O 65: Solid-liquid interfaces: Reactions and electrochemistry II

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

O 65.1 Wed 15:00 TRE/PHYS

Effect of Organic Additives in Aqueous Dye-Sensitized Solar Cells with TEMPO$^{+/0}$ Radicals as Redox Mediator Studied by Perturbation Techniques — •Daniel Holzhacker and Derck Schlettwein — Justus-Liebig-Universität Gießen, Institut für Angewandte Physik, Heinrich-Buff-Ring 16, D-35392 Gießen

Understanding the complex interactions among the electrolyte, dye, and semiconductor (TiO_2) in dye-sensitized solar cells (DSSCs) is crucial to uncover and optimize the individual roles of each component. Organic electrolyte additives, such as 1-methylbenzimidazole (1MBI), are commonly used to enhance cell performance. In aqueous TEMPO$^+$ solutions, a distinctive color change was observed upon addition of 1MBI. Cyclic voltammetry revealed that the redox potential of the electrolyte shifted systematically to higher potentials with increasing 1MBI concentration. Photoelectrochemical analysis of DSSCs demonstrated a clear effect of 1MBI on the conduction band edge, which shifted in parallel to the redox potential of the electrolyte. It was shown that reduced recombination losses, i.e., a shift of the electron Fermi level in the TiO_2 closer to the conduction band edge, were responsible for an increased open-circuit voltage. Additionally, the shifts of both the conduction band edge and the redox level of the electrolyte may facilitate electron injection from the dye into TiO_2 and/or the regeneration of the oxidized dye by the redox mediator, thereby explaining the higher photocurrents, also observed at increased 1MBI concentrations.

O 65.2 Wed 15:15 TRE/PHYS

Laser-treated activated carbon derived from date stone for energy storage and environmental remediation applications — •Ahmad Jabr[1], Iyad Sadeddin[1], Amer El Hamouz[1], Hyun Jungb[2], and JeongWon Parkb[2] — [1]An-Najah National university, Nablus, Palestine — [2]Dongguk University, Seoul-Campus, Korea

In this study, Activated Carbon (AC) was synthesized via traditional ZnCl* and KOH routes followed by surface modification process using pulsed Nd:YAG laser (1064 nm) under aqueous conditions to produce laser-modified activated carbon (LAC).

Structural and surface analyses revealed that laser introduced new surface functionalities, increased surface roughness, promoted additional micropores and mesopores formation, resulting in 17% enhancement in SSA. Nitrogen adsorption isotherms indicated higher monolayer adsorption and more developed pore volume distribution in LAC compared with AC. Also, LAC exhibited improved surface chemistry with newly developed OCFGs, attributed to laser bombardment effects.

Electrochemical characterizations showed that AC and LAC exhibit typical EDLC behavior, with LAC achieving 70% higher specific capacitance, enhanced energy and power densities, reduced ESR, and better stability after 10000 cycles compared to AC. Furthermore, adsorption studies showed that LAC overcame AC with 400% enhancement in maximum adsorption capacity and initial rate adsorption, signifying improved surface heterogeneity and multilayer adsorption features.

O 65.3 Wed 15:30 TRE/PHYS

rationalizing capacitance differences across metal/water interfaces within a unified quantum electric double layer model — •Lang Li, Nicolas Hörmann, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

Electrochemical routes to hydrogen and synthetic fuels promise sustainable energy storage, yet their advancement is limited by an incomplete microscopic picture of the electric double layer (EDL) that governs electrode behavior. Using extensive density-functional theory-based *ab initio* molecular dynamics simulations, we examine a series of noble-metal surfaces and capture the experimental capacitance trend Pt(111) > Cu(111) > Ag(111) ≈ Au(111). Subsequent data analysis rationalizes this trend within a unified EDL picture that rests upon a universal four-state interfacial water structure and material-dependent electron spillover [1]. We probe the generality of this understanding by performing alloy- or strain-mimicking "cross-geometry" simulations at interchanged lattice constants, and obtain capacitance variations in full accordance with the model predictions. This suggests applicability of the model for the rational design of next-generation electrode materials.

[1] L. Li, T. Eggert, K. Reuter, N. Hörmann, *J. Am. Chem. Soc.*, **147**, 22778 (2025).

