

## O 23: Solid-Liquid Interfaces II: Electrode Surfaces

Time: Tuesday 10:30–13:00

Location: H5

## Invited Talk

O 23.1 Tue 10:30 H5  
**Investigating atomic scale structure of liquid metal–electrolyte interfaces** — ●BRIDGET M. MURPHY — Ruprecht Haensel Laboratory — Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel

Electrochemical interfaces between immiscible liquids have lately received renewed interest, both for gaining fundamental insight as well as for applications in nanomaterial synthesis. In this contribution, we demonstrate how the atomic scale structure of these previously inaccessible interfaces nowadays is explored by *in situ* synchrotron-based X-ray scattering techniques. Exemplary studies of a prototypical electrochemical system — a liquid mercury electrode in pure NaCl solution — reveal that the liquid metal is terminated by a well-defined atomic layer. This layering decays on length scales of 0.5 nm into the Hg bulk and displays a potential- and temperature-dependent behaviour that can be explained by electrocapillary effects and contributions of the electronic charge distribution on the electrode. In similar studies of nanomaterial growth, performed for the electrochemical deposition of PbFBr, a complex nucleation and growth behaviour is found, involving a crystalline precursor layer prior to the 3D crystal growth. *Operando* X-ray scattering measurements provide detailed data on the processes of nanoscale film formation [1].

[1] B. M. Murphy, S. Festersen, and O. M. Magnussen, *Nanoscale*, 2016, 8, 13859

O 23.2 Tue 11:00 H5  
**Resolving the chemical identity of H<sub>2</sub>SO<sub>4</sub> derived anions adsorbed on a Pt(111) electrode: they are sulfate.** — R. KRAMER CAMPEN, GREGOR ZWASCHKA, IGOR YING ZHANG, MARTIN WOLF, and ●YUJIN TONG — Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany

One of the model systems in electrochemistry that has been extensively studied is the adsorption of sulfuric acid anions on Pt(111) electrode in acidic solution. While many properties of the adsorbed anion have been well resolved, its chemical nature, whether it is sulfate (SO<sub>4</sub><sup>2-</sup>) or bisulfate (HSO<sub>4</sub><sup>-</sup>) is still under debate. The controversy mainly originates from the difficulty in assigning the vibrational mode around 1250 cm<sup>-1</sup> which has been observed in previous infrared spectroscopic measurements. Here we apply interface-specific, vibrational sum frequency generation (VSF) spectroscopy and theoretical simulation to this problem. By taking advantage of the background-free nature of VSF spectroscopy, we are able to perform more reliable isotope exchange measurements than those done with conventional infrared spectroscopy. The chemical identity of the adsorbate is unambiguously revealed: it is SO<sub>4</sub><sup>2-</sup> rather than HSO<sub>4</sub><sup>-</sup> that adsorbed at the surface even in acidic solution (pH=0), where the dominant solute is essentially HSO<sub>4</sub><sup>-</sup>. The distinct different chemical nature of the anion at the surface and in the bulk suggests intriguing interaction between the electrode and the anions.

O 23.3 Tue 11:15 H5  
**Influence of the polarization of the electrode on the surface plasmon resonance angle shift during adsorption processes on Au(111)** — ●KARIN SCHLAG, DETLEF NATTLAND, and ROLF SCHUSTER — Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Knowledge about the structure and composition of the double layer is essential for the understanding of electrochemical reactions. We therefore investigated the sulfate adsorption on Au(111) with cyclic voltammetry and *in-situ* surface plasmon resonance (SPR) spectroscopy. SPR is sensitive to changes of the refractive index at the electrolyte-electrode interface, which is connected to concentration changes of the constituents of the double layer. We observed an increase of the SPR angle during the adsorption process of sulfate on Au(111) by 0.14°.

A multi-layer model based on Abeles' formalism was used to quantify the potential dependent refractive index of the double layer. We found that the experimentally determined, unexpectedly strong shift of the SPR angle can only partly be explained by the increase of the sulfate concentration at the interface. It is suggested that the polarization of the interface and the subsequent changes of the electron density in the metal surface have to be included in the model.

