O 65: Solid-Liquid Interfaces: Reactions and Electrochemistry III

Time: Wednesday 15:00–17:45 Location: H6

O 65.1 Wed 15:00 H6

Potential Pulsed CO2 Reduction Reaction on Polycrystalline Copper Electrodes Studied with Operando Plasmonic Interface Analysis — •Hagen Übele, Katharina Krischer, and Moritz Josef Feil — Chemische Physik fern des Gleichgewichts Technische Universität München, München, Deutschland

This contribution highlights the use of polished polycrystalline Cu electrodes for the CO2 reduction reaction. By applying time-periodic potential pulses, long-term stability and enhanced selectivity towards hydrocarbon products like methane, ethylene, and ethanol are achieved. These methods rival the performance of nano-structured oxide-derived catalysts or Cu single crystal electrodes while improving electrode longevity.

Operando monitoring is conducted using a plasmonic interface analysis technique with a time resolution of 100 ms. This enables real-time tracking of the Cu oxidation state and the nano-morphology of the electrode surface during potential pulses. The study demonstrates that optimized pulsing protocols can significantly extend the stability of Cu electrodes without the need for pre-manufactured nanostructures.

O 65.2 Wed 15:15 H6

Au(111) in the Ionic Liquid [MPPip][TFSI]: Corrosion, Reconstruction and Other Surface Restructuring Phenomena — •Maren-Kathrin Heubach[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.

In fundamental electrochemistry, Au single-crystals are a good benchmarking standard because of the ease of their preparation and high chemical stability.[1-4] Nevertheless, the morphological stability of Au under measurement conditions is rather limited. In this study, we utilize *in situ* scanning tunnelling microscopy (STM) to investigate the stability of a Au(111) electrode in the ionic liquid *N*-methyl-*N*-propylpiperidinium bis(trifluoromethane)sulfonimide ([MPPip][TFSI]). We will provide an overview of the observed surface structures and the corresponding potential ranges in which they remain stable.

[1] J. M. Hermann, *et al.* Electrochim Acta 2020, 347, 136287. [2] M.-K. Heubach, *et al.* ChemElectroChem 2022, 9, e202200722. [3] X. Hu, *et al.* Sci. Bull. (Beijing) 2015, 60, 877-883. [4] L. A. Kibler, *et al.* in Encyclopedia of Solid-Liquid Interfaces, Elsevier, 2024, pp. 426-449.

O 65.3 Wed 15:30 H6

The relationship between composition, structure and activity of well-defined Pt-Ru alloys during electroreduction of acetone — •Robert Hübsch[1], Pankaj Kumar Samal[2], Frederike Jäschke[1], Tomáš Skála[2], Nataliya Tsud[2], Josef Mysliveček[2], Olaf Brummel[1], Yaroslava Lykhach[1], and Jörg Libuda[1] — [1]Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — [2]Department of Surface and Plasma Science, Charles University, Prague, Czech Republic

The isopropanol/acetone couple can be used as an electrochemically active liquid organic hydrogen carrier (EC-LOHC). PtRu-based alloys are the state-of-the-art catalysts for the electrooxidation of isopropanol. We have investigated the reverse reaction, i.e. electrochemical reduction of acetone, on well-defined PtxRu1-x alloys by means of cyclic voltammetry (CV), synchrotron radiation photoelectron spectroscopy (SRPES) coupled with an ex-situ emersion electrochemical cell, electrochemical infrared reflection absorption spectroscopy (EC-IRRAS), and differential electrochemical mass spectrometry (DEMS). In a systematic study, we established structure-activity relationships for well-ordered PtxRu1-x alloys and surfaces subjected to dealloying in pure and acetone-containing electrolyte. We found that the active state of the catalyst corresponds to the presence of ultra-small Pt aggregates supported on partially oxidized Ru(0001). While Pt(110) forms propane as reduction product, the dealloyed catalysts form the target product isopropanol and suppress propane formation.

O 65.4 Wed 15:45 H6

Electrochemical XPS for probing the electrified solid-liquid interface of tungsten carbide — Christoph Griesser, Toni Moser, Sergio Diaz-Coello, and •Julia Kunze-Liebhäuser — Institute of Physical Chemistry, University of Innsbruck, Innsbruck, Austria

A profound understanding of the solid/liquid interface is central in electrochemistry and electrocatalysis, as the interfacial properties determine the electro-reactivity of the system. This study reveals the in-situ surface chemistry evolution of tungsten carbide (WC) powders during electrochemical polarization. WC is known for its platinum-like properties and its high activity towards the hydrogen evolution reaction (HER), but prone to passivation upon air or electrolyte exposure. It is found that the unpreventable surface passivation layer on WC dissolves into the electrolyte under HER conditions, which explains the typically measured high HER electrocatalytic activity of this compound material. The electrochemical (EC-)XPS data provide profound chemical understanding of the electrode/electrolyte interface during operation. This enables fundamental contribution to bottom-up electrocatalyst development, and thus to the advancement of energy conversion and storage technologies.

