O 39: Focus Session: Structure and Dynamics of Solvent at Electrochemical Interfaces I

Understanding how solvent molecules organize and move at electrochemical interfaces is central to catalysis, energy conversion, and electrochemical materials science. This Focus Session will bring together experimental and theoretical leaders using complementary surface specific spectroscopies as vibrational sum frequency generation, advanced X ray/electron techniques, and multiscale simulations to reveal intermolecular structure, hydrogen bond networks, ion-solvent coupling, and field driven dynamics from single crystal electrodes to complex battery interfaces. By highlighting recent breakthroughs in time-resolved measurements and operando platforms, the session aims to connect fundamental interfacial physics with macroscopic performance in electrocatalysis, corrosion, and electrochemical energy storage.

Organized by Yujin Tong (U Duisburg-Essen) and Angelika Kühnle (U Bielefeld).

Time: Tuesday 10:30–12:30 Location: WILL/A317

O 39.1 Tue 10:30 WILL/A317

Influence of Tip Apex Modification on Force Microscopy at the Solid-Liquid Interface — ●Lucas Andreas Scheibel and Andrea Auer — Institute of Physical Chemistry, Innsbruck, Austria

Recent advances in electrochemical atomic force microscopy (EC-AFM) at the electrified solid-liquid interface using stiff, self-sensing quartz cantilevers (qPlus sensors [1]) have enabled high-resolution imaging of both electrode surfaces and interfacial solvent structures.[2,3] This interfacial region plays a decisive role in determining the performance of electrocatalysts, fuel cells, and electrochemical processes. In this work, we introduce chemically modified Si tips functionalized with charge-neutral hydrophobic or hydrophilic groups to identify how charge buildup at the tip apex influences the ability to resolve solvent structures and distinguish water from ion layering at the Au(111)-electrolyte interfaces across a range of pH values. These strategies provide new insight into atomic-scale contrast mechanisms of liquid AFM and highlight the role of tip-apex chemistry[2] in resolving the interfacial organization of solvent molecules at well-defined electrified solid-liquid interface.

[1] F. J. Giessibl, Rev. Sci. Instrum. 90, 011101 (2019)

[2] A. Auer, F. J. Giessibl, J. Kunze-Liebhäuser, ACS Nano, 19, 9, 8401-8410 (2025)

[3] A. Auer, X. Ding, A. S. Bandarenka, J. Kunze-Liebhäuser, J. Phys. Chem. C, 125, 9, 5020-5028 (2021)

O 39.2 Tue 10:45 WILL/A317

High-Resolution Hydration Layer Mapping: Does a Hydration Structure above Gold Imply a Clean Surface? — ●Antonia Köhler[1], Ralf Bechstein[1], Michael Reichling[2], and Angelika Kühnle[1] — [1]Bielefeld University, Bielefeld, Germany — [2]Institut für Physik, Osnabrück, Germany

Solid-liquid interfaces are pivotal in a broad range of fields, including electrochemistry, catalysis and geochemistry. In electrochemistry, the molecular structure of the electrode-water interface is decisive for understanding and improving electrochemical reactions. In this context, the Au(111) surface constitutes a prototypical model system as gold is believed to be a relatively inert and well-characterized sample material. So far, however, little is known about the hydration structure at the Au(111)-water interface at the molecular level. Here, we present atomic force microscopy data on a gold sample carefully cleaned according to standard electrochemistry preparation recipes. Our three-dimensional atomic force microscopy data reveal a vertically ordered hydration structure with layer-to-layer distances of 0.36 nm as expected for water. Strikingly, despite our extensive cleaning efforts (validated by cyclic voltammetry measurements), our two-dimensional data reveal stripe-like structures at the Au(111)-water interface. The dimensions of these structures differ from the well-known herringbone reconstruction of the gold surface, which is why we interpret them as surface contamination. Our work, hence, demonstrates that the presence of a hydration structure is no evidence for a clean gold surface.

Invited Talk O 39.3 Tue 11:00 WILL/A317

Electric double layer of platinum electrodes — ●Marc Koper — Leiden University

Platinum is the most studied electrode material in electrocatalysis, but its electric double layer properties are still incompletely understood. Only Pt(111) has a true double layer window, which charges purely electrostatically. However, the properties of the electric double layer of Pt(111) do not follow the classic Gouy-Chapman-Stern theory. Lower coordination sites and facets on platinum are always covered by either hydrogen or hydroxyl adsorbates, which have an important influence on its double layer properties, as will be illustrated by recent results of double-layer measurements on stepped Pt single-crystal electrodes combined with ab initio molecular dynamics simulations and mean-field modeling. In addition, we show that at low electrolyte concentrations, which are often necessary for double-layer measurements, Pt(111) displays strong constant-phase element behavior, which complicates the accurate measurement of its double layer capacitance. The possible origin of this nonideality will be discussed. Finally, the effect of adsorbates on the electric double layer of platinum will be discussed on the basis on hydrogen-covered Pt(111).

