

## O 10: Solid-liquid Interfaces I

Time: Monday 10:30–13:15

Location: WIL A317

O 10.1 Mon 10:30 WIL A317

**On the stability of strained Cu overlayers on Pt(111), Au(111) and Au(100) electrodes under low potential conditions and in presence of CO and CO<sub>2</sub>** — ●CHRISTIAN SCHLAUP and SEBASTIAN HORCH — Center for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark (DTU), DK-2800 Kongens Lyngby, Denmark

Copper is known for its outstanding catalytic activity for the electroreduction of carbon dioxide. However, a tremendous overpotential in the order of 1 V needs to be overcome in order to drive this reaction. An approach to tune the reactivity of copper surfaces is to introduce strain into the surface, yielding in different binding situations of the involved reaction species.

A convenient experimental access to such strained copper surfaces is the electrodeposition of pseudomorphic films on electrodes with a bigger lattice constant. Yet, their stability under the desired reaction conditions is of crucial importance. By means of in-situ STM, the influence of CO<sub>2</sub> and the important reaction intermediate CO has been studied under low potential conditions. For the Pt(111) substrate, a CO induced restructuring, driven by attractive Pt-CO bindings was found. In contrast, Au-CO bindings are much less attractive, however, for Au(111) the stability of Cu films is limited by desorption of coadsorbed anions at low potentials. For Au(100) neither effect was found, instead a surface alloy forms under the desired reaction conditions.

O 10.2 Mon 10:45 WIL A317

**Structural degradation of PtRu model electrodes during CO electrooxidation and its influence on the reaction characteristics** — ●ALBERT K. ENGSTFELD, JENS KLEIN, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

The stability of an (electro-)catalyst under reaction conditions is important for the proper understanding of the underlying (electro-) catalytic processes. In this work we present the structural modifications of a PtRu model electrode during the electrooxidation of CO and the resulting changes in the electrocatalytic behavior.

The electrodes are prepared by deposition of Pt ( $\leq 1$  ML) on Ru(0001) under ultra high vacuum (UHV) conditions, leading to Pt monolayer islands with different sizes and densities. Subsequent to the structural characterization by scanning tunneling microscopy (STM), the samples are transferred to a pre-chamber equipped with an electrochemical laminar flow cell. The electrochemical/-catalytic properties of the PtRu electrodes were characterized by base cyclic voltammetry in 0.5 M H<sub>2</sub>SO<sub>4</sub> (potential range of 0 V to 0.9 V or 1.25 V) and by evaluating their activity for CO bulk electrooxidation. Subsequently, the samples were transferred back to the UHV to study modifications of the electrode surface structure by STM. After exposure to higher potentials the surface shows pronounced modifications of the Ru(0001) surface and small Pt islands, which influences the CO oxidation in a distinct way. Correlations between electrode structure / structure modification and reactivity will be discussed.

O 10.3 Mon 11:00 WIL A317

**Photoelectrochemical CO<sub>2</sub> reduction on silicon electrodes functionalized with pyridine** — ●QI LI<sup>1</sup>, SEBASTIAN LINDNER<sup>1</sup>, ANTON TOSOLINI<sup>1</sup>, KATRIN BICKEL<sup>1</sup>, SIMON FILSER<sup>1</sup>, KONRAD SCHÖNLEBER<sup>1</sup>, IGNAZ HÖHLEIN<sup>2</sup>, BERNHARD RIEGER<sup>2</sup>, IRENE GRILL<sup>3</sup>, REGINA WYRWICH<sup>3</sup>, JOOST WINTTERLIN<sup>3</sup>, and KATHARINA KRISCHER<sup>1</sup> — <sup>1</sup>Nonequilibrium Chemical Physics, Physics Department, Technical University Munich, Germany — <sup>2</sup>WACKER-Lehrstuhl für Makromolekulare Chemie, Chemistry Department, Technical University Munich, Germany — <sup>3</sup>Chemistry Department, Ludwig-Maximilians-Universität Munich, Germany

Solar driven CO<sub>2</sub> conversion to fuels or basic chemicals could provide an exciting new energy storage pathway. Attempts of creating such a photochemical solar cell have to deal with the large activation barrier of CO<sub>2</sub> reduction which leads to low yields and efficiencies. Bocarsly et al. reported that in the presence of dissolved pyridine, CO<sub>2</sub> can be electrochemically reduced to methanol at illuminated p-GaP electrodes at a comparably low overpotential [1]. We demonstrate that a functionalized p-Si electrode constitutes a promising interface for CO<sub>2</sub> reduction. The interface consists of pyridine molecules which are immobilized via

an electrografting process to the Si-surface. Modified electrodes have been characterized using electrochemical methods and XPS. Besides its protective attributes against surface oxidation, the pyridine layer on top of the p-Si electrode shows increased electrochemical reactivity towards CO<sub>2</sub> reduction. [1] E. Barton, D. Rampulla, A. B. Bocarsly; J. Am. Chem. Soc., 2008, 130, 6342-6344

O 10.4 Mon 11:15 WIL A317

**Implicit solvation model for the first-principles description of methanol electro-oxidation on Pt electrodes** — ●SUNG SAKONG and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

Within a conventional density functional theory (DFT) framework, the atomistic description of the electrochemical reactions in a direct methanol fuel cell often ignores the presence of the aqueous environment or the dispersion interactions between reaction intermediates and electrode that can be crucial for a realistic modeling. Recently, Arias has introduced a joint scheme to treat solute/solvent simultaneously with combining DFT calculations and an implicit solvent based on the polarizable continuum model [Modelling Simul. Mater. Sci. Eng. **21** (2013) 074005], which allows to assess electrochemical systems including the electrolyte within a first-principles approach.