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O 65.5 Wed 16:00 H6

Degradation of TiO$_2$/Pt catalyst interfaces during operation — •Sergej Levashov[1], Tim Rieth[1,2], Ian D. Sharp[1,2], and Johanna Eichhorn[1] — [1]TUM School of Natural Sciences — [2]Walter Schottky Institut

Photoelectrochemical (PEC) water splitting is a promising approach for generating green fuels. However, photosystems often degrade in the harsh chemical environment required for PEC water splitting. To overcome this limitation, understanding the starting point of the degradation and the exact degradation mechanism at the nanoscale is required. In this work, we study TiO$_2$ thin films grown by atomic layer deposition (ALD) combined with Pt catalyst layers, deposited by sputtering and two different ALD processes, by in-situ/operando atomic force microscopy and elucidate their changes in topography and mechanical properties under operation conditions. The main difference between the Pt is the growth mechanics: while sputtering yields a continuous film, the ALD growth results in Pt islands. On the macroscale, the ALD grown Pt catalysts show similar onset potentials and saturation current densities as the sputtered ones. At the nanoscale, we observe that the ALD Pt films are more stable than sputtered Pt under operation conditions. Complementary, we performed X-ray photoelectron spectroscopy (XPS) before and after PEC operation to reveal chemical changes. Overall, ALD grown Pt catalysts improve the system performance compared to sputtered Pt. These measurements provide important insights into the underlying reaction mechanism and the role of surface restructuring and delamination of catalyst interfaces.

O 65.6 Wed 16:15 H6

TiO2 passivation of GaInP(100) surfaces — •David Ostheimer[1], Julius Kühne[2,3], Sahar Shekarabi[1], Agnieszka Paszuk[1], Mohammad Amin Zare Pour[1], Ian D. Sharp[2,3], Wolfram Jägermann[4], and Thomas Hannappel[1] — [1]TU Ilmenau, Inst. of Physics, Fundamentals of Energy Materials, Ilmenau, Germany — [2]TU Munich, Walter Schottky Institute, Garching, Germany — [3]TU Munich, Physics Department, TUM School of Nat. Sciences, Garching, Germany — [4]TU Darmstadt, Surface Science Lab, Darmstadt, Germany

GaInP is widely used in III-V-based photoelectrochemical devices as a top photoabsorber or charge-selective contact, achieving high solar-to-fuel conversion efficiencies. To enhance stability under HER conditions, a thin TiO2 protection layer can be applied. This study investigates the electronic structure of the TiO2/GaInP(100) interface. TiO2 was deposited via atomic layer deposition (ALD) on p-type GaInP(100) grown on GaAs(100) substrates. Two surfaces were prepared: a phosphorus-rich (P-rich) (2x1)-like surface transferred contamination-free under ultra-high vacuum (UHV) and a naturally oxidized surface. X-ray and UV photoelectron spectroscopy revealed a slightly thinner interfacial oxide in the UHV-transferred sample. Initial ALD cycles formed an oxide nearly stoichiometric to the native oxide, but both samples exhibited strong Fermi level pinning, resulting in similar band alignments. These findings highlight the influence of initial oxides on interface control in III-V semiconductors.

O 65.7 Wed 16:30 H6

Influence of pH and Electrolyte Flow on the Oxidation of Ni anodes at High Overpotentials — •Justus Leist[1], Timo Jacob[1,2,3], and Albert K. Engstfeld[1] — [1]Institute of Electrochemistry, Ulm, Germany — [2]Helmholtz-Institute-Ulm (HIU), Ulm, Germany — [3]Karlsruhe Institute of Technology, Karlsruhe, Germany

The electrocalalytic splitting of aqueous electrolytes is typically impeded by the sluggish kinetics of the oxygen evolution reaction (OER). Ni-based catalysts are considered as cost-effective alternatives to the currently used rare metal oxides, such as Ir or Ru. While the fundamental properties of Ni have been studied intensively usually at or around the onset potential for the OER, here we study the OER activity at high overpotentials, which are more closely related to application.

The OER characteristics are studied by means of cyclic voltammetry and polarization curves using Ni electrodes in alkaline solutions. Depending on the experimental conditions, electrolyte pH and flow, the current voltage traces show several features at high overpotentials, which can be attributed to the pH-dependent change in OER kinetics. Based on additional in-situ Raman spectroscopy and electrochemical quartz crystal microbalance measurements we discuss possible structures formed and the degradation of the Ni electrodes under these conditions.