O 65.4 Wed 15:45 TRE/PHYS

Formic Acid Oxidation on Gold Electrodes — •Johannes M. Hermann[1], Areeg Abdelrahman[1], Heiko Müller[1], Ludwig A. Kibler[1], and Timo Jacob[1,2,3] — [1]Institute of Electrochemistry, Ulm University, Ulm, Germany — [2]Helmholtz-Institute-Ulm (HIU), Ulm, Germany — [3]Karlsruhe Institute of Technology, Karlsruhe, Germany

Adsorption processes are an integral part of electrocatalysis. The use of extensively studied and structurally well-defined Au(111) single crystal electrodes allows for a better understanding of such processes. Formally, the formic acid oxidation (FAOR) is a relatively simple reaction as only one proton and two electrons have to be released to obtain CO_2. However, the reaction exhibits a self-inhibition on Au(111) electrodes due to the blocking of active sites by strongly adsorbed formate indicated by a bell-shaped current density-potential curve [1]. Similarly, the addition of specifically adsorbing anions typically lowers the catalytic activity [2]. In contrast, certain adsorbates enhance the reaction by orders of magnitude. An intersting example is irreversibly adsorbed 4-mercaptopyridine forming a self-assembled monolayer (SAM) on Au(111) with the enhancement being related to the highly ordered SAM structure [3]. Several aspects of FAOR on gold single crystals will be discussed.

[1] L.A. Kibler, M. Al-Shakran, J. Phys. Chem. C 120 (2016) 16238*16245. [2] J.M. Hermann, A. Abdelrahman, T. Jacob, L.A. Kibler, Electrochim. Acta 385 (2021) 138279. [3] J.M. Hermann, H. Müller, L. Daccache, C. Adler, S. Keller, M. Metzler, T. Jacob, L.A. Kibler, Electrochim. Acta 388 (2021) 138547.

O 65.5 Wed 16:00 TRE/PHYS

Improving Carbon Dioxide Reduction Reactivity and Stability of Ultra-High Vacuum Prepared Cu(111) Surfaces by Crystalline Ultrathin Oxide Films — •Patrick Giesbrecht[1], Mauricio Prieto[1], Mikhail Belozertsev[1], Sergio Tosoni[2], Markus Heyde[1], Thomas Schmidt[1], Beatriz Roldan Cuenya[1], and Juan Navarro[1] — [1]Department of Interface Science, Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany — [2]Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Milano, Italy

Electrocatalytic carbon dioxide reduction reactions (CO2RR) to hydrocarbons at copper cathodes is one promising but complex route towards carbon capture and reutilization, where ultra-high vacuum (UHV) prepared single crystal electrodes can provide precise precatalyst structures to inform reactivity trends.[1,2] This work develops ultrathin crystalline Cu oxide phases and silica on Cu(111) electrodes under UHV conditions that activate Cu(111) toward hydrocarbon production and alter corrosion pathways under CO2RR conditions.[3] Ex situ and quasi-in situ UHV surface characterization as well as DFT computational analyses are presented that relate this altered reactivity and surface reconstruction to the pre-catalyst oxide structure, highlighting how atomic scale modifications of the surface can lead to macroscopic changes in electrocatalyst reactivity.

[1] Nguyen, K.C., et al. ACS Energy Lett. 9, 644-652 (2024). [2] Cheng, D., et al. Nat. Commun. 16, 4064 (2025). [3] Navarro, J.J., et al. J. Phys. Chem. C 124, 20942-20949 (2020).

O 65.6 Wed 16:15 TRE/PHYS

Mechanistic insights into liquid phase photocatalysis by studying the photoconversion of tertiary alcohols on titania — •Lucia Mengel, Elena Dietz, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85748 Garching, Germany

Titania loaded with a metal co-catalyst represents a well-studied model photocatalyst, e.g. for investigating hydrogen evolution. For the reaction of most alcohols, the use of a co-catalyst is vital to enable hydrogen evolution and thus a fully catalytic reaction. Tertiary alcohols, however, can be employed as probe for the intrinsic photoactivity of bare titania, as they are catalytically converted in a surface photoreaction discovered by us on single crystals in UHV. In this work, we focus on the applicability of these findings to a liquid phase environment by performing photoconversion of 2-methyl-2-butanol on titania nanopowder. We investigate the catalytic activity under water- and oxygen-free conditions and discuss the reaction behavior under consideration of the catalyst's properties.

