Book of Abstracts of the

# 11th Spring Meeting of the International Society of Electrochemistry

## Theoretical and Computational Electrochemistry

23 to 25 May, 2012, Georgetown University
Washington, DC, USA

Training School, 21 and 22 May, 2012

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# Computational and Experimental Approaches for the Design of Novel Materials for Electrical Energy Storage Applications

Héctor D. Abruña
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*Energy Materials Center at Cornell (emc$^2$)*
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This presentation will deal with a combined computational/experimental approach for the design of novel materials for electrical energy storage applications with emphasis on hybrid materials containing a conducting polymer backbone with redox-active (Faradaic) pendants. We present a computational screening study for downselection of pendant candidates and a systematic study of structure-electrochemical properties relationships. From this study, a generalized approach for determining the formal potential of oxidation of organic pendants is presented. Many of the structural parameters with which the oxidations can be tuned are independently addressable. Results from the computational studies are validated against experimental measurements. Similar formalisms can be applied to other systems where the ability to rationally tune redox active components is desireable.

# Some Problems in Modern Electrochemistry How Can Theory Help?

Allen J. Bard
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A brief overview of the current approaches to studies of electrochemical reactions and will be followed by more detailed examples from our labs.

One area of interest is understanding the mechanisms of heterogeneous electrocatalysis, Important in such experimental studies is the determination of adsorbed surface species, preferably with good spatial and temporal resolution A new scanning electrochemical microscopy (SECM) technique operating in the transient feedback mode, called substrate interrogation SECM,[i] allows the detection and direct quantification of adsorbed species on the surface of electrodes at sub monolayer coverage. In this method the substrate electrode is held at a potential for a given time, then brought to open circuit. An SECM tip, operating in the cyclic voltammetry mode, generates a species from a reversible redox mediator that interrogates the substrate and reacts chemically with (titrates) the adsorbed species. In this mode, the substrate diameter must be of the order of the tip diameter and the tip positioned very close to the substrate, i.e. at a distance ~ 0.1 of the tip radius. The sensing mechanism provides a contrast between positive and negative feedback, which allows a direct quantification of the amount of species reacted at the substrate. Results based on oxygen, hydrogen, CO and others at Au and Pt electrodes will be described. Simulations of this mode of operation show good agreement with the experimental results.

In the area of nanoelectrochemistry, electrochemical studies of single molecules or nanoparticles (NPs) are emerging, but are challenging. Because one cannot yet measure the transfer of a single electron, methods that amplify the signal obtained from single molecules or NPs by many orders of magnitdue are required. Experiments like trapping a molecule in a small cavity where it can make repeated excursions between two electrodes or studies of immobilized molecules with appropriate optical properties (e.g. appropriate polymer molecules) by single molecule spectroelectrochemistry (SMS-EC) have appeared. A more general direct electrochemical approach involves collisions of metal or other catalytic NPs with an electrode by using a novel current amplification scheme.[ii] A number of different NPs and electrode reactions have been employed in such studies and information about particle size, collision frequency and potentially the details of the nature of the charge transfer process at the electrode surface obtained. Understanding the details of such stochastic responses in principle allow insights into questions that cannot be addressed in ensemble measurements.

Finally the theoretical needs for the above projects and other electrochemical problems will be addressed.

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[i] J. Rodríguez-López, M. A. Alpuche-Avilés, A. J. Bard "Interrogation of Surfaces for the Quantification of Adsorbed Species on Electrodes: Oxygen on Gold and Platinum in Neutral Media" J. Am. Chem. Soc. 130, 16985-16995 (2008).

[ii] S. J. Kwon, H. Zhou, F.-R. F. Fan, V. Vorobyev, B. Zhang, A. J. Bard "Stochastic Electrochemistry with Electrocatalytic Nanoparticles at Inert Ultramicroelectrodes-Theory and Experiments" Phys. Chem. Chem. Phys. 13, 5394-5402 (2011).

# Quantum Mechanical Evaluation of Photoelectrochemical and Solid Oxide Fuel Cells

Emily A. Carter
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We have launched a major research effort to use quantum mechanics techniques to search for robust, efficient, and inexpensive materials for photo-catalytic electrodes (PCEs) that convert sunlight, carbon dioxide, and water into fuels and for solid oxide fuel cells (SOFCs) that convert fuels to electricity. PCEs providing fuels to SOFCs could represent a pathway to clean, efficient, renewable electricity. Various observables that are key metrics for determining the utility of a given material can be accurately calculated from quantum mechanics; we will discuss our theoretical schemes for each observable and how we validate our approach. In the solar energy conversion arena, despite periodic media reports to the contrary, no efficient PCEs are available yet. I will discuss why it is so difficult to find effective PCE materials; in particular I will enumerate the nontrivial constraints that they must satisfy to achieve high efficiency. Limiting oneself to abundant elements further constrains the design space. As a result, we focus primarily on first row transition metal oxide parent materials. In our SOFC research, we are focused on cathode optimization, often considered the limiting factor in reducing the high operating temperatures of current SOFCs. Porous electrodes can be readily synthesized for SOFCs such that gas transport is facile. If oxide ion diffusion and electron transport could be enhanced, along with rapid dissociative adsorption of dioxygen on the cathode surface, lower temperatures could be used, which would facilitate wider deployment. Key properties of conventional and novel materials, along with some new design principles, will be discussed. The work is revealing which dopants or mixed oxides are likely to provide the most efficient energy conversion materials.

# Physics of supercapacitors and electroactuators at the nanoscale

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This *keynote lecture* will overview the current status of the theory of equilibrium and dynamic properties of the modern double layer capacitors and electroactuators (artificial muscles). Special attention will be paid to the effects related to nanostructured electrodes and the systems based on ionic liquids.

The presentation will focus on the predictions of the theory that can be experimentally verified and those that have been verified already. The revealed dependencies will be analyzed in the context of optimization of performance of these devices, under the slogan: *what is the best structure for the best performance?* These will include such issues as the optimal pore size of nanotemplated electrodes for the maximal energy storage and power delivery, maximal bending of an electroactuator and the fastest time response - for a given voltage.

Overview-like in character the talk will compare approaches of different groups, being, however, centred around original results based on the cooperation projects of the presenter's group at Imperial (including, in the first place, Slava Kondrat and Alpha Lee) and the groups of Yuri Gogotsi (Drexel University), Ralf Colby (PennState), Martin Bazant (MIT), and Maxim Fedorov (University of Strathclyde).

# Trends in activity for the HER and OER on metal and metal-oxide catalysts

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Design and synthesis of energy efficient and stable electrochemical interfaces (materials and double layer components) with tailor properties for accelerating and directing chemical transformations is the key to developing new alternative energy systems. For example, improving the sluggish kinetics of the electrochemical transformation of water to molecular hydrogen and oxygen in alkaline environments is essential for reducing the massive energy losses associated water-alkali electrolyzers. Although a very large number of materials have been tested for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), the two key reactions associated with water-alkali electrolyzers, all of the currently used catalysts operate with rather low efficiency. One of the major reasons for a such slow progress is that the selection of these materials has been guided by a purely trial-and-error and/or a combinatorial approach, and no studies focusing on systematic understanding of trends in the fundamental, atomic-scale catalytic properties of these reactions on well-characterized materials have been established.

In this lecture, we demonstrate that by studying the breaking up and making up of the H-OH bond on well characterized, stable, and conductive *3d-M(M=Ni,Co,Fe,Mn)* (hydr(oxy)oxides on metal (Pt and Au) substrates, it is possible to find the guiding principles (descriptors) that control the rates of the HER and the OER in alkaline environments. The stoichiometry, oxidation state and morphology of 3d-M (hydr(oxy)oxides on Pt surfaces are studied by a combination of x-ray absorption spectroscopy (XAS) and scanning tunneling microscopy (STM). The overall picture that emerges from the XAS and STM analysis is similar for all of the *3d* elements considered here; the stoichiometry of nanometer-scale 3d-M (hydr(oxy)oxides clusters changes from predominantly $M(OH)_2$ ($\sim M^{2+}$) in the HER to an MOOH ($\sim M^{3+}$) type oxide in the OER region. These consistent trends in the oxidation state and structure of the 3*d* series provides strong evidence that we have a series of well-characterized electrodes which can be used as a basis for finding trends in the kinetics of the HER and the OER.

We also demonstrate that for these two reactions, with completely different reaction mechanisms, the order in activity is the same and increases monotonically from $Ni^{n+}$ to $Mn^{n+}$. Activity trends follow the OH- - -$M^{n+}$ bond strength, which we identify as be the key descriptor for the HER and the OER; indeed, we also find that the same descriptor also describes trends in yet another important reaction, CO electrooxidation. Thus, for the 3*d* elements considered here, $Ni^{n+}$, with its optimal interaction strength with $OH_{ad}$, satisfies the Sabatier principle for catalyst design. For the OER, it is critical to consider the balance for the energetics of $OH^-$ adsorption and the recombination of $OH_{ad}$ intermediates on MOOH materials. We found that controlled arrangement of nanoscale NiOOH clusters manifests a factor of 5 activity increase in catalyzing the OER relative to PtO. In the case of the HER, a balance must be found between the transition state energies for water dissociation and the final state energies of adsorbed $OH_{ad}$ on $M(OH)_2$. The most active $Ni(OH)_2$ and $Co(OH)_2$ catalysts manifest more than a five-fold increase in HER activity relative to the state of the art metal and metal oxide clusters.

We conclude that understanding the complexity (simplicity) of electrochemical interfaces would open new avenues for design and deployment of alternative energy systems.

# Electrocatalysis from First Principles: Mechanistic Insights into the Oxygen Reduction Reaction

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Electrocatalysis is controlled by the elementary reactions that occur at the interface between the electrode and the solution phase along with the electrochemical potential that results across this interface. Elucidating the electrochemical behavior at this interface, however, presents a considerable challenge due to complexity of the surface chemistry, the explicit atomic and molecular structure of the solution phase at the interface, the presence and formation different ions and their specific location in solution or on the surface, and the surface potentials and electric fields that results as a function of the surface reactivity. First principles based simulations of electrocatalysis tend to be limited due the size of the systems required to appropriately model the interfacial structure, and by the fact that ab initio methods are typically constant charge rather than constant potential systems. We present an approach that can begin to simulate the elementary pathways and kinetics for constant potential systems and highlight the challenges of this approach. The results are used to construct first principles based kinetic Monte Carlo simulations to model different electrochemical systems. We discuss the application of the approach to simulate the electrocatalytic reduction of oxygen over transition metal surfaces as well as nitrogen doped carbon-based substrates.

# Electron transfer in Electrocatalysis

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Electrochemical electron transfer reactions involve a change in the solvation sphere of the reactants, and thermal fluctuations to overcome the activation energy; in addition, they depend strongly on the electrode potential. Therefore, they cannot be treated by DFT alone, or only within oversimplified models. In our group we have developed our own approach, which combines electron transfer theory with DFT [1]. The basic idea is the following: DFT provides the electronic energy of the initial and the final state as a function of distance; our theory interpolates between the electronic energies in order to describe electron transfer, and introduces the coupling to the solvent together with the fluctuations.

So far, we have applied our theory to hydrogen evolution both on bare metal electrodes and on a variety of nanostructured surfaces. The results are encouraging [2], and we will present a number of examples. However, hydrogen is a particularly simple case since the electronic energy of the hydrogen atom or molecule is easily obtained by DFT, and the electronic energy of the corresponding ion, the proton, is zero. An application to other reactions involves performing DFT calculations for ions, and an extension of our interpolation scheme. We have chosen the reaction:

$$OH^{-}(sol) \;\rightarrow\; OH_{ad} + e^{-}$$

as a first example. Correspondingly, we have performed DFT calculations both for the OH radical and the anions – the latter involve a few technical tricks to localize the excess negative charge. The Coulomb repulsion $U$ between electrons on the same orbital is adjusted so that it provides the correct interpolation between the two states. With these data, we have calculated the free energy surface for this reaction at various electrode potentials.

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# The Computational Electrochemistry of Metal Oxides

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Metal oxides vary in electronic structure from metals to wide gap semiconductors. Examples of metallic systems are transition metal oxides with partially filled d-shells. The best electrocatalysts (e.g. $RuO_2$ with a $d^5$ configuration) belong to this category. Wide gap semiconductors, while often poor electrocatalysts, are used in photocatalysis, in particular $d^0$ and $d^{10}$ compounds such as $TiO_2$ and $SnO_2$. A most prominent application of metal oxides is as anode in either the electro or photo catalysis of oxidation reactions (notably water electrolysis). However, the nature of the HOMO of metallic electrocatalysts is predominantly of d-character (with some oxygen admixture) while the HOMO of $d^0$ and $d^{10}$ photocatalysts consists almost entirely of O2p orbitals. This raises interesting chemical questions. Can the mechanism for electro and photocatalysis of anode reactions be the same when the nature of holes is so different?
The electrocatalysis of water oxidation has been investigated in detail by density functional theory (DFT) based electronic calculation methods (see for example the talks by Norskov, Rossmeisl and Liu in this conference). The computational study of oxidation by photogenerated holes is at a less advanced stage. The difficulty holding such calculations back is the treatment of holes in O2p bands. The DFT methods used for extended systems have a tendency to delocalize holes. Experimentalists seem to agree however, that the holes involved in surface reactions are localized.
Recent progress in the implementation of exact exchange in periodic systems has overcome some of these problems[1]. In this talk we will report and discuss our results using these methods focusing on the formation of radical defects on aqueous $TiO_2$[2]. Redox levels of the solid, absorbed species and the uncatalyzed reaction in homogeneous solution are treated at the same level of theory using a recently developed molecular dynamics normal hydrogen electrode[3,4]. This method uses the solvation free energy of the proton computed by free energy perturbation as energy reference. This also enables us to account for another property of metal oxides namely their acid/base character leading to proton exchange with the electrolyte charging the surface[5]. We also comment on the general question raised above concerning possible differences in anodic catalysis by metallic and semiconducting metal oxides.

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# New Directions in Nanoscale Electrochemical Imaging: Revealing the True Activity of Surface Steps, Terraces, Nanoparticles and Nanotubes

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Many computational and theoretical methods applied to electrochemistry describe processes at the molecular-level and nanoscale, but the overwhelming majority of experimental techniques have remained stuck at the macroscale. Indeed, after about half a century, cyclic voltammetry at mm-sized electrodes is probably still the main method for electrochemical investigations.

Although more technically challenging, nanoscale methods, and particularly nanoscale electrochemical microscopy, open up the possibility of investigating interfacial charge transfer at a level commensurate with theory and computation. In particular, shrinking the length scale of electrochemical measurements allows single facets and surface features to be investigated, providing a natural bridge between experiment and theory.

This paper will provide an overview of our recent developments of scanning electrochemical cell microscopy (SECCM)[1,2] and intermittent-contact scanning electrochemical microscopy (IC-SECM)[3] for nanoscale imaging. We will show how these techniques can be described by detailed 3-D finite element models, providing a foundation for quantitative applications. Through studies of carbon-based electrodes and catalytic nanoparticles, it will be shown that oft-quoted models for the electrochemical activity of some of these materials[4] require significant revision, providing new opportunities for theoretical and computational chemists.

We thank the European Union FP7 programme, through an ERC award and Marie Curie Fellowships, along with EPSRC, for supporting much of this research.

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# Oral Presentations

# Application of the Condensed Fukui Function to Predict Reactivity in Core-Shell Transition Metal Nanoparticles

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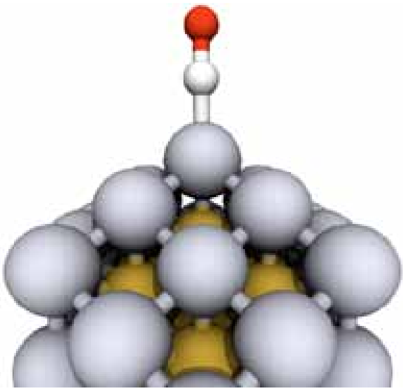
Frontier molecular orbital (FMO) theory has been very successful in explaining and predicting organic chemistry reactions. FMO concepts have been given a theoretical foundation within conceptual density functional theory (DFT) making these concepts amenable to computation. In particular, the Fukui function has emerged as a powerful predictor of chemical reactivity. It is further possible to localize the Fukui function to atomic sites using the "condensed" Fukui function. This condensed function provides a particularly powerful tool for analysis.



Despite the success of the Fukui function in the realm of organic chemistry, there are comparatively few studies of the Fukui function on transition metal surfaces and nanoparticles. Thus, validation of the Fukui function as a reliable predictor of chemical reactivity on transition metal surfaces and nanoparticles is of considerable interest.

Our previous work on transition metal nanoparticles has established that the condensed Fukui function yields information consistent with the predictions made by the d-band center model. In this talk, we will describe our efforts to extend use of the condensed Fukui function as a predictor of chemical reactivity for core-shell transition metal nanoparticles. Using density functional theory calculations, we investigated Au@Pt and Ru@Pt nanoparticles with a CO molecule bound to various surface Pt atoms. The results of the calculations on these molecules will be compared to the available theoretical and experimental data, and to the predictions made by the d-band center model.

# Effects of Acid Medium Dealloying on Oxygen Reduction Reaction Activity

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Nanoalloy particles are state-of-the art electrocatalysts for the oxygen reduction reaction (ORR) in acid medium. In particular, Pt-based nanoscale alloys show enhanced activity with respect to pure-Pt. However, upon contact with an acid oxidative environment, several of the most effective alloy components are prone to easy dissolution leaving behind a modified structure that may contain different degrees of nanoporosity.[1,2] Interestingly, the dealloying process has been found to be a useful technique for enhancing the ORR catalytic activity, and various dealloying protocols are being tested to maximize activity of the resultant nanoporous matrix while maintaining reasonable long lifetimes. Therefore, elucidating the origins of the enhanced activity and its associated durability features is a crucial step where theory and experiment may contribute.