Using the method, we address the electro-oxidation of methanol on Pt electrodes and compare it to the corresponding reaction steps at Pt in vacuum. Practically, we model the electrode as a Pt(111) surface and investigate the energetics of the reaction intermediates with and without implicit solution. Furthermore, we test the influence of an explicit water bilayer at the interface in addition to the implicit solution on the energetics. The contribution of dispersion interaction to the stability of reaction intermediates and the height of reaction barriers in both vacuum and an aqueous environment will also be addressed using a correction scheme suggested by Tkatchenko and Scheffler [Phys. Rev. Lett. **102** (2009) 073005].

O 10.5 Mon 11:30 WIL A317

**The structure of water at metal interfaces** — ●TANGLAW ROMAN and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

The structure of water and adsorbed ions at the interface between a metal electrode and an electrolyte solution directly impacts the electrode potential, and vice versa [1]. Although water has been the subject of countless experimental and theoretical investigations, the details of its structure at electrochemical interfaces are still the subject of debate [2]. In this talk, we will discuss ab initio molecular dynamics investigations for interfaces involving Cu, Pt, and Ag. Water is introduced using different surface area densities through supercells that are unbiased to the formation of bilayers. Dispersion corrections are added to energies obtained using the RPBE functional which is necessary in order to obtain the correct wetting behavior of water [3].

[1] S. Schnur and A. Groß, New J. Phys. **11**, 125003 (2009). [2] T. Roman and A. Groß, Catal. Today. **202**, 183 (2013). [3] K. Tonigold and A. Groß, J. Comput. Chem. **33**, 695 (2012).

O 10.6 Mon 11:45 WIL A317

**Development of a Neural Network Potential for Protonated Water Clusters** — ●SURESH KONDATI NATARAJAN, TOBIAS MORAWIETZ, and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr Universität Bochum, D-44780 Bochum, Germany

Protonated water clusters are important model systems for the dissociation of water, proton transport and acids in aqueous solution. Many classical force fields are not applicable to the dissociation of water or proton transport due to their inability to describe the making and breaking of bonds. Recently, high-dimensional neural networks (NNs) [1-2] have been introduced as an efficient way to represent interatomic potentials based on electronic structure calculations. Here, we present a NN potential for protonated water clusters with up to eight water molecules. The results are discussed and compared to density functional theory data.

[1] J. Behler and M. Parrinello, Phys. Rev. Lett., vol. 98, p.146401, 2007.

[2] J. Behler, Phys. Chem. Chem. Phys., vol. 13, p.17930, 2011.

O 10.7 Mon 12:00 WIL A317

**The electrostatic double layer of Pt/water interfaces from first principles molecular dynamics.** — ●CLOTILDE S. CUCINOTTA and STEFANO SANVITO — School of Physics and CRANN, Trinity College Dublin, College Green, Dublin 2, Ireland

The formation of the electrostatic double layer is the most basic phenomenon taking place at electrified interfaces. However, even in the relatively simple case of a Pt/water interface, none of the current theoretical approaches provides a realistic microscopic view of this double layer (DL), accounting for electronic, polarization and solvent reorganization effects. Here we provide for the first time a comprehensive description of the DL of a Pt-water interface, based on ab initio computations, including charge polarization effects at both sides of the interface, explicit solvent and its rearrangements upon changing the electrode polarization. This interface has been modeled with up to 1000 atoms. A simple, fully dissociated salt in solution has been explicitly included. Varying the relative number of cations and anions provides a way to control the charge on the electrode, controlling, in turn, the applied potential. The proposed approach allows to provide a detailed description of the structure of the Pt/water DL reproducing the localization of electric field and potential energy drop within a microscopic distance from the metal surface. An a posteriori calibration of the relation between charge and potential is performed, analyzing the potential energy profile vs. the distance from the electrode for any given charge, providing for the first time a realistic ab initio determination of the interface capacitance and the point of zero charge.

