

## O 42: Solid-Liquid Interfaces: Reactions and Electrochemistry - Theory II

Time: Tuesday 14:00–16:00

Location: WIL B321

O 42.1 Tue 14:00 WIL B321

**First-principles free-energy barriers for photoelectrochemical surface reactions: Proton abstraction at TiO<sub>2</sub>(110)** — •THOMAS STECHER, KARSTEN REUTER, and HARALD OBERHOFER — Technische Universität München, Garching, Deutschland

First-principles modelling of electrocatalytic surface reactions is still largely defined by the computational hydrogen approach. This approach evaluates free energy differences between consecutive reaction steps and thereby accounts only for thermodynamic barriers. In order to access additional kinetic barriers in the photocatalytic oxidation of water, we present an approach based on *ab initio* molecular dynamics (AIMD) simulations and umbrella sampling. [1] We showcase the method by explicitly calculating the free-energy barrier for the initial proton abstraction in the water splitting reaction at rutile TiO<sub>2</sub>(110), which was previously studied within the computational hydrogen electrode approach. [2] Combining electrostatic QM/MM embedding, an energy based reaction coordinate and state-of-the-art free-energy reconstruction techniques renders the calculation tractable at the hybrid density-functional theory level, which is required for a realistic description particularly of the transition state. The obtained free-energy barrier of approximately 0.2 eV, depending slightly on the orientation of the first acceptor water-molecule, suggests a hindered reaction on the pristine rutile surface.

[1] T. Stecher, K. Reuter and H. Oberhofer, *Phys. Rev. Lett.*, accepted for publication (2016).

[2] H. Oberhofer and K. Reuter, *J. Chem. Phys.* **139**, 044710 (2013).

O 42.2 Tue 14:15 WIL B321

**Thermodynamic sampling of the electrode potential on a Pt(111) electrode from first principles** — •SUNG SAKONG and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

The potential of zero charge (pzc) is an important electrochemical quantity that is determined by the work function of a metal covered by an ion-free water film. Recently we derived the pzc from large scale *ab initio* molecular dynamics simulations by statistically averaging the work function [1] and reproduced the experimentally observed value. However, hydronium and hydroxyl ions can be present in the water film at metal electrodes created by the self-ionization of water. We have studied the consequences of the creation of these ions on the water properties separately. They modify the charge distribution at the water-metal interface. Consequently, the local dipole field and thus also the work function are influenced by the ions. Furthermore, we will establish a connection to computationally less demanding methods for the description of electrochemical water metal interfaces [2].

[1] S. Sakong, K. Forster-Tonigold, and A. Groß *J. Chem. Phys.* **144**, 194701 (2016)

[2] S. Sakong and A. Gross, *ACS Catal.* **6**, 5575 (2016).

O 42.3 Tue 14:30 WIL B321

**Computational hydrogen electrode modelling of water electrolysis at IrO<sub>2</sub> nanoparticles** — •DANIEL OPALKA and KARSTEN REUTER — Technische Universität München, Germany

IrO<sub>2</sub> is the primary active anode component of proton-exchange membrane cells for water electrolysis in acidic operating conditions. Its superior performance has generally been rationalized through the optimized binding of relevant reaction intermediates at IrO<sub>2</sub>(110) as assessed within the computational hydrogen electrode (CHE) approach based on density-functional theory (DFT) calculations. At present, it is unclear though whether this level of theory is sufficient to guide ongoing activities that aim at improving the anode activity and stability through nanostructuring and doping. To this end we revisit critical practical components of the CHE approach, such as the employed DFT functional or the degree of hydroxylation under operating conditions. Extending the calculations to other low-index facets allows to attempt a first description of IrO<sub>2</sub> nanoparticles through an *ab initio* thermodynamics based Wulff-construction.

O 42.4 Tue 14:45 WIL B321

**Coadsorption of anions and cations on platinum** — •FLORIAN GOSSENBERGER and AXEL GROSS — Institute of Theoretical Chem-

istry, Ulm University, D-89069 Ulm/Germany

The relevant reaction steps in electrochemistry occur in the region where ion-conduction of the electrolyte merges electron-conduction of the electrode. This area is crucially influenced by the presence or absence of both anions and cations, which are - dependent on the electrode potential - specifically adsorbed on the electrode.

To understand the structure and stability of the adsorbate layer, we have investigated the simultaneous adsorption of different anions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>/HSO<sub>4</sub><sup>-</sup>) and protons/hydronium on platinum, using density functional theory [1]. The dependence of the adsorption structures on the ionic concentrations in the electrolyte and on electrode potential have been derived using the concept of the computational hydrogen electrode, allowing to derive phase diagrams and Pourbaix diagrams. Thus we have been able to reproduce the experimental finding of the competitive adsorption of hydrogen and halides on Pt(111). With respect to sulphate adsorption our results suggest the need to revisit previously suggest structural models.

[1] F. Gossenberger, T. Roman, A. Groß, *Electrochim. Acta* **216**, 152-159 (2016).