O 65.8 Wed 16:45 H6

DFT Study of Aldehyde Oxidation and Hydrogen Evolution on Flat and Stepped Gold Surfaces — •Samuel Mattoso[1], Stefan Wipperman[1,2], Mira Todorova[1], and Jörg Neugebauer[1] — [1]Max-Planck-Institut für Nachhaltige Materialien, Max-Planck-Straße 1, 40237 Düsseldorf — [2]Philipps-Universität Marburg, Renthof 5, Marburg, 35032, Germany

Significant investments are being made in the development of greener industrial processes, with heterogeneous electrocatalysis playing a major role. Gold is known as a catalyst, which selectively oxidizes aldehydes to carboxylic acid. It may also catalyze the hydrogen evolution reaction (HER). These chemical reactions take place at the solid-liquid interface, where the role of step sites, pH, adsorption of intermediates, solvation and applied bias are largely unknown but may be relevant to understand in order to improve performance. We employ DFT simulations to provide mechanistic insights into this system, by probing the interaction of Au(111) and Au(331) surfaces with H, OH and acetaldehyde. The adsorption energies and work function changes as a function of H and OH coverage for different observed patterns will be reported for the two surfaces. In addition, we find that surface imperfections such as step edges are essential for the HER and aldehyde oxidation to proceed, as they dissociatively bind the aldehyde, leading to adsorbed H.

O 65.9 Wed 17:00 H6

On the pH-dependence of the H_{upd} peak in cyclic voltammograms of Pt-group nanoparticles — •Hedda Oschinski[1,2], Simeon Beinlich[1,2], Karsten Reuter[1,2], and Nicolas Hörmann[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Technische Universität München, München

Understanding the electrochemical behavior of hydrogen adsorption at Pt-group metal surfaces, particularly in the context of non-well-defined nanoparticle surfaces, is crucial for advancing electrocatalytic applications such as the hydrogen evolution reaction (HER). To this end, we provide insights into the non-Nernstian pH shifts observed for underpotential deposited H_{upd}-like cyclic voltammetry (CV) peaks on Pt, Ir, Pd, and Rh nanoparticles. Utilizing density-functional theory, we explore the potential-dependent stability of H and OH adsorbates at undercoordinated surface sites, emphasizing the role of non-ideal electrosorption valencies in these shifts. This identifies direct H-OH replacement as predominant mechanism behind the CV peaks and reveals a primary influence of partial charge transfer. The theoretical predictions show good agreement with experimental observations across various Pt-group metals, even over various surface coordinations, and provide insights into cation-specific effects at Pt across the entire pH scale. This work not only clarifies the origin of the H_{upd}-like peak shift within the water stability region, but also suggests the interfacial capacitance as a main descriptor for cation effects in the HER, paving the way for more detailed analyses of cation type, concentration, and interfacial solvent structure.

O 65.10 Wed 17:15 H6

From model to realistic copper sulfide electrocatalyst — •Roser Fernandez Climent, Jesus Redondo, and Martin Setvín — Charles University, Prague, Czech Republic

Copper sulfide is a widely studied material in electrocatalysis. In this study, we synthesized copper sulfide thin films electrochemically under inert conditions, enabling precise control of material properties and minimizing contamination risks. The films were transferred in-vacuum for surface characterization using X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and scanning transmission electron microscopy (STEM).

O 65.11 Wed 17:30 H6

Stability of Pd-Rh core-shell electrocatalysts supported on Co3O4(111) in alkaline environment — Alexander Simanenko[1], Jan Škvára[2], Pankaj Kumar Samal[2], Evanie Franz[1], Robert Hübsch[1], Tomáš Skála[2], Nataliya Tsud[2], Sascha Mehl[3], Viktor Johánek[2], Josef Mysliveček[2], Olaf Brummel[1], •Yaroslava Lykhach[1], and Jörg Libuda[1] — [1]Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — [2]Charles University, Prague, Czech Republic — [3]Elettra-Sincrotrone Trieste SCpA, Basovizza-Trieste, Italy

The electronic metal-support interaction (EMSI) is considered as an efficient strategy to stabilize the noble metal nanoparticles against sintering, but its consequences under the electrochemical conditions remain elusive. We investigated the effect of the EMSI on the stability of bimetallic Pd@Rh and Rh@Pd core@shell nanoparticles supported on well-ordered Co3O4(111) films in alkaline electrochemical environment by means of synchrotron radiation photoelectron spectroscopy (SRPES) coupled with ex-situ emersion electrochemical cell. We found that the EMSI promotes strong oxidation of Rh metal. The extent of Rh oxidation strongly depends on the specific metal/oxide interface configuration below the core@shell nanoparticles. Our study suggests that decoupling the Rh metal and the Co3O4(111) substrate by constructing the Pd/Co3O4(111) interface below Pd@Rh core@shell nanoparticles reduces the effect of the EMSI and improves the stability of the electrocatalyst toward oxidation.