

O 13: Solid-Liquid Interfaces I: Electrocatalysis and Photoelectrochemistry

Time: Monday 15:00–17:30

Location: H16

O 13.1 Mon 15:00 H16

Operando studies of well-defined Co oxide films for OER catalysis with surface X-ray diffraction — ●TIM WIEGMANN^{1,2}, FINN REIKOWSKI¹, FIRAS FAISAL⁴, MANON BERTRAM⁴, JAKUB DRNEC², FOUAD MAROUN³, JÖRG LIBUDA⁴, and OLAF MAGNUSSEN¹ — ¹Christian-Albrechts-Universität, 24118 Kiel, Germany — ²European Synchrotron Radiation Facility, 38000 Grenoble, France — ³Ecole Polytechnique, 91128 Palaiseau, France — ⁴Friedrich-Alexander-Universität, 91054 Erlangen, Germany

Transition metal oxides have recently received great attention as highly active, noble-metal-free catalysts for the oxygen evolution reaction (OER), which is a key reaction in electrochemical water splitting. To establish the relationship between their structure and catalytic activity, we conducted operando surface X-ray diffraction (XRD) studies on epitaxial Co₃O₄(111) thin films prepared by different methods. In addition to grazing incidence XRD, transmission surface XRD, a novel technique for fast capture of in-plane surface structure, was employed. For Co₃O₄ films electrodeposited as 3D islands on Au(111) and Au(100), a potential-dependent, reversible change of bulk lattice constant as well as the formation of a nm-thin skin layer can be observed over a wide potential range before the onset of OER. In comparison, smooth films grown in UHV on Ir(100) are structurally stable while exhibiting a much lower catalytic performance. The influence of the films' granular morphology on their behaviour in the pseudo-capacitive regime and catalytic activity will be discussed.

O 13.2 Mon 15:15 H16

In operando surface X-ray diffraction studies of Co oxide catalysts films for electrochemical water splitting — ●CANRONG QIU, FINN REIKOWSKI, OLAF MAGNUSSEN, and JOCHIM STETTNER — Christian-Albrechts-Universität zu Kiel, Institut für Experimentelle und Angewandte Physik, Leibnizstraße 19, 24118 Kiel

Transition metal oxide have been receiving much recent interest as active and stable electrocatalysts for the anodic oxygen evolution reaction (OER). We present operando surface X-ray diffraction studies of two structurally well-defined epitaxial Co₃O₄(111) and CoOOH(001) films electrodeposited on Au(111). The potential-dependent structural changes were monitored with high time resolution up to OER current densities as high as 150 mA cm². The CoOOH(001) film is found to be smooth and perfectly stable over a wide potential range. In the case of Co₃O₄(111), fast and fully reversible structural changes are observed. The surface region of Co₃O₄(111) starts restructuring at potentials 300 mV negative of the onset of the OER, indicating that the process is related to the thermodynamically predicted Co₃O₄/CoOOH(001) transition. The formed skin layer changes linearly with applied potential. The results are at variance with previous suggestions that di-*oxo bridged Co cations are exclusively responsible for the OER activity of Co oxides.

O 13.3 Mon 15:30 H16

Overpotentials of the Oxygen Evolution Reaction on Rutile TiO₂: Effect of the Solvent — ●PATRICK GONO, FRANCESCO AMBROSIO, and ALFREDO PASQUARELLO — *Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

We investigate the solvation effect of water on the overpotentials of the oxygen evolution reaction on rutile TiO₂ through first-principles density functional theory calculations. Applying the thermodynamic integration method on an atomistic semiconductor-water interface, we calculate the free energy steps corresponding to the oxygen evolution reaction treating the solvent explicitly. These results are compared with those achieved by employing a computational method in which solvent effects are neglected. The modifications in the free energy steps are analysed in terms of hydrogen bonds between adsorbates and the water molecules of the solvent, as well as the electronic structure of the reaction intermediates.