O 65.7 Wed 16:30 TRE/PHYS

Simulation of catalytic and corrosive processes via Thermopotentiostat Molecular Dynamics — •Andreas Kretschmer[1], Samuel H. Mattoso[2], Jing Yang[2], Ahmed Abdelkawy[2], Mira Todorova[2], Jörg Neugebauer[2], and Markus Valtiner[1] — [1]Institute of Applied Physics, TU Wien, 1040 Wien, Austria — [2]Max-Planck-Insitute of Sustainable Materials GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

Ab Initio Molecular Dynamics (MD) provides valuable insights in dynamic processes at solid liquid interfaces on the electronic level. However, electrified interfaces have been inaccessible due to the interaction of charged systems with the periodic images. The recently developed thermopotentiostat enables the use of electric fields across a solid/liquid interface by a computational electrode. This electrode consists of a fixed layer of Ne atoms, which confines the water, and provides a compensating charge to keep the cell charge-neutral. The thermopotentiostat updates the charge of the Ne atoms after every MD step to drive the potential difference towards a desired value on average. The electronic minimization then distributes the charge, leading to a corresponding counter charge on the electrode surface, allowing the study of dynamic processes under the influence of electric fields. We apply this method to 2 model systems, one is a single Pt atom supported on two layers of graphene to study catalytic processes with water, the second is a Zn surface to study corrosion processes under H evolution at the interface in anodic and cathodic conditions.

O 65.8 Wed 16:45 TRE/PHYS

First Steps Matter Most: Free Energy Barriers of the Volmer Step in Hydrogen Evolution at Pt(111) — •Barbara Sumić, Karsten Reuter, and Nicolas G. Hörmann — Fritz-Haber-Institut der MPG, Berlin

The Hydrogen Evolution Reaction (HER) plays a central role in hydrogen-based energy conversion. The initial Volmer step, involving proton adsorption at the electrode interface, is key to understanding reaction kinetics and the influence of pH. Conventional approaches to estimating barrier heights based on density-functional theory are limited by the need for reduced system sizes and short simulation times, which restrict statistical sampling and hinder fully converged free-energy calculations, particularly when solvent reorganisation is involved.

Here, we explore machine-learned interatomic potentials (MLIPs) combined with enhanced sampling techniques to gain more comprehensive insight into the reaction mechanism and barrier for the Volmer step at Pt(111) in dynamically described interfacial water. Using data-driven collective variables, we aim to capture dynamic environmental and solvent effects that are difficult to access with standard sampling. We also investigate the applicability of the RAZOR (Response Analysis in z-ORientation) framework [1] for barrier calculations at applied bias to probe potential-dependent behavior.

Together, these approaches provide a pathway toward more consistent and physically grounded modelling of HER across different pH conditions.

[1] N. Bergmann *et al.*, Phys. Rev. Lett. **135, 146201 (2025).**

O 65.9 Wed 17:00 TRE/PHYS

Modeling chemical trends of Hydrogen adsorption and reactivity on Pt (111) surface alloyed with transition metals — •Bingxin Li, Jing Yang, Mira Todorova, and Jörg Neugebauer — MPI for Sustainable Materials, Düsseldorf, Germany

Platinum's near-optimal hydrogen binding energy, as dictated by the Sabatier principle, makes it the benchmark electrocatalyst for the hydrogen evolution reaction (HER). Alloying Pt with transition metals (TMs) is known to enhance catalytic activity, though the underlying mechanisms vary substantially across alloying elements. Here, we employ ab initio molecular dynamics to investigate hydrogen adsorption on Pt (111) surfaces whose top layer is alloyed with different TMs at varying concentrations. By generating lateral free-energy maps of chemisorbed hydrogen and combining them with nudged-elastic-band calculations, we determine the Tafel-step barriers of HER. We find that Tafel-step kinetics improves as on-top-site hydrogen binding is weakened on alloyed Pt surfaces. Electronic-structure analyses, coupled with a machine-learning model, reveal that on-top-site hydrogen binding energy (key HER activity descriptor) can be quantitatively predicted from d-band centre characteristics. These results link compositional tuning of Pt-based alloys to predictable changes in HER-activity, offering a rational design route for next-generation hydrogen evolution catalysts.

