O 97: Solid-liquid interfaces: Reactions and electrochemistry III

Time: Friday 9:30–12:30 Location: TRE/PHYS

Invited Talk O 97.1 Fri 9:30 TRE/PHYS

Questions of Selectivity in Electrocatalysis — •Vanessa J. Bukas — Fritz-Haber-Institut der MPG, Berlin

Heterogeneous electrocatalysis is at the heart of developing sustainable energy technologies. The rational design of suitable electrocatalysts, however, depends on a deeper understanding of the underlying reaction mechanisms. Product selectivity, in particular, remains poorly understood and cannot be rationalized by popular thermodynamic models that currently define the state-of-the-art in computational electrocatalysis. In this talk, I will address a number of possible scenarios as to why this may be while challenging prevalent mechanistic assumptions. Atomistic models, based mainly on density-functional theory, will explore microscopic reaction mechanisms to demonstrate effects due to the local field at the electrical double layer, the delicate kinetic competition between electrochemical and non-electrochemical reaction steps, as well as the key role of mesoscopic mass transport. The emerging insight adds to our fundamental understanding of electrocatalysis and supports ongoing efforts toward optimal process design.

O 97.2 Fri 10:00 TRE/PHYS

Mechanism of Fe(II) Chemisorption on Hematite(001) Revealed by Machine Learning Molecular Dynamics — •Kit Joll[1], Philipp Schienbein[1,2], Kevin Rosso[3], and Jochen Blumberger[1] — [1]Department of Physics and Astronomy and Thomas Young Centre, University College London, London WC1E 6BT, United Kingdom; — [2]Ruhr-Universität Bochum, 44780 Bochum, Germany; Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, 44780 Bochum, Germany — [3]Pacific Northwest National Laboratory, Richland, Washington 99354, United States;

Understanding ion adsorption at mineral-water interfaces is key to explaining geochemical processes such as redox cycling, dissolution, and crystal growth. However, probing these reactions experimentally at atomic resolution remains challenging. Here, we employ reactive neural network potential molecular dynamics (NNP-MD) with umbrella sampling and reactive flux transition state theory to simulate the chemisorption of aqueous Fe^{2+} on hematite(001) at density-functional theory (DFT) accuracy and nanosecond time scales. We identify a dissociative mechanism for Fe^{2+} water-ligand exchange and multiple stable surface complexes, nonadsorbed, physisorbed, monodentate, and tridentate chemisorbed species, along the adsorption pathway. The overall process is exergonic, in contrast to previous classical force-field predictions. These results demonstrate how machine-learning potentials bridge the accuracy of ab-initio methods with the sampling efficiency of classical molecular dynamics, providing new atomistic insight into reactive processes at oxide-water interfaces.

O 97.3 Fri 10:15 TRE/PHYS

How to Best Achieve a Steady State: Comparison of Different Methods to Acquire Tafel Plots — •Maren-Kathrin Heubach and Gregory Jerkiewicz — Department of Chemistry, Queen's University, Kingston, Canada.

The performance of an electrocatalyst is typically characterized by Tafel plots, which show a natural logarithm of the current density of a reaction as a function of the overpotential. Hereby, the exchange current density and the Tafel slope can be determined, giving insights into the mechanism of the electrocatalytic reaction. Even though Tafel plots are widely used, there is a large variety in performing the measurements to create Tafel plots.

In this contribution, we will discuss and compare several approaches to achieve the closest approximation to the desired steady state. These approaches will be showcased with the benchmark system of a polycrystalline Pt sample in an aqueous sulphuric acid solution.

O 97.4 Fri 10:30 TRE/PHYS

Exploring the Surface Structure of Ni Anodes and the Role of pH for Alkaline Oxygen Evolution Using SERS — •Justus Leist, Annika Neufischer, Roman Jocher, Benjamin Schilling, Timo Jacob, and Albert Engstfeld — Ulm University, Institute of Electrochemistry, Ulm, Germany

Sustainable hydrogen can be generated by electrochemical water splitting, but the process is typically limited by the sluggish kinetics of the oxygen evolution reaction (OER) at the anode. To avoid reliance on noble-metal catalysts such as Ir and Ru, Ni-based catalysts have attracted considerable interest due to their abundance and efficiency. Under OER conditions, where the Ni anode surface is accepted to be NiOOH, Raman spectroscopy enables *in situ* monitoring of both the surface structure and possible OER intermediates. In this work, using Surface-enhanced Raman spectroscopy (SERS) combined with DFT, we challenge the assumed presence of NiOOH under OER conditions.[1]

To probe the atomic composition of the oxidized Ni anodes, isotope-labelled Raman experiments were performed, revealing the absence of hydrogen in the lattice. The presence of NiO*, rather than NiOOH, is further supported by DFT-calculated spectra. Additionally, we illustrate that a band previously attributed to an OO- species is more likely related to overtones. By varying the pH from alkaline to near-neutral conditions, we examine the impact of pH on the Raman spectra during the OER and discuss these changes in relation to the vibrational Stark effect and possible OER intermediates.

