O 13: Solid-liquid interfaces: Reactions and electrochemistry I

Time: Monday 15:00–18:00 Location: TRE/PHYS

O 13.1 Mon 15:00 TRE/PHYS

The Weak Spots of IrO_2: Sampling Defect Landscapes at Operation Conditions — •Jimiben V. Patel, Nikhil Bapat, Karsten Reuter, and Hendrik H. Heenen — Fritz-Haber-Institut der MPG, Berlin

Under the harsh oxidative potentials required for the oxygen evolution reaction, rutile IrO_2 surfaces undergo restructuring that leads to Ir dissolution and undermines catalyst durability, eventually impacting device performance. To mitigate the catalyst degradation via robust design principles, a fundamental atomistic understanding of how surface reconstructions initiate and propagate dissolution is urgently needed. Since high-resolution *operando* characterization remains challenging, atomistic simulations are essential for uncovering the underlying microscopic mechanisms. However, achieving realistic insight requires approaches that go well beyond conventional, idealized modeling frameworks. In this work, we employ machine-learned interatomic potentials trained on density-functional theory to systematically sample vacancy formation across a wide range of electrochemical environments. This allows us to resolve how surface defects nucleate, interact, and evolve under relevant oxidizing conditions. We find that vacancy formation becomes increasingly favorable at higher potentials, with isolated defects stabilizing and subsequently coalescing into larger surface pits – structures that likely act as precursors for accelerated dissolution. These findings provide a first link between applied potential and defect thermodynamics, offering predictive insight into potential-dependent degradation pathways of IrO_2.

O 13.2 Mon 15:15 TRE/PHYS

Electrochemical Free Energy Barriers at Constant Potential — •Elias Diesen, Karsten Reuter, and Vanessa J. Bukas — Fritz-Haber-Institut der MPG, Berlin

Simulating barriers for electrocatalytic reactions is methodologically very challenging due to the intricate dynamics at the electrified solid/liquid interface. In addition, standard atomistic simulations based on periodic density-functional theory (DFT) keep the charge of the simulation cell constant instead of allowing it to fluctuate during the reaction in order to maintain a (fixed) electrode potential. Here, we introduce a method to compute electrochemical free energy barriers under well-defined potential conditions. Our approach relies on umbrella sampling on top of DFT-based molecular dynamics to access the free energy of activation, including both enthalpic and entropic contributions [1]. By carefully sampling the work function along the reaction coordinate, a Legendre transformation of the resulting canonical (constant-charge) energetics is then used to obtain grand canonical (constant-potential) results [2]. The method is demonstrated for proton deposition over Au(111). We extract potential-dependent barriers and examine kinetic scaling relations as well as use our results to benchmark common approximations in the recent literature. This work paves the way for systematic studies under realistic electrochemical conditions at e.g. varying temperatures or considering different proton-donating species.

[1] E. Diesen *et al.*, ACS Catal. **15**, 5403 (2025).

[2] S.D. Beinlich *et al.*, J. Chem. Theory Comput. **19**, 8323 (2023).

O 13.3 Mon 15:30 TRE/PHYS

Customizable Electrostatic Potentials in DFT Supercell Calculations: Implementation and Application to Electrified Interfaces — •Samuel Mattoso[1], Jing Yang[1], Florian Florian Deissenbeck[1], Ahmed Abdelkawy[1], Christoph Freysoldt[1], Stefan Wippermann[1,2], Mira Todorova[1], and Jörg Neugebauer Jörg Neugebauer[1] — [1]Max Planck Institute for Sustainable Materials, Max-Planck-Straße 1, 40237 Düsseldorf, Germany — [2]Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany

Electric fields drive reactions, reshape surfaces, guide protein folding and dictate selectivity in chemistry and materials science. While Density Functional Theory (DFT) is a standard tool for modelling such phenomena, introducing user-defined customizable electrostatic potentials usually requires invasive code modifications and deep coding expertise. We will present a lightweight, Python-based implementation that allows adding external electric fields to supercell DFT calculations via a new VASP-Python interface. We outline the necessary energy- and force-corrections, describe the computational setup, and provide a streamlined workflow that works entirely within VASP without altering the source code. The method's versatility is demonstrated on several case studies: molecular adsorption on charged surfaces, field-ion microscopy, electrochemical solid-water interfaces, and implicit solvent models. This approach offers a simple, flexible route for researchers to incorporate external fields into DFT simulations, enabling exploration of field-dependent phenomena across chemistry and materials science.