Recently we introduced a new concept associated with enhancement of the catalytic activity driven by geometric and electronic confinement caused by the interaction of metallic surfaces separated by sub-nanometer distances.[3-5] It was found that the electronic density distribution arising from the particular confined geometry may induce significant changes in reactivity of the exposed molecules which is translated in lower activation barriers, alternative reaction mechanisms, and formation of radicals thus changing the catalytic pathways based on a single surface. Here we apply this concept and present our most recent findings using density functional theory related to the effect of nanoporosity on ORR catalysis with Pt-based alloys. Specifically, our DFT analysis follows individual ORR steps based on model geometries that represent the nanoporous matrix. In addition, we discuss and present preliminary results of a Kinetic Monte Carlo model emulating the dealloying process where the various variables affecting the process such as electrochemical potential, electrolyte composition, and extent of surface oxidation are incorporated into the model.

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# Overlimiting Current in Porous Media

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Salt transport in bulk electrolytes occurs by diffusion and convection, but in microfluidic devices and porous media, surface conduction and electro-osmotic flow also contribute to ionic fluxes. The classical theory of electrokinetic phenomena in porous media assumes linear response to a small voltage, where the electrolyte concentration is only weakly perturbed. When a large voltage or concentration gradient is imposed, some surprising nonlinear electrokinetic phenomena result from the competition between bulk and interfacial transport in a microstructure. At constant voltage, the microstructure can sustain an over-limiting current (exceeding diffusion limitation) without any hydrodynamic or chemical instability [1]. At constant current, a "deionization shock" can propagate through the microstructure, leaving behind a macroscopic region depleted of ions and particles. This talk will present the mathematical theory [2] and new experimental evidence for surface-driven overlimiting current and deioniziation shocks in porous glass frits, as well as applications to water deionization by ``shock electrodialysis" [3].

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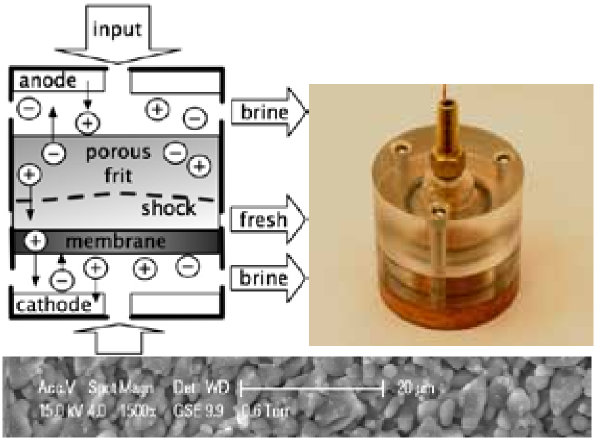

Fig 1. Prototype shock electrodialysis system [3]

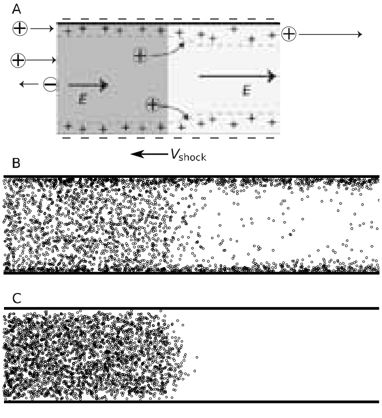

Fig 2. Physics of deionization shocks[2].

# Ab Initio Studies Of Proton Coupled Electron Transfer Paths Between Catalytic Polypyridyl Ruthenium Complexes and Carbon Electrodes In Aqueous Media

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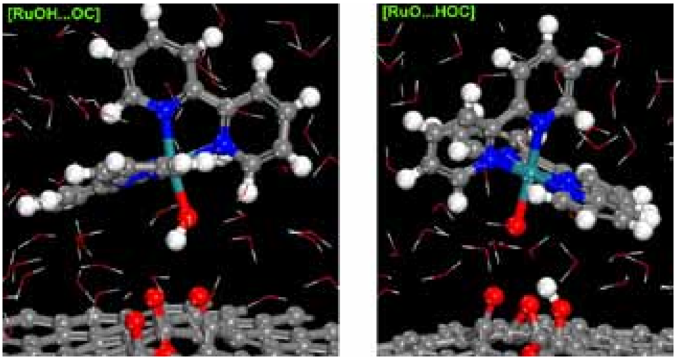
Proton coupled electron transfer is an elementary step in many electrochemical and photoelectrochemical reactions. Understanding such paths may ultimately aid in the design of inorganic complexes that can help to promote such PCET reactions in electrocatalytic reaction systems. In this paper ab initio density functional theory was used to examine the proton coupled electron transfer in aqueous phase from the polypyridyl ruthenium complex to surface ketone groups on a graphene substrate. Three different graphene surfaces were investigated including oxygen-modified graphene surface, graphene armchair edge, and graphene zigzag edge. The proton transfer reactivity depends on the surface composition, i.e. the number of ketone groups on graphene basal plane. The ketone groups at the graphene edges were shown to have a higher reactivity than those on the basal plane. The potential dependent energies for two proton transfer states [RuOH…OC] and [RuO…HOC] (see figure below) were calculated for graphene basal plane and edges.



# Origin and Extent of the Scaling Relationships between Adsorption Energies

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The discovery of linear relations between the adsorption energies of atoms and their hydrogenated species on various surfaces is one of the major advances of theoretical heterogeneous catalysis of the past decade [1, 2]. These relationships provide the necessary atomic-scale insight to test rapidly reaction mechanisms, which ultimately allows determining trends in catalytic and electrocatalytic activity [3-5]. In spite of their fundamental importance and numerous applications, their origin and extent are not clear. In this talk we will present the results of a systematic DFT study of the adsorption energies of C, Si, N, P, O, S, F and Cl onto the Near-Surface Alloys (NSAs) of Pt(111) and transition metals, and the scaling relationships between them [6].

Our studies show that scaling relations are not restricted to atoms and their hydrogenated species and provide evidence for the existence of generalized scaling relations. Moreover, our results suggest that the existence of generalized scaling relations is a result of identical variations of adsorption energies with respect to suitable electronic-structure parameter(s). For the particular case of NSAs of Pt and transition metals, the combined number of valence electrons of the adsorbate and the surface components appears to be the key parameter. Besides, there is predictive power in this analysis, since the minimal adsorption energies are normally displayed by systems with optimal electronic configurations. This reveals the search for higher stability that underlies adsorption processes.

Finally, we will provide a simple solution to non-scalability based on electron-counting rules.

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# Nanoscale Phenomena in Fuel Cell Electrocatalysis

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Improvements in power density, cost reduction, and durability of polymer electrolyte fuel cells hinge on progress in catalyst layer design.[1] The overall objective is to maximize the rate of desired electrochemical reactions, in particular the oxygen reduction reaction (ORR), at drastically reduced loading of platinum. Pertinent targets in electrode research are the intrinsic activity of electrocatalytic materials and the mass-specific effectiveness factor of catalyst utilization. Physical theory and *ab initio* electrochemical approaches are needed to establish a profound basis for materials design and structural optimization of catalyst layers in view of these targets. The variable that controls thermodynamic state and electrocatalytic properties of catalyst nanomaterials and catalyst layers is the metal phase potential. It determines the oxidation state of Pt, the surface charge density at Pt-Ox, the concentration of protons in electrolyte solution, and the solution phase potential. Obtaining the solution for these coupled structure-sensitive functions represents a self-consistency problem. For the case of ultrathin ionomer-free catalyst layers, we have developed a phenomenological approach to study this coupling.[2] The model consists of a water-filled cylindrical nanopore with Pt deposited at pore walls. Proton and potential distributions in the pore depend on the properties of the charged metal|solution interface, including potential of zero charge, Helmholtz capacitance and ORR kinetic parameters, as well as on the pore geometry. The impact of these parameters on the effectiveness of Pt utilization will be discussed. The impedance variant of the model provides capabilities to separate the kinetic, electrostatic, and transport contributions to the Faradaic current density, and to extract metal|solution interfacial parameters.[3] The key aspect in the model that defines the ORR activity and effectiveness factor of Pt in nanostructured electrodes is the dependence of the metal charging behaviour on metal phase potential and oxidation state. To this end, we employ DFT-based ab initio studies and develop a kinetic model of Pt oxide formation and reduction; preliminary results of these efforts will be presented.

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# Electrochemical Vs. Electromechanical Effects: Rationalizing Electrochemical Reactivity at Interfaces

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The need to reduce $CO_2$ production and to find more powerful and lighter batteries for our always more demanding electronic devices necessitates to design more efficient electrochemical systems. Therefore, there is a great need to model them at the atomic scale using *ab initio* methods.

Most of the bulk thermodynamics of electrochemical reactions can be directly extracted from conventional density functional (DFT) calculation. Nevertheless, whenever the electrochemical reactions at the interfaces dominate, in particular, in heterogeneous systems like in fuel cells, the knowledge of the bulk properties is not enough: the interfacial electrochemistry cannot be simply extracted from standard uncharged calculations as the effect of the applied voltage and local electric field has to be accounted for and modifies strongly the reactivity. Therefore, one of the most challenging issues for the computation of the electrochemical reactions is to take into account the electric field and the electrode potential change at the interface.

We have implemented methods[1,2,3] using the powerful periodic density functional theory (DFT), to compute surfaces under an applied potential. We then show the validity of the approach by looking at the effect of an electric field on a CO/Pt(111) surface: the CO molecule stretch frequency shifts with the applied electric field as observed experimentally.

We subsequently investigate the reasons for the property changes with the applied potential. Two main effects dominate: the first one is the interaction of the electric field with the surface dipole moment that causes a mechanical distortion of the surface structure; the second one is a modification of the electronic structure induced by the charging and the potential modification. We show that the dominant effect can directly be found by using the surface Fukui function that gives some good insights in the surface electrochemistry.

Finally, we show that the electrochemical approach can also be useful to understand some surface phenomena[4,5] by generalizing the disproportionation concept to surfaces.

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# Oxygen Reduction for Fuel Cells and Batteries: Mechanistic Studies and the Design of New Catalysts

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In this talk, we discuss aspects of our work related to the structure and reactivity of electrode surfaces. We report on our efforts directed at establishing the mechanism of oxygen and peroxide reduction on many different metal surfaces. By using a combination of spectroscopic, imaging, and x-ray scattering techniques combined with detailed calculations, we show that a crucial step involves the spontaneous clevage of the O-O bond to form a mixed metal-hydroxide complex. This hydroxide complex is reduced during the electron transfer event, leading to the product water. The understanding derived from the mechanistic work provides directions for synthesis of advanced catalysts for oxygen reduction. In particular, we have synthesized a series of bio-insipired metal coordination polymers exhibiting oxygen reduction activity. Extension of this work to the oxygen reduction/evolution system in metal-air battery cathodes will be reported.

# Density Functional Theory studies of interfacial electrochemistry and catalysis

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In this talk, I will outline some of our recent work in the use of Density Functional Theory to study interfacial phenomena of relevance to energy storage materials and to electrocatalysts. I will describe simple models to determine semiconductor and metal surface thermodynamics in electrochemical environments, and I will apply these models to the lithiation of different surface terminations of silicon and various oxides, with a goal of determining the structure sensitivity and stability of these materials to lithiation. If time permits, I will also discuss aspects of the structure sensitivity of the electrooxidation of small organic molecules on metal surfaces, including metal facets and bifunctional oxide-metal interfaces.

# A density-functional theory study of hydrogen evolution reaction at a platinum(111)/water interface

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Understanding the mechanism of electrochemical reactions at the electrode/solution interfaces (electrode reactions) is of fundamental and technological importance. This is because they have great implication to real applications such as in photovoltaics and fuel cells. However, even for the simplest hydrogen evolution reaction (HER, $H^{+}+e^{-} \rightarrow 1/2H_2$) experimental and theoretical clarification of the reaction mechanism is still a big challenge. This is because of the complexity associated with electrode/solution interface. Here, my focus is on the HER at a platinum (111)/water interface. It is the cathodic reaction of water electrolysis, which is the reverse reaction in the hydrogen fuel cell. Thus, clarifying its mechanism may contribute to the development of an efficient electrode catalyst. In this talk, after a brief introduction on our modeling of electrode/solution interface using the effective screening medium method [1], I will discuss microscopic details of the initial adsorption of proton in HER ($H^{+}+e^{-} \rightarrow H_{ad}$, the Volmer step) [2], followed by the adsorption properties of hydrogen [3], obtained by molecular dynamics simulations based on density-functional theory. Preliminary results for the hydrogen evolution via Tafel ($H_{ad} + H_{ad} \rightarrow H_2$) as well as Heyrovsky ($H^{+}+ H_{ad} +e^{-} \rightarrow H_2$) steps [4] will be also introduced.

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# Theoretical Studies on the Electrooxidation of Pt

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The surface oxidation of Pt(111) seems to be a rather basic and quite simple reaction but nevertheless plays an important role for a wide range of catalytic reactions in gas-phase surface science and electrochemistry. Despite the fact that many experimental studies are focused on single crystal systems with (almost) perfect surfaces, realistic catalysts always contain step-edges, kinks, vacancies and other imperfections on the surface. Especially these lower coordinated sites are believed to play a decisive role for surface reactions and the catalytic performance.

In this talk we will provide a detailed theoretical investigation of the adsorption of oxygen on perfect and stepped Pt(111) using density functional theory and the extended *ab initio* thermodynamics approach. By comparing the temperature and pressure phase diagram for the system in contact with a gaseous $O_2$ atmosphere with the corresponding electrochemical ($p$,$T$,□) phase diagram, characteristics of the surface morphology under specific conditions were evaluated. Comparison to experimental CV measurements revealed the presence of step edge oxide structures prior to the bulk oxidation, which might have interesting implications for electrocatalytic reactions operating under these conditions (*e.g.* the oxygen reduction reaction).

Furthermore, we will extend these concepts from single crystals to the regime of nanoparticles that are often used for electro-catalytic reactions. Focusing on mono- and bi-metallic alloys we will show that nanoparticles are not rigid objects but might change their morphologies and compositions under reaction conditions.

# First principles study on vibration frequencies of sulfate on Pt(111) electrode

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Specific adsorption of sulfuric acid anion on Pt(111) has been extensively studied because of its scientific and technological importance as a model system of the fuel cells.[1] However, there still remains an essential question: which is the major adsorbate, sulfate or bisulfate? This question is exemplified by contradicting interpretations of absorption bands at 1250 and 950 $cm^{-1}$ measured by *in situ* infrared reflection absorption spectroscopy (IRAS) in sulfuric acid solutions.[1] Despite intensive studies, a consensus has not been reached for more than 20 years.

For solving the long-time problem, a density functional theory (DFT) combined with a continuum solvation theory[2] was applied.[3] Figure 1 (A) shows the simulated IRA spectra and the displacement vectors of two vibration modes of sulfate. The 1250-$cm^{-1}$ band ($\nu_4$) and the 950-$cm^{-1}$ band ($\nu_1$) are assigned respectively to the S–O (uncoordinated) stretching mode and the totally symmetric S-O stretching mode of sulfate. Potential dependence of the frequencies (Fig. 1 (B)) also supports sulfate. The 1250-$cm^{-1}$ band strongly depends on the electrode potential (a slope of 58 $cm^{-1}\cdot V^{-1}$), while the 950-$cm^{-1}$ band does not (a slope of –20 $cm^{-1}\cdot V^{-1}$). The trend is similar to that observed in the experiments reported in the literature.[1] As reported previously,[4] other properties, such as the free energy and the electrosorption valency, also support sulfate. In summary, all the theoretical results indicate that sulfate is the major adsorbate.

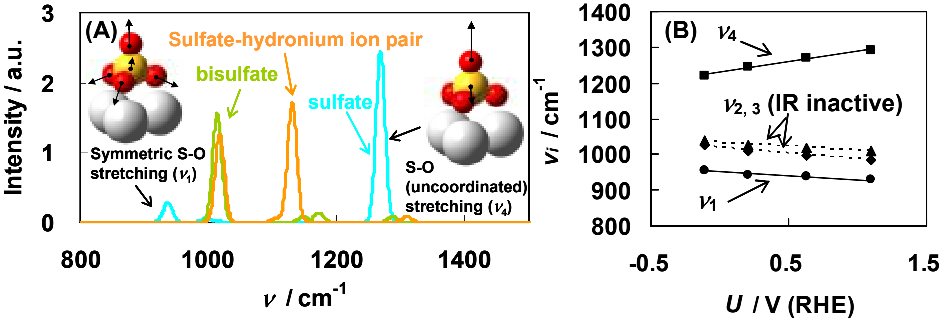

**Fig. 1 (A) Simulated IRA spectra and (B) potential dependent frequencies**

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# Oxygen-Induced Roughening of Pt Nanoparticles

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Since high-index surfaces often show higher chemical activity in comparison to their close-packed counterparts, nanoparticles (NPs) consisting of open surfaces can be promising candidates for various electrocatalytic applications. Recently the group of Sun found that unusual tetrahexahedral (THH) NPs bounded by 24 high-index faces can be prepared by an electrochemical treatment of Pt nanospheres using a square-wave potential [1]. Through a combination of transmission electron microscopy (TEM) and density functional theory (DFT) we studied the equilibrium shape of Pt NPs under electrochemical conditions. Constructing the electrochemical phase diagram for Pt NPs in contact with an oxygen-containing electrolyte, we find that at low and medium potentials (<1.18 V) the polyhedra shapes dominated by low-index (111) faces are stable, while increasing the potential stabilizes the THH shape enclosed only by high-index Pt(520) faces [2]. At high oxygen coverage, obtained at high electrode potentials, the (520) faces are reconstructed to form oxide-like structures. Higher stability of these faces compared to their low-index counterparts results in formation of the rough THH NPs. Our studies suggest that it is possible to stabilize atomically rough NPs by tuning the electrolyte composition and electrode potential in electrochemical systems. As the surface morphology has a strong influence on materials' behaviour in electrocatalytic reactions, the present work has important implications for electrocatalysts that work under oxygen-rich environments.

