

O 86: Solid-Liquid Interfaces II: Reactions and Electrochemistry I

Time: Thursday 15:00–17:45

Location: TRE Phy

O 86.1 Thu 15:00 TRE Phy

Enter the Void: Cavity Formation at Metal-Water Interfaces — ●THORBEN EGGERT^{1,2}, NICOLAS G. HÖRMANN¹, and KARSTEN REUTER¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Technical University of Munich, Munich, Germany

Cavity formation is an important concept when rationalizing the solvation of ions. However, most studies only analyze cavities 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 classical molecular dynamics simulations. Specifically, we use a particle insertion approach, as well as thermodynamical integration via the Multistate Bennett Acceptance Ratio. We demonstrate that cavity formation at interfaces depends on the substrate material, which can be rationalized by the strength of the substrate-water interaction. Furthermore, we observe deviations from the bulk behavior in the second solvation layer, which underlines the importance of the substrate-specific interfacial water structure. Finally, we validate our findings with *ab initio* molecular dynamics simulations.

These results allow a quantification of the competitive nature of adsorption processes at solid-liquid interfaces. Ultimately, they could improve implicit solvation models, which typically neglect substrate-specificity.

O 86.2 Thu 15:15 TRE Phy

first-principles molecular dynamics simulations of electrified Pt(111)/H₂O interfaces — ●LANG LI^{1,2}, NICOLAS HÖRMANN¹, and KARSTEN REUTER¹ — ¹Fritz haber institut of Max planck socirty — ²Humboldt-Universität zu Berlin

Metal-water interfaces play a fundamental role in electrochemistry. An accurate understanding of their properties is required in any attempt to describe electrochemical phenomena such as electrocatalytic reactions or charge transfer processes.

In this work, we benchmark the description of electrified Pt(111)/water interfaces based on first-principles molecular dynamics simulations at applied potential conditions using density functional theory. We apply the potential by introducing excess electrons that are counterbalanced by partially charged hydrogen atoms. This method is tested with a variety of slab setups and cell sizes.

We analyze in detail the structure of the interface as well as the obtained capacitance vs. potential curves and compare these with published theoretical and experimental results [1]. Our results highlight the response of interfacial water to an applied potential and its importance for understanding the hump in the capacitance, observed at high electrolyte concentrations [2].

[1] L. Li, J. -B. Le, J. Cheng, Cell Rep. Phys. Sci., 3, 100759 (2022).
[2] J.B. Le, Q.Y. Fan, J.Q. Li, J. Cheng, Sci. Adv., 6, eabb1219 (2020).

Topical Talk

O 86.3 Thu 15:30 TRE Phy

Novel concepts to simulate electrified liquid/solid interfaces from first principles — FLORIAN DEISSENBECK¹, CHRISTOPH FREYSOLDT¹, MIRA TODOROVA¹, JÖRG NEUGEBAUER¹, and ●STEFAN WIPPERMANN^{1,2} — ¹Max-Planck-Institut für Eisenforschung — ²Philipps-Universität Marburg

Ab initio techniques have revolutionized the way how theory can help practitioners to discover and design new materials, and explore critical mechanisms. Achieving an atomistic understanding of electrochemical processes is imperative to realize disruptive innovations, e.g. power-to-X devices, supercapacitors, metal-air batteries, new concepts in sustainable metallurgy. A well known example, how novel concepts can impact our ability to perform such studies is the introduction of temperature control into *ab initio* simulations. The analogous technique to model electrochemical systems - potential control - is just emerging.

We recently introduced a “thermopotentiostat”: a novel approach to control the electrode potential in molecular dynamics (MD) simulations [1], that can be straightforwardly implemented into any density-functional code [2]. Here, we provide a perspective on the key concepts of simulating electrified liquid/solid interfaces via *ab initio* MD at controlled electrode potential. To highlight the opportunities provided by these developments we discuss the dielectric response and splitting of liquid water in contact with electrified semiconductor surfaces.

[1] F. Deisenbeck, C. Freysoldt, M. Todorova, J. Neugebauer, S.

