O 21: Poster Session II: Solid-liquid interfaces: Reactions and electrochemistry I

Time: Monday 13:30–15:30 Location: P

O 21.1 Mon 13:30 P

Stable and cost-efficient core-shell catalysts for enhanced acidic oxygen evolution–a first principles approach — •Yonghyuk Lee[1,2], Christoph Scheurer[1,2], and Karsten Reuter[1,2] — [1]Technical University Munich, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Most commercial oxygen evolution reaction (OER) catalysts in proton exchange membrane electrolyzers contain precious IrO_2 due to its high catalytic activity and favorable stability in acidic electrolytes. IrO_2 supported on rutile TiO_2 has been utilized in order to reduce the price without sacrificing activity. However, thin IrO_2 films seem generally not stable on titania and a gradual dewetting of the film takes place.

In the present work, we use density-functional theory (DFT) calculations to further scrutinize the feasibility of encapsulating a cheap rutile TiO_2 core with thin coherent IrO_2 or RuO_2 films as potentially stable catalyst materials for water electrolysis. We calculate facet-resolved interface formation energies and works of adhesion to quantify the effect of interfacial strain, the stability of the oxide interfaces and their strong directional dependence. A wetting tendency results only for some low-index facets under experimental gas-phase synthesis conditions. Surprisingly, *ab initio* thermodynamics indicates a significantly better wetting stability for lattice-matched RuO_2 films in more oxidizing conditions such as under OER operation. The calculations also predict an enhanced OER activity of epitaxial RuO_2/TiO_2 core-shell particles. [1] D. Opalka *et al.*, ACS Catal. **9**, 4944 (2019).

O 21.2 Mon 13:30 P

Interaction of Small Alcohols with TiO_2 studied by Vibrational Sum Frequency Spectroscopy — •Anupam Bera, Denise Bullert, and Eckart Hasselbrink — Fakultät für Chemie, Universität Duisburg-Essen, D-45117 Essen, Germany

The interaction of alcohols with oxide surfaces such as TiO_2 attracts interest as the oxidation of these species is of large industrial relevance. The interaction of TiO_2 with alcohols has attracted less interest although oxidation of the latter is of large industrial relevance.Surface-sensitive vibrational sum frequency spectroscopy (vSFS) has been utilised to study the adsorption chemistry of small alcohols namely methanol, ethanol, 1-propanol and 2-propanol on TiO_2 thin films under vapour pressure conditions at which a condensed molecular film is maintained. The vSF spectra in the C-H region reveal that methanol and ethanol adsorb both molecularly and dissociatively, while 1-propanol and 2-propanol are solely detected in molecular form. The different adsorption behaviour suggests that the extend of dissociation decreases from methanol to propanol. Moreover, polarisation analysis of the spectra reveals that the methyl groups are preferentially oriented with their symmetry axis pointing in a direction close to the surface normal for methanol, ethanol and 1-propanol. That seems not to be the case for 2-propanol.

O 21.3 Mon 13:30 P

Cooperative Effect of Carbonaceous Material with Water Enhances the Growth of SiOx on Si — •Rémi Dupuy[1], Clemens Richter[1], Pip CJ Clark[2], Rossella Yivlialin[2], Michael J Sear[2], Marco Favaro[2], Robert Schlögl[1], David E Starr[2], and Hendrik Bluhm[1] — [1]Fritz Haber Institute of the Max Planck Society, D-14195 Berlin, Germany — [2]Institute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, D-14109 Berlin, Germany

We have investigated the influence of carbonaceous materials on the growth of SiOx layers on Si under dry conditions and in the presence of water and/or water vapor. Dip-and-pull experiments were carried out using the SpAnTeX endstation using tender X-rays (3 keV) from the KMC-1 beamline at BESSY II. Si wafers (n-doped) cleaned using the RCA-method exhibited initially a uniform SiOx film thickness of the order of 1 nm, as determined from Si 2p and Si 1s spectra.

In the dip-and-pull experiments the Si wafers were partly immersed into pure water or octanoic acid, as well as mixtures of water and stearic or octanoic acid. The XPS data clearly show a correlation between the thickness of the SiOx layer and the amount of carbon present at the surface. However, this effect is only observed in experiments where the Si wafer was exposed to both water and carbonaceous species. Oxide growth was not observed for experimental conditions where the SiOx/Si surface was exposed to only either water or carbonaceous material. These results thus point to a cooperative effect between water and carbonaceous species that induces SiOx growth.

O 21.4 Mon 13:30 P

2D water structures on low index Pt surfaces — •Alexandra C. Dávila[1], Nicolas G. Hörmann[1,2], Thorben Eggert[1], and Karsten Reuter[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany — [2]Chair of Theoretical Chemistry and Catalysis Research Center, Technische Universität München, Germany

It is a common approximation in *ab initio* calculations of electrocatalytic metal-water interfaces, to use static ice-like water adlayers to represent the first solvent shell on the electrode [1,2]. To date, these ice-like layers are typically created manually and in an *ad-hoc* fashion. To extend this to a better defined protocol that also allows to generate a larger statistical ensemble of ice-like adlayers, we here develop a versatile construction recipe leveraging lattice-matching algorithms in combination with a database of metastable 2D water polymorphs. We illustrate the approach for Pt (100), (110) and (111) surfaces, and systematically compute the energetics, as well as geometric and electronic properties of the created structures using density-functional theory. Comparison to corresponding literature data from full *ab initio* molecular dynamics simulations allows to gauge the accuracy of the prevalent single ice-adlayer approximation and assess ice-ensemble averaging as a controlled and cost-efficient proxy.