O 13.4 Mon 15:45 TRE/PHYS

Ion-specific charge transfer and capacitance in the compact double layer of solvated cations at metal electrodes — •Fabiola Dominguez Flores, Axel Gross, and Wolfgang Schmickler — Institute of Theoretical Chemistry, Ulm University, 89081 Ulm, Germany

A molecular-scale understanding of the compact double layer is essential for fundamental electrochemistry. Using density-functional theory with a hybrid implicit-explicit solvation model, we investigate the adsorption of solvated cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) on metal electrodes. This approach captures the local hydration structure while modeling a dilute electrolyte where no diffuse layer forms. Our results reveal two distinct physical regimes: alkali ions retain their unit charge, while divalent ions exhibit substantial partial charge transfer, directly quantified by Bader analysis. This charge transfer governs the interfacial capacitance, which we calculate to be 10-20 μF cm^{-2}, in excellent agreement with experiment. We demonstrate that the electrosorption valency equals the negative of this partial charge. Interpreting these results with a parallel-plate model yields an effective dielectric constant dictated by the polarizabilities of the metal and the water layer. This work provides fundamental microscopic insight into how ion-specific electronic interactions control the properties of the electrochemical double layer.

O 13.5 Mon 16:00 TRE/PHYS

Electrokinetic spectroscopy of ion dynamics near charged surfaces using modulated surface acoustic waves — •Ofer Manor, Li Yifan, and Sudeepthi Aremanda — Technion, Haifa, Israel

We use MHz-level frequency-modulated surface acoustic waves (SAWs) to study the dynamics of ions in the electrical double layer (EDL) to appear near the charged glass/electrolyte interface. The SAW travels in the solid; the EDL exists in the electrolyte; both phenomena are entangled through a field effect, a mechanical evanescent wave, which is invoked in the electrolyte by the SAW and vibrates ions in the EDL to result in the leakage of an electrical field off the glass/electrolyte interface. We show measured spectra of electrolyte comprising different types and concentrations of salts and salt mixtures. This is a spectroscopy of ion dynamics in isolated and unique EDLs.

EDLs are nanometer-thick clouds of ions that appear at the charged interface between a substrate and an electrolyte solution and determines its electrical properties. Ions migrate through the EDL within micro- to nano-seconds: These are the EDL relaxation-times for charging and discharging, which are a product of the EDL structure and ion species therein.

Ion relaxation-times similar to the SAW periodic time result in an ion electro-mechanical synchronization, which maximizes ion vibration and the leakage of electrical fields off the EDL. The leakage identifies ion relaxation-time spectra for different electrolytes and the presence of ions and the intrinsic rate by which they charge and discharge EDLs.

O 13.6 Mon 16:15 TRE/PHYS

Impact of the Negative Dielectric Responses on Solvation and Adsorption at Electrified Interfaces — •Zhenyu Wang[1], Mira Todorova[1], Christoph Freysoldt[1], Stefan Wippermann[2], and Jörg Neugebauer[1] — [1]Department of Computational Materials Design, Max Planck Institute for Sustainable Materials, Düsseldorf, Germany — [2]Department of Physics, Philipps-Universität Marburg, Marburg, Germany

Understanding processes at electrified solid-liquid interfaces is central to electrocatalysis, corrosion, and water-splitting, yet the dielectric response of interfacial water remains poorly understood. Using a capacitor geometry in which water is confined between oppositely charged electrodes, we perform several hundred nanoseconds-long molecular dynamics simulations to probe both the dielectric behaviour of neat water and the solvation of ions under bias. The simulations reveal pronounced oscillations in the screening of interfacial water, giving rise to regions in which the local dielectric constant becomes negative. This dielectric response gives rise to weakly bound adsorption states. By correlating the computed potential profiles with the evolution of Na^+ and Cl^- solvation shells, we demonstrate that the rate-limiting step is not related to the charge transfer barrier but originates from the reorganization of the ion solvation shell when transferring through the negative-dielectric regions. This insight bridges atomistic dielectric anomalies with macroscopic electrochemical behaviour and provides a quantitative basis to describe ion migration in the vicinity of the electrified interface.