O 39.4 Tue 11:30 WILL/A317

Nonequilibrium density-potential functional theoretical approach of electrochemical plasmonics — ●Lulu Zhang[1,2], Michael Eikerling[1,2], and Jun Huang[1,2] — [1]Forschungszentrum Juelich GmbH, Juelich, Germany — [2]RWTH Aachen University, Aachen, Germany

Electrochemical plasmonics enables in-situ optical probing and modulation of electrochemical interfaces. Experiments have revealed that localized surface plasmon resonance (LSPR) in metal nanoparticle-solution systems is sensitive to surface charge, morphology, electrolyte composition and chemisorption. However, resolving nanoscale interfacial structures from the measured LSPR is rarely practiced; all existing theoretical methods fall in short of simulating the electrochemical plasmonics of nanoparticles under realistic conditions, namely, at a constant electrode potential for a particle with a diameter above 10 nm immersed in an electrolyte solution with a moderate concentration below 100 mM. We are developing a nonequilibrium density-potential functional theoretical (DPFT) approach to enable LSPR simulations under realistic conditions, considering coupled electron-ion-solvent interactions under a terahertz electromagnetic perturbation and on the mesoscale. It ensures constant-potential simulations, scalability to realistic systems, consistency for electronic effects under equilibrium and nonequilibrium, and systematic analysis under working conditions. The fundamental insights into coupled light-electron interactions at electrochemical interfaces are provided, including the extinction spectra, enhanced electric fields and perturbed electron densities.

O 39.5 Tue 11:45 WILL/A317

Insights into the Structure and Dynamics of Co_3O_4–Water Interfaces Using a High-Dimensional Neural Network Potential — ●Amir Omranpour[1,2] and Jörg Behler[1,2] — [1]Theoretische Chemie II, Ruhr-Universität Bochum, Germany — [2]Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany

Co_3O_4 is an important catalyst for the oxygen evolution reaction and for the oxidation of organic molecules in the liquid phase. Therefore, understanding the Co_3O_4–water interface is essential for understanding the mechanistic aspects of those catalytic processes. The interactions at such complex interfaces, including hydrogen-bond fluctuations, hydroxylation, proton transfer, and solvent structuring, are inherently reactive atomistic processes that cannot be fully described by continuum or implicit-solvent models. On the other hand, *ab initio* molecular dynamics with explicit solvent remain restricted to only a few picoseconds and a few hundred atoms. In this work, we overcome these limitations by training a high-dimensional neural network potential (HDNNP) on density functional theory data, which enables us to greatly extend the accessible time and length scales. Using this HDNNP, we carry out simulations that uncover the structure, dynamics, and reactivity of Co_3O_4–water interfaces in detail. Our simulations show that different surface terminations give rise to significantly different hydration structures. They also reveal how each termination templates the interfacial water network, affects hydroxylation, and determines the degree of structural ordering at the interface.

Invited Talk O 39.6 Tue 12:00 WILL/A317

First-principles modelling of electrochemical interfaces — •Axel Gross — Institute of Theoretical Chemistry, Ulm University, 89069 Ulm

Electrochemical processes occur at the interface between an electron conductor, the electrode, and an ion conductor, the electrolyte. From an atomistic point of view, the liquid nature of electrolytes requires appropriate statistical averages which can be numerically rather demanding. Still it has become possible to model these interfaces using using first-principles quantum chemical methods [1,2]. In this talk I will present which insights can be gained from such studies, but I will also identify limititations of this approach and discuss how they can be overcome, contrasting the cases of solvated cations and anions [3, 4] as one example.

[1] A. Groß and S. Sakong, Chem. Rev. **122**, 10746 (2022).
[2] A. Groß, Curr. Opin. Electrochem. **40**, 101345 (2023).
[3] F. Gossenberger, F. Juarez, A. Groß, Front. Chem. **8**, 634 (2020).
[4] F. Dominguez-Flores, A. Groß, W. Schmickler, J. Phys. Chem. C **129**, 9179 (2025).