

## O 38: Solid-Liquid Interfaces 4: Reactions and Electrochemistry

Time: Wednesday 10:30–12:30

Location: H4

**Topical Talk**

O 38.1 Wed 10:30 H4

**Electrochemical Microcalorimetry** — ●ROLF SCHUSTER and MARCO SCHÖNIG — Institute of Physical Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

We investigate electrochemical reactions at single electrodes by measuring the accompanying heat changes. The heat reversibly exchanged during an electrode process is directly correlated to the reaction entropy of the half-cell reaction including all side reactions, e.g., ordering processes of the solvent or coadsorption processes of anions. Thus, measuring the heat exchange during an electrochemical process provides independent information on the ongoing reaction, which is complementary, e.g., to the potential-current relation, usually measured by cyclic voltammetry or impedance spectroscopy.

In this contribution we will briefly discuss some theoretical aspects of electrochemical microcalorimetry of single electrodes and present our strategy to measure the heat evolution upon surface electrochemical processes. With our setup we are sensitive to heat effects originating from minute conversions of a few percent of a monolayer of an electroactive species.

We will present examples for entropy changes upon anion adsorption and double layer charging on Au(111) and discuss the effect of configurational entropy of the adlayer. The hydrogen adsorption on Pt-films deals as an example of a prototypical surface electrochemical reaction. Time-resolved studies of the heat evolution during Cu bulk deposition will demonstrate the implications from heat measurements on the subsequent reaction steps of this complex reaction.

O 38.2 Wed 11:00 H4

**Direct Assessment of the Proton Affinity of Individual Surface Hydroxyls with AFM and DFT** — ●BERND MEYER<sup>1</sup>, MARGARETA WAGNER<sup>2</sup>, MARTIN SETVIN<sup>2</sup>, MICHAEL SCHMID<sup>2</sup>, and ULRIKE DIEBOLD<sup>2</sup> — <sup>1</sup>Interdisciplinary Center for Molecular Materials and Computer Chemistry Center, FAU Erlangen-Nürnberg, Germany — <sup>2</sup>Institute of Applied Physics, TU Wien, Austria

The state of protonation/deprotonation of individual surface sites has far-ranging implications in all areas of chemistry. However, common experimental measurements of surface acidity are integral techniques which give only average quantities integrated over the whole surface. Here we show that an OH-functionalized tip of an atomic force microscope (AFM) can be used for quantitative insights into the acidity of individual surface OH groups [1]. The chosen model oxide, In<sub>2</sub>O<sub>3</sub>(111), offers four types of surface O atoms with distinct properties, each giving rise to a characteristic force–distance curve after protonation. Density-functional theory (DFT) calculations demonstrate a linear correlation between the force minimum and the proton affinity of the surface hydroxyls. By benchmarking the calculations to known proton affinities and pK<sub>a</sub> values of gas-phase molecules, the force minima provide a direct measure of proton affinity distributions and pK<sub>a</sub> differences at the atomic scale.

[1] M. Wagner, B. Meyer, M. Setvin, M. Schmid, U. Diebold, *Nature* **592** (2021) 722–725

O 38.3 Wed 11:15 H4

**Revisiting the OH adsorption on Pt(111) in static water environments** — ●ALEXANDRA C. DÁVILA LÓPEZ, NICOLAS G. HÖRMANN, THORBEN EGGERT, and KARSTEN REUTER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The partial solvation of adsorbates typically leads to altered adsorption energies at solid-liquid interfaces as compared to vacuum. While such solvation effects can be treated most accurately based on *ab initio* molecular dynamics simulations, an according description is hardly feasible for a large number of systems e.g. across different substrates, adsorbates and adsorbate coverages due to prohibitive computational costs. As a result, many studies rely on an approximate treatment based on static water environments. In this work, we study solvation effects based on our previously introduced method [1] to generate a wide range of different static water adlayers. In particular, we analyze the adsorption energy of solvated OH on Pt(111) for a variety of explicit solvation environments and OH configurations. The results are benchmarked against available theoretical and experimental literature data [2, 3], and they highlight prevailing uncertainties in the description of solvation effects.

- [1] A. C. Dávila *et al.*, *J. Chem. Phys.* **155**, 194702 (2021).  
 [2] V. Tripković *et al.*, *Electrochim. Acta* **55**, 7975\*7981 (2010).  
 [3] H. H. Kristoffersen *et al.*, *Chem. Sci.*, **9**, 6912-6921 (2018).

O 38.4 Wed 11:30 H4

**Measuring the reaction volume of an electrochemical surface process: Cu underpotential deposition on Au(111)** — ●LISA HIRSCH, BIANCA KRUMM, TAMARA MEYER, and ROLF SCHUSTER — Karlsruhe Institute of Technology

Information about the reaction volume of electrochemical surface reactions is rather scarce [1-3] albeit this thermodynamic quantity would allow conclusions on solvent contribution and possible side processes. With a specifically designed electrochemical cell, we determined the variation of the cell potential of a (111)-textured Au-film in CuSO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> vs a Cu reference electrode, while applying pressure pulses of moderate amplitude (< 10 bar) and durations of several seconds, starting at different rest potentials. According to the pressure dependent potential variation, we calculated the reaction volume  $\Delta_R V$  of the processes at the working electrode. For rest potentials in the Cu UPD region,  $\Delta_R V$  varies only slightly ( $\pm 8 \text{ cm}^3/\text{mol}$ ) around  $\Delta_R V = 18 \text{ cm}^3/\text{mol}$ , its value for Cu bulk deposition, moderately peaking upon formation of the  $(\sqrt{3} \times \sqrt{3})$  Cu UPD structure. Positive of the Cu UPD, in the sulfate adsorption region,  $\Delta_R V$  drops to smaller values. We check the integrity of the measured potential variations by their dependence on the pressure amplitude as well as by measuring the symmetrical Cu|Cu<sup>2+</sup>,SO<sub>4</sub><sup>2-</sup>|Cu cells.