O 23.4 Tue 11:30 H5

**Strain controlled electrocatalysis during Methanol oxidation on gold thin film** — ●XINYAN WU<sup>1</sup>, MATTHIAS GRAF<sup>2,3</sup>, and JÖRG WEISSMÜLLER<sup>1,3</sup> — <sup>1</sup>Institute for Materials Physics and Technology, Hamburg University of Technology, Hamburg — <sup>2</sup>Institute for Electronic and Optical Materials, Hamburg University of Technology, Hamburg — <sup>3</sup>Institute for Materials Technology, Helmholtz-Zentrum Geesthacht, Geesthacht

It is well known that one method of enhancing the electrocatalytic performance is to tune the surface strain of nanomaterials, by which the adsorption enthalpies could be modified. Based on theories and experiments towards this mechanism, the underlying strain-adsorption-reactivity relationship gradually becomes acknowledged. However, quantifiable experimental observations of the impact of strain for reactivity of catalyst are still rare, which means this field lacks a quantitative experimental database.

Here we explore a method, Dynamic Electro-Chemo-Mechanical analysis (DECMA), in order to investigate the impact of elastic strain on the electrocatalytic methanol oxidation reaction on gold thin film surface. In this approach, a sinusoidal strain is applied on the surface of gold electrode during this whole process, and simultaneously the corresponding reaction current and potential signals caused by this known strain are collected through a lock-in technology. In this way, coupling parameters such as potential-strain and current-strain coefficients will be measured and provide effective information for each reaction step.

O 23.5 Tue 11:45 H5  
**Influence of steps and atomic ensembles for the CO electro-oxidation** — ●JENS KLEIN, ALBERT K. ENGSTFELD, VALERIA CHESNYAK, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The rate of electrocatalytic reactions is often highly sensitive to the surface structure of the metal catalysts.<sup>[1,2]</sup> To improve the performance of catalyst materials it is inevitable to identify active surface sites and to understand the electrocatalytic processes at the surface sites on an atomic scale.

In this work we report on the role of Pt steps and atomic PtRu ensembles in the CO electro-oxidation i) on Pt(111) model electrodes with varying step density and ii) on Pt<sub>x</sub>Ru<sub>1-x</sub>/Ru(0001) surface alloys with varying Pt content, respectively. The model electrodes were prepared and structurally characterized by scanning tunneling microscopy (STM) under ultra-high vacuum (UHV) conditions. The electrocatalytic measurements were performed in an electrochemical flow cell attached to the UHV system. To investigate the role of Pt step sites for the CO electro-oxidation, the steps of the Pt(111) electrodes were passivated for the reaction by condensation of Au. The CO oxidation activity of Pt<sub>x</sub>Ru<sub>1-x</sub>/Ru(0001) surface alloys with different Pt contents was correlated with the abundance of specific PtRu ensembles on the surface. We will discuss the influence and importance of defect sites as well as ensemble sites for the electro-catalytic CO oxidation.

[1] M. T. M. Koper, *Nanoscale* **3** (2011) 2054. [2] A. K. Engstfeld et al., *Angew. Chem. Int. Ed.* **53** (2014) 12936.

O 23.6 Tue 12:00 H5  
**DFT calculations of self-diffusion at an Au(001) electrochemical interface** — ●ALEXANDRA C. DÁVILA and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, CAU Kiel, Germany

In surface X-ray scattering experiments at the interface between an Au(100) electrode and HCl+HAuCl<sub>4</sub> containing electrolyte Krug et al. [1] have observed that the growth mode depends on the electrode potential and Au-concentration. Transitions from 3D to layer-by-layer and to step-flow growth mode were observed at positive potentials ( $V_{Ag/AgCl}$ ), where the unreconstructed substrate surface is stable. Pichardo-Pedrero et al. [2] have observed an increase of the decay rate of Au islands on Au(001) with sample potential and, in particular, when chloride is present in the electrolyte. The atomic-scale mechanism of self-diffusion on coinage metal surfaces has been investigated by DFT calculations before [3,4], however, the detailed role of the co-adsorbed anions on the diffusion is not yet fully understood. We present diffusion paths on  $c(\sqrt{2} \times 2\sqrt{2})R45^\circ\text{-Cl}$  and  $c(2 \times 2)\text{-Cl}$  Au(001) surfaces. The dependence of the diffusion rate on sample potential as derived from the variation of the induced dipole moment along the paths gives an increase of the Au self-diffusion energy barrier with

increasing potential. Thus, we speculate that other factors, like nucleation, determine the sample potential dependence of Au growth mode.