Wippermann, Phys. Rev. Lett **126**, 136803 (2021)

[2] F. Deisenbeck, S. Wippermann, arXiv:2209.04363

O 86.4 Thu 16:00 TRE Phy

Entropic contributions to the stability of electrochemically adsorbed anion layers on Au(111), a microcalorimetric study — ●MARCO SCHÖNIG and ROLF SCHUSTER — Karlsruhe Institute of Technology, Germany

The understanding of the solid/electrolyte interface is detrimental for rationalizing of electrochemical processes. In this contribution we use electrochemical microcalorimetry to study the entropy of formation of the interface for anion (Cl⁻, Br⁻, I⁻, SO₄²⁻) adsorption on Au(111) [1]. The entropy of formation of the interface provides information on the structure, order and composition of this interface, which are often used as descriptors in electrochemical processes. The specific adsorption of anions on Au(111) is an important model system, since the nearly ideal polarizability of the gold surface over a large potential window allows to study the formation of surface adlayers up to high surface coverages. We found a negative reaction entropy during the adsorption process, with a distinct minimum around two thirds of the maximum coverage. Additionally, we observed that the course of the reaction entropy vs. potential changes with the employed cation (Li⁺, K⁺, Cs⁺) in solution. We will discuss contributions of the solvent and the electrolyte to the entropy of formation of the interface and provide statistical mechanics models to describe the measured data. We found that it was imperative to include repulsive interactions between the adsorbates to account for the experimental results. [1] M. Schoenig and R. Schuster Phys. Chem. Chem. Phys., 2022, Accepted Manuscript

O 86.5 Thu 16:15 TRE Phy

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

O 86.6 Thu 16:30 TRE Phy

Dynamics of the Iridium-Oxide/Water Interface from Machine Learning Potential Simulations — ●NIKHIL BAPAT, SIMON WENGERT, HENDRIK H. HEENEN, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin, Germany

The interaction of liquid water with a solid substrate at an electrified solid/liquid interface plays a crucial role in the activity and stability for electrocatalysts such as IrO₂. It is therefore important to obtain detailed insights about the underlying processes on these interfaces. Here, resolving the dynamical evolution at the atomic scale requires highly accurate yet efficient models that overcome the length and time scale restrictions imposed by traditional *ab initio* molecular dynamics simulations. To that end, we use the Gaussian approximation potential framework to construct a machine-learned model trained on density-functional theory data for the IrO₂(110)/water interface. The established training protocol uses an automated and iterative procedure to ensure that the training data covers the *a priori* unknown geometric and compositional motifs of the evolving working interface.

The model is then used to run reactive molecular dynamics simula-

tions with varying surface compositions. Crucial for electrolysis, the reduced computational cost allows to efficiently explore the diverse configuration space of adsorbed intermediates in the oxygen evolution reaction. Furthermore, we investigate the mobility of water in dependence of the underlying surface composition in which, long-range effects are reflected in a strong variation of water mobility as a function of distance to the surface.

O 86.7 Thu 16:45 TRE Phy

First-principles study of electrochemical effects in Si/SiO_x-water interfaces — ●KAMILA SAVVIDI¹ and ROBERT H. MEISSNER^{1,2} — ¹Institute of Polymer and Composites, Hamburg University of Technology, Hamburg, Germany — ²Institute of Surface Science, Helmholtz-Zentrum Hereon, Geesthacht, Germany

Nanoporous silicon is a prominent candidate for application in energy storage devices as silicon can be conductive under certain conditions. Computer simulations offer an understanding of the electrified semiconductor/water interfaces on the atomistic level; essential for the efficient design and optimization of these devices. We use *ab-initio* molecular dynamics (AIMD) to study the capacitive properties of Si/water interface in the presence of an electrostatic potential. A doped Ne crystal is used as counter electrode to a SiO_x slab and to a hydrogenated Si(100) slab to apply a constant bias potential while explicit water molecules constitute the electrolyte solution.[1] Differential capacitance is estimated by the time-averaged atomic charge fluctuations for each system. To obtain more information about the influence of individual electrode atoms to the differential capacitance, the charge fluctuations of each atom are used to calculate a charge-charge covariance matrix \mathbf{K}_{qq}^- . [2] Results are compared to the simulation of a single electrode with water on either side in an electric field.