[1] S. Schnur *et al.*, New J. Phys. **11**, 125003 (2009).

[2] J. Rossmeisl *et al.*, Chem. Phys. Lett **466**, 68 (2008).

O 21.5 Mon 13:30 P

Ni modified Fe3O4(001) surface as a simple model system for understanding the Oxygen Evolution Reaction — •Francesca Mirabella[1,2], Matthias Müllner[2], Thomas Touzalin[3], Michael Schmid[2], Marc Koper[3], Gareth Parkinson[2], and Ulrike Diebold[2] — [1]Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany — [2]TU Wien, Vienna, Austria — [3]Leiden Institute of Chemistry, Leiden University, The Netherlands

Electrochemical water splitting is an environmentally friendly technology to store renewable energy in the form of chemical fuels. Among the Earth-abundant first-row transition metal-based catalysts, mixed Ni-Fe oxides have shown promising performance for effective and low-cost catalysis of the oxygen evolution reaction (OER) in alkaline media, but the synergistic roles of Fe and Ni cations in the OER mechanism remain unclear. In this work, we report how the Ni-modification changes the reactivity of a model iron oxide catalyst using a combination of surface science techniques in ultra-high-vacuum (LEED, XPS, LEIS, STM), AFM in air, and electrochemical methods (CV and EIS) in alkaline media. A significant improvement in the OER activity is observed when the surface presents an Fe:Ni ratio in the range 20-40%, which is in good agreement with what has been observed for powder catalysts. EIS suggests that the OER precursor species observed on the clean and Ni-modified surfaces are similar, but form at lower overpotentials when the surface Fe:Ni ratio is optimized. We propose that the well-defined Fe3O4(001) surface can serve as a model system for understanding the OER mechanism on mixed Fe/Ni oxides.

O 21.6 Mon 13:30 P

Active-Site Computational Screening: Role of Structural and Compositional Diversity for the Electrochemical CO2 Reduction at Mo Carbide Catalysts — •Haobo Li[1] and Karsten Reuter[1,2] — [1]Technical University of Munich, Lichtenbergstr. 4, D-85747 Garching, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany

The surfaces of compound catalyst materials generally exhibit a wide range of geometric and compositional motives that could act as active sites. We address this inherent complexity by extending computational materials screening over a diverse set of such sites. For the electrochemical CO2 reduction reaction (CO2RR) at molybdenum carbides, extensive density functional theory (DFT) calculations for key reaction intermediates at these sites show that di*ering adsorption modes break many of the scaling relations known to hold across transition metals. Despite the resulting inherently rich reduction chemistry, clear trends emerge. Notably, this includes a product selectivity governed by the metal/carbon ratio of the active site. The trend toward methanol formation for C-containing active sites mirrors thermal heterogeneous CO2 activation and suggests a shift of focus toward more C-rich carbides for CO2RR to methanol [1].

[1] H. Li and K. Reuter, ACS Catal. 10, 11814 (2020).

O 21.7 Mon 13:30 P

When to stop the count? - Time scales of liquid water on metal substrates — •Thorben Eggert, Nicolas G. Hörmann, and Karsten Reuter — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

The detailed arrangement of water layers at a metal surface plays a crucial role for a plethora of different properties concerning the solid-liquid interface like the work function or the adsorption energy [1]. However, reliably determining this arrangement through predictive-quality simulations generally requires computationally most demanding *ab initio* molecular dynamics (MD) simulations with explicit water. In practice, the high costs then often allow to acquire trajectories only over limited simulation times and in simulation cells of limited size.

We examine this problem with reactive force field MD simulations, collecting data over extended time scales of a few nanoseconds. As a test system, we study water films on Pt(111) for various thicknesses. While running averages look highly converged on the limited time scale of *ab initio* MD simulations, significant differences are found when comparing them to results obtained on the nanosecond time scale. This showcases the difficulty of generating a representative subset of the relevant configurational space in a controlled fashion.

[1] A. Groß *et al.*, J. Electrochem. Soc. **161**, E3015-E3020 (2014).

O 21.8 Mon 13:30 P

Boosting Hydrogen Evolution Reaction Activity by Lateral Electrode Structuring — •Thomas L. Maier[1], Matthias Golibrzuch[2], Tina Angerer[1], Markus Becherer[2], and Katharina Krischer[1] — [1]Nonequilibrium Chemical Physics, Technical University of Munich, Garching, Germany — [2]Nanoelectronics, Technical University of Munich, Munich, Germany

Producing solar fuels with devices based on metal-insulator-semiconductor (MIS) interfaces is a very promising future technology for a renewable energy economy. The semiconductor part of such hybrid devices can provide efficient light absorption while the metal part facilitates fast reaction kinetics. However, in order to fulfil these two functionalities, the device requires patterning of the MIS interface.

We show that lateral structuring of silicon-based electrodes with well-defined gold arrays exhibits cooperative effects, i.e. strongly altered catalytic activities compared to bare metal surfaces. We demonstrate this with the hydrogen evolution reaction (HER) in acidic and alkaline medium and show that the HER rate scales with the interfacial area between the metal catalyst and the adjacent silicon oxide support. The rate of alkaline HER can be enhanced by an order of magnitude, which results in a very similar HER activity in alkaline and acidic medium. We explain this increase by a bifunctional mechanism at the metal/silicon oxide interface and argue that the lateral structuring changes locally the electric field, which increases the reaction rate of alkaline HER at the interface compared to the rate at the metal bulk.