- [1] K. Krug *et al.*, Phys. Rev. Lett. **96**, 246101 (2006).
- [2] E. Pichardo-Pedrero *et al.*, Appl. Phys. A, **87**, 461 (2007).
- [3] J. E. Müller *et al.*, Phys. Rev. B **74**, 085408 (2006).
- [4] M. Mesgar *et al.*, ChemPhysChem **14**, 233 (2013).

O 23.7 Tue 12:15 H5

**Investigation of ion mobility and material transport on KBr surfaces in air in dependence of the relative humidity.** — DOMINIK KIRPAL, KORBINIAN PÜRCKHAUER und FRANZ GIESSIBL — University of Regensburg, Regensburg, Germany

On every surface exposed to humid air a thin film of water molecules forms. The presence of water plays an important role for chemical reactions, material exchange and movement. The effect of condensed water layer, present in ambient conditions plays a significant role especially on surfaces that dissolve easily in water [1]. Surface atoms can easily diffuse into the thin water layer and, when surface conditions are favourable, they can re-attach to the surface. We collected FM-AFM images of the KBr surface in a climate-controlled glove box at various values of relative humidity. By scratching the surface with the AFM tip, we construct energetically unfavourable hills and scratch sites. We observe the time evolution of these sites. We propose that there is a critical value around 25% relative humidity, under which dissolution and reattachment occurs relatively slowly, in contrast to our observations at 28% relative humidity where these processes occur quickly.

- [1] M. Luna, *et al.*, Journal of Physical Chemistry A, 102.34 (1998) 6793-6800.

O 23.8 Tue 12:30 H5

**Boosting the Scalability of Car-Parrinello Molecular Dynamics for Large-Scale Simulations of Solid-Liquid Interfaces** — TOBIAS KLÖFFEL<sup>1</sup>, PAWEŁ RODZIEWICZ<sup>2</sup>, GERALD MATHIAS<sup>3</sup>, and BERND MEYER<sup>1</sup> — <sup>1</sup>Interdisciplinary Center for Molecular Mate-

rials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg — <sup>2</sup>Department of Chemistry, Jan Kochanowski University, Kielce, Poland — <sup>3</sup>Leibnitz Supercomputing Centre (LRZ), Garching

We present our recent optimizations of the ultra-soft pseudo-potential (USPP) code path of the *ab initio* Car-Parrinello molecular dynamics program CPMD (www.cpmc.org). All relevant USPP routines have been revised to fully support hybrid MPI+OpenMP parallelization. For two time-critical routines, namely the multiple distributed 3d FFTs of the electronic states and a key distributed matrix-matrix multiplication, we have implemented hybrid parallel algorithms with overlapping computation and communication. The achievements in performance and scalability are demonstrated on simulations of liquid water with 128 and up to 2048 molecules. Performance evaluation shows gains of up to one order of magnitude and around 50% peak performance on the node level. The improved CPMD code has been applied to sample the free energy landscape for a hydrolysis reaction in explicit liquid water on a ZnO surface as catalyst. The unit cell contained 735 atoms and 3332 electrons. A 50 ps trajectory required about 10 days on 18 SuperMUC2 compute nodes.

O 23.9 Tue 12:45 H5

**The nanoscopic structure of Pt-water electrified interface under bias revealed** — CLOTILDE CUCINOTTA — Imperial College London

In this talk I will introduce some issues connected with the simulation of electrified interfaces at the nanoscale focusing in particular on modelling the effect of an applied potential to an EC cell. I will present some recent progress in the simulation of the double layer of the fundamental Pt-water interface and its response to changes of potential applied to the cell. I will show that the metal/surface charging cannot be described using a traditional simple capacitor model and that the double layer nanoscopic structure, mass density and charge distribution, strongly depend on the applied potential.