O 65.10 Wed 17:15 TRE/PHYS

Atomic-scale insights into enhanced oxygen reduction on Au(100) in alkaline solutions from ab initio molecular dynamics simulations — •Alexander von Rueden[1,2], Mal-Soon Lee[1], Vassiliki-Alexandra Glezakou[3], Roger Rousseau[3], and Manos Mavrikakis[2] — [1]Pacific Northwest National Laboratory, Richland, WA, USA — [2]University of Wisconsin-Madison, Madison, WI, USA — [3]Oak Ridge National Laboratory, Oak Ridge, TN, USA

The unusually high 4e$^-$ oxygen reduction reaction (ORR) activity of the Au(100) surface in alkaline environments has motivated numerous experimental and theoretical studies. Even so, atomic-scale insights into the origin of its high activity remain elusive, with static density functional theory (DFT) calculations under vacuum typically proving insufficient. Here, we instead developed atomistic models of Au(100)-water interfaces featuring fully explicit neutral or alkaline solvent environments. Using these models, we performed DFT-based ab initio molecular dynamics (AIMD) simulations to probe the dynamic atomic structures of ORR intermediates adsorbed on Au(100) in different solvent environments. Additionally combining the Blue moon ensemble enhanced sampling technique with AIMD, we demonstrated a low free energy barrier for O_2 dissociation and hydrogenation by water molecules to yield OH* on Au(100), which is consistent with its high experimental activity. Further, our alkaline simulations revealed these OH* products can form complexes with near-surface Na^+ cations, possibly leading to a more downhill reaction free energy.

O 65.11 Wed 17:30 TRE/PHYS

When Charged Intermediates Escape the Surface: Mass Transport Effects on the Electrocatalytic Selectivity of NO_3 Reduction — •Hemanth S. Pillai, Karsten Reuter, and Vanessa J. Bukas — Fritz-Haber-Institut der MPG, Berlin

Electrocatalytic selectivity is often discussed at the atomic level on the basis of the active site, while ignoring effects of mesoscopic mass transport. And yet, transport can critically shape selectivity through the exchange of surface-bound intermediates between the electrode and bulk electrolyte. We recently explored this mechanism, originally coined “desorption–re-adsorption–reaction” [1], by developing a simple model that couples the surface reaction kinetics with diffusion [2]. Here, we advance and extend our approach to describe charged intermediates such as nitrite (NO_2^-) during the electrochemical NO_3 reduction reaction. Ion transport augments a mean-field microkinetic model and is treated at varying levels of sophistication to capture different double layer characteristics. Our simulations show that both the applied potential and catalyst morphology uniquely shape NO_2^- selectivity within the desorption–re-adsorption–reaction mechanism. The emerging trends are in qualitative agreement with experiments, while distinctly different from those obtained for analogous charge-neutral intermediates during e.g. CO_2 reduction. This comparison shows how the double layer affects selectivity due to transport and allows to gauge the level of detail that is required in corresponding reaction models.

[1] H. Wang *et al.*, J. Phys. Chem. B **108**, 19413 (2004).

[2] H.H. Heenen *et al.*, Nature Catal. **7**, 847 (2024).

O 65.12 Wed 17:45 TRE/PHYS

Electroreduction of Acetone on PtRu Model Catalysts — •Robert Hübsch[1], Daniel Schauermann[1], Pankaj Kumar Samal[2], Jan Škvára[2], Frederike Jäschke[1], Lesia Piliai[2], Tomáš Skála[2], Nataliya Tsud[2], Josef Mysliveček[2], Olaf Brummel[1], Yaroslava Lykhach[1], and Jörg Libuda[1] — [1]Interface Research and Catalysis, ECRC, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany — [2]Charles University, Faculty of Mathematics and Physics, Department of Surface and Plasma Science, V Holešovičkách 2, Prague, 18000, Czech Republic

The isopropanol/acetone system functions as an electrochemically active liquid organic hydrogen carrier (EC-LOHC). In this context, direct electrochemical charging is particularly attractive but requires highly active and selective catalysts. In this study, we investigated acetone reduction on well-defined PtRu model surface alloys. Our approach combined cyclic voltammetry (CV), ex-situ emersion synchrotron radiation photoelectron spectroscopy (SRPES), electrochemical infrared reflection absorption spectroscopy (EC-IRRAS), and differential electrochemical mass spectrometry (DEMS). The PtRu/Ru(0001) surface exhibits low intrinsic catalytic activity; but can be activated through a dealloying procedure. This treatment produces small Pt aggregates on a rough Ru support. In contrast, the PtRu/Ru(10 10) surface, characterized by a lower coordination number, does not require dealloying. Unlike Pt(110), which predominantly produces propane, the PtRu model catalysts selectively yield the target product isopropanol.