[1] J. Leist et al. *ChemRxiv* DOI: 10.26434/chemrxiv-2025-jb73p

O 97.5 Fri 10:45 TRE/PHYS

Optimizing oxygen vacancies through grain boundary engineering to enhance electrocatalytic nitrogen reduction — •Xiu Zhong[1], Fu Yang[2], and Yong Lei[1] — [1]Institut für Physik & IMN MacroNano (ZIK), Technische Universität Ilmenau, Ilmenau 98693, Germany — [2]School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212100, China

This study develops an efficient N2-reduction catalyst by in-situ anchoring ultrafine MoO2 nanograins on N-doped carbon fibers. Optimized thermal treatment generates abundant grain boundaries that increase oxygen-vacancy concentration, enhance electron transfer, and create highly active N2-trapping sites. The optimal MoO2/C700 catalyst delivers superior performance, achieving an NH3 yield of 173.7 μg h-1 mgcat -1 and a Faradaic efficiency of 27.6% at -0.7 V vs. RHE in 1 M KOH. In-situ XPS and DFT confirm the electronic-structure modulation and strong N2-oxygen-vacancy interaction, revealing electron transfer between adsorbed nitrogen and Mo(IV). Correlating activity with interfacial effects further clarifies the origin of enhancement. The catalyst also shows stable operation for 60 h, demonstrating the promise of grain-boundary engineering to boost oxygen vacancies for efficient and sustainable electrochemical ammonia synthesis.

O 97.6 Fri 11:00 TRE/PHYS

Investigating the Role of Nuclear Quantum Effects at Zinc Oxide-Water Interfaces with High-Dimensional Neural Network Potentials — •Jan Elsner[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

Zinc oxide is a promising material for sustainable hydrogen production via catalytic water splitting. The interface of ZnO with water exhibits complex dynamical behaviour, including water dissociation and recombination, as well as long-range proton transport. Previous studies [1] have elucidated these mechanisms using High-Dimensional Neural Network Potentials (HDNNPs), which enable simulations at the system sizes and timescales needed for statistically converged interfacial properties. However, the validity of the classical approximation for atomic nuclei in such systems, particularly for describing interfacial proton transfer (PT), remains poorly understood. Here, we employ a new efficient parallel implementation of path-integral molecular dynamics with HDNNPs [2] to investigate the role of nuclear quantum effects (NQEs) at the ZnO-water interface. We show that NQEs significantly lower free energy barriers for PT, and discuss the resulting implications for the interfacial dynamics of the system.

[1] Quaranta V., Hellström M., Behler J., J. Phys. Chem. Lett. 2017, 8, 1476-1483

[2] Shiga M., Elsner J., Behler J., Thomsen B., J. Chem. Phys. 2025, 163, 134119

O 97.7 Fri 11:15 TRE/PHYS

Linking Water Structure to Proton-Coupled Electron Transfer at Metal Interfaces — •Julius Lonnes[1,2], Nicolas G. Hörmann[1], and Karsten Reuter[1] — [1]Fritz-Haber-Institut der MPG — [2]Technische Universität München

Understanding the kinetics of interfacial electrochemical reactions is essential for optimizing technologies such as fuel cells and batteries. To this end, the interfacial water structure plays a key role in determining the effects of pH and electrolyte cations on reaction rates, yet the mechanistic link between water arrangement and reaction barriers remains unclear. By examining the acidic Volmer step on Pt(111) and tuning the hydrogen-bond network surrounding the proton, we uncover how interfacial solvation modulates electrochemical activation barriers. We find that proton stability at the metal-water interface strongly influences the barrier height, a relationship that can be rationalized with Hammond's postulate:[1] variation in electrochemical potential shifts the transition state position along the reaction coordinate, altering its sensitivity to local solvation structure. We establish that interfacial solvation is a decisive factor in determining electrochemical activation energies, advancing fundamental understanding of proton-coupled electron transfer at charged interfaces.

[1] G.S. Hammond, J. Am. Chem. Soc. **77**, 334 (1955).

O 97.8 Fri 11:30 TRE/PHYS

Understanding of degradation of catalyst/semiconductor interfaces — Sergej Levashov[1], Tim Rieth[1,2], Ian D. Sharp[1,2], and •Johanna Eichhorn[1] — [1]TUM School of Natural Sciences, TU Munich — [2]Walter Schottky Institute, TU Munich

The performance of photoelectrochemical (PEC) materials are governed by interfacial processes where atomic structure, electronic states, and chemical reactions meet. Local defects and dynamic surface transformations at the nanoscale can dominate charge transfer and often trigger degradation under operating conditions. Accessing such mechanisms requires in-situ/operando techniques that probe interfacial structure and dynamics with nanoscale resolution. We employ in situ scanning probe microscopy to study the interfacial stability of TiO2/Pt photocathodes by monitoring local surface transformations and detachment events during operation. Pt catalysts are deposited on conformal TiO2 coatings either by sputtering, yielding continuous films, or by atomic layer deposition (ALD), forming discrete nanoislands and enabling atom-efficient utilization of precious metals. Under PEC conditions, both architectures show comparable onset potentials and saturation current densities, yet chronoamperometry reveals an enhanced long-term stability for the nanostructured ALD-Pt electrodes. We attribute this contrasting behavior to different bubble formation and detachment dynamics at the catalyst-semiconductor interface. These nanoscale insights highlight the importance of interfacial and morphological engineering, as well as the necessity of controlling reaction processes, to achieve durable and efficient PEC material systems.

