O 58: Solid-Liquid Interfaces: Reactions and Electrochemistry II

Time: Wednesday 10:30–13:00 Location: H4

O 58.1 Wed 10:30 H4

Step Bunching Instability and its Effects in Electrocatalysis on Platinum Surfaces — •Francesc Valls Mascaró[1], Marc T. M. Koper[2], and Marcel J. Rost[3] — [1]Departement of Physical Chemistry, University of Innsbruck — [2]Leiden Institute of Chemistry, Leiden University — [3]Huygens-Kamerlingh Onnes Laboratory, Leiden Institute of Physics, Leiden University

The atomic-scale surface structure plays a major role in the electrochemical behaviour of a catalyst. The electrocatalytic activity towards many relevant reactions, such as the oxygen reduction reaction on platinum, exhibits a linear dependency with the number of steps until this linear scaling breaks down at high step densities. In this work we show, using Pt(111)-vicinal surfaces and in situ electrochemical scanning tunnelling microscopy, that this anomalous behaviour at high step densities has a structural origin and is attributed to the bunching of closely spaced steps. While Pt(554) presents parallel single steps and terrace widths that correspond to its nominal, expected value, most steps on Pt(553) are bunched. Our findings challenge the common assumption in electrochemistry that all stepped surfaces are composed of homogeneously spaced steps of monoatomic height and can successfully explain the anomalous trends documented in the literature linking step density to both activity and potential of zero total charge [1].

[1] F. Valls Mascaró, M. T. M. Koper, and M. J. Rost, Nat. Catal. 7, 1165 (2024)

O 58.2 Wed 10:45 H4

ALD coatings on 1D and 3D structures for electrochemical applications — •Siow Woon Ng — Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

Atomic layer deposition (ALD) utilizes self-limiting surface reactions to construct ultrathin films layer by layer. Among many deposition techniques, ALD uniquely offers conformal deposition and excellent coating thickness control. Hence, the technique is particularly attractive for depositing structures with complex geometries, such as spheres, foams, 1D nanostructures, and 3D structures. This presentation discusses the preparation of 1D nanostructure and 3D-printed structures, followed by ALD inorganic and semiconductor coatings on these scaffolds. The influence of surface properties on the ALD coatings, and how the coatings enhance the electrical, mechanical, optical, and chemical properties or introduce new functionalities to the host structures will be presented. In particular, we will demonstrate that thin coatings in nanometer thicknesses are optimized for sensing and photo- and electrocatalytic applications.

O 58.3 Wed 11:00 H4

echemdb - a Database for Electrochemical and -catalytic Data of Metal Single-Crystal Electrodes — •Johannes Hermann[1], Julian Rüth[2], Nicolas G. Hörmann[3], Nicolas Bergmann[3], Karsten Reuter[3], Timo Jacob[1], and Albert K. Engstfeld[1] — [1]Institute of Electrochemistry, Ulm, DE — [2]Julian Rüth GmbH, DE — [3]Fritz-Haber-Institut der MPG, Berlin, DE

Over the last decades and still today, electrochemical and catalytic studies on metal single-crystal electrodes form the basis of our fundamental understanding of atomic-scale processes on such electrodes and more complex catalyst materials, such as supported nanoparticles, found in applications. So far, experimental data and information on the data are mostly only available as traces and plain text in published works, which limits the FAIR (findable, accessible, interoperable, and reusable) use of the data in further experimental and theoretical works. To mitigate this issue, we present an open-source community approach to store such data and metadata in a structured way in a dedicated database, using the frictionless framework combined with a simple metadata standard. We illustrate the challenges associated with setting up such a system for the underlying data types, highlight tools that allow recovering data from published works and storing new data from experimental and theoretical works similarly. We demonstrate that these tools are equally applicable to other research areas. Finally, we provide some examples of using such a database in daily routines (finding and comparing experimental and theoretical data) and system-specific studies (reusability).