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# First-Principles Study of Carbon Supported Metal Free Boron-Nitrogen ORR Electrocatalyst

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Fuel cells continue to attract significant attention and are prime candidates for energy generation. Currently, this technology is limited by rare and expensive platinum group metal (PGM) cathode electrocatalysts for the oxygen reduction reaction (ORR). Therefore, it is important to develop non-PGM catalysts to reduce or eliminate current challenges of fuel cell technology. Recently, ORR activity of boron (B) doped and boron-nitrogen (BN) co-doped carbon nanostructures have been reported [1,2]. XPS characterization of ORR active BN co-doped carbon supported electrocatalysts revealed B-C bonds and various B-N-C moieties in the sample [2]. However, the chemistry and the geometry of the active sites in BN co-doped carbon supported catalysts remain unclear. Previous simulations have demonstrated ORR activity of graphitic edge BCN and $BN_2$ moieties [3]. Importantly, non-edge defects could dominate over edge defects for catalysts with sufficiently large surface area. Here, we present results from density-functional-theory (DFT) computations on the ORR activity of combined BN graphitic defect motifs of composition $BN_2$, BCN and $BC_2$ in alkaline medium.

The preliminary results show $O_2$ chemisorption on boron in all BN defect motifs considered in this study. $OOH^-$ chemisorbs on $BC_2$ and decomposes on $BN_2$ and BCN defects such that O is chemisorbed on B and $OH^-$ desorbs. These predictions are consistent with a single site $2x2e^-$ ORR pathway. However, the calculations predict that $O_2$ binds more (less) strongly than $OH^-$ on $BN_2$ (BCN and $BC_2$) defect motifs. This result suggests that $BN_2$ is most active for ORR among the graphitic BN defects considered in this study. However, the calculations also show that the $BN_2$ defect has a higher formation energy as compared to the $BC_2$ and the BCN defects. This prediction implies that graphitic BN defects may only contribute little to the overall ORR activity of BN co-doped electrocatalyst, in contrast to carbon supported $TM-N_x$ (TM=Fe, Co) electrocatalysts where graphitic defect motifs may dominate.

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# Solid-Liquid Interface Electrocatalysis from Periodic DFT-MPB Model: Interface Properties and Tafel Kinetics

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In this talk, I will present our recent progress in understanding solid-liquid interface catalysis [1-4]. Methodologically, we developed a periodic continuum solvation model based on the modified-Poisson-Boltzmann equation within the periodic DFT slab framework, which is designed for studying complex catalytic reactions at the solid-liquid reactions under the influence of electrochemical potentials, surface charges and solution [3,4]. Using the approach, we investigated water oxidation on $RuO_2$ surface and oxygen reduction on Pt surface, and calculated Tafel kinetics quantitatively. We show that the elementary electrocatalytic reactions on surface can be classified into two general classes according to their redox properties, whose activity exhibits distinct potential dependence. Our approach has also been utilized to investigate some other catalytic reactions on nanoparticles in aqueous surroundings [1,2].

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# Effect of molecular adsorption on metal nanoparticles.

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Colloidally prepared metal nanoparticles are gaining attention for catalytic applications because of the advanced possibilities to tailor their size and shape, which are often important factors governing catalytic activity and selectivity. In the case of bimetallic catalysts, composition is usually difficult to control by traditional techniques, but by colloidal chemistry the relative portions of the metals in the nanoparticles can be exactly predefined. This approach offers the advantage of controlling structure and composition of the resulting particles.

Preparation, conservation and protection of metallic or multimetallic nanoparticles require protection with organic ligand molecules if they will remains in a colloidal suspension. When nanoparticles are made of gold, a relatively easy way of protect them is through organic molecular self-assembly, particularly with thiols molecules due to the strong interaction between sulfur and gold atoms. Self-assembly monolayer's (SAM's) have been intensively studied, at experimental[1,2,3] and theoretical level[4,5,6,7], on extended gold (111) surfaces and small Au clusters[8],[9],[10]

In the present talk we show the application of a new semiempirical potential, recently developed in our Lab, to describe molecule-metal interfaces in a more realistic way[11],[12]. Using Density Functional calculations (DFT) in combination with the bond-order concept we have developed a new semiempirical framework which is very simple and easy to implement in standard MD/MC codes. In particular we show the effect of soft and hard surfactant on the structure of gold nanoparticles of > 1nm.

Finally, we will show very recent studies which involve the nucleation and growth processes of bimetallic NPs carried out in solution under control of the chemical potential of the metal ions.

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# Structure Sensitivity of Dimethyl Ether Electro-oxidation

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Dimethyl Ether (DME) is an attractive chemical for both on-board hydrogen generation as well as a fuel in direct electro-oxidation in fuel cells.[1, 2] Experimental studies of the electro-oxidation have demonstrated significant structure sensitivity on Pt – specifically when comparing the (111) and (100) facets.[3] Using periodic, self-consistent density functional theory calculations, we evaluate the thermodynamics of dimethyl ether (DME) electro-oxidation on a number of model (100) and (111) facets of monometallic fcc catalysts, including Au, Ag, Cu, Pt, Pd, Ni, Ir, Rh. Using the results, we predict the most-probable reaction mechanism on each of these catalysts. Based on these proposed mechanisms, we predict the energy efficiency and catalytic activity of each of these metals. Furthermore, by comparing results on the (111) and (100) facets, we attempt to elucidate the origins of the experimentally observed structure sensitivity of DME electro-oxidation.

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# Understanding the Charging Mechanism of Nanoporous Carbon Electrodes from Molecular Dynamics Simulations

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A major challenge in moving towards sustainable and renewable energy sources is to develop lightweight and low-cost storage systems with the capability of leveling the cyclic nature of these sources to satisfy energy demands. Electrochemical double layer capacitors (supercapacitors) store energy at the electrolyte/electrode interface through reversible ion adsorption leading to higher charge/discharge rates and better cyclability but lower energy density compared to batteries. Nevertheless, the recent demonstration that ions from the electrolyte could enter sub-nanometer pores increasing greatly the capacitance [1] opened the way for valuable improvements of the supercapacitors performances. Despite the recent experimental and fundamental studies on that subject, the molecular mechanism at the origin of this capacitance enhancement is still not quite clear. We report here molecular dynamics simulations including two key features: the use of realistic electrode structures comparable with carbide-derived carbons [2] and the polarization of the electrode atoms by the electrolyte. This original design of an electrochemical cell allows us to recover capacitance values in quantitative agreement with experiment and to gain knowledge about the local structure of the ionic liquid inside the pores (local ionic densities, local coordination numbers). Then, from the comparison between planar (graphite) [3] and porous electrodes, we propose a new mechanism explaining the capacitance enhancement in nanoporous carbons.

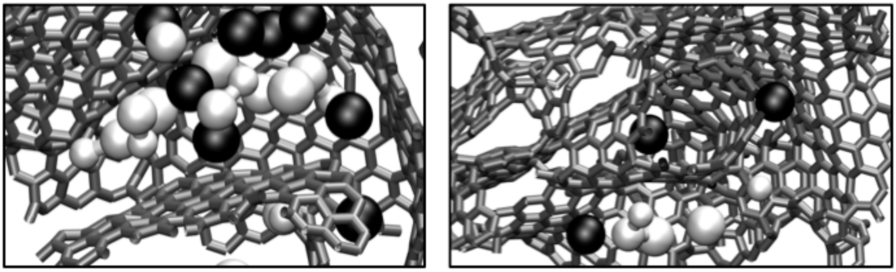

**Fig. 1.** Local structure of the pure ionic liquid inside positively charged nanopores of different geometries (white: $BMI^+$ cations, black: $PF_6^-$ anions, gray: carbon atoms).

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# Island formation on gold surfaces under electrochemical Conditions

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The anion-enhanced mobility of gold atoms is believed to be the basis of the so-called *electrochemical annealing* and formation of gold islands on electrode surfaces (*e.g.* Au(100)) [1]. Although many experimental and theoretical studies already focused on the adatom diffusion, much less is known about how coadsorbates or specifically adsorbed electrolyte ions might influence diffusion barriers or even entire migration mechanisms, which could lead to modifications in the surface morphology.

Performing density functional theory (DFT) studies we have investigated the anion-modified self-diffusion on Au(100). We investigated the adsorption and various migration mechanisms of Au atoms on clean [2] and Cl-covered Au(100) with and without surface defects (*e.g.* step-edges, kink sites, or vacancies). Our studies indicate that in both systems (*i.e.* clean and Cl-covered) the exchange mechanism is the most favorable mechanism for terrace diffusion. Further, we find that for all diffusion processes the presence of co-adsorbed Cl leads to the formation of AuCl-complexes, which remain stable during the diffusion processes. Further, due to this complex formation all diffusion barriers are reduced, which overall should result in faster island formation. Based on our DFT results the next aim will be to generate a reactive forcefield for Au−Au and Au−Cl interactions [3], which will then be used to extract the rates of all possible diffusion processes and which will provide the basis for large-scale kinetic Monte−Carlo simulations, offering macroscopic quantities (*e.g.* diffusion coefficients or island shapes) readily comparable to experiments.

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# Ab Initio Prediction of Oxygen Reduction Performance of Solid Oxide Fuel Cell Cathodes

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Solid oxide fuel cell (SOFC) cathodes made from perovskite oxides can effectively catalyze the oxygen reduction reaction (ORR), which consists of the reaction $O_2$(gas) → $2O^{2-}$(bulk). However, SOFC efficiency is significantly reduced by overpotential in the cathodic ORR, a problem that is likely to get worse as researchers push to lower SOFC operating temperatures. Therefore, there is increasing interest in enhancing the catalytic ability of perovskite cathodes. We have used *ab-initio* density functional theory methods and thermokinetic theory to model properties relevant for the ORR on SOFC cathodes. We have demonstrated for (La,Sr)$MnO_3$ that *ab-initio* energetics can provide insight into the stable defects and their formation energetics[1], enabling improved modeling of defect chemistry critical for the ORR. We have also applied *ab-initio* based thermokinetic modeling to understand effects on ORR of strain in (La,Sr)$CoO_3$ thin films[2] and activity enhancement at interfaces between perovskite (La,Sr)$CoO_3$ and $K_2NiF_4$ (La,Sr)$_2CoO_4$[3]. Despite these and other successes in the community, the goal of robust *ab-initio* prediction of SOFC ORR activity for arbitrary complex oxide systems still remains elusive. However, we have demonstrated an *ab-initio* descriptor that can be simply calculated and then correlated with ORR related energetics and processes in conducting perovskites[4]. This and other descriptors are opening the door to practical tools for *ab-initio* based materials design of SOFC cathodes. This work was supported financially by the U.S. DOE, Award DE-SC0001284, and computationally by the NSF TeraGrid, Grant [TG-DMR090023].

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# DFT Studies of Electrochemical Reduction of $CO_2$ to Methanol on Cu Metal and Cu Oxide Catalysts

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Direct conversion of solar or electrical energy to chemical energy using abundant sources of $CO_2$ and water presents opportunities to produce high energy density fuels and reduce atmospheric $CO_2$ levels. Electrochemical reduction of $CO_2$ to alcohols is highly desired, but still poses significant research challenges [1-3]. In particular, the large overpotential and poor understanding of the factors that affect the selectivity. Recent experimental results from our collaborators at Louisiana State University (LSU) show that Cu/ZnO and oxidized Cu catalysts produce methanol instead of methane [3]. This result is the inverse of the findings from Hori and co-workers for Cu metal [4], where they observe methane production but no methanol. Based on Density Functional Theory (DFT) calculations, Nørskov and co-workers have reported a pathway for methanol production on Cu(111) and Cu(211) through formation of a surface methoxy ($CH_3O^*$) [1-2]. We have performed DFT calculations to map out the energetics of $CO_2$ electrochemical reduction to methanol versus methane on several surface models including Cu metals, Cu/ZnO(10-10), and $Cu_2O(111)$. The methane and methanol branching from the key intermediate methoxy species on the various surface models will be presented. There are strong differences in the stability of species in comparison of Cu metal with Cu oxide. In particular, on one monolayer of Cu on ZnO(10-10), we found a facile downhill pathway to methoxy species ($CH_3O^* + H^*$) on the surface. Our DFT results on $Cu_2O(111)$ surface suggest that the hydrogenation of O* versus H* on the $CH_2O^*$ intermediate might lead to the experimentally observed selectivity to methanol on Cu oxide surfaces [3]. We will also discuss ongoing work to examine the role of kinetics (i.e. barriers to reaction steps) and other factors (e.g. solvation) on the selectivity for $CO_2$ reduction on Cu-based catalysts.

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# Simulation of Electrochemical Problems Using Conformal and Quasiconformal Mappings

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Conformal and quasiconformal mappings are spatial transformations which obey a system of first-order partial differential equations (Cauchy-Riemann equations for conformal mappings and more general equations for quasiconformal ones). Due to an intrinsic interrelation of the defining system of the mapping with higher order differential equations (diffusion, diffusion-convection, biharmonic equations etc.) they are extremely useful for the solution of boundary value problems. These extraordinary properties of (quasi)conformal mappings are already been used for about a couple of centuries for solving problems in electrostatics, aerodynamics, geoscience etc. [1] However, turning of the science towards micro- and nanodimensions brings a new realm of experimental situations with a vast variety of geometries and sets of boundary conditions. Moreover most of electrochemical problems are characterized by sharp concentration gradients, which are difficult to treat numerically.

In this respect, conformal and quasiconformal mappings represent an efficient approach since they allow the creation of highly non-uniform grids consistent with the underlying mass transfer processes thereby facilitating greatly numerical solution of a given problem. Besides of this, the main advantages of the application of (quasi)conformal mappings consist in i) possibility of obtaining an analytical solution or analytical approximation for the steady-state formulation of the problem; ii) higher numerical convergence rates; iii) mapping of a (semi)infinite space onto a closed simulation space; iv) possibility of grid density redistribution by means of additional transforms.

During the last decade we developed a set of mappings for numerical solution of electrochemical problems for different electrodes and their assemblies. These include, but are not limited to, the systems with disk, ring, band, double band, double hemicylinders, channel microband, recessed disk (and their arrays), droplet-modified electrodes as well as for vesicular release, transport in nanotubes etc. For the specified electrode geometries, various experimental situations were investigated including E, EC, ECE etc. mechanisms, electrochemiluminescence, generator-collector as well as generator-generator assemblies (see for example [2, 3]). An overview of these works as well as emphasis on the particular advantages of the (quasi)conformal mapping approach will be presented.

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# Multi-scale structure/function modeling of fuel cell electrolytes

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Proton exchange membranes (PEMs) are the electrolyte in current state-of-the-art fuel cells and function as not only the separator of the electrodes and reactant gases ($H_2$ and $O_2$) but importantly as the internal ion conductor.[1] Efficient operation of these energy conversion devices in diverse applications (vehicular, portable, and stationary) places demands on the PEM which include: long-time thermal and chemical stability (including resistance to oxidation and degradation by reactive species) at temperatures as high as 120°C, and high proton conductivity ($\approx 10^{-1}$ $\mathrm{Scm^{-1}}$) under low humidity conditions (25-50% relative humidity). Although a large number of strategies have been devised in the pursuit of membranes that meet these requirements,[2] current PEM fuel cells still utilize perfluorosulfonic acid (PFSA) ionomers such as Nafion®. Recently, proton conduction in these polymeric materials has been developed within a framework consisting of: *complexity, connectivity,* and *cooperativity*.[3]Experiments and modeling have shown that the transport of water and hydrated protons within PFSAs is dependent upon: the characteristic dimensions of the phase-separated hydrated polymer morphology (typically on the order of only a few nanometers); acidity, density, and distribution of the sulfonic acid groups; and the external conditions including humidity, temperature, and pressure. A complete understanding of how all these factors may be used in a synergetic fashion in the engineering of novel high performance materials remains forth-coming.[4] This talk will describe our multi-scale modeling effort in securing a fundamental molecular-level understanding of how structure determines function and properties.[5-9]

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# Computer Simulation Studies on the Properties of Molecular Wires

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Single molecules attached to nanosized metal contacts have been proposed as building blocks for ultra small electronic circuits. This is in part due to the fact that the properties of these nanosized devices may be tailored by changing the chemical nature of the molecule and modifying the anchoring group.

In the present work two types of approaches have been undertaken to consider the properties of molecular wires. On one side, density functional calculations using the SIESTA computer code[1] were performed to analyze the binding energy, rupture forces, kinetic stability and conductances of molecular wires involving different anchoring groups(-NH2, -S, -COO, -COOH, -P(CH3)2, -CN, -NC) and metal electrodes(Au and Pt). On the other side, the dynamic properties of molecular wires involving alcanedithiols were studied by means of accelerated dynamics using semiemipirical interatomic potentials. With this purpose, we performed molecular dynamics simulations in the framework of hyperdynamics as formulated by Voter[2], using the bias function proposed by Hamelberg et al[3]. This methodology allowed to study the contribution of different molecular conformations to the average conductivity of the system.

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# Surface Morphology on Water Dissociation Coupled with Electron Transfer and OH Adsorption: First Principles Study

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First principles molecular dynamics has been used to simulate the interface between defect Pt(111) surface which contains a pit with OH coadsorption ($OH_{ad}$) and the liquid water. Electric bias was applied by the ESM method [1,2]. Water dissociation coupled with electron transfer

$$H_2O \rightarrow H^+ + OH_{ad} + e^-$$

does not happen even under a strong bias ($\sigma = 14\ \mu C/cm^2$), but reversibly happens on the flat surface with $\sigma = 7\ \mu C/cm^2$ [3]. Calculations of OH adsorption on various sites of both Pt surface show OH adsorption energy on pitted surface are enhanced. $OH_{ad}$ is located on a top site of the flat surface, but it is on a bridge site at the pitted surface. Therefore different OH adsorption structure results in different hydrogen bond properties between $OH_{ad}$ and water molecule. $OH_{ad}$ promotes water dissociation on the flat surface, since it makes a hydrogen bond with a water molecule adsorbed on the Pt top site, but at the pitted surface water dissociation is prohibited due to an unfavorable formation of the hydrogen bond between $OH_{ad}$ on the bridge site and $H_2O$ on the Pt top site. Electronic structure calculation shows an unsymmetrical electron distribution between the two OH bonds of the water molecule, in which the OH bond with lesser electrons (opposite side of the hydrogen bond with $OH_{ad}$) is broken to produce $H_3O^+$ with nearby water molecule.