O 13.7 Mon 16:30 TRE/PHYS

Selectivity in Electrochemical Oxidation Reactions: Challenges in Ethylene Epoxidation — •Pauline Schütt and Alexander Bagger — Department of Physics, Technical University of Denmark

Electrochemical technologies play a central role in the sustainable production of fuels and chemicals, but their applications remain limited due to significant overpotentials and challenges in controlling selectivity. Alternative oxidation reactions could potentially generate value-added products on the anode side of electrochemical cells, but typically suffer from competition with the oxygen evolution reaction (OER).[1] Density functional theory (DFT) predictions and concepts from computational catalysis provide useful tools to systematically analyze selectivity and establish trends across different catalyst and reaction systems.[2] We here discuss key challenges restricting such alternative oxidation reactions and their competition with the OER, with a focus on ethylene epoxidation.

[1] L. F. T. Novaes *et al.* Chemical Society Reviews **50**(14), 7941-8002 (2021).

[2] P. Schütt, L. Karlsson and A. Bagger, in preparation, (2026).

O 13.8 Mon 16:45 TRE/PHYS

Bias, Barriers, and Beyond: Perturbative Insights into Electrochemical Reactivity — •Nicolas G. Hörmann and Karsten Reuter — Fritz-Haber-Institut der MPG

Electrochemical processes at solid-liquid interfaces are strongly shaped by the applied potential, yet capturing these effects efficiently remains a central challenge for atomistic modelling. In this talk, I will provide an overview of recent advances made in our group, focusing on perturbative and response-based approaches for electrochemical energetics and kinetics. Building on a rigorous connection between the constant-charge and constant-potential ensembles, we establish general connections between computational formalisms and clarify how potential-dependent properties emerge.

These insights enable efficient Taylor-expanded descriptions of energetics that avoid explicit simulations at different applied biases and allow analytical assessments of non-Nernstian shifts in hydrogen underpotential deposition, potential-dependent symmetry factors and potentiostat-free barrier calculations. Implementing them into bias-aware ML potentials opens the door to long-timescale molecular dynamics and accelerated exploration of electrochemical reaction pathways.

O 13.9 Mon 17:00 TRE/PHYS

Electro-osmotic Flow in Nano-capillaries via Optical Imaging and I/V Measurements: Influence of different salts and concentrations — •Aleksei Overchenko[1], Simon Brauburger[2], Frank Cichos[1], and Ulrich Keyser[2] — [1]Leipzig University, Peter Debye Institute for Soft Matter Physics, Linnéstr. 5, 04103 Leipzig — [2]University of Cambridge, Cavendish Laboratory, JJ Thomson Ave

Electro-osmotic flow (EOF) is of great interest in solid-state nanopores (SSNPs) due to its ability to pump, mix, and separate fluids in micro- and nanofluidic devices without mechanical components. However, EOF remains insufficiently explored at the nanoscale. Although KCl, NaCl, and LiCl are the most commonly used salts for driving matter through nanopores, no systematic qualitative or quantitative study has yet evaluated how different ions and concentrations affect EOF magnitude in nanopores.

We investigated the influence of various salts and their concentrations (10 mM to 1 M) on EOF behavior in 100 nm SiO2 glass capillaries. Flow visualization was performed using dark-field optical microscopy with simultaneous I/V measurements via a custom-designed flow cell. Tracer particles included 250 nm polystyrene and AuNPs.

This study provides higher spatial resolution and more detailed characterization of EOF than previously reported, offering new insights into nanoscale behavior. Understanding EOF under different ionic conditions is essential for future applications, including controlled manipulation of single DNA molecules and proteins.