O 58.4 Wed 11:15 H4

The direct comparison of Pt and Cu particles on a TiO_2 photocatalyst in the hydrogen evolution reaction — •Lucia Mengel[1], Pieter van den Berg[2], Martin Tschurl[1], Neill Goosen[2], and Ueli Heiz[1] — [1]Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany — [2]Department of Process Engineering, Stellenbosch University, Banghoek Rd, Stellenbosch Central, Stellenbosch, 7599, South Africa

Anatase TiO_2 loaded with a metal co-catalyst is a well-known photocatalyst for hydrogen evolution. Fundamental studies on this system often employ photoreforming of alcohols as model reaction, utilizing noble metals such as platinum as a co-catalyst. The hole-mediated photooxidation reaction of the alcohol yields hydrogen next to valuable organic compounds such as aldehydes. Recent efforts aim at a replacement of platinum as co-catalyst by the more abundant and less expensive copper. In our work, we focus on the evolution of hydrogen on copper-loaded anatase by performing ethanol photoreforming in the liquid phase in oxygen- and water-free conditions. We study the hydrogen evolution reaction under excitation with UV-light and compare the photoactivity of the system to a common platinum-loaded catalyst and discuss possible scenarios for the interpretation of the reaction behavior.

O 58.5 Wed 11:30 H4

Microkinetic Modeling of the Hydrogen Evolution Reaction in Alkaline Conditions — •Dipam Patel and Georg Kastlunger — Technical University of Denmark

The Hydrogen Evolution Reaction (HER) in alkaline media is distinguished from the acidic case by the source of H. Significant theoretical work has investigated and diagnosed activity in acidic conditions, but this understanding does not necessarily correspond to alkaline. The implications of the stronger O-H bond in H2O compared to that in H3O+ are not yet fully understood. Using constant-potential electrochemical barriers, we developed a microkinetic model of alkaline HER activity on a selection of close-packed metallic surfaces. By accounting for the different potential responses of catalysts, we are able to reproduce the relative rates and tafel slopes seen in experiment. By relating the calculated activities to electrochemical descriptors, we show that the application of solely hydrogen binding descriptors, as in acidic HER, does not fully explain HER activity in alkaline.

O 58.6 Wed 11:45 H4

Predicting Charge Effects at 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]Laboratory of Theory and Simulation of Materials, EPFL, Lausanne

Computational modeling of electrified solid-liquid interfaces must account for capacitive contributions at potentials beyond the point of zero charge (PZC) [1]. These contributions can approximately be obtained from first-principles calculations at constant charge, employing a second-order Taylor expansion that involves the surface's free energy, the work function, and the interfacial capacitance at the PZC [2]. Machine learning (ML) surrogate models have already successfully been employed to predict the PZC energies at significantly reduced computational costs. Here, we extend this by presenting a ML model for work functions and apply this to two standard electrode modeling setups. By including the derivatives of the atomic forces with charge, we stabilize our model and predict the atomic effective charge. As an outlook, we show how this methodology could be utilized to run molecular dynamics simulations at charged conditions and electrochemical barrier calculations.

[1] N. Bergmann, N.G. Hörmann, and K. Reuter, J. Chem. Theory Comput. **19**, 8815 (2023).

[2] N.G. Hörmann and K. Reuter, J. Chem. Theory Comput. **17**, 1782 (2021).

O 58.7 Wed 12:00 H4

Dynamics at metal-water interfaces for catalytic hydrogenation — Tien Le[1], Shoutian Sun[1], and •Bin Wang[1,2] — [1]University of Oklahoma, Norman, Oklahoma, US — [2]Max Planck Institute for

Sustainable Materials GmbH, Düsseldorf, Germany

The presence of water has been shown to enhance hydrogenation of polar chemical functional groups, such as C=O and N=O bonds, through proton shuttling. To demonstrate such rather sophisticated reaction pathways, explicit solvent models with dynamic change of local solvent structures should be considered. Beyond what we reported previously for water-promoted C=O hydrogenation in furfural, in this presentation, we will highlight how the dynamics of the local water structures within the first solvation shell may affect the hydrogenation kinetics. Specifically, we find that the activation barriers correlate well with some collective variables that determine the local configuration and relative positions of surface hydrogen and water. We further show that such dynamics of the metal-water interfaces can be manipulated by different approaches to tune the reaction kinetics. Our findings thus provide fundamental insights of this dynamic transformation at the solid-liquid interface and its impact on catalytic activity and selectivity.

