air Batteries

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Highly ionic conductive solid electrolytes are utilized in Li-ion and Li-air batteries as for solid electrolyte and ion conductive membranes [1]. $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) glass ceramic membranes are the most promising candidates to be functionalized in Li-air battery systems owing to their high electrochemical stability and corrosion resistance. Although great strides have been achieved, ionic conductivity of these electrolytes is required to be increased further for better electrochemical performance of batteries [2].

In this study we report the succesful synthesis of sulfur doped LATP(S-LATP) glass ceramic membranes by combining sol-gel method with sulfur-ethylene diamine chemistry. It is aimed to replace oxygen with sulfur in $(PO_4)_3$ tetrahedra and decrease the activation energy of lithium ion movements and increase the conductivity of LATP electrolyte. Surface morphologies of the produced S-LATP membranes were characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) was used to determine the elemental surface composition of the S-LATP membrane. Structural and phase characterization of the S-LATP were performed using Raman spectroscopy and X-ray diffraction (XRD) patterns. Compatibility of S-LATP with lithium metal shown by long term chronoamperometric cycling in symmetric cells. Charge transfer resistance (R_{ct}), ionic conductivity and activation energy of the membrane were measured via EIS using Nyquist curves. Eventually, ionic conductivity of the LATP membrane was increased without sacrificing the mechanical properties of LATP membrane.

Keywords: Solid electrolyte, Sulfide Doping, LATP, Ionic conductivity

Acknowledgments

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Effect of different lithium salts on the electrochemical performance of PVDF-HFP gel polymer electrolytes for Li-O_2 battery

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Among rechargeable batteries, lithium-oxygen (Li-O_2) batteries offer one of the highest theoretical specific energy density (approximetly 11.5 kWh/kg). A conventionel non-aqueous rechargable lithium-oxygen battery (LOB) consists of lithium metal anode, a porous cathode, and a Li^+ conducting liquid electrolyte and seperator to prevent short circuit between two electrodes. However, there are several issues which prevents to use liquid electrolytes for LOB such as low volatile temperature, passivation of metal anode surface and decomposition of electrolyte at higher potential after 4.0 V. Another issue for using liquid electrolyte is leakeage problem [1, 2].

Here, our aim is to replace volatile, flammable and leakable liquid electrolytes with polyvinylidenefluoride-hexafluoropropylene (PVDF-HFP) based gel-polymer electrolyte. The gel-polymer electrolyte was prepared with dissolving of PVDF-HFP polymer into acetone and ammended type of lithium salts and its concentration. We have prepared $LiPF_6$/PVDF-HFP, $LiClO_4$/PVDF-HFP and LiTFSI/PVDF-HFP polymer electrolytes and molar concentration ratio of lithium salts ammended from 1.0 M to 2.0 M to investigate effect of lithium salts on the ionic conductivity and electrochemical performance of polymer gel electrolyte for lithium oxygen batteries. Electrochemical performance of gel polymer electrolytes were tested using ECC-Air test cell. In this cell, lithium foil was used as anode, gas diffusion layer (GDL, Sigracet 24BC) as cathode and gel polymer as electrolyte~~.~~. Ionic conductivity and actvitation energy of the gel polymer electrolytes were calculated via EIS measurements. Reaction potentials of the Li-O_2 cells were conducted by cyclic voltammetry. Galvanostatic charge-discharge profile of cells were performed between 2 V and 4.5 V at 0.1 mA/cm^2. According to results, we have found the optimum salt concentration for high ionic conductivity and the best reversible cycleability.

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Fe-doped Manganese Dioxide films for supercapacitors

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Manganese Dioxide (MD) thin films are considered as cheap and environmentally friendly material for supercapacitors. There are various modification of MDs with different physical and electrochemical properties. In presented work the films with desired properties were obtained in Fe^{2+} containing solutions on platinum electrode by electrodeposition. The optimal composition of the solution, determined experimentally, was the following: $2\cdot10^{-3}$ M Mn^{2+} + 10^{-3} M Fe^{2+} + 0,4 M Na_2SO_4 + $5\cdot10^{-3}$ M H_2SO_4. The electrodeposition of the film was fulfilled at room temperature, at 1,2 V potential (vs. Ag/AgCl). The pseudocapacitance of the film is based on the reversible redox reaction:

$$MnO_2 + H^+ + e^- = MnOOH$$

The electrochemical properties of the film were studied by cyclic voltammetry in 0,5 M Na_2SO_4 solution at 50 mV/s scan rate. For determination of specific capacitance, the following equation was used:

$$C=(I\triangle t)/\ m\triangle V$$

where I (A) is the discharge current, t (s) is the discharge time, m (g) is the mass of the MD film, and $\triangle V$ (V) is the voltage interval (0,9 V). Doping of MD film with Fe increased the capacitance. Moreover, was improved the shape of voltammogram curve – it become more rectangular. The increasing of the thickness of the films from 50 nm to 300 nm also enhanced the capacitance. However, the film capacitance without doping was less depended on the thickness of the film and after 150 nm was slightly changed. Apparently, intercalation of iron in MD structure increases its electro conductivity and furthermore, improves diffusion of the proton in solid phase.