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# Atomic scale modeling of the electrochemical interface

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The fundamental properties of the electrochemical interface are important for many aspects of electrochemistry. And for theoretically addressing selectivity of electrochemical reactions it is necessary to explicitly model the interface. The challenge is that density functional simulations normally are done for constant charge whereas the electrochemical reactions take place at constant chemical potential.

There exist a handful of methods to circumvent this problem, most of these are based on performing a number of constant charge calculations and link a change in potential to a change in work function and thereby obtaining the reaction path at constant work function. This introduces another challenge that is how to translate the work function scale into a thermo electrochemical reference such as the standard hydrogen electrode. We have previously developed a method that offers a route forward [1] and it has been used to calculate the work function corresponding to the standard hydrogen electrode[2].

However, it turns out that for some structures of the interfaces it is not possible to use the work function as a measure of the potential, this is related the size of the ionization potential of the water electrolyte structure relative to the work function of the metal electrode. This has implications on many present studies in the field where barriers for charge transfer reactions are calculated and on the interpretation of potential of zero charge in atomistic simulation of the electrochemical interface. This represents a step towards a general atomic scale framework for modeling the electrochemical interfaces.

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# Building Polarizable Force Fields for Lithium Fluorophosphate Materials

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Many modeling problems in materials science involve finite temperature simulations with a realistic representation of the interatomic interactions. In ionic systems, it is possible to introduce physically motivated model potentials for the interactions, in which additional degrees of freedom provide a ‘cartoon’ of the response of the electronic structure of the ions to their changing coordination environments. These potentials may then be parametrized by fitting the predicted forces and multipoles to a large body of information generated from DFT calculations [1]. Such potentials are predictive, of first-principles accuracy, and have a high degree of transferability between different systems [2]. Recently, lithium-based fluorophosphate materials have showed promising performances as positive electrodes for lithium-ion batteries [3]. In order to study the physical properties of this family of compounds, we have developed a polarizable potential for $LiMgSO_4F$. By performing long molecular dynamic simulations involving large simulation cells, we study the diffusion mechanism of $Li^+$ ions. The formation of preferential pathways is observed (Fig.1), which leads to important collective effects.

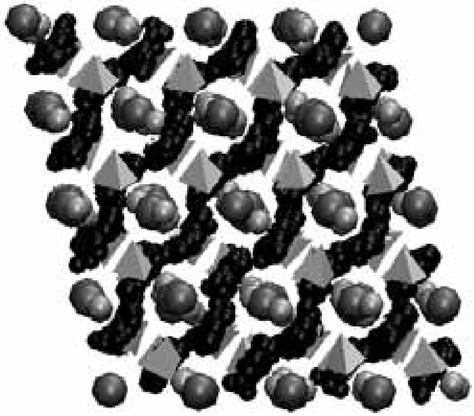

**Fig. 1.** Diffusion pathways for $Li^+$ ions in the $LiMgSO_4F$ material (Gray tetrahedra: $SO_4^{2-}$ units, Black, gray and silver spheres: $Li^+$, $Mg^{2+}$ and $F^-$ ions).

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# Design Principles for Oxygen Reduction and Evolution on Oxide Catalysts

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Driven by growing concerns about global warming and the depletion of petroleum resources, developing renewable energy production and storage technologies represent one of the major scientific challenges of the 21st century. A critical element in pursuit of this quest is the discovery of efficient and cost-effective catalysts used in solar fuel production via electrochemical energy conversion processes such as oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), both of which are central to the efficiencies of direct-solar and electrolytic water-splitting devices, fuel cells, and metal-air batteries. Although the Sabatier's principle provides a qualitative argument in tuning catalytic activity by varying the bond strength between catalyst surface and reactant/product (neither too strong nor too weak leading to the maximum activity at moderate bond strength), it has no predictive power to find catalysts with enhanced activity. Identifying a "design principle" that links catalyst properties to the catalytic activity is critical to accelerate the search for highly active catalysts based on abundant elements, and minimize the use of precious metals.

Recently we report a molecular principle that governs the activities of oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) for oxide catalysts, where the activities primarily correlate to the $\sigma^*$ orbital ("$e_g$") occupation of surface transition-metal cations established by systematic examination of more than ten to fifteen transition-metal oxides. The intrinsic ORR and OER activities exhibit a volcano-shaped dependence on the $e_g$ occupancy and the activities peak at an $e_g$ occupancy close to unity. Our findings reflect the critical influence of the $\sigma^*$ orbital on the energetics of surface reaction intermediates on surface transition metal ions such as the $O_2^{2-}/OH^-$ displacement and the $OH^-$ regeneration, and thus highlight the importance of surface oxide electronic structure in controlling catalytic activities. Using the established molecular principle, we further demonstrate that an alkaline earth cobalt oxide with a chemical formula of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), catalyzes the OER with intrinsic activity that is at least an order of magnitude higher than the state-of-the-art iridium oxide catalyst in basic solutions.

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# Proton Discharge on Charged Metal Surfaces. A Reactive Trajectory Approach

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A reactive trajectory approach for the study of proton discharge from aqueous environments on charged metal surfaces is reviewed. It is based on an extension of a minimalistic empirical valence bond (EVB) model to study proton transfer in the bulk. Extensive quantum mechanical density functional theory calculations were parametrized for the EVB force field [1]. The model is used to investigate reactive (discharging) proton trajectories that were started in the bulk of a water film adsorbed on charged metal electrodes. The results indicate a transition between a reaction-dominated regime at moderate negative charges, where the rate constant increases exponentially, to a ``transport limited'' regime where the transfer rate is almost independent of the surface charge density (at more negative surface charge densities) [2,3].

Recent extensions of the model to introduce background electrolytes with and without specific ion adsorption are discussed. Comparison between the electrochemically active Pt(111) surface and the much less reactive Ag(111) surface indicate that proton discharge on silver occurs only at unrealistically large negative potentials. This trend is in good agreement with experiment. The simulation results hint that part of the large differences in electrochemical behavior between the two metals might -- at least partially -- be due to the strikingly different water structure at the two interfaces.

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# DFT-MD Analysis of Interfacial Charge Transfer at $TiO_2$/ Solution Interfaces for Photocatalysis and Solar Cell

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Atomistic mechanisms of charge transfer processes at the $TiO_2$/solution interfaces of photocatalysis (PC) and dye-sensitized solar cell (DSC) have been still open questions because of the experimental and computational difficulty in analyzing such buried interfaces. In order to solve these problems, it is necessary to specify initial and final equilibrium states of the processes and estimate the free energies associated with them, at the solid/liquid interfaces.

In this work, we explore possible interfacial structures and electronic states of $TiO_2$/liquid water interfaces for PC and $TiO_2$/liquid acetonitrile for DSC under thermal equilibrium, by using density functional theory based molecular dynamics (DFTMD) analysis. With the averaged electronic states and the view of semiconductor junctions involving electric double and space-charge layers, we discuss possible pathways of the charge transfer processes.

For PC interfaces, we first clarified the water adsorption manners, the interfacial hydrogen bonding, and the stability of surface defects & nanostructures[1]. The averaged electronic states show variation of electronic levels at the interfaces, indicating probable electron and hole transfer pathways[2]. For DSC, we clarified the interfacial $CH_3CN$ adsorption and its water contamination effect[3]. These alter the $TiO_2$ electronic states, which affects the probability of interfacial charge transfer, crucial for the DSC photovoltaics and durability. These calculations correspond to the flatband conditions, which also gives electrochemical implications.

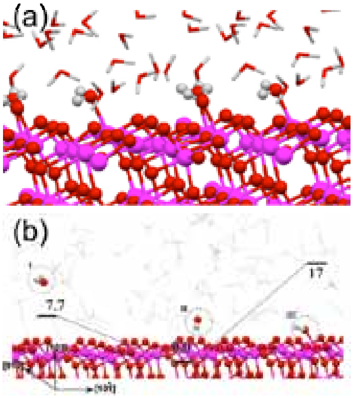

Fig. (a) Equilibrium structure of $TiO_2$ anatase (101)/ liquid water interfaces. Molecular adsorption of water with strong hydrogen bond is observed. The water coverage is around 0.6. (b) Equilibrium structures of water contamination at $TiO_2$ anatase (101)/acetonitrile interfaces for DSC. Structure II with unusual hydrogen bond is found the most stable. This water can be a cation radical by accepting a hole.

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# Electrowetting with Electrolytes

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Interfaces between two immiscible electrolytic solutions (ITIES) provide significant contact-angle variation at substantially lower operating voltages than conventional electrowetting systems require. A theory of electrowetting with ITIES is developed that differs from standard theories of electrowetting with both liquids are insulating, and even when insulating is the surrounding medium only [1,2]. We have shown that in these systems, nonlinear electrostatics and the ionic impermeability of the liquid/liquid interface dominate the potential response of the contact angle. These effects rationalize contact-angle saturation and droplet dewetting, both of which have been observed experimentally in similar systems. The analysis also provides surprising predictions (for instance, a nonmonotonic change in the contact angle with potential) that can be explored in the laboratory and after verification used for new designs of electrotunable microlenses.

Contact angle hysteresis caused by random pinning forces, which are originated from surface roughness and heterogeneity, is a major obstacle for operation of microfluidic devices. To achieve efficient motion, one has to either prepare samples with sufficiently low heterogeneity, i.e., with minimum contact angle hysteresis or to provide sufficient “vibrational energy” to overcome the pinning forces. Recently we demonstrated experimentally [3] that the contact angle hysteresis can be eliminated applying short voltage pulses in addition to the steady-state bias voltage. These pulses activate the droplet, facilitating depinning of the three phase boundary on its way to its final position. If the duration of each pulse is very short, the energy cost of pulsing is minor.

We have developed a theory [4] that describes the effect of electric pulses on the droplet motion and predicts dependencies of the dynamical response on material parameters. Theory shows that important counterparts of the electrowetting dynamics under pulsing are: the physical properties of the droplet, the nature and magnitude of the friction force, the free energy profile as a function of droplet diameter, and the duration and height of the pulse.

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# A new multiscale model for the transient analysis of Lithium-ion batteries

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We propose here a new multiscale model for the numerical simulation of Lithium-ion batteries based on the simulation package MEMEPhys®, previously developed by Franco *et al.* for PEMFCs [1]. In contrast to the classical Butler-Volmer approach used in Newman-like models [2] our approach is based on a *bottom-up* framework and uses kinetics data coming from atomistic calculations. In our description we have used and adapted the non-equilibrium thermodynamics description of electrified interfaces, developed by Franco *et al.* [1] and firstly applied on fuel cells, to describe the electrochemical double layer formation at the vicinity of the Li insertion material in contact with carbonates electrolyte. Starting from the nanoscale level, an elementary kinetic model describing the $Li^+$ insertion/delithiation processes occurring in both positive and negative electrodes is implemented with energy barriers calculated at the atomistic level by using DFT and DFT+U approach. At the mesoscale level, the model introduces a structural-resolved description of the $Li^+$ transport. The capabilities of this model are illustrated through several simulation results on a $LiFePO_4$//Graphite cell in close comparison with experimental data: this includes the influence of electrodes structural parameters on the charge and discharge curves at different operating conditions, and the impact of some irreversible aging phenomena, such as graphite exfoliation and $FePO_4$ passivation on the long-term performance decay.

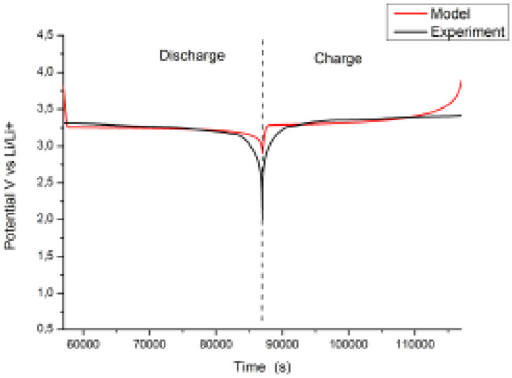

Figure 1 : First comparison between a discharge/charge curve calculated with our new model and an experimental result for $LifePO_4$ battery.

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# Transport in Nanometer-Wide Electrochemical Cells

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The current-voltage response of thin-layer electrochemical cells in which the electrodes are separated by tens of nanometers will be described. At such close separation distances, the electrical double layers of the two electrodes overlap, resulting in large electric field effects on the transport of ions. We have computed the current-voltage response of these cells using finite-element methods to solve the Poisson and Nernst-Planck equations for cells containing one or more reversible redox couples. Our results demonstrate that the electrical current in the limit of overlapping double layers can be greatly enhanced or suppressed depending on the charge of the redox ions, supporting electrolyte, and surface charge on the electrodes. Atomic layer deposition, photolithography, and chemical etching have been used to create thin-layer cells with spacing between two Au electrodes as short as 30 nm. Experimental and simulated results will be presented in this lecture.

# Quantum Chemistry Calculations on Photoinduced Catalytic Reactions on Nanostructured Silver Electrodes

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Nanoparticles of noble metals have the special photocatalytic properties due to the large surface-to-volume ratio and special hot electron behavior due to surface Plasmon resonance in visible light region. The light excites metal surface electrons to hot electrons, which can tunnel to the solution side to form hydrated electrons and to split water then. Meanwhile, a proper energy match results in photoinduced charge transfer from the highest occupied molecular orbital to the metal unoccupied energy band above the Fermi level. The surface-enhanced vibrational spectroscopy can be used to provide fingerprint information of these processes at molecular levels in electrochemical interfaces. However, the complexity of interfacial structures makes a difficulty to understand the spectroscopic signals. By combining quantum chemistry calculations to the Raman measurements of adsorbed molecule, we can deeply understand the photoelectrochemical processes of hydrogen evolution reaction and other important reaction processes, like aromatic amine oxidation on nanoscale silver electrodes.

In the communication we first present the photoinduced surface catalytic discharging process of hydrated proton clusters on a silver cathode of nanoparticles. The hybrid exchange-correlation functionals (B3LYP) were used for geometry optimizations, electron transitions, and vibrational analysis calculations. For C, N, O and H atoms, the basis sets of 6-311+G** and Aug-cc-pVTZ were used. For Ag atoms, the valence electrons and the internal shells were described by the basis set, LANL2DZ, and the corresponding relativistic effective core potentials, respectively. The validity of these basis sets has been demonstrated in our recent studies of a water molecule and its coinage metallic complexes. On the basis of density functional theory calculations of metallic cluster models, a series novel intermediates were proposed for the photocatalytic hydrogen evolution reaction. We further studied electrochemical oxidation of aromatic amine adsorbed on nanostructured silver electrode. In the case, the photo-oxidation product is aromatic azo dye, which displays strong Raman signal. This interprets that the surface-enhanced Raman spectra of p-aminothiophenol adsorbed on nanostructured silver electrode. In the surface catalytic coupling reaction, the charge transfer and the proton transfer are involved.

# A first principle study of bisulfate and sulfate anion adsorption over a Pt(111) electrode

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Specific adsorption of ions is an important phenomenon in electrocatalysis, as ions may block active sites or alter the electronic structure of the surface and electrode-electrolyte interface. Although Pt(111) electrodes in sulfuric acid solutions have been widely investigated using electrochemical experiments and surface characterization techniques, the identity of the dominant adsorbed species and coadsorbed species as well as the mechanistic cause of features in the adsorption voltammogram remain debated. We employ a series of density functional theory-based electrochemical models to examine the specific adsorption of sulfate and bisulfate anions to Pt(111) electrodes. The origins of experimentally observed voltammetric features have been assigned based on comparison of calculated vibrational frequencies and simulated linear sweep voltammograms (LSVs) to experimental data available in the literature.

We have assigned the experimental characteristic vibrational mode of adsorbed (bi)sulfate in the 1200-1300 $cm^{-1}$ range as an $S\text{-}O_{uncoordinated}$ stretch. Combining a solvated electrochemical model with vibrational frequency analysis, sulfate is identified as the dominant adsorbed species over the (bi)sulfate adsorption potential region. The simulated isotherm and voltammogram shown in Fig. 1 suggests rapid increase of coverage with electrode potential causes a sharp peak in the voltammogram. The molecular structure of ordered sulfate containing ($\sqrt{3}x\sqrt{7}$) adlayers on the Pt(111) surface (an example is shown in Fig. 2), are examined as well. A reduced Stark tuning slopes of the $S\text{-}O_{uncoordinated}$ frequency between a ((H)$H_2O\text{-}SO_4$) and a ($HO\text{-}SO_4$) adlayer within the ($\sqrt{3}x\sqrt{7}$) unit cell explains an experimentally observed slope change.

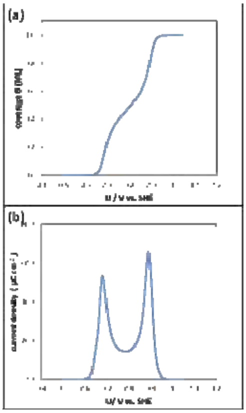
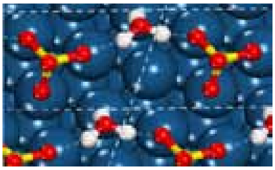


**Figure 1.** Simulated (a) isotherm and (b) voltammogram for a 0.1 M $H_2SO_4$ solution at the vacuum/Pt(111) interface using coverage dependent sulfate adsorption calculations. The sweep rate used is 50 mV $s^{-1}$.

**Figure 2.** Optimized structures of $SO_4\text{-}H_3O$ over Pt(111) surface within the ($\sqrt{3}x\sqrt{7}$) unit cell.