O 13.4 Mon 15:45 H16

Modelling cost-effective RuO₂ catalysts for the electrochemical oxygen evolution reaction via a core-shell approach — ●YONGHYUK LEE, DANIEL OPALKA, CHRISTOPH SCHEURER, and KARSTEN REUTER — Technische Universität München

Rutile-type transition metal oxides such as RuO₂ and IrO₂ currently

receive great attention due to their high catalytic activity for the oxygen evolution reaction (OER) in acidic electrolytes. While most OER catalysts in proton exchange membrane electrolyzers rely currently on expensive IrO₂ catalysts due to their favorable stability, RuO₂ shows even higher activity at substantially reduced costs. In the present work, we explore a core-shell approach coating RuO₂ on lattice-matched rutile oxides to potentially yield highly active, relatively inexpensive and chemically stable catalyst materials for water electrolysis. For a first characterization of RuO₂ surfaces, we employed *ab initio* thermodynamics and the computational hydrogen electrode model to determine relative stabilities of pristine and hydrated surfaces as a function of applied potential. Relevant RuO₂ structures at OER operating conditions are compared to core-shell designs, and key factors which further stabilize the system are discussed. Finally, we present thermodynamic reaction barriers for anodic water oxidation and illustrate potential OER pathways that demonstrate enhanced OER activity at surfaces of core-shell materials.

O 13.5 Mon 16:00 H16

A Kinetics-Based Computational Catalyst Design Strategy for the Oxygen Evolution Reaction on Transition Metal Oxide Surfaces — ●SIMEON D. BEINLICH¹, CRAIG P. PLAISANCE², and KARSTEN REUTER¹ — ¹Technische Universität München, Germany — ²Louisiana State University, USA

Aiming to extend over prevalent thermodynamical models, we present a catalyst design strategy for the oxygen evolution reaction (OER) at transition metal oxide (TMO) surfaces that explicitly considers aspects of the reaction kinetics. This strategy is based on extensive DFT+U calculations for a large number of doped active sites on three different surface terminations of cobalt(II,II) oxide.

On this basis, we adapt existing Brønsted-Evans-Polanyi relationships to achieve an accurate description of the two-step nature of the rate-limiting water addition step in the OER. This reveals that the electrochemical and nonelectrochemical pathways of water addition are kinetically equivalent under certain conditions. It also yields a simplified kinetic model to derive a generalized expression for the catalytic activity. We use this model to formulate design criteria for optimal catalytic performance, which pose structure-sensitive and electrode-potential-dependent restrictions for the oxidation potentials of the metal centers involved in the reaction.

The kinetics-based design strategy as well as these design criteria are expected to be transferable to other TMOs and similar electrocatalytic systems dominated by kinetic barriers.

O 13.6 Mon 16:15 H16

Kinetic and transport effects in the ORR on Pt/Ru(0001) model catalysts — ●ALBERT K. ENGSTFELD, KLEIN JENS, FUCHS STEFAN, JUSYS ZENONAS, and R.JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The efficiency of a fuel cell (fueled with, e.g., H₂, MeOH) could be enhanced by decreasing the overpotential for the oxygen reduction reaction (ORR) at the cathode at low current densities (kinetic limitations). At high overpotentials (high current densities), the reaction is mass transport limited and thus only depends on the geometric arrangement as well as the loading of the active catalyst material. In this work, we report on the ORR on monolayer high Pt island modified Ru(0001) model electrodes. The surfaces are prepared and characterized by STM under UHV conditions, while the electrocatalytic investigation is performed in an electrochemical flow cell system attached to the main UHV system.[1] We will first discuss the influence of the Pt coverage on the kinetic currents and show that electrodes with high Pt coverages are more active than bare Pt(111). Second, we demonstrate that at high overpotentials electrodes with low Pt coverages show a much larger turn-over frequency per Pt atom compared to high Pt coverages. Finally, we observed that our model catalyst also forms significant amounts of H₂O₂. Possible reasons will be discussed in relation to the structural