O 10.8 Mon 12:15 WIL A317

**Ab initio molecular dynamics approach to adsorption processes of water molecules on Pt surface** — ●MARYAM NADERIAN and AXEL GROSS — Institute of Theoretical Chemistry, University of Ulm, D-89069 Ulm, Germany

The processes involved in the interaction of water with surfaces play a very important role in the fields of electrochemistry and surface science. We perform ab initio molecular dynamics (AIMD) simulations to address the adsorption process of water molecules on Pt(111). The AIMD simulations are based on periodic density functional theory calculations using the RPBE functional in connection with dispersion correction, as the correct wetting behavior of water on close-packed metal surfaces is reproduced by using the RPBE-D3 approach [1]. Special attention is paid to the role of the internal degrees of freedom of the water molecules upon impinging on the Pt substrate, as temporary kinetic energy from the center-of-mass motion might be transferred into vibrations and rotations thus leading to a more efficient energy dissipation which is crucial for molecular adsorption [2]. Furthermore, the sticking probability will be presented as a function of initial kinetic energy of water and/or water coverage. Also the initial processes of the water network formation on metal surfaces shall be addressed based on AIMD trajectories.

- [1] K. Tonigold and A. Groß, *J. Comput. Chem.* **33**, 695-701 (2012).  
 [2] A. Groß *et al*, *Surf. Sci.* **539**, L542-L548 (2003).

O 10.9 Mon 12:30 WIL A317

**Copper (110) surface in thermodynamic equilibrium with water vapor - Entropy effect** — ●AMIRREZA BAGHBANPOURASL<sup>1</sup>, KURT HINGERL<sup>1</sup>, and WOLF GERO SCHMIDT<sup>2</sup> — <sup>1</sup>Johannes Kepler University Linz — <sup>2</sup>University of Paderborn

In this contribution we study the interaction of Cu(110) surface with water vapor in a wide range of environment conditions. Theoretical and experimental studies for determining the adsorption structures of water on Cu(110) surface, are mostly performed for/in UHV and

low temperature condition. For extending the validity of the studies to higher pressure and temperature it is needed to include the thermodynamic properties of water in the environment and the effect of vibrations of adsorbed molecules in the calculation of free energy. We applied Density Functional Theory on a relatively large group of known structures of locally stable water/Hydroxyl on Cu(110) surface, as a starting point, to calculate different contributions to adsorption free energy, coming from electronic interaction, zero point and thermal vibrations. The study shows that vibrational effects are negligible on the phase diagram. The net effect of zero point and thermal vibrations is increasing the temperature of the phase transition (for each pressure) with about 20 K.

O 10.10 Mon 12:45 WIL A317

**First-principles study of the water structure on flat and stepped Pb surfaces** — ●XIAOHANG LIN and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

The geometric structure and electronic properties of single water layers on flat and stepped Pb surfaces have been addressed by periodic density functional theory (DFT) calculations. Pb is often used as an electrode material in electrochemical applications such as the electrochemical atomic-scale quantum conductance switch [1]. As a first step in the modeling of this switch, we had considered Pb deposition and diffusion processes on stepped Pb surfaces. As the next step, we study the interaction between water and flat and stepped Pb substrates which is important for an understanding of the switching processes. Because of the large lattice constant, water layers on Pb surfaces exhibit completely different structures than, e.g., on transition metals such as Au, Ag and Pt [2, 3]. In order to understand the structure formation and the Pb-water interaction, the electronic structure of water layers on Pb surfaces, in particular on stepped surfaces, will be discussed.

- [1] F.-Q. Xie *et al.*, *Phys. Rev. Lett.* **93**, 128303 (2004).  
 [2] X. Lin and A. Groß, *Surf. Sci.* **606**, 886 (2012).  
 [3] S. Schnur and A. Groß, *New J. Phys.* **11**, 125003 (2009).

O 10.11 Mon 13:00 WIL A317

**Insights on the Microscopic Mechanisms of Anisotropic Growth of Gold Nanorods from Molecular dynamics simulations** — ●SANTOSH MEENA and MARIALORE SULPIZI — Condensed Matter Theory, Institute of Physics, Johannes Gutenberg University, Staudingerweg 7, 55128 Mainz, Germany

Gold nanorods are normally prepared using seed-mediated growth technique, which require gold seeds, ascorbic acid and aqueous cetyltrimethylammonium bromide (CTAB) solution of HAuCl<sub>4</sub>. Crystal twinning of seeds results into formation of pentatetrahedral nanorod structure with different facets[1]. Although possible mechanism have been proposed, the microscopic understanding of the anisotropic growth is still missing. We provide the first atomistic model of adsorption of CTAB on different surfaces, namely (111), (110) and (100) in growing electrolyte solution. We find that on all the investigated surfaces, the CTAB form a layer of distorted cylindrical micelles where channels among micelles would provide direct ions access to the surface. In particular, we show how AuCl<sub>2</sub><sup>-</sup> ions, can freely diffuse from the bulk solution to the gold surface[2]. Furthermore, we investigate the effect of halide ions (X= Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) on adsorption of CTAX on the (111) surface and we provide a rational for the influence of halide ions on anisotropy of gold nanoparticles.

- [1] C. J. Murphy, T. K. Sau, A. M. Gole, C. J. Orendorff, J. Gao, L. Gou, S. E. Hunyadi, T. Li, *J. Phys. Chem. B* **2005**, *109*, 13857-13870  
 [2] S. K. Meena, M. Sulpizi, *Langmuir* **2013**, DOI: 10.1021/la403843n