O 58.8 Wed 12:15 H4

Rough Choice: Comparing 1- and 2D Representations of Electrocatalyst Morphology in Multiscale Models — •Hemanth S. Pillai, Hendrik H. Heenen, Karsten Reuter, and Vanessa J. Bukas — Fritz Haber Institute der MPG, Berlin

While electrocatalyst morphology is often used to tune product selectivity in electrochemical systems, the precise mechanism underpinning this relationship still remains elusive. Recently, we highlighted the role of morphology impacting product selectivity through a "Desorption–Re-adsorption–Reaction" mechanism [*Nat. Catal.* 7, 847*854 (2024)]. In particular, the catalyst morphology steers the competition between two elementary steps: either the desorption and diffusion of an intermediary byproduct or its re-adsorption and further reaction. Within such a model, morphology is captured in an effective manner via a surface roughness descriptor, however some systems may require a more explicit representation of the catalyst morphology. To assess this we employ a transport coupled kinetic model and systematically improve the representation of the catalyst from an effective one-dimensional descriptor to an explicit two-dimensional catalyst morphology. We find that deviations between the two descriptions are governed by morphological and transport parameters, i.e. diffusion length, particle size, shape, and interparticle distance. To conclude, we demonstrate that detailed morphological descriptions are only necessary within a narrow parameter window, thus providing guidance for selecting appropriate representations.

O 58.9 Wed 12:30 H4

Atomistic Simulation of Platinum-Water Interface: Deep Potential Molecular Dynamics (DP-MD) — •Muhammad Saleh[1], Alexander Lozovoi[2], Riccardo Martina[1], Matthew Darby[2], Clotilde Cucinotta[2], and Marialore Sulpizi[1] — [1]Theoretical Physics of electrified liquid-solid interface, Ruhr-University Bochum, Germany — [2]Department of Chemistry, Imperial College London, UK

The interaction between platinum surfaces and water holds significant importance due to its extensive applications in catalysis and electrochemical reactions. However, investigating these interactions at the atomistic level presents considerable experimental challenges. Moreover, accurately modeling such systems demands a substantial number of atoms (exceeding 1000), which can impede computational efficiency, particularly when using high-quality methods. In this study, we utilize the capabilities of machine learning potentials, specifically Deep Potential Molecular Dynamics (DP-MD), to overcome these challenges and achieve comprehensive simulation trajectories. This approach allows for an in-depth analysis, providing valuable insights into the surface properties.

O 58.10 Wed 12:45 H4

Preparation and Electrochemical Characterization of Metal Bicrystal Electrodes — •Nadine Wölfel, Albert K. Engstfeld, and Timo Jacob — Institute of Electrochemistry, Ulm, DE

The activity of a metal-based electrocatalyst strongly depends on its structural properties, where grain boundaries (GB) can play a significant role. One approach to study the impact of GBs is by varying the grain size of a material, which changes the GB density. In our study we aim at gaining fundamental insights into the atomic scale electrochemical and -catalytic processes at a GB, separating two surfaces with specific crystallographic orientation. We demonstrate how such electrodes can be prepared from Pt wires using the controlled atmosphere flame fusion method [1]. Here, poly-oriented single crystals are formed from two wires, crystallizing as a poly-oriented bicrystal from a common melt. By carefully polishing the poly-oriented crystal along the surface orientation of interest, a planar bicrystal surface with a single GB can be created. The structural properties of the prepared electrodes are determined by Laue X-ray diffraction, scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD) spectroscopy. Electrochemical measurements, such as cyclic voltammetry (CV) are presented, which, based on the features in the CV, provide insights into the available facets and defects. The local electrocatalytic activity of the GB can be elucidated by scanning electrochemical microscopy (SECM) measurements.

[1] FM Schuett et al., Angewandte Chemie, 132 (2020) 13348-13354