# Effect of ligand, support, and solvent on the $O_2$ binding of non-precious metal catalysts: An *ab initio* study

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Non-precious metals, due to their abundance and low cost, have received considerable attention as potential substitutes for Pt as catalysts in the Oxidative Reductive Reaction (ORR) of PEM fuel cells. One of the most promising non-precious metal oxygen reduction catalysts is carbon supported transition metal/nitrogen ($M/N_x/C$) materials.[1-2] The nature of their active sites remains elusive, although different catalytically active structures have been proposed including $M\text{-}N_4/C$, $M\text{-}N_2/C$ and N-C species.[3]
In this work, we examine the $O_2$ binding of a series of non-precious metal catalysts $ML_n$ where M = $Cu^+$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Ni^{2+}$, and $Co^{2+}$; and L = diaminetriazole ($M\text{-}N_2$) or porphyrin ($M\text{-}N_4$). Results were obtained from Density Functional Theory (DFT) calculations based on the Becke-Perdew exchange-correlation functional and standard triple-$\zeta$ basis sets for all atoms, using the Amsterdam Density Functional (ADF) program.[4] $O_2$ binding was further investigated by the Bond Decomposition Analysis[5] to understand the orbital interactions between the catalysts and $O_2$. The effect of various factors on $O_2$ binding, including: catalyst ligand, solvent, and support, is investigated.
When only the ligand is considered, $Fe^{2+}$ shows the strongest $O_2$ binding, followed by $Co^{2+}$, $Fe^{3+}$, $Ni^{2+}$ and $Cu^+$, whereas $Cu^{2+}$ exhibited inactivity towards $O_2$. This order in the binding seems to correlate with energy gap between the d orbitals of the metal cation and the $\pi^*$ of the triplet $O_2$ with the smaller the gap resulting in the stronger $O_2$ binding. When support and explicit solvent molecules are considered, catalysts with the porphyrin ligand demonstrate better $O_2$ binding than their counterparts with diaminetriazole. The initial structural change of the catalysts due to attachment to the support and the competition between $O_2$ and $H_2O$ for the binding of the catalysts are considered responsible.

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# Chemical amplitude: A quantitative descriptor for the surface reactivity of metals

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The d-band center has become a popular language in the community of heterogeneous catalysis, including electrocatalysis. In some particular cases, the d-band center of transition-metal surface seems to be a good reactivity index, but it can hardly be a satisfactory one when a wide range of transition metals are involved (Fig. 1A), not to mention its disability in comparing different adsorbates on the same surface.

In our recent research on new discription for chemical bond, we use a complex number, termed the chemical amplitude ($R = ae^{i\theta}$), to charaterize a reactant (be it an atom or a surface); and the bond energy is deduced to be the absolute square of the interfered chemical amplitudes of two involved reactants. This model turns out to work very well for both covalent bonds in molecules and adsorption bonds on transition metal surfaces. As an example, we show in Fig. 1B the result of Cl adsorption on 25 transition metals, the model-predicted bond energy matches the DFT-calculated adsorption energy with satisfied accuracy.

Detailed information about the theoretical model and relevant calculations will be presented in the meeting.

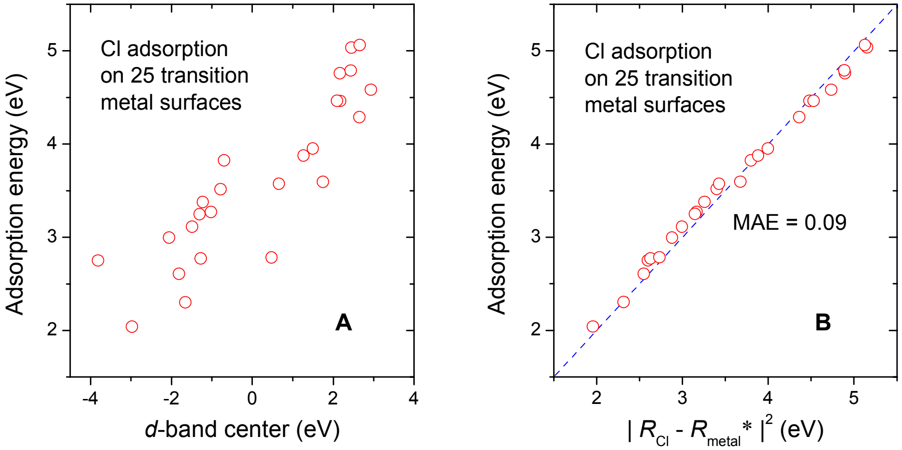

Fig.1 (A) The d-band center is not able to describe the surface reactivity for a wide range of transition metals; (B) The chemical-amplitude model proposed in this work can predict the adsorption energy in an accuracy within the error of DFT calculations.

# Trends in the transition metals for heterogeneous electrochemical $CO^2$ reduction

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The ability to efficiently convert carbon dioxide into hydrocarbons and alcohols could simultaneously address renewable fuel production and the intermittency of renewable electricity production. A cathodic electrocatalyst that could produce hydrocarbons or alcohols with low overpotentials, high yields, and high selectivities is essential for this process to be successful. Despite years of effort studying transition-metal heterogeneous electrocatalysts, only copper has been repeatedly shown to be able to produce high yields and selectivities of hydrocarbons, albeit with a large overpotential. In this work, we use electronic structure calculations to understand the mechanism of hydrocarbon formation on Cu and scale this reaction mechanism to the other late transition metals. One obvious requirement of a good catalyst for CO2 reduction is comparatively poor activity in the hydrogen evolution reaction. We will show data that suggests the other key criterion for a good electrocatalysts is not the ability of the catalyst to reduce CO2, but rather to perform the elementary protonation of adsorbed carbon monoxide to CHO or COH.

# Poster Presentations

P-001

# Water Oxidation at Transition Metal Oxides from a Binuclear Perspective

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Splitting of water into oxygen and hydrogen by means of photo/electrochemistry constitutes a key reaction for storing solar energy. The anodic oxygen evolution reaction (OER) is mostly discussed in terms of a mononuclear reaction between a surface TM=O species and a water molecule [1]. Here, a complementary binuclear reaction mechanism will be discussed using Density Functional Theory (DFT). A molecular biomimetic μ-OH bridged Mn(III-V)-dimer, inspired by Photosystem II and related homogenous biomimetic systems [2,3], is employed as model catalyst.

The water oxidation steps comprise the consecutive abstractions of 4 $H^+/e^-$ reducing equivalents. Catalyst recovery is achieved via the formation of an intramolecular O-O bond between 2 Mn(V)=O/Mn(IV)-O• moieties to form a μ-peroxo bridge. $^3O_2$ is released by subsequent replacement of the Mn-O bonds with water [4].

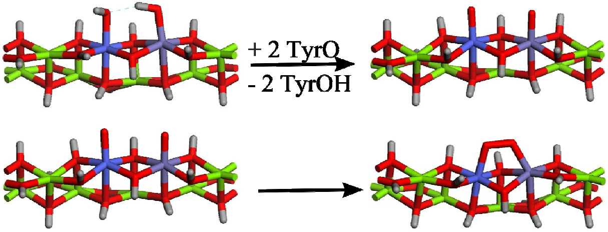

**Figure 1: The key reaction steps used to describe the reactivity of the embedded candidate catalysts are shown.**

Insights gained from the molecular system are generalized for a set of embedded 3d transition metal oxide dimers using the key reaction steps as descriptors [5] and discussed with respect to experimental results for $RuO_2$ [6] and $IrO_x$. Taking advantage of the binuclear nature of the OER novel mixed transition metal oxide catalysts are arrived at. The validity of this concept is evaluated for a set of mixed 3d transition metal oxides. Additionally the possibility to block the binuclear OER path and use the high oxidative power of the TM=O intermediates to produce valuable chemicals such as oxirane is discussed [6].

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## P-002

# The Study of Electrochemical Performance of LiFePO4/C Composites Doped with Na and V

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$LiFePO_4$/C, Na-doped $LiFePO_4$/C, V-doped $LiFePO_4$/C, and Na, V-doped $LiFePO_4$/C composites were synthesized by sol-gel method. Shown in Table 1 are the molar ratios of elements in all samples. All samples were characterized by inductively coupled plasma (ICP), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). ICP and XRD analyses indicated that Na and V ions were sufficiently doped in LiFePO4 and did not alter its crystal structure and exhibited the variation of lattice parameters with the doped ions. Electrochemical test results showed that the V-doped $LiFePO_4$/C exhibits the best electrochemical performance with initial specific discharge capacity of 143.31 mAh/g at 0.1 C. EIS results demonstrated that the charge transfer resistances of metal-doped $LiFePO_4$/C decrease, and the $Li^+$ ionic diffusion coefficients of these samples also were improved. Furthermore, the lattice structure stability of $LiFePO_4$ is also enhanced by doping Na and V. From the results, it is noted that metal ions doping can improve performance of $LiFePO_4$, especially on the aspect of stable cycle-life at higher C rate.

Table 1 The molar ratios of elements in the samples.

| Sample | Li | Na | Fe | V | P |
|---|---|---|---|---|---|
| **$LiFePO_4$/C** | 1.03(4) | - | 1.00(1) | - | 1 |
| **Na-doped $LiFePO_4$/C** | 0.97(7) | 0.01(9) | 1.02(3) | - | 1 |
| **V-doped $LiFePO_4$/C** | 1.01(5) | - | 0.97(1) | 0.02(4) | 1 |
| **Na,V-doped $LiFePO_4$/C** | 0.99(0) | 0.02(1) | 0.98(1) | 0.02(5) | 1 |

P-003

# The Nature of Proton Transport in Polymer Electrolyte Membranes: Insights from First Principles Molecular Dynamics Simulations

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The nature of proton transport in hydrated polymer electrolyte membranes is investigated using various simulation techniques including first-principle molecular dynamics simulations. Especially, focus is on how details of molecular structure and local morphology of membranes affect the water channel structure and proton transport. We found that the structure of water channel inside membranes strongly affects the proton transport. Also, for typical hydrocarbon membranes, e.g. sulfonated polyethersulfone (SPES) [1], where water channel structure is rather scattered compared to that of Nafion [2], we found that hydrophilic functional groups such carbonyl or sulfone groups affect the nature of proton transport under low water content conditions [1]. Some other polymer electrolytes are also under the investigation.

The free energy potential surfaces of constructive and non-constructive proton transfers by the Grotthus mechanism are also obtained. It shows that structure change plays an important role for the constructive proton transfer.

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### P-004

# Prediction of Process Parameters of an Electrochemical System via Artificial Neural Networks

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In terms of modelling of chemical and physical processes by computer usage, one of the most popular methodologies is the Artificial Neural Networks (ANNs) approach. It is defined as an information processor forced with analytical capabilities and considered as an alternative way to other mathematical approaches in modelling of complex data sets. This technique is primarily software based and it can learn the system performance characteristics by monitoring the system test or running data. Optimising the network structure and inner parameters, its training speed and the prediction accuracy can be enhanced. Therefore, the ANN-approach may be easily used in chemical or electrochemical research for parameter estimation. Modelling by ANN, a trained network is ran to obtain a chemical system model. In training, the network is repeatedly presented with input-output pairs, which are being modelled. The advantage of a neural network is to make generalization within defined limits from the known examples to unknown values. The model is established for an available data set. Such data sets include very interesting features or valuable information, which cannot be deduced by known classical methods. On the other hand, in recent decades, there has been considerable interest in the subject of glucose oxidation in connection with the problem of devising a sensor to determine blood sugar concentrations and a fuel cell to power an artificial heart. By this sense, under the process modelling approach, current study presents the estimation of the peak current values for the electrooxidation of D-glucose on noble metal electrodes in different experimental conditions. The structure named back-propagation (BP) algorithm, which is the most widely used in the ANN-model, is utilized in this study. BP-ANN is trained to learn a possible correlation between potential sweep rate and peak current densities obtained for the electrooxidation reaction of D-glucose. A three layer feed-forward ANN with error back-propagation learning algorithm is used for this experimental modelling . Using this methodology, the results can be safely extended to the larger measurement range safely and it can be used as an alternative tool for inadequate measurement capabilities. Hence, this study plays an important role, showing the potential application of ANNs in electrochemical process modelling and parameter estimation.

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P-005

# Fault Diagnosis of a Glucose Sensor via Neural Computational Approach

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Neural computation approach represents a comparatively new trend in the study of Artificial Neural Networks (ANNs) such as modelling, calibration, prediction and fitting problems. They are mathematical models of biological neural systems. Computation strategies based on neural models facilitate the solution of complex problems that reguire a great deal of time and calculation when solved by traditional methods. ANNs consist of simple processing elements or ‘neurons’ linked with each other in a particular configuration. Each neuron is a non-linear transducer of input signals which are given weight coefficients, summed and transferred to a non-linear function of activation that forms an output signal. Biosensor response functions are often characterized by significant deviations from linearity, requiring complex mathematical descriptions. Accordingly, coupling biosensors with ANNs is growing in importance as a tool for determination processes. In the current study, glucose oxidase enzyme that is specific for the glucose determination is entrapped into polypyrrole matrix containing p.benzoquinone in biological (PIPES) buffer and glucose sensitivity of the biosensor is investigated. Then, neural computation analysis is applied on our glucose sensor. This implementation can be used for the sensor failure detection i.e. fault diagnosis, in a wide sense. Failure or normal condition of the sensor can be monitored through the difference between actual sensor output and its estimated value. If this difference is less than or equal to a threshold value ($\varepsilon$), the sensor is in the normal condition or has a good calibration. Otherwise, it is failure. Moreover, the estimation power of the neural network used in the direct and inverse modeling is examined by statistical methods. The estimation power of the neural networks in the training process, which is the measure of the neural network performances, can be defined by correlation coefficient between the actual and estimated values for their training data sets. According to these computational results, it shows a very good prediction ability with correlation coefficients $r_1= r_2= 0.99$, i.e. it presents the good performance for the estimation power. The neural network structures used in this application are presented by the same topology which are replaced into the sensor calibration modelling and inverse modelling.

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P-006

# Supercapacitor Using Binderless Composite Electrodes from Carbon Nanotubes and Carbon Derived from Biomass Residues

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Binderless composite electrodes (BCMs) in the monolithic form prepared from carbon nanotubes (CNTs) and self-adhesive carbon grains (SACG) were used as electrodes in a symmetrical supercapacitor. The SACG1, SACG2 and SACG3 were prepared by a low carbonization temperature from three different types of biomass residues, i.e. fibers of oil palm empty fruit bunches (*Elaeis guineensis*), roughbark lignum-vitae (*Guaiacum officinale*) and pakistanis-flora(*Heliotropium dasy*carpum), respectively. For each biomass, the BCMs were prepared from green monoliths (GMs) contain SACG treated with KOH (5 % by weight) and SACG mixed with carbon nanotubes (CNTs) (5% by weight) treated with KOH (5 % by weight), respectively. These GMs were carbonized at 800$^o$C under $N_2$ environment and activated by $CO_2$ gas at 800$^o$C for 1 hour to produce BCMs. The electrochemical properties (specific capacitance, internal resistance, specific energy and specific power) and physical properties (density, electrical conductivity, porosity, interlayer spacing, crystallite dimension and microstructure) of the BCMs from these three different biomass residues will be compared and discussed. The role of CNTs on both the electrochemical and physical properties of the BCMs will also be discussed.

### P-007

# DFT and Electrochemical SHINERS Studies on the Co-adsorption of sulfate and water on Au (111)

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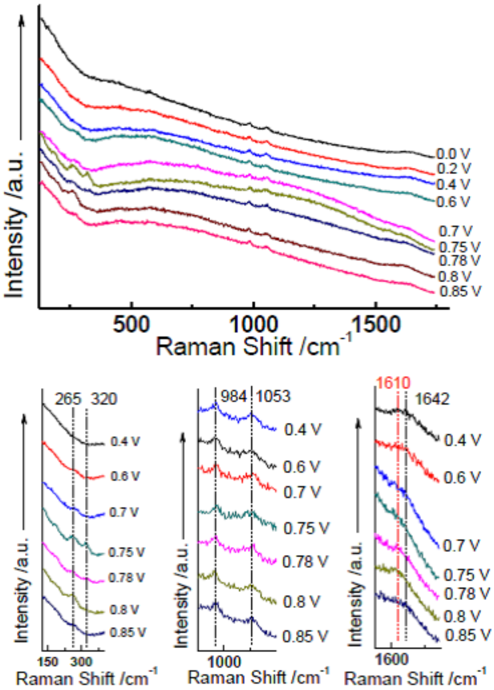
Density functional theory (DFT) and electrochemical shell-isolated nanoparticle-enhanced Raman spectroscopy (EC-SHINERS) studies were performed for the well-known (√3×√7) structure that the co-adsorption of (bi)sulfate/water on the Au (111) single crystal. With the surface specificity of SHINERS [1], we successfully ruled out the Raman signal from solution and obtained the EC-SHINERS spectra from the surfaces (see Figure 1).

Based on Jocob's previous systematic DFT studies of the various (co)-adsorption structure of water and sulfate complexes without external electrostatic field on the energy level [2], we performed a periodic DFT frequency calculations of these complexes using VASP with the PBE functional with and without electrostatic field. A preliminary result showed that a complex with one bi-sulfate and two water molecules is indeed energy-preferable in the absence of the external field. The simulated frequencies of bi-sulfate and two water molecules agreed well with the experimental results, especially for the 984 and 1053 cm$^{-1}$ and the bending mode 1610 cm$^{-1}$.



In summary, the co-adsorption of bi-sulfate and two water molecules is the most probable configuration for the (√3×√7) structure on Au (111).

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P-008

# Towards a more reliable method for electrochemical parameter estimation considering experimental systematic error

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A quantitative, accurate and statistically founded modeling of electrochemical reactions to determine the charge and mass transfer parameters from linear sweep voltammetry experiments with a rotating disk electrode (LSV/RDE) has been developed in our group and used to study a one electron-transfer reaction [1,2]. The model is derived from the proposed mechanism for the electrochemical reaction as an analytical expression representing the voltammograms. By means of a parameter fitting procedure, the model parameters are estimated as the arguments that minimize a weighted least squares cost function, which measures the distance between model and experiment. After a statistical evaluation of the best-fit values it is decided whether the model is able to describe the experiments. The experimental current-potential data for the modeling are multiple experiments performed under identical conditions. Those are required to design the weighting factor of the cost function, defined as the standard deviation of the current over the set of experimental curves. This experimental standard deviation is considered, in practice, as a good approximation of the standard deviation of the stochastic noise, which is known to minimize the estimated standard deviation of the best-fit parameters. Yet it provides not only a measure of the stochastic noise but also of the experimental systematic noise. Hence the latter is carried along the modeling and, consequently, its influence is reflected in the parameter estimation.