[1] S. Surendralal *et al.*, Phys. Rev. Lett. 120, 246801 (2018)

[2] J. Seebeck, C. Merlet, R. H. Meißner, Phys. Rev. Lett. 128, 086001 (2022)

O 86.8 Thu 17:00 TRE Phy

Thermodynamic Cyclic Voltammograms from First Principles — ●NICOLAS BERGMANN, NICOLAS G. HÖRMANN, and KARSTEN REUTER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Cyclic voltammograms (CVs) are a central experimental tool for assessing the structure and activity of electrochemical interfaces. Computationally, a predictive-quality modeling of CVs is challenging due to the entangled need to accurately account for the interactions and reactive chemistry at the liquid electrolyte/solid electrode interface as well as for the applied potential [1]. For sufficiently small scan rates, thermodynamic approaches help to meet these challenges.

Here, we compare different options to derive thermodynamic CVs consistently and at low computational cost, using the well-studied model system of Ag(100) in a Br-containing electrolyte as a test case. We present our generalized ansatz to derive continuous expressions within a mean-field (MF) model, using non-parametric Gaussian process regression. We also shine light on the inherent accuracy limitations of MF theory, by comparing it to CVs from grand-canonical lattice Monte Carlo simulations. Finally, we show how augmenting traditional zero-field calculations (computational hydrogen electrode,

CHE) with capacitive double layer energetics (CHE+DL) [1] within an implicit solvent model influences the theoretical results.

[1] N.G. Hörmann *et al.*, J. Chem. Theory Comput. 2021, 17, 1782

O 86.9 Thu 17:15 TRE Phy

Electrodeposition and Electrochemical Characterization of Thin Nickel Overlayers on Au(111) — ●MARKUS WITTMANN, LUDWIG A. KIBLER, and TIMO JACOB — Ulm University, Institute of Electrochemistry, 89069 Ulm, Germany

Nickel is widely used in energy storage and conversion, *e.g.* nickel-iron, nickel-cadmium, and nickel-metal hydride batteries. The behavior of nickel electrodes has been investigated extensively. However, a detailed understanding of adsorption and absorption processes on the atomic level is still missing. In particular, the distinction between surface and bulk atoms, as well as adsorbed hydrogen during electrooxidation is difficult.[1,2] Here we report on the electrochemical fabrication of thin nickel overlayers on Au(111) and their electrochemical characterization. Stable nickel overlayers have been electrochemically deposited onto Au(111) from a 1 mM NiSO₄ solution and subsequently characterized by cyclic voltammetry in a 10 mM KOH solution. The current density–potential curves of nickel overlayers on an Au(111) single crystal in comparison with the behavior of Au(111) and Ni(111) in 10 mM KOH help separating surface and bulk contributions of nickel electrooxidation. This is especially relevant for small deposits with a high surface-to-bulk ratio. In addition, relations between the structure of the nickel electrodeposit and its electrochemical behavior are addressed.

[1] D. S. Hall *et al.*, J. Electrochem. Soc. **160** (2003) 235–243.

[2] L. F. Huang *et al.*, J. Phys. Chem. C **121** (2017) 782–9789.

O 86.10 Thu 17:30 TRE Phy

Cu Underpotential Deposition on Au(111) in Presence of Carboxylic Acids — ●SEBASTIAN FACKLER, MARKUS WITTMANN, LUDWIG A. KIBLER, and TIMO JACOB — Ulm University, Institute of Electrochemistry, 89069 Ulm, Germany

The underpotential deposition (UPD) of foreign metals on different host metals has been extensively studied, especially for Cu on Au(111).[1] Apart from the nature of the metals, the nature and concentration of anions in the solution govern the initial stages of the deposition process. The influence is usually explained with respect to non-specific and specific adsorbing anions, with the ability of the latter to stabilize sub-monolayers of the deposited metal on the host metal by co-adsorption on top of well-ordered superstructures.[1]

Similarities and differences of the Cu UPD on Au(111) with short-chained carboxylic acids in comparison with known inorganic anions were systematically investigated by cyclic voltammetry and current transients. Despite the non-specifically adsorbing nature of perchlorate ions, the present study demonstrates that perchlorate can influence the Cu deposition in presence of specifically adsorbing acetate ions. Similarly, it has been found by in-situ STM studies that the presence of perchlorate influences the adsorption structure of strongly adsorbing formate on Au(111).[2]

[1] E. Herrero, *et al.*, Chem. Rev. 2001, 101, 187–1930.

[2] A. Abdelrahman, Dissertation, Ulm University, 2019.