O 13.10 Mon 17:15 TRE/PHYS

Facet-dependent restructuring and catalytic activity of Cu single crystals during CO electro-oxidation — Matthias Leitner, Francesc Valls Mascaro, •Andrea Auer, and Julia Kunze-Liebhäuser — Institute of Physical Chemistry, University of Innsbruck, Austria

Understanding how surface structure relates to catalytic activity is essential for designing efficient electrocatalysts. Copper (Cu) is known to restructure under reaction conditions, yet the precise impact of this dynamic behavior on activity remains largely unclear. Here, we combine electrochemistry with in situ electrochemical scanning tunneling microscopy (EC-STM) to investigate CO electro-oxidation on Cu(111) and Cu(100) single crystals and correlate activity with facet-specific structural changes. Both surfaces undergo nanometer-scale restructuring, forming undercoordinated Cu adatoms that act as active sites. Their evolution, however, differs significantly: Cu(111) shows dynamic, reversible restructuring that maintains a high density of adatom nanoclusters, whereas Cu(100) forms clusters that evolve less reversibly, with a gradual reduction in density. Interestingly, the evolution of clusters and their density does not directly correlate with the observed catalytic activity for either facet. Instead, we propose that the differences in activity stem primarily from variations in the effective density of the catalytically active Cu adatoms and their distinct interaction with reactants, rather than from different structural motifs. These results underscore the crucial role of dynamic restructuring in guiding the design of Cu-based electrocatalysts.

O 13.11 Mon 17:30 TRE/PHYS

In-situ magneto-optical tracking of redox reactions in NiFe electrocatalysts — •Sandhya Chandola[1,2], Karuppasamy Dharmaraj[2], Jörg Rappich[2], and Norbert Esser[1] — [1]Institut für Festkörperphysik,TU Berlin, Hardenbergstr. 36, 10623 Berlin, Germany — [2]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Schwarzschildstr. 8, 12489 Berlin, Germany

Nickel/Iron (NiFe)-based electrocatalysts are known to be efficient catalysts for the oxygen evolution reaction (OER), involved in water splitting. By using a polarization sensitive optical spectroscopy technique, Reflection Anisotropy Spectroscopy (RAS), at near normal incidence, we show how the polarization state of the reflected light can be directly correlated with the oxidation state changes of NiFe catalysts via two entangled magnetic effects, which are the magneto-optical Kerr effect (MOKE) at the surface of the NiFe layer and Faraday rotation within the layer. The polarization state can be used to monitor phase transitions which are not observed in unpolarized absorption spectra.

Increasing amounts of Fe in the NiFe films correspond to greater changes in the RAS/MOKE intensities, up to the solubility limit of ˜ 25% Fe, after which the spectra do not show any more changes. RAS/MOKE is shown to be a valuable spectroscopic technique which can probe changes in the redox states for different NiFe ratios, due to the indirect influence of magneto-optical effects with the implied role of ferromagnetic ordering in enhancing catalytic activity.

O 13.12 Mon 17:45 TRE/PHYS

Size Dependent Stability of Pt-supported Ceria Nanoparticles in Alkaline Electrolyte — Lukáš Fusek[1], Pankaj Kumar Samal[1], Jiří Kerešteš[1], Ivan Khalakhan[1], Viktor Johánek[1], Yaroslava Lykhach[2], Jörg Libuda[2], Olaf Brummel[2], and •Josef Mysliveček[1] — [1]Charles University, Faculty of Mathematics and Physics, V Holešovičkách 2, 180 00 Praha 8, Czech Republic — [2]Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

Ceria nanoparticles find applications in electrocatalysis as co-catalysts for alcohol and CO oxidation, and for fuel cell and water electrolysis reactions. Synergistic effects of ceria are expected to critically depend on the cerium phases established under electrochemical conditions.

We perform a combined surface science and electrochemical study of CeO2(111) nanoparticles on Pt(111). Under electrochemical operation conditions, large ceria nanoparticles exhibit a stable redox behavior, while nanoparticles smaller than 5 nm destabilize and convert to a fully hydrated phase. Both types of nanoparticles block OH adsorption and H evolution on Pt(111), but do not block H adsorption, indicating H intercalation.

Our results reveal the nature of the electrocatalytically active cerium phases [10.1039/d3cp03831a] and underline the relevance of combined surface science and electrochemical experiments [10.1021/acs.jpclett.5c01465] for obtaining in-operando information on model electrocatalyst systems.