This work presents the local polynomial model to identify the stochastic noise on one experimental curve. It is based on approximating the current locally as a polynomial function of the potential. Estimates of the current (polarization curve) and the standard deviation of the current (calculated from the estimated standard deviation of the noise) are extracted from only one experiment. They can be subject of the fitting procedure, where the new estimated standard deviation of the current is the weighting factor. In a set of "identical" experiments, the combination of the local polynomial model and the fitting procedure enables to estimate the model parameters and their standard deviations for every polarization curve. The evaluation of all best-fit values determined from the individual voltammograms within the set of experiments shows the influence of the experimental systematic error in the parameter estimation. Furthermore, these best-fit parameters and standard deviations are compared to the ones estimated by the previous modeling method [1], using the whole set of voltammograms. The improvement of the parameter precision with the new modeling strategy confirms its strength for a quantitative study of electrochemical reactions.

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### P-009

# Stability Improvement of an $MnO_2$ Electro-catalyst for the Oxygen Evolution Reaction under Acidic Conditions

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Developing new electro-catalysts for the Oxygen evolution reaction composes a major challenge if hydrogen production from electrolysis is to play a role in the future energy society. Electrolysers based on PEM cells possess a high potential due to compact systems and high current densities compared to alkaline based electrolysers but the best performing catalysts in such cells are scarce materials such as Ruthenium and Iridium. Finding better catalysts for the reaction is complicated due to the newly established scaling relations between reaction intermediate adsorption energies [1]. Inspired by the Photosystem II Mn based oxides was investigated experimentally and found to be active by Gorlin et al [2]. Rossmeisl et al. investigated rutile oxides by the use of Density functional theory and at an overpotential around 0.5 V the (110) surface of rutile $MnO_2$ should perform well, however dissolution at low pH is an issue [3]. This study seeks to improve the dissolution potential on stepped and kinked (120) surfaces of $MnO_2$ by the use of Density Functional Theory calculations. Terminating steps and kinks with a more stable oxide can lead to a meta stable surface structure with promising oxides being $TiO_2$ and $IrO_2$ . For $TiO_2$ a process in which the local oxygen coordination for Ti is 2 was found to result in a driving force towards terminating steps. For $IrO_2$ a local oxygen coordination of 3 for Ir was needed to establish a driving force. The result of introducing $TiO_2$ in this way could lead to an improvement of the dissolution potential of up to 0.5 V. This concept of improving of dissolution potential by terminating under-coordinated sites could be applied to other catalyst systems in which the facets are active.

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## P-010

# Charge Transfer in the Course of Adsorption of Inorganic and Organic Species from Aqueous and Biological Media

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The nature or mechanism of the elementary act in the course of electrochemical processes is a subject of perennial interest. The inherent difficulties of elucidating the mechanism of the elementary act are obvious, especially if the electrode surface is superfine and complex in its chemical composition (e.g., is highly functionalized). For such electrodes the probability of several simultaneous processes at the interface with different mechanisms is quite high, even for single-component electrolytes.

However, it is possible to characterize the nature of the predominant process as either faradaic or nonfaradaic based on the amount of charge transferred across the interface. If the electrode can be treated as a perfectly polarizable electrode, i.e. if the surface condition is defined uniquely by the amount of charge consumed and if the electrochemical reaction is reversible, it is possible to compute the effective amount of charge transferred across the electrode/electrolyte interface if the change in potential and adsorption are measured in an open circuit. If the total differential of charge $dQ$ is expressed as a function of electrode potential $E$ and adsorption $\Gamma$, the following expression is obtained, equal to zero when measurements are made in an open circuit: $dQ = (\partial Q/\partial E)_\Gamma\, dE + (\partial Q/\partial \Gamma)_E\, d\Gamma = 0$, where $(\partial Q/\partial E)_\Gamma = C_{\mathrm{EDL}}$, $(\partial Q/\partial \Gamma)_E = -nF$. If the differentials $dE$, $d\Gamma$ are approximated by total changes $\Delta E$, $\Delta\Gamma$, this can be rewritten: $n = (C_{\mathrm{EDL}}\, \Delta E)/(F\, \Delta\Gamma)$, and the effective number of electrons $n$ transferred in the course of the elementary act can be calculated for each experiment.

In the present work, such measurements and computations have been performed for processes of adsorption of cupric ions, *t*-butanol, isopropanol, acetone, and hemoglobin from aqueous solutions. The values of effective numbers of electrons computed for different initial open-circuit potentials of activated carbon electrodes have, indeed, allowed for the faradaic contribution to be identified.

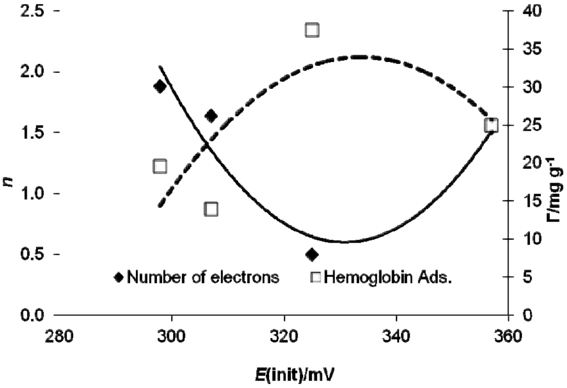

Fig. 1. Adsorption of hemoglobin on act. carbon

## P-011

# Theory of Interfacial Proton Transport in Polymer Electrolyte Membranes

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Polymer electrolyte fuel cells (PEFC) are highly efficient and environmentally benign electrochemical power sources. Major issues persist, however, with water and thermal management under PEFC operation. Electro-osmotically driven water depletion on the anode side or evaporative water loss at $T > 90°C$ lead to a dramatic decrease in proton conductivity of the polymer electrolyte membrane (PEM). A rational approach in designing PEM that could tolerate such changes demands fundamental understanding of proton transport mechanisms under almost dry conditions. Our theoretical work focuses on interfacial mechanisms of proton transport prevailing if a minimal amount of water is tightly bound to the polymeric host. As indicated by experimental studies, highly efficient interfacial proton transport becomes feasible at a high density of acid-bearing interfacial surface groups (SG). Our model system is a dense 2D array of flexible protogenic SG (vertices) and mobile hydronium ions (filled triangles), as depicted in Fig.1. Previous quantum mechanical simulations have revealed a structural interfacial transition to a condensed state at a critical packing density of SG, accompanied by a hydrophilic-to-hydrophobic transition.[1,2,3] Motivated by results of ab initio metadynamics simulations,[4] we focus on concerted lateral proton moves at the critical packing density. We develop a soltion model of collective hydronium ion transitions for the two-component lattice of SG and hydronium ions, Fig. 2. The collective process corresponds to a traveling solitary wave. During these transitions, the number of hydrogen bonds per SG is conserved, rendering such a process energetically much less expensive compared to single hydronium ion moves. Advised by ab initio simulations, we consider the influence of different potential profiles created by the SG on the soliton properties such as velocity of propagation, energy, shape, and size. Then we derive an expression for the conductivity. The combination of ab initio calculations with soliton theory allows relating microscopic parameters defining the structure of the array, such as chemical composition, length and density of SG, to its proton conductivity.

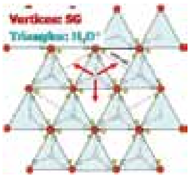

Fig.1
2D array of SG and hydronium ions

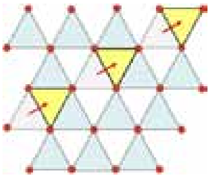

Fig.2
Concerted motion of hydronium ions

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## P-012

# Phase Field Modeling of Electrochemical Transport in Nanoparticles for Medical Applications

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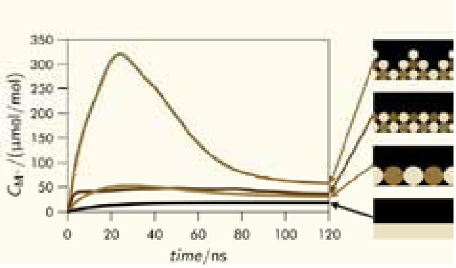
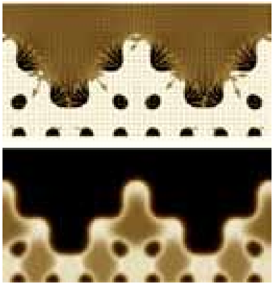
Nano-particulate silver systems are widely used in wound dressings, surgical masks, and catheter coatings as anti-microbial agents. The increased antimicrobial efficacy relative to bulk material is presumably due to increased silver ion solubility due to capillarity. Electrocapillary driving forces around complex, evolving nanostructures are difficult to estimate from analytical treatments. We have shown [1,2] that a phase field model of the electrochemical interface captures behaviors including electrocapillary phenomena, differential capacitance curves that resemble experimental measurements, and non-linear kinetics consistent with the empirical Butler-Volmer relation. Although numerical constraints limit the applicability of this model to dimensions of a few nanometers, the model is capable of making predictions at precisely the spatial and temporal scale that we are interested in for studying medical applications of silver nanoparticles and we find that our simulations compare favorably with experimental measurements [3]. We will discuss the impact of particle size, solution concentration, and particle aggregation on ion release and surface charge, which not only impact the anti-microbial efficacy and system stability, but may also affect biocompatibility. We have recently extended the model to include the effects of stabilizing coatings. We have found that even a chemically inert, charge-neutral adsorbate has a dramatic effect on the double layer structure, and hence on the ion release behavior and nanoparticle stability. Finally, we will discuss our numerical and theoretical efforts to extend the length and time scales of the model.



Ion release for different configurations of nanoparticles



Electric field and ion concentration in vicinity of coarsening nanoparticles

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## P-013

# Understanding Lithium-Oxygen Cell Chemistry

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To satisfy the energy storage needs of society in the long-term, an advance in battery energy density is required. The lithium-oxygen battery (Fig. 1) is one of the emerging opportunities in available for enhanced energy storage [1]. The challenge for the Li-$O_2$ cell is the progress of development of the air-cathode that allows reversible formation of $Li_2O_2$ in a stable electrolyte within its pores [2]. A typical air-cathode comprises of a carbon black mixed with a polymeric binder. The porous air-cathode is required to accommodate the insoluble discharge product ($Li_2O_2$) as well as to facilitate oxygen diffusion to the reaction site through the cathode film. In addition, the porous carbon should provide sufficient network conductivity to deliver electrons to the reaction site efficiently with little overall impedance. A homogenous distribution of nano-sized catalyst may also be required to maximize the performance by increasing the round-trip efficiency by lowering the voltage gap between charge and discharge processes. Understanding the atomic-scale factors governing the properties of the air-cathode interface is crucial for the development of the Li-$O_2$ cell. This in turn requires the possibility to access the physical parameters governing both the thermodynamics and kinetics of the electrochemical processes at the air-cathode. Since such insight can, at least partly, be provided by simulation and modeling, interplay between experiment and theory is expected to underpin the development of novel solutions for the Li-$O_2$ cell. Here we present experimental work and discuss the aspects (such as characterisation of the air-cathode structure, thermodynamics and kinetics also with respect to parasitic side reactions) where theoretical input could be highly beneficial.

$$2Li^+ + 2e^- + O_2 \leftrightharpoons Li_2O_2$$

**Figure 1.** Non-aqueous rechargeable Li-$O_2$ cell

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P-014

# Solid ionic conductor and its interface with metal: first principles molecular dynamics

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Development of fast ionic conductors is currently focused on $Li^+$, $H^+$, and $O^{2-}$ for use in batteries or fuel cells. Solid-state Li ion conductors could be applied to solid lithium secondary batteries, which are safer and easier to handle than batteries using electrolytes in organic solvents. A new type of solid Li ion conductor that has high Li ion conductivity and high chemical stability in anode and cathode regions is required for further development of lithium secondary batteries.

Recently, $LiBH_4$ was found to be superionic at $T > 390$ K ($Li^+$ conductivity, $\sigma = 5 \times 10^{-3}$ S cm$^{-1}$ at 423 K) [1], where it changes from an orthorhombic to a hexagonal structure. It shows a reversible electron transfer between $Li^+$ and Li metal. It has a large electrochemical window, though it is a strong reducing agent.

First principles molecular dynamics (FPMF) simulation showed that hexagonal $LiBH_4$ originates from the atom occupation splitting in the c-direction that results in a dumbbell-like density profile [2]. Activation barrier between two sites was found to be lower than 0.01 eV. This low barrier causes high ionic conductivity in bulk and polarized structure on electrode. It may be a reason of the reversible reaction of $Li^+ + e^- \leftarrow\rightarrow Li$.

Li atoms diffuse in the following way by the large-scale first principles molecular dynamics (FPMD) simulations [3]. A Li atom, at first, moves to a metastable interstitial site by thermal excitation, leaving a vacancy. The metastable-state is at 0.29 eV higher energy and the barrier surrounding it is at 0.30 eV. Then, another Li atom moves to this vacancy through a connection region having a barrier of 0.31 eV.

When a bias is added to the $LiBH_4$ and Li metal interface, Li is occupied only one side of the double well occupation. It takes reversibly with no memory effect.

Hexagonal-phase $LiBH_4$ was modeled using 300 or 1200 atoms. DFT based FPMD code of FEMTECK (finite element basis set with O(N)) and STATE (plane wave basis set) were used.

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## P-015

# DFT study of potential-dependent iodide adsorption at Au(111) electrode

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Experimental studies of ordered adlayers at well-defined single crystal electrodes has shed light on many problems related to applied electrochemistry [1]. In this work a well-known Au(111) | $I^{\gamma}$ interface has been investigated at density functional theory (DFT) level in order to describe potential-dependence of iodide adsorption theoretically. Optimized structure, all electron density, and free energy of the system as a function of coverage were computed using Grid-based projector-augmented wave calculator (GPAW) [2] with similar parameters as in ref. [3]. The interface free energy dependence on the surface coverage and electrode potential was treated according to previously developed atomistic model [3]. For the range of coverages from 1/3 to 0.442 formation of a commensurate $(\sqrt{3}\times\sqrt{3})R30°$, an uniaxial-incommensurate $8\times\sqrt{3}$, $5\times\sqrt{3}$ and $6\times\sqrt{3}$, and an incommensurate rotated hexagonal (7×7)21.8° atomic iodine adlayers at Au(111) surface was investigated. Single-ion specific adsorption was studied at coverages smaller than 1/3. Calculated energy for single iodide-ion adsorption (−1.5 eV at 2.40 Å) is lower than the value calculated in a study made by Pašti and Mentus (−2.03 eV at 2.38 Å) [4]. However, significant charge transfer, indicated via Bader analysis, from $I^-$ to a gold surface, but not from $F^-$, confirms formation of a strong covalent Au–I bond. Atomistic model analysis also reveals, that adsorption process may be separated into three stages: formation of commensurate adlayer characterized by high capacitance; adlayer compression with lower capacitance; and formation of rotated hexagonal structure (7×7)21.8°. Additional calculations show, that at higher coverages the influence of water is weak, as iodine charge does not change, and Au–I distance is only slightly suppressed by 0.05 Å.

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## P-016

# Surface Stability and Activity of Pt based Alloys

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The search for new improved Pt based catalysts for the oxygen reduction reaction, ORR, has procured various interesting alloys, such as $Pt_3Y$ and $Pt_3Ni$ [1]. These catalysts must possess two important properties, i.e. they should bind the intermediates with a certain strength in order to achieve high activity, according to Sabatier's principle, and they should be stable towards various mechanisms deteriorating the functionality, e.g. corrosion, phase separation and dissolution. Investigating and evaluating new catalysts in general entails the assumption that the activity and stability are uncorrelated parameters.

In this present study, the surface stability of Pt terminated alloys is investigated using density functional theory to find whether any correlation between this surface stability and corresponding binding energies of the ORR adsorbates exists. Assuming that the binding energy of the adsorbates is given in terms of two contributions; 1) strain effects and 2) ligand effects, as explained by the d-band model [2], the results indicate that the ligand part of the binding energy, i.e. the binding energy corrected for strain effects, scale linearly with the surface stability. This can be rationalized by the fact that high surface stability implies a top surface layer bonded strongly to the near surface layer. This, in contrary, leads to a weakening of the adsorbate layer thus leading to reduced binding energies.

Furthermore, the study also investigates alloys with concentrations of the alloying element of 33 % and 25 % in the second and third layer respectively, requiring comprehensive computational systems to model. Here, the results suggest that structures with 33 % of the alloying element in the near surface layer could be of significant importance.

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P-017

# Electrochemical Stark Effect on Raman Spectroscopy: Model Calculation of CO Molecule

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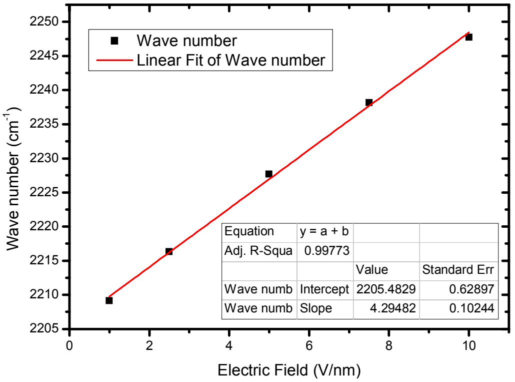
Spectroscopic technique is a key approach to investigate adsorption configurations and dynamic properties of molecules in electrochemical reactions. The binding interaction changes the electronic properties of adsorbed molecules. Meanwhile the static electric (Stark) field in the interfacial double layer polarizes adsorbed molecules. In potential dependent vibrational spectra, electrochemical vibrational Stark effect mainly displays as the frequency shift and intensity variation of some vibrational peaks at certain potential range.

