

## O 35: Solid-Liquid Interfaces: Reactions and Electrochemistry - Theory I

Time: Tuesday 12:15–13:15

Location: HSZ 101

O 35.1 Tue 12:15 HSZ 101

**Towards a generally applicable parametrization protocol for first-principles implicit solvation approaches based on the Poisson-Boltzmann method** — ●STEFAN RINGE, HARALD OBERHOFFER, and KARSTEN REUTER — TU Munich, Garching, Germany

Implicit solvation models are a standard means for efficient first-principles descriptions of solvated systems. Poisson-Boltzmann (PB) methods in particular even provide a mean-field account of ionic effects in electrolytes, which are known to crucially impact chemical stability, geometries or dissociation constants. Although PB methods have been extensively applied, generally applicable parametrization protocols are lacking so far. Recently, we have implemented PB solvation functionality into the full-potential density-functional theory package FHI-aims [1]. Here we argue that experimentally measured Setschenow coefficients, which probe the stability change of solutes with varying ionic strength, offer an intriguing route to determine the ionic parameters entering the PB approach. With a slight modification of the original PB model in terms of a Stern or ion exclusion layer, parameterized as a function of the solute's electron density, we achieve generally good agreement with experimental data for different alkali halide aqueous solutions.

[1] Ringe, S., Oberhofer, H., Hille, C., Matera, S., Reuter, K., *J. Chem. Theory Comput.*, **2016**, *12* (8), pp 4052–4066.

O 35.2 Tue 12:30 HSZ 101

**Quantum Chemistry of the Oxygen Evolution Reaction on Transition Metal Oxides** — ●CRAIG PLAISANCE<sup>1</sup>, RUTGER VAN SANTEN<sup>2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Technische Universität München, Germany — <sup>2</sup>Technische Universiteit Eindhoven, The Netherlands

Density functional theory (DFT) is used to examine the changes in electronic structure that occur during the oxygen evolution reaction (OER) on a model oxide catalyst containing different 3d transition metal cations (Cr, Mn, Fe, Co, Ni). Active sites identified in previous work [1] consisting of both one and two redox-active metal centers were examined. For all sites, the important water addition step was determined to occur by the transfer of two holes from the metal cation(s) to the O-O antibonding orbital of the resulting hydroperoxo. Of the sites examined, Fe was found to have the most efficient single-center site while Co was found to have the most efficient dual-center site. In line with our previous work on Co oxide [2], the activity of an active site is seen to be related to the energy required to localize holes on the oxygen species participating in the reaction, calculated with a constrained-orbital DFT method we have developed. The hole-localization process is further analyzed in terms of screening and changes in metal-oxygen hybridization to identify how the unique electronic structures of Fe and Co lead to their superior performance for the OER.

[1] Plaisance, C.P., van Santen, R.A., *J. Am. Chem. Soc.* **2015**, *137*, 14660-72. [2] Plaisance, C.P., Reuter, K., van Santen, R.A.; *Faraday Discuss.* **2016**, *188*, 199-226.

O 35.3 Tue 12:45 HSZ 101

**Metallic nanoparticles under realistic electrochemical conditions** — ●NICOLAS G. HÖRMANN, OLIVIERO ANDREUSSI, and NICOLA MARZARI — Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), EPFL, CH-1015 Lausanne, Switzerland

We present a study of the stability and equilibrium shape of metallic nanoparticles in electrochemical environments based on periodic density functional theory (DFT) calculations. Metallic surfaces in water are modelled within the self-consistent continuum solvation scheme (SCCS) [2] as recently implemented in the ENVIRON module of Quantum-ESPRESSO [3]. We analyse in detail the effect of the dielectric environment and different adsorbates on surface structure, energetics and potential. The effects of applied potential are treated by studying appropriately charged systems, with explicit countercharge layers in the solution to mimic the effects of the electrical double layer [4]. We will also discuss the difference between this approach and the widely applied “computational hydrogen electrode” [5] with respect to surface termination and adsorbate species. Our results shed light on how to apply ab-initio thermodynamics in electrochemical environments.

[1] A. Jain et al., *APL Materials* **1**, 011002 (2013); [2] O. Andreussi, et al., *J. Chem. Phys.* **136**, 064102 (2012); [3] P. Giannozzi, et al., *J. Phys.: Condens. Matter* **21**, 395502 (2009); [4] N. Bonnet, et al., *Phys. Rev. Lett.* **110** 086104 (2013); [5] J. K. Norskov, et al., *J. Phys. Chem. B* **108** 17886 (2004);

O 35.4 Tue 13:00 HSZ 101

**Insights into the mechanism of photocatalytic water splitting on rutile (110) from quantum dynamical calculations** — ●THORBEN PETERSEN and THORSTEN KLÜNER — Carl von Ossietzky Universität, Oldenburg, Germany

In order to understand the elementary steps involved in photochemical reactions, quantum dynamical calculations are an exceptional tool to acquire a detailed insight into reaction paths on a femtosecond time scale including quantum effects like tunneling as well. Using this approach we want to study the photodissociation mechanism of water on an ideal rutile (110) surface.

Based on previously generated potential energy surfaces [1], the dissociation mechanism will be investigated including the five most relevant degrees of freedom. Regarding the photocatalytic properties of titanium dioxide, a cationic H<sub>2</sub>O-adsorbate as a result of a hole attack of the surface has been assumed for the excited state.

By propagating a wave packet representing the adsorbate on the excited state potential energy surface, we obtain dissociation probabilities in dependence of the movement of the resulting OH-group. For a fixed OH-group no complete dissociation occurs [2]. However, by allowing its movement, the potential barrier for a complete dissociation process can be overcome.

[1] J. Mitschker, T. Klüner, *Phys. Chem. Chem. Phys.* **2015**, *17*, 268

[2] J. Mitschker, T. Klüner, *J. Theor. Comput. Chem.* **2016**, *15*, 1650013