In many researchers opinion, diffusion defines the rate of the operating redox reaction. Each film with the thickness 100, 200 and 300 nm underwent 1000 cycle of redox reaction. For the first two film, the capacity after 50 cycle almost did not change and for 100 nm thick film it was equal to 390 F/g, but for the 200 nm film - 370 F/g. The voltammogram shape also did not change. After 1000 cycle, the loss of capacitance, compared to the first cycle, was 10 %. At this point, the resource of the cycling was not thoroughly depleted. The thick film (300 nm) at the same conditions lost his capacity quite fast and at the end of the cycling was 35% of the initial capacitance. In addition, the shape of the voltamogram was deteriorated sharply.

The investigation of influence of Fe^{3+} ions on the properties of MD film was carried out in condition of separated anodic and cathodic spaces. The capacity of obtained film was increased by 25 % and for 50 nm thick film it was 500 F/g. Moreover, the potential scan interval was increased to 100 mV. For determination of the mechanism of formation of manganese dioxide and intercalation of iron ions in the structure of MD was fulfilled the following experiments: manganese dioxide film was kept in Mn^{2+} ions solution, then was thoroughly washed with DI water and measured voltametric curve in 0,5 M Na_2SO_4 solution. The curve had peak shape at the potential of electrodeposition of MD. Obviously, there takes place chemosorption of Mn^{2+} on MD surface and MnOOH is obtained, which is then oxidized to MnO_2. If the MD film was previously kept in Fe^{2+} ions solution, the current of voltamogram peak was two times smaller. In this case, undergoes chemosorbtion of Fe^{2+} ions and the amount of MnOOH is two times less. At the same conditions, keeping of MD film in the solution containing Fe^{3+} ions, no peak occurred on voltamogram. Therefore, it can be conclude, that intercalation of Fe^{3+} ions in the structure of manganese dioxide occurs by adsorption.

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Fe(II) Mixed Ligand Complexes for High Energy Density Non-aqueous Redox Flow Batteries

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Redox flow batteries are recently considered as a promising technology for large scale energy storage systems. Although some types of the battery have been commercialized, their low working voltages caused by the aqueous electrolytes limit their further applications. Using organic solvents has previously been attempted and the idea of non-aqueous redox flow batteries is proposed. However, the low solubilities and poor electrochemical properties of the redox couples inside the organic electrolytes have become the main issue. In this work, to improve the solubility, a series of Fe (II) based “mixed ligand” complexes were designed and synthesized and their chemical and electrochemical properties were measured and discussed. We confirm that for Fe (II) complexes the ligand equilibration occurs in solution. We also propose the mechanism of the redox processes of these complexes and understand how the mixed ligands will affect the redox potentials of the Fe (II) complexes. Furthermore, we confirm that the mixed ligand structure can improve the solubilities and diffusion rate of the complexes. We believe that at least one of these complexes is suitable as the redox couple in a flow battery. The mixed ligand effect will also be beneficial for designing other new high solubility redox materials in non- aqueous flow batteries.

Screen-Printable Thixotropic Gel Electrolytes Consisting of Fluoropolymers and Cellulose Derivatives for Form-Factor-Free Lithium-ion Batteries

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All-solid-state lithium-ion batteries are receiving considerable attention due to their safety superiority and high energy density achieved by bipolar configuration. Inorganic solid electrolytes are explored as a key-enabling material of the all-solid-state lithium-ion batteries. However, their critical challenges, including grain boundary resistance, interfacial instability with electrode materials and complicated processability, remain yet unresolved. Here, we demonstrate a new class of gel electrolyte with reversible thixotropic transformation between gel and sol states and abuse tolerance as an effective and scalable approach to address the longstanding issues. The gel electrolyte consists of cellulose derivative/fluoropolymer matrix and conventional liquid electrolyte. The representative polymer species of hydroxypropylcellulose (HPC) and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) are schematically shown in the Figure below. The thixotropicity is appeared particularly when the polymer system consists of flexible polymer chain molecules (e.g., PVdF-HFP) and rigid rod-like (or liquid crystalline) polymer molecules (e.g., HPC) with the optimized compositions. The reversible thixotropic transformation is realized via sol-gel transition based on Coulombic interaction of polymer matrix with carbonate-based liquid electrolyte. This unusual rheological feature allows the gel electrolyte to be printed in various forms to prepare form-factor-free cells. In addition, the gel electrolyte shows low crystallinity playing a viable role in delivering high ionic conductivity. Based on understanding of rheological and electrochemical characteristics of the gel electrolyte, we also fabricate a pouch-type form-factor-free cell assembled with the gel electrolyte using sequential screen-printing process. The resultant lithium-ion cell shows exceptional safety upon exposure to various abuse conditions, along with decent electrochemical performance.