Previous theoretical methods need complicated calculation processes and involves many variables with unclear physical meanings [1-3]. This is very difficult to discuss the perturbation correction of anharmonic potentials. In the present work, we concentrated on the following aspects. The Stark effect of the electric field is introduced into the perturbative potential in a relatively compact expression. We use a diagrammatic method to simplify the calculation of anharmonic contributions. The advantages of the diagrammatic method is easy to consider the influence of the anharmonic coefficients from the static electric field polarization on the spectroscopic frequencies and intensities. We performed *ab initio* calculations to determine the potential energy functions and then numerically calculated the Stark slope of frequency shift and Raman intensity variation of free CO molecule under an external field. The refined result of the frequency-field slope is shown in Figure 1.



| Equation | y = a + b | | |
|---|---|---|---|
| Adj. R-Squa | 0.99773 | | |
| | | Value | Standard Err |
| Wave numb | Intercept | 2205.4829 | 0.62897 |
| Wave numb | Slope | 4.29482 | 0.10244 |

**Figure 1**. The calculated Stark slope of CO molecule.

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### P-018

# Performance Comparison of Co/Fe-$N_x$ (x=2, 4) ORR Electrocatalyst in Acidic and Alkaline Media: A Density Functional Theory Study

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The generation of energy is expected to be one of the major challenges in the 21st century largely due to declining fossil fuels and the reduction of greenhouse gas emissions. Fuel cell is an attractive and promising technology that can address both constraints simultaneously. However, currently this technology relies on expensive and rare platinum group metal (PGM) electrocatalysts. For this reason self-assembled pyrolyzed TM-$N_x$ (TM=Co, Fe, x=2, 4) based cathode electrocatalysts have attracted significant interest for oxygen reduction (ORR). Several experimental studies have reported ORR activity of these catalysts [1]. However, the stability of TM-$N_x$ defects, and the detailed ORR mechanism/pathway remain presently unclear.

Here, we have explored the stability and ORR activity on TM-$N_x$ defect motifs through density-functional-theory (DFT) calculations. The TM-$N_x$ defect motifs are embedded in monolayer graphene. We find that the embedded TM-$N_x$ motifs are thermodynamically stable. TM-$N_4$ defects are predicted to be energetically more favorable as compared to the competing TM-$N_2$ defects. The ORR activity and mechanism of TM-$N_x$ defect motifs are explored by their interactions with $O_2$ and the peroxide intermediate ($OOH^-$ in alkaline and $H_2O_2$ in acidic media). Focusing on the energetically favorable TM-$N_4$ defect motifs, we find that $O_2$ chemisorbs. In contrast, $OOH^-$ is predicted to decompose into $OH^-$ and O on Fe-$N_4$ where O remains chemisorbed on Fe and $OH^-$ desorbs. This observation suggests that ORR proceeds via a single site $2x2e^-$ process. In contrast, $OOH^-$ is physisorbed on Co-$N_4$ and requires a second reaction site for further reduction, thus ORR is predicted to be a dual site $2x2e^-$ process. In acidic medium, $H_2O_2$ is physisorbed on Fe/Co-$N_4$ supporting a dual site $2x2e^-$ mechanism. A similar analysis for the less stable TM-$N_2$ defects shows that ORR can proceed via a single site mechanism in acidic and alkaline electrolyte. In summary these preliminary results provide a rationale for the experimental observation that Fe-$N_x$ based ORR electrocatalysts are superior to Co-$N_x$ especially in alkaline medium [2,3].

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P-019

# Ab initio study of low-coordinated sites on the MgO(001)-surface using Hybrid Functionals

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Nano-particles and thin films of metal oxides play a large role in catalysis, so understanding their underlying properties is of crucial importance to optimize the catalytic process. It is widely accepted the low-coordinated surface sites, such as surface oxygen vacancies, step edges, and reverse corners represent the reactive centers for example at the MgO(001) surface. Unravelling the role of these particular centers in chemical reactions by accurately modelling their localized electronic states is pivotal to understanding the chemical properties of these materials.

Standard density functional theory together with the local density or generalized gradient approximation for the exchange-correlation functional, however, underestimates the band gap of metal oxides by a large margin and often even fails to describe the bonding correctly. However, employing hybrid functionals like the HSE06, which include a fraction of screened Hartree-Fock exchange, are known [1] to improve the description of metal oxides considerably.

Magnesium oxide is a prototype for metal oxides with ionic bonding. We investigate surface color centers at the MgO (001) surface including the surface oxygen vacancy, step edges, and vacancies at step edges using the DFT-HSE06 approach and a slab model. This enables a proper description of localized and extended states, e.g. the dispersion of shallow surface states at the step edge. For the relevant surface and localized states within the band gap we find large corrections to the standard approach. In addition, the calculations reveal a negative electron-affinity in agreement with recent calculations within in the many body perturbation theory [2]. Also we compare our results with recent STM-experiments on vacancy centers at step edges of MgO-films [3].

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### P-020

# Facile fabrication of graphene film by electrodepostion from doped graphene

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Graphene is doped using various doping agents: HCl, $HNO_3$, or $H_2SO_4$; and then the doped graphene are dispersed in acetonitrile. Graphene-deposition is carried out by applying a voltage to a conducting polymer, PEDOT, coated electrode. The behavior of the graphene-deposition is confirmed by QCM and Raman spectra as a function of the doping agent. This method is powerful for the fabrication of graphene layers on desired substrates and for applications requiring large areas due to its wrinkled structure.

Keyword : graphene, electrodeposition, electrode

P-021

# Density Functional Study of Curvature Effects on Carbon Nanotube Unzipping

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Graphene nanoribbons (GNRs) are promising materials for a wide range of applications, due to its unique conductive, catalytic and biocompatible properties, which make them very attractive as an alternative to carbon nanotubes (CNTs). One way of obtaining this material is from CNTs. Kosynkin [1], by means of a chemical treatment with a solution of potassium permanganate in acid medium, obtained GNRs from longitudinal opening of multi-walled CNTs. This procedure offers the possibility of producing at large-scale GNRs of controlled width, which are of interest because their electric properties vary with their width.

The aim of the present work is to contribute to the understanding of the unzipping mechanism of CNTs, to yield GNRs of zig-zag edges by means of quantum mechanical calculations based on Density Functional Theory (DFT), considering the role played by the radius of the CNT. With this purpose, we use the SIESTA computer code [2]. We consider a set of arm-chair CNTs of different radii, as well as corrugated sheets which emulate the curvature of CNT of larger radii. This approach was found useful to reduce the number of atoms and so the computational cost. Thus, we could study the properties of a wide range of nanotube radii involving only 80 carbon atoms in the calculations.

The minimum energy configuration was obtained with the conjugate gradient (CG) technique. The minimum energy path (MEP) for the oxidation reaction was undertaken using the Nudged Elastic Band method (NEB) [3]. This is a very useful calculation method that allows obtaining the MEP of an elementary step with the only assumption of its initial and final states. The charges on the different atoms were evaluated by means of the Mulliken population analysis.

It was found that permanganate adsorption energies become more negative with increasing curvature of the surface. This favors the energetic of the oxidative reaction, since for smaller radii the reaction of the CNTs becomes spontaneous, leading to diona formation and the generation of a hole in the CNT.

As the unzipping process goes on, a second permanganate group is adsorbed in the C-C bond adjacent to the hole, leading to longitudinal unzipping and yielding nanoribbons of zig-zag edges.

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P-022

# Hydrogen Storage Optimization on Nanoporous Carbonaceous Material: A Theoretical Study

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Carbonaceous compounds appear as promising materials for gas storage, as they have large surface area. In the case of hydrogen, this property is of particular interest, since it is the optimum fuel in an economy based on renewable resources [1], where hydrogen should be generated by electrolysis. The use of hydrogen as fuel requires the improvement of tanks on board of vehicles, so that with moderate pressure a storage capacity of the order 6.5% should be achieved. However, pure carbonaceous materials have low storage capacity of hydrogen at room temperature and they do not meet the requirements. In recent years, many theoretical studies were made of carbonaceous materials decorated with metals to improve their performance. From the theoretical perspective, it appears that this kind of hybrid materials should be very promising, but experiments did not accompany these predictions. We found that problems arise because oxygen acts as an interferent in the storage process, by oxidizing the metal decoration or by blocking the hydrogen adsorption site [1-3]. Given the larger dynamic radius of the oxygen molecule as compared with hydrogen, it appears as possible to avoid oxygen access to the binding sites by optimizing the pore size of these materials. This possibility is investigated in the present work by means of a molecular dynamics model using GROMACS package with Lennard-Jones potential at room temperature and mixtures of gases (hydrogen, oxygen) up to a pressure of 200 bar.

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P-023

# First-principle density functional theoretical study on the potential dependence of the oxygen reduction reaction over catalytically active Fe/Co-$N_4$-graphene centers

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Density functional theoretical calculations were carried out to examine the oxygen reduction over model Fe and Co sites on nitrogen-containing graphene surfaces that mimic the active Fe-$N_4$ and Co-$N_4$ sites on graphene substrates found by Dodelet for systems resemble the active sites in heme macromolecules[1][2]. The predominant reaction pathways that lead to the partial and complete oxygen reduction are examined on both the Fe and Co-$N_4$ active sites located on the basal plane of graphene in an aqueous environment. The potential-dependent reaction energies and barriers for the important reduction pathways were calculated using the double reference method developed by Filhol and Neurock[3]. The Fe-$N_4$ active sites were found to promote the complete oxygen reduction for potentials between 0.8~1.2V v.s. NHE, while the Co-$N_4$ active sites promote the reduction to hydrogen peroxide as the main reduction product.
Recent experiments suggest that the main active sites may reside between graphene edge planes[2]. We have therefore examined the ORR paths at the Fe-$N_4$ and Co-$N_4$ sites located at the hydrogen-terminated graphene edges to determine their role in the reduction of oxygen.

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## P-024

# Influence of cation chemical composition and structure on the specific interactions at Bi(111) | room temperature ionic liquid interface

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Room temperature ionic liquid (RTIL) | electrode interface is highly interesting object both for fundamental and applied electrochemistry [1]. This work focuses mainly on the theoretical description of 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$) and 1-butyl-4-methylpyridinium tetrafluoroborate ($BMPyBF_4$) interaction with bismuth single crystal plane (111) surface. B3LYP density functional theory was used for investigation of single-ion and cation-anion pair adsorption at Bi(111) in different orientations and at various surface sites. Bismuth surface was modeled by $Bi_{24}$ and $Bi_{54}$ clusters, described with LanL2MB basis-set, and 6-31g** approximation was used for lighter atoms. The interaction energy of ion with neutral bismuth cluster is low and almost equal for $EMIm^+$ and $BMPy^+$ cations, but interaction is much stronger for $BF_4^-$ anion. Therefore, the anion position determines the position of cation-anion pair at the Bi(111) surface. Herewith, cation-anion relative orientation is similar for isolated and adsorbed pairs. On the whole, the adsorption is quite strong (~ −180 kJ/mol), which is indicated by redistribution of charge density (more details are given in ref. [2]). However, ion-surface interaction energy is heigher than the cation-anion bond energy (~ −400 kJ/mol). The latter is attributed mainly to Coulomb-interaction, while binding to the surface has complex nature explained with projected density of states. Experimental data [2–4] indicate the noticable differences between Bi(111) | $BMPyBF_4$ and Bi(111) | $EMImBF_4$ interfaces. Both cations bind weakly to the surface in a similar way through aromatic π-electron system and we address observed differences to the structural peculiarity located in adsorbate layer. We emphasized, that besides ion size and alkyl chain length, the hydrogen-bonds affect relative orientation of ions in isolated cation-anion pair as well as in adsorbate layer near Bi(111) the electrode surface, lowering the energy path for reorientation and, consequently, the adsorption layer reorganization energy [5]. Therefore, Bi(111) | room temperature ionic liquid interface structure is strongly influenced by the cation structure due to the specific cation-anion interaction.

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P-025

# The Mechanism of Electrocatalytic Oxidation of Formic Acid at Pt Electrodes

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The mechanism and kinetics of electrocatalytic oxidation of formic acid at Pt electrodes is discussed in detail based on previous electrochemical in situ ATR-FTIRS data [1-4]. A kinetic model with formic acid adsorption (and probably the simultaneous C-H bond activation) as the rate determining step, which contributes to the majority of reaction current for formic acid oxidation, was proposed for the direct pathway. The model simulates well the IR spectroscopic results obtained under conditions where the poisoning effect of carbon monoxide (CO) is negligible and formic acid concentration is below 0.1 M. The kinetic simulation predicts that in the direct pathway formic acid oxidation only needs one Pt atom as active site; formate is the site blocking species instead of being the active intermediate.

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## P-026

# Hydrogen Oxidation on Pt-Sn Intermetallic Phases

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Ordered intermetallic phases are a special class of materials inside the group usually called metal alloys. Such materials can be applied as electrocatalysts for fuel cell related reactions [1, 2]. Their principal characteristic is that one can obtain well ordered samples with crystallographic properties and electronic structure quite distinct from those usually found in the original metal constituents. In this work we have investigated the hydrogen oxidation on $Pt_3Sn$, PtSn and $PtSn_2$ ordered intermetallic phases by means of the Density Functional Theory (DFT) and the theory developed by Santos and Schmickler [3, 4]. The calculations were carried out with Dacapo code [5] that uses plane-wave basis set to expand the wave functions of the electronic states and describes the core-electron interactions with Vanderbilt pseudo-potentials [6]. An 8 x 8 x 1 k-point grid was used to perform the Brillouin-zone integration following the Monkhorst-Pack scheme [7]. It was observed that in all intermetallic compounds the d band of platinum lies below the Fermi level and it is supposed to be filled since tin is reported as electron-donor. $Pt_3Sn$ is the intermetallic with higher content of platinum; it is a good electrocatalyst for hydrogen oxidation and showed a variety of sites that are exergonic for hydrogen adsorption suggesting the occurrence of underpotential deposition (upd) of hydrogen. PtSn is almost as good, and this is attributed to two effects: absence of strongly adsorbed hydrogen, which can inhibit the reaction [4], and the large coupling constant with the hydrogen 1s orbital. $PtSn_2$ is considered inactive as it presented endergonic hydrogen adsorption energies on all studied sites. Furthermore, our calculations agree well with experimental data.

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P-027

# Vanadium speciation in the mixed acid based electrolytes of Redox Flow Batteries

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Redox Flow Batteries (RFB) is emerging as potential candidate for grid scale energy storage systems owing to their ability to store energy in multi megawatt scale. The RFB is also an efficient storage device for renewable energy sources such as wind turbine and hybrid photovoltaic cells. In particular, RFB can help us to successfully integrate the intermittent renewable energy sources in to large scale electrical supply grid. The RFB operates on the redox potential between two electrolytes containing redox active species. Among various redox couples, all-vanadium based redox flow batteries (here after called VRFB) is suitable for large scale storage due to long lifespan, quick response time, deep-discharge capability and low maintenance cost. However a serious limiting factor in total energy density of this VRFB system comes from poor solubility of vanadium in electrolyte solutions. For example, the fully charged $V^{5+}$ electrolyte solution displays poor stability at elevated temperatures (>310 K) and also at high vanadium concentrations (>2M) [1]. Recently we reported a novel mixed acid system (i.e. solution containing sulfuric and hydrochloric acids) which offers electrolytes with relatively higher vanadium concentrations (>2M) [2]. These electrolyte systems shows tremendous increase in electrolyte stability and has nearly two times energy density over conventional sulfuric acid based VRFB.

However, the chemistry behind this higher stability of $V^{n+}$ species in mixed acid system is not well understood. Understanding the chemistry behind this higher solubility is imperative for developing a better or even a new vanadium electrolyte solution, which can further increase the life cycle, energy density and reduce the operating cost of the VRFB. In this work, a combination of Nuclear Magnetic Resonance (NMR) and density functional theoretical (DFT) studies were carried out to provide a clear view about structure of $V^{n+}$ species in various electrolytes and their thermal stability. In particular we examined the various possible ligand exchange reactions and dimerization reaction involving $V^{n+}$ cations, which are related to observed increase in the solubility of vanadium in electrolyte solutions. We will discuss the DFT predicted molecular structure and properties along with the experimentally observed spectroscopic results.

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## P-028

# Calculations of Near-edge X-ray Absorption Spectra of Biased Pt/water Interface

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Detailed understanding of electrochemical reactions at the metal/electrolyte interface is fundamental to improve the efficiency and durability of electrode catalysis for renewable energy resources. Since the electrochemical reactions take place at the complex metal/electrolyte interface where ions and solution distribute a specific structure and strong electric field is across near the electrode surface, it is difficult to understand precise electronic structures at the interface using only experimental data. Recently we started to develop an *ab-initio* computational framework to elucidate the electronic structure at the interface under an electrochemical condition in conjunction with an x-ray absorption spectroscopy (XAS) experiment.

So far, we have developed both the modeling of an electrochemical reaction at the metal/electrolyte interface [1-5] and the simulation tool for a XAS experiment [6]. By connecting these methods, we are trying to simulate near-edge x-ray absorption fine structure (NEXAFS) spectrum of biased Pt/water interface. We will present some bias potential dependence of the oxygen K-edge NEXAFS spectrum at the interface.

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P-029

# Kinetic Monte Carlo Simulations of $Pt_{1-x}Co_x$ Nanoparticle Catalyst Dealloying

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Nanoparticle Pt alloy fuel cell catalysts have the advantage of higher oxygen reduction activity and lower cost than pure Pt catalysts. However, the high potential and acidic operating environment leads to dealloying and loss of activity over time. Optimizing the design of nanoparticle alloy catalysts depends on developing a better understanding of the process by which nanoparticles dealloy. In bulk materials, dealloying is often understood in terms of a "parting limit" and "critical potential", the concentration and potential above which massive dealloying of the less noble metal will occur. The parting limit is determined by a competition between dissolution of the more active element and repassivation by surface diffusion of the more noble element. [1] At the nano-scale the parting limit may be different from the bulk value since both the dissolution and diffusion rates may be affected by particle size and morphology.

In this work, we use kinetic Monte Carlo (KMC) simulations with the modified embedded atom method to investigate dealloying of $Pt_{1-x}Co_x$ nanoparticles. We consider the effect of particle size and morphology on the parting limit and critical potential. We also consider the effect of concentration, potential, and particle size on depth and rate of dealloying, surface concentration, surface area, and particle morphology.