O 42.5 Tue 15:00 WIL B321

**Experimental and theoretical investigation of Prussian blue type catalysts for photoelectrochemical water-splitting** —

•FRANZISKA HEGNER, NÚRIA LÓPEZ, and JOSÉ-RAMÓN GALÁN-MASCARÓS — Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain

The development of an efficient, cheap and robust water-oxidation catalyst remains the bottleneck step to realizing artificial photosynthesis. Materials based on Prussian blue (iron hexacyanoferrate), which fulfill all those criteria, have shown high catalytic activities with exceeding long-term stabilities.

In combining experimental methods with theoretical calculations we aim to elucidate the underlying photo-physical mechanisms and its determining factors. Catalytic systems were prepared by modifying the well-known photo-catalytic material BiVO<sub>4</sub>, with cobalt iron analogues of Prussian blue (CoFe-PB), which largely increases the photocurrent and significantly lowers the onset potential of light-induced water oxidation.

It was found that common density functional theory (DFT) methods are insufficient to accurately describe the complex electronic and magnetic structure of Prussian blues and functionals of higher degree of complexity are needed. We developed a robust computational scheme to evaluate electronic structure relationships of the combined semiconductor system, which might be crucial to its photo-catalytic applications.

O 42.6 Tue 15:15 WIL B321

**Driving Forces for Aggregation and Dissociation of Water on Zinc Oxide** — •P. ULRICH BIEDERMANN<sup>1</sup> and STEPHANE KENMOE<sup>1,2</sup> — <sup>1</sup>Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany — <sup>2</sup>current address Department of Theoretical Chemistry, University of Duisburg-Essen, Essen, Germany

The interactions of water with zinc oxide play an important role in the fields of catalysis, corrosion protection and biomedical applications. The properties of water adsorbed at the interface of oxides are significantly different from bulk water. In particular, the high degree of water dissociation observed in the contact layer indicates O-H bond activation. This facilitates proton transfers, an important step in many catalytic processes. We present a comprehensive DFT study of water adsorbed on the non-polar ZnO (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) surfaces using PBE. In view of the band-gap problem of GGA-DFT, the results are benchmarked against hybrid DFT results. Several new interface structures have been discovered in the coverage regime of 0-3 ML. Water aggregation on ZnO is controlled by a subtle interplay of direct water-water interactions including H-bonds and dipole-dipole interactions versus surface- or adsorption-mediated interactions including enhanced water-surface interactions and reduced relaxation energies required to optimize the geometry of the water molecules and ZnO surface for adsorption. While water dissociation also depends on aggregation and the geometrical arrangement of the molecules on the surface, direct water-water interactions do not contribute to this process. Water dissociation is driven by enhanced water-surface interactions.

O 42.7 Tue 15:30 WIL B321

**Proton dynamics and structure of confined sulfuric acid liquid between graphene sheets from ab-initio molecular dynamics** — ●STEFFEN SEILER and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

The wet-chemical exfoliation of graphite via Hummers' method [1,2] is a promising route for large-scale graphene production. The first relevant reaction intermediate, the stage-1 sulfuric acid graphite intercalation compound, is an interesting model system of a confined liquid. To unravel the proton dynamics and the structural properties of the confined liquid in this compound, extensive Car-Parrinello molecular dynamics simulations were performed. We show that the stability of the hydrogen-bond network in the sulfuric acid film is affected neither by the extreme confinement (mono-molecular layer) nor by graphite oxidation. Also the proton-transfer reaction barrier is not increased upon confinement. In contrast, oxidation of graphite reduces the barrier, which provides an explanation for the fast and efficient intercalation of graphite with sulfuric acid in the presence of oxidizing agents.

[1] W.S. Hummers, *J. Am. Chem. Soc.* **80**, 1339 (1958).

[2] D.C. Marcano, et al., *ACS Nano* **4**, 4806 (2010).

O 42.8 Tue 15:45 WIL B321

**Functionalization of Oxide Surfaces: Chemical Reactions at the Solid/Liquid Interface** — ●PAUL SCHWARZ and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

Using ab-initio molecular dynamics we have studied the anchoring of methylsilanetriol (MST) linker units to aluminum oxide surfaces via condensation reactions in the presence of residual water and liquid isopropanol at standard temperature and pressure. While in vacuum MST molecules spontaneously attach to the surface Al ions via one of their oxygen atoms, adding the residual water molecules and the liquid isopropanol suppresses the direct approach of MST to the surface and solvent molecules have to be displaced. To accelerate this process and to study the mechanism of the subsequent condensation reaction, the metadynamics technique is applied. The simulations show a variety of reaction pathways which differ in how MST deprotonates and how the OH group at the same Al site is converted to water and desorbs. In addition, several competing processes are observed: 1) reprotonation of MST with a subsequent detachment of the molecule and diffusion into the liquid; 2) detachment of MST and spontaneous reaction with a neighboring surface Al atom; 3) binding of a second OH group of MST to the same Al site. Free energy profiles of these paths will be compared and the stability of reaction intermediates will be compared by static DFT calculations.