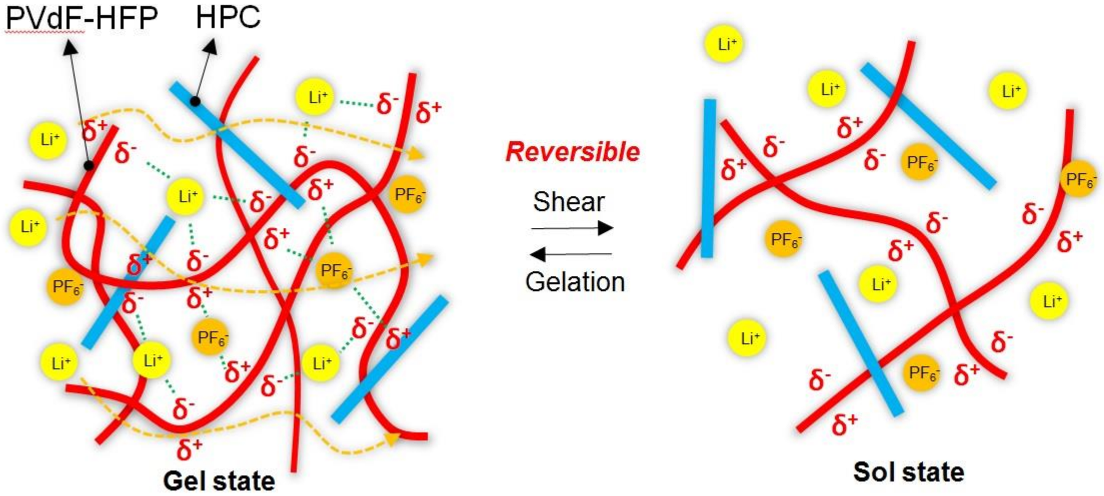

Figure. Schematic illustration of molecular interaction of thixotropic gel electrolyte.

UV-cured Novel Polymer Electrolyte Directly Pendant Lithium Fluorosulfonyimide (LiFSI) for Li-ion batteries

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In this paper, we report the synthesis and characterization of novel fluorosulfonyimide acrylic based polymer electrolyte membranes for lithium batteries. The characteristic structure of this monomer is containing lithium salt inside, not blend type. The solid polymer electrolyte was prepared by UV-curing process, which is well known for being easy, low cost, fast and reliable. Novel fluorosulfonyimide acrylic monomer was synthesized from fluorosulfonyisocyanate and acrylamide. Fluorosulfonylisocyanate was synthesized by exchange reaction from chloride to fluoride using antimony trifluoride. It consists of a free radical photo polymerization of poly-functional monomers with new fluorosulfonyimide acrylic monomer. Tetra-acrylate functional monomer was chosen as it can readily form flexible 3D networks. And also glycidyl methacrylate and isobonyl acrylate were additionally enhance the flexibility of movement of Li^+-ions inside the polymer matrix. The tests on the ion conductivity, electrochemical stability and performance of the membranes put in evidence the importance of the polymerization in presence of multi-methacrylates acting as reactive crosslinking co-monomers. A series of membranes were studied by ^1H NMR spectroscopy, thermo-gravimetric analysis. Also surface morphologies were assessed by atomic force microscope (AFM).

Keywords: UV-curing; Lithium-ion batteries; Electrolyte; Ionic conductivity; Electrochemical stability.

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Novel Non-Aqueous Electrolytes and Enhancement of its Electrochemical Performances by using Sulfonyl Imide as Additives for Li-ion Battery

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Novel non-aqueous organic electrolytes with wide electrochemical window and high ionic conductivity have great potential for rechargeable lithium-ion batteries. Herein, we report the synthesis of a novel ionic salt, lithium carbonylbis(fluorosulfonyl)imide (LiCFSI) as an electrolyte for the application in lithium-ion battery (LIB). The as-synthesized LiCFSI exhibited high purity and yield, which was characterized by various spectroscopic techniques. The LiCFSI electrolyte showed wide electrochemical stability (ca. 4.8 V *vs.* Li/Li^+) and high thermal stability (330 ºC), good Li^+ conductivity (ca. 8.15 mS/cm at 30 ºC), and low intrinsic viscosity, which concurrently delivered a specific discharge capacity of ca. 134.92 $mAhg^{-1}$ at 0.1 C with the full LIB configuration of $LiFePO_4$/electrolytes/graphite. The performance of this LiFSMIPFSI electrolyte was enhanced further by the addition of conventional lithium bis(fluoro-sulfonyl)imide (LiFSI) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) ionic salts (20% each) as additives with the specific discharge capacity of ca. 156.92 and 149.27 $mAhg^{-1}$, respectively, at 0.1 C. This is mainly due to the additional enhancement of Li^+ conductivity and its concentrations in the electrolytes induced by the additives. The LiCFSI electrolyte with LiFSI additive based LIB showed the highest cycling stability (capacity retention ca. 99.55%) among the electrolytes after 500 charge-discharge cycles. Thus, the present work contributes to the development of new ionic salts and its effects upon the addition of additives on LIB performance.

Keywords: Ionic conductivity, Lithium-ion batteries, Electrolyte, Solid electrolyte interface, Cyclic Stability

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