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## P-030

# Water (Dis)order on a Hydrogen-covered Electrode

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Up until now, little attention has been paid to the fact that under electrochemical conditions and low potentials, Pt(111) is covered by hydrogen. There is still some disagreement between experiment and theory□regarding the hydrogen equilibrium coverage: whereas experiments□indicate that at 0 V relative to the normal hydrogen electrode (NHE)□the hydrogen coverage should be about 0.66 ML [1], density functional theory calculations yield a hydrogen coverage of□1 ML [2,3]. Still, there is a qualitative□agreement that there is significant hydrogen coverage, and it is very likely that the presence of these adsorbed species has a severe influence on the structure of the electrochemical electrode-electrolyte interfaces and on the processes occurring at these interfaces.

In this presentation, we will address the structure of water layers above hydrogen-covered Pt(111) surfaces, which have been examined at room temperature through ab initio molecular dynamics simulations based on periodic DFT calculations. Fully hydrogen-covered Pt(111) (Fig. 1) with additionally either a hydrogen vacancy or another hydrogen adatom have been considered. The resulting structures are analyzed in detail as a function of the hydrogen coverage. In particular, the thermal disorder in the water layer is examined in terms of deviations from the ordered ice lattice, orientational inhomogeneity within a water bilayer, as well as the onset of proton transfer. We also comment on associated work function changes, the effect of water on the structure and stability of the hydrogen cover, and time permitting, the effect of charged electrodes on our numbers.

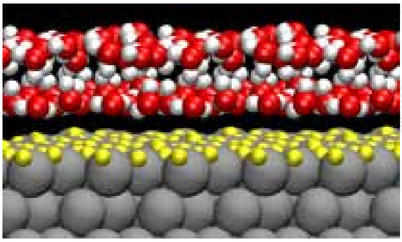

**Fig. 1.** Snapshot of the molecular dynamics run for water on H-covered Pt

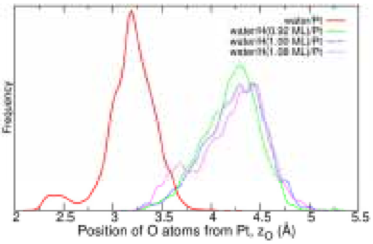

**Fig. 2.** Distribution function for the distance of the oxygen atoms from Pt

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## P-031

# Exploring $Li^+$ Potential Energy Surface in Poly(ethylene oxide)-based Sulfonate Ionomers

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Ion-containing polymers are of interest as single-ion conductors for use as electrolytes in electrochemical devices, including lithium ion batteries. Current ion conductivities of the best ionomers are roughly 100X too small for practical applications and have a small fraction of their $Li^+$ counterions participating in conduction. We are using *ab initio* methods to investigate the $Li^+$ conduction mechanism, and specifically the role of transient positive triple ions ($Li^+A^-Li^+$) in the conduction process. The positive triple ion has a lower energy separated state that allows for facile transport, if there is a pair within 1.4 nm. We will discuss the competition between cation solvation with ether oxygen atoms and cation-anion interaction. The importance of anion-anion separation in altering $Li^+$ hopping barriers will be examined, as well as the variation in hopping rates with solvent identity. *Ab initio* calculations are used to evaluate the relative energy of ion states (contact and separated states), and this analysis is used to explain experimental phenomena of $Li^+$ mobility in ionomers.

## P-032

# Effect of Nano Particle Geometry on Diffusion Impedance of Battery Electrodes

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Short diffusion length in confined nanoparticles makes the capacitive behavior of diffusion impedance accessible in impedance experiments, which is hard to see in impedance spectra of large particles. Transport properties of charge carriers come most accurately from the low frequency capacitive behavior of diffusion impedance. In this work, we study properties of the diffusion impedance based on linearized transport theory in model geometries of nanoparticles, including flat film, cylinder, sphere, and cubic. While some theoretical formulae of the diffusion impedance for various geometries have been suggested in the community, they have not been well appreciated so far by experimentalists. [1, 2] Mostly, the flat film expression was employed, or the semi-infinite Warburg expression was used excluding the capacitive part of spectra to interpret diffusion impedance. We reilluminate and apply the theoretical advances to some of published experimental impedance data of silicon nanowire electrode and mesocarbon microbead (MCMB) electrode. [3, 4] In the application, we show that it is essential to account for the right particle geometries to correctly interpret impedance data of battery electrodes with nanoparticles.

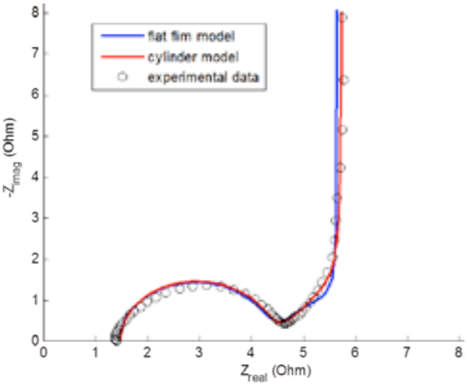

Figure 1. Impedance data of silicon nanowire electrode were fitted using flat film and cylindrical diffusion impedance, and significantly different diffusivities were obtained. (The original data were kindly provided by Prof. Yi Cui at Stanford University.)

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## P-033

# Microstructure of electrolytes

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Mechanism of metals and their compounds dissolving in inorganic water solutions, formation of their microstructure and microstructure of oxide melts are explained in terms of spontaneous electrolytic dissociation at first order phase transition. Over thirty years we studied electrolytes conductivity, effects of alternating magnetic fields on electric conductivity and structures of these liquid systems, as well as the effects of mechanical vibrations on structural features of oxide melts and metallurgical slag. We obtained experimental data which can not be explained considering that molecules in melts are dissociated into cations and anions.

Such synthesized slag as of compositions, (%): $SiO_2$ - 24-47; $Al_2O_3$ – 8-10; Fe oxides – 0-53; CaO – 14-40 were used in experiments. It was found the following:

- Mechanical vibrations induce division of melts into 2 or 3 phases of different chemical compositions and structures;
- Alternating magnetic fields induce division of melts into 2 phases (total mass and mass in inter-electrodes space), differing by their chemical compositions and structures;
- At melt temperature increasing up to $1500^0$C we managed to identify endothermic and exothermic effects occurred at different temperatures;
- At iron-free melt temperature increasing it was found that its electric conductivity (which was measured by means of potentiometer equipped with platinum and platinum-rhodium thermocouples) was started at $1450^0$C and above, where exothermic effect occurred at the cooling branch and electric conductivity stepped-down to value below instrument sensitivity;
- Anisotropy of electric conductivity for hyperthermal melts was identified; effects of molecular dipole orientation on melt conductivity value were shown; a series of exotic phenomena was revealed in electric conductivity of melts and water solutions occurred under the effects of electromagnetic fields and electric current parameters (i.e., decrease in electric conductivity of melt with temperature increasing; increase in electric conductivity of melt with temperature decreasing; stepwise variation of electric conductivity where effects of alternating magnetic fields are removed off; sharp increase in electric conductivity where retrograde compounds disintegration is occurred in cold slag etc.);
- Potential excessive electrophoretic mobility is proved for solid particles in melts;
- Potential chemical interactions are proved for oxide melts/gas phase components within a wide range of chemical compositions under the effects of pulse electric current where carbon monoxide may serve as a melt oxidizing agent.

Similar phenomena were identified through study of different copper slags.

### P-034

# Effects of electric current parameters on metals solubility in inorganic water solutions

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We studied aluminium, iron and molybdenum solubility in alkali solutions of concentrations below 10% under the effects of sinusoidal alternating electric current. A two-electrode cell was used. Electrodes were made of soluble metal. Electrical frequency varied in range of 20 Hz to 200 000 Hz. Metal wires of 2.5 mm diameter were used as electrodes in studies of metal aluminium solubility. Electrodes were immersed in alkali water solution of 1.46; 3.58 and 5.7% KOH concentrations (by chemical analysis). A granular KOH ("pure" grade) was used to prepare raw liquors. Current intensity increasing leaded to specimen mass losses to 0.042-0.044 g at equal electrical frequency and alkali concentration. Further current intensity increasing practically suppressed electrode dissolving: mass varied up to 0.005-0.007 g of Al. Alkali concentrations increasing up to 5.7% KOH substantially decreased aluminum dissolving with mass losses up to 0.009 g. Total electrode surface after 6 hours of dissolving process was covered with film. Phase analysis of aluminum surface proved that the film is a phase mainly represented by potassium. Thickness of potassium film varied depending on the depth of electrodes immersion into solution and experiment time duration. We failed to identify structures and compositions of potassium and aluminum compounds. Wires of 1.5 mm diameter were used as electrodes for molybdenum dissolving. Chemical composition of wire was determined with X-ray metals analyzer InnovXSystems (USA). Chemical composition of electrode wire was as follows, %: Mo 96.8; Cr 2.60; Fe 0.59. Dissolving was performed in thermostated cell within 25-80 °C temperature range. Electrode voltage reached 1.0-3.2 V and was restrained by capacity features of UZG-33 ultrasonic generator. Current intensity varied from 200 mA to 500 mA, while dissolving rate increased prorate to current intensity and reached 0.5-4.3 mg/min. It was shown the following:

- Dissolving rate was not proportional to electrical frequency, starting at 20 Hz frequency and stopping at increased current frequency;
- Dissolving stopped at different current parameters and concentrations of potassium oxide where temperature reached 75°C;
- Molybdenum dissolving was not occurred at any current parameters where concentrations of potassium oxide exceeded 9 %;
- Successive increasing of current intensity resulted in increased electrical frequency at which reaction stopped. For temperature 25°C and current intensity 90 mA reactions stopped at 66 Hz, 200-130, 270-250, 360-350, and 450-400 Hz.

### P-035

# New Software for Computational Electrochemistry

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The new software is designed for automatic simulation of any electrochemical reaction mechanisms at the most frequently employed electrode geometries such as the one-dimensional planar, sphere and cylinder (KISSA-1D) as well as the two-dimensional disk and band (KISSA-2D).

Simulations are performed using a novel approach [1, 2] developed by the authors, which involves the use of (quasi)conformal transformations of the simulation space to avoid numerical difficulties arising from diffusional propagation of species near electrode/insulator edges and a NEW algorithm for adaptive tracking of sharp reaction fronts in the solution and corresponding adjustment of computational grid to obtain accurate results for both concentrations and electrochemical currents. This approach allows for efficient resolution of all physicochemical and mathematical issues connected both with edge effects (for microelectrodes) and considerable disparity of time and length scales of the underlying processes arising due to quickly changing electrode potential and/or rapid homogeneous chemical reactions resulting in steep concentration gradients [3-5].

The software offers a possibility to take into account spontaneous natural convection which limits the extent of the diffusion layer and leads to the establishment of a steady state current even at macroelectrodes. Furthermore, this enables setting correct and thermodynamically consistent initial conditions within the stagnant layer when the system is pre-equilibrated at a given rest potential for a finite period of time. The software also allows simulating adsorption equilibria and chemical reactions between surface-bound species [6].

The program's graphical interface offers convenient entry of an electrochemical reaction mechanism and parameters and provides access to the computed distributions of all important quantities such as concentration distributions, currents (CV) and current densities as well as ECL intensity when applicable.

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## P-036

# Constrained Density Functional Theory in ONETEP

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In the pursuit of a more sustainable energy-economy, great efforts are currently being made to develop improved, industrially viable electrochemical energy conversion and storage devices. Understanding the different materials and interfaces constituting such devices is crucial for the development of novel solutions. This, in turn, requires the possibility of accessing the atomic-scale parameters governing the thermodynamics and kinetics of the electrochemical processes at the device interfaces.

Recently, very encouraging results have appeared regarding the potential of constrained Density Functional Theory (cDFT) for the study of ground-state electron transfer and chemical reactivity [1]. Here we present the implementation of cDFT in the ONETEP program [2], based on the existing framework of tensorial invariance and self-consistency for non-orthogonal projectors [3,4]. The linear-scaling (LS) nature of the cDFT implementation and its compatibility with the LS-DFT+U functionality in ONETEP [5] open up for cDFT(+U) simulation of systems up to several thousands of atoms on academically available hardware. This should make the method valuable for the study of the extended electrochemical interfaces present in fuel-cells, batteries and supercapacitors.

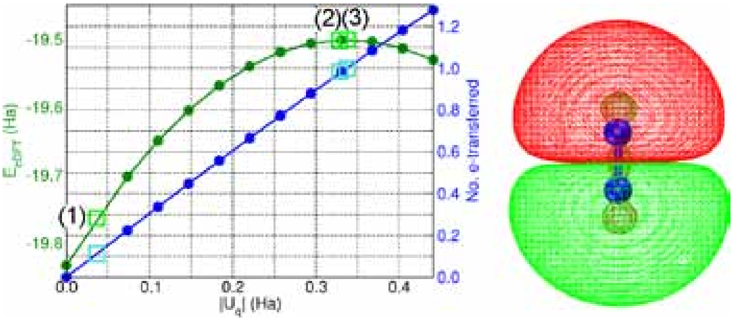

**Figure 1. (Left)** cDFT energy (green) and calculated electron transfer (blue) of the $N^{(+)}=N^{(-)}$ system (bond-length: 1.1 Å) as a function of the constraining potential ($U_q$). Circles refer to single-point (fixed-$U_q$) simulations. Squares indicate the Conjugated Gradient iterations (labeled in brackets) needed to converge the cDFT solution to within $\pm 10^{-4}$ e. **(Right)** Calculated electron-charge density change ($\Delta\rho = \rho_{cDFT} - \rho_{DFT}$) between the constrained and unconstrained solutions. Green: $+10^{3}$ e Å$^{-3}$, red: $-10^{3}$ e Å$^{-3}$.

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P-037

# Molecular Modelling of Proton Transport in Polymer Electrolyte Membranes

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Polymer electrolyte fuel cells (PEFC) have garnered foremost interest in research and technology development due to their unrivalled efficiency and their environmentally friendly operation. The polymer electrolyte membrane is a central component of a PEFC; the proton conductivity of these separator membranes is crucial for attaining high efficiency and power density of PEFC. The most widely employed perfluorosulfonic acid ionomer membranes, such as Nafion, attain high proton conductivity only with sufficient hydration. Proton conductivity decreases dramatically at low hydration levels and at elevated temperature. Hence, there is a huge continuing interest in designing new membranes for high temperature fuel cells that could provide high proton conductivity under lower humidification conditions. In order to understand the fundamental proton transport mechanisms at minimal hydration and rationalize the impact of chemical structure and composition of ionomer systems on long range proton transport, we have performed *ab initio* metadynamics simulations of interfacial proton transfer. The considered model system consists of a densely packed array of functional surface groups that mimic sidechains in PEM. The end groups of these surface groups are fixed at positions of a hexagonal grid on a basal plane. Sulfonic acid head groups of the SG are allowed to move unrestrictedly. We evaluate this system under conditions of minimal hydration. From calculated free energy surfaces, we determined activation energy barriers and lowest free energy paths for the concerted and non-concerted hydronium ion transitions. Transitions involve concerted sequences of hydrogen bond breaking between hydronium ions and sulfonate anions, orientational fluctuations of surface groups and hydronium ion shift. Results show that highly efficient collective proton transport could occur at a critical spacing of ~6.7 Å between surface groups. This critical separation is in good agreement with experimental assertions of highly efficient interfacial proton transport at biomembranes and Langmuir monolayers.

## P-038

# Stochastic cellular automata and its applications in simulations of adsorptions kinetics of electrochemical active species at electrode surface and their electrochemical behaviors

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Cellular automaton (CA) method was originally developed by John Von Neumann back to 1950 as self-reproduced cellular automata. Nowadays, it has been become one kind of powerful simulation methods, and widely used in many areas such as physics, chemistry, biological, environmental science as well as geographic sciences. The introduction of probability concept into CA, and called probabilistic cellular automata (PCA) or stochastic cellular automata (SCA), which shows not only the statistic properties as monte carlo simulation does, but also CA characteristics such as mutual interactions with its neighbors, fast computation speed with all cells act at one sep.

In this report, we briefly introduce stochastic cellular automata simulation method, its characteristics, applications in chemistry as well as electrochemistry, and then give out two examples of applied systems: (1) the cyclic voltammogram of electrochemical active species adsorbed on electrode surface; (2) cyclic voltammogram of cysteine adsorbed on nano silver particle modified clustered carbon fibre electrode.

The first example is a one-component reversible electrochemical system, such as polyamine, adsorbed ferricyanide, and so on. The electrode was discretized into 100×100 two dimensional lettice, the adsorption dynamics of electrochemical active species randomly adsorbed and distributed on the surface with some probability was simulated with SCA. The cyclic voltammogram of the adsorbed molecule was simulated based on the normal distribution of electrochemical activities around equilibrium potential.

The secondary example is a two-component system with irreversible electrochemical behavior. The nano silver particles modified clustered carbon fibre electrode was used to extract cysteine molecules from solution simulated by SCA. The deposited silver surface was discretized with five grids, which gives out an irreversible cyclic voltammogram with a pair of redox peaks. After the modified electrode contact with solution including cysteine, cysteine molecules adsorbed on the silver particle surface, and give out a different irreversible cyclic voltammogram. During the adsorption process the redox peaks of silver particles decrease, and the redox peaks of silver-cysteine increase, the whole process was described with the simulated cyclic voltammograms, which are accord well with the experimental results. All the simulations were carried out on a personal computer within SCILAB 5.03 software.

## P-039

# Electrocatalysis on Cubic Pt-M Alloy Nanocrystals

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Particle size, shape and composition are crucial factors in determining the catalytic activity of Pt-alloy nanoparticles. In most of the previous studies, particle shape is not well controlled, and the comparison of activity is therefore complicated by the shape (i.e. surface structure) difference. The development of nanocrystal synthesis enables production of high quality nanocrystals with monodisperse size and shape. In this presentation, electrocatalytic activities of $Pt_3M$ (M = Mn, Fe, Co, and Ni) nanocubes towards oxygen reduction reaction (ORR) and methanol oxidation reactions (MOR) will be compared and discussed. Results from particle structural characterization will be demonstrated to confirm the quality of the nanocrystals. It will be shown that both ORR and MOR activities depend on the particle composition. The observed systematic activity changes will be discussed in the frame work of the d-band theory. These studies underscore the importance of controlling particle shape in fuel cell catalyst development.