O 97.9 Fri 11:45 TRE/PHYS

An Analytical Description for Atomic Diffusion involved Peaks in Cyclic Voltammograms: the Reversible Place-Exchange on Pt(111) — Jon Bjarke Valbaek Mygind[1], Francesc Valls Mascaró[2], Gerard J. Verbiest[3], and •Marcel J. Rost[4] — [1]Catalan Institute of Nanoscience and Nanotechnology, Campus UAB, Barcelona, Spain — [2]Faculty of Physical Chemistry, University of Innsbruck, Innsbruck, Austria — [3]Department of Precision and Microsystems Engineering, Delft University, Delft, The Netherlands — [4]Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands

Cyclic voltammetry (CV) is one of the most powerful tools for the experimental investigation and characterization of electron transfer processes in electrochemistry. As the unique electrochemical fingerprint of a particular system is given by specific (current) peaks in the cyclic voltammogram, it is not surprising that great effort is done to understand, describe, and model these peaks. However, the underlying thermodynamic and kinetic processes make this a difficult task, especially when features in the fingerprint change with the applied CV sweep rate. Here we show, on the example of the reversible Place-Exchange peak, a precursor in the electrochemical oxidation of the Pt(111) surface, that a combination of a Frumkin isotherm followed by an Arrhenius (atomic) diffusion process delivers a rather good description. We present an analytical theory that fits all peaks of all CVs, measured with different sweep rates, with only six fit variables. These variables deliver hard quantitative thermodynamic values.

O 97.10 Fri 12:00 TRE/PHYS

Machine Learning the Energetics of Electrified Solid-Liquid Interfaces — •Nicolas Bergmann[1], Nicéphore Bonnet[2], Nicola Marzari[2], Karsten Reuter[1], and Nicolas G. Hörmann[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Theory and Simulation of Materials, EPFL, Lausanne

Machine learning interatomic potentials (MLIPs) accelerate many aspects of computational chemistry. However, MLIPs fail to describe the biases introduced at applied potential conditions for typical electrocatalytic systems, where effects of the inner double layer play a critical role [1]. Here, we present the "Response Analysis in z-ORientation" (RAZOR) model [2], which machine-learns the work function, the first-order energy change to bias charges q. RAZOR is stabilized by additionally learning the atomic force derivative to q, equivalent to Born effective charges. The approach extends MLIPs to the variable charge case, by adding bias-induced energy and force changes to traditional zero-bias MLIPs. This enables large-scale molecular dynamics simulations at finite bias. We demonstrate RAZOR's capabilities by investigating OH adsorption on Cu(100) and explicit Pt(111)-H_2O interfaces, faithfully recreating *ab initio* and experimental results.

[1] N. Bergmann *et al.*, J. Chem. Theory Comput. **19**, 8815 (2023).
[2] N. Bergmann *et al.*, Phys. Rev. Lett. **135**, 146201 (2025).

O 97.11 Fri 12:15 TRE/PHYS

Entropy-Enthalpy Relationships in Heterogeneous Electrocatalysis: A Case Study of the Hydrogen Evolution Reaction — •Andrew J. Wong, Barbara Sumić, Elias Diesen, Nicolas G. Hörmann, Hendrik H. Heenen, Karsten Reuter, and Vanessa J. Bukas — Fritz-Haber-Institut der MPG, Berlin

Temperature is a key parameter in industrial electrolyzers. And yet, the vast majority of mechanistic lab-scale studies ignores temperature variations by operating at room temperature. This is surprising since existing experimental evidence has shown that even modest heating can significantly affect the rate and selectivity of electrocatalytic reactions. Understanding the origin of such effects is crucial for advancing fundamental electrocatalysis and exploiting temperature as a control parameter. Here, we explore temperature effects on the hydrogen evolution reaction (HER) by developing a simple mean-field microkinetic model based on first-principles energetics. An Arrhenius analysis on the HER rates across different metal catalysts reveals distinct entropy-enthalpy correlations, reflected in the apparent activation enthalpy and entropy-dependent prefactor. Despite the simplicity of our model, these trends are in remarkable qualitative agreement with experiments. A degree of rate control analysis explains the kinetic fingerprints in terms of a change in the rate-determining step, inducing a shift in kinetic regime. We thus conclude that the enthalpy-entropy compensation effect is explained, at least to a first approximation, by the surface kinetics. Our work overall highlights the subtle interplay between temperature, applied potential, and catalyst reactivity.