- [1] Conway, B. E., Currie, J. C., *J. Chem. Soc.*, **74**, 1978, 1390-1402.  
 [2] Loewe, T., Baltruschat, H., *Phys. Chem. Chem. Phys.*, **7**, 2005, 379-384. [3] Heusler, K. E., Gaiser, L., *Ber. Bunsenges. Phys. Chem.*, **73**, 1969, 1059-1068.

O 38.5 Wed 11:45 H4

**Enter the Void: Cavity Formation at Metal-Water Interfaces** — ●THORBEN EGGERT<sup>1,2</sup>, NICOLAS G. HÖRMANN<sup>1</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>Technical University of Munich, Munich, Germany

Cavity formation is an important concept when rationalizing the solvation of ions. However, most studies analyze cavities only in bulk liquids, omitting that their properties may change dramatically at solid-liquid interfaces.

Here, we study cavities at interfaces, particularly their free energy of formation based on molecular dynamics simulations. Specifically, we use a particle insertion approach, as well as the Multistate Bennett Acceptance Ratio method. We demonstrate that cavity formation at interfaces is dependent on the substrate material, which can be partially rationalized by the substrate-specific interfacial water structure. Furthermore, we observe stabilized cavities behind the first solvation layer of water.

These results might on the one hand rationalize recent theoretical suggestions of a non-electrostatic, attractive force on ions near interfaces, and on the other hand enable the improvement of implicit solvation models, which typically neglect substrate-specificity in their description.

O 38.6 Wed 12:00 H4

**Impact of confined water on solvation and adsorption/desorption energetics of charged ions at the electrified interface** — ●ZHENYU WANG, MIRA TODOROVA, and JÖRG NEUGEBAUER — Department of Computational Materials Design, Max-Planck-Institut für Eisenforschung, Max-Planck-Str.-1, D-40237, Düsseldorf, Germany

Understanding processes at electrified solid/liquid interfaces is crucial for many systems and a wide range of applications in electrochemical industry, catalytic sciences and biological engineering. Using a prototypical model system of a single ion in water confined between two charged electrodes, we perform nanosecond-scale atomistic molecular dynamics simulations to study the dielectric behavior of chemically pure water as well as the solvation of ions in the presence of an electric field. For weak electric fields we find that the screening charge density of water is proportional to the external electric intensity, in agreement with classical polarization theory. Probing the interface structure by

the single  $\text{Na}^+/\text{Cl}^-$  ion we investigate the formation and evolution of the ion's solvation shell as function of the electrode-ion distance. Comparing potential profiles from  $\text{Na}^+/\text{Cl}^-$  calculations for different charge states and positions, we elucidate the role of screening and solvation shell size on reorganization energies and transmission barrier of the ions close to the interface.

O 38.7 Wed 12:15 H4

**Are organic solvents key to enable  $\text{CO}_2$  electro-reduction on  $\text{Mo}_2\text{C}$  as promised in theory?** — •THOMAS MAIREGGER<sup>1</sup>, CHRISTOPH GRIESSER<sup>1</sup>, HAOBO LI<sup>2</sup>, NICOLAS HÖRMANN<sup>3</sup>, KARSTEN REUTER<sup>3</sup>, and JULIA KUNZE-LIEBHÄUSER<sup>1</sup> — <sup>1</sup>Department of Physical Chemistry, Innsbruck, Austria — <sup>2</sup>University of Adelaide, Adelaide, Australia — <sup>3</sup>Fritz Haber Institute, Berlin, Germany

It has been proposed in active-site computational screening studies

that  $\text{Mo}_2\text{C}$  is an effective electrocatalyst for the electrochemical  $\text{CO}_2$  reduction reaction ( $\text{CO}_2\text{RR}$ ) to valuable fuels, such as hydrocarbons and alcohols. However, the competing hydrogen evolution reaction (HER) has been found to exclusively take place.[1] Reason for this is the formation of a surface oxide film upon air exposure or immersion of  $\text{Mo}_2\text{C}$  into aqueous electrolytes that impedes the formation of the desired higher reduction products.[1]

Here we investigate the  $\text{CO}_2\text{RR}$  activity of polycrystalline hexagonal  $\text{Mo}_2\text{C}$  in non-aqueous electrolyte to avoid passivation of the electrode and circumvent the high HER activity. We show that  $\text{Mo}_2\text{C}$  is capable of reducing  $\text{CO}_2$  in reasonable amounts in an acetonitrile electrolyte, with an onset at  $-1.08 V_{SHE}$ . [1] The nature of the products, among them gaseous  $\text{CO}$ , depends on the concentration of water in the electrolyte. Furthermore, we show that the acetonitrile has a stronger impact on the  $\text{CO}_2$  electro-reduction than previously believed.

[1] Griesser, C., et. al., ACS Catalysis 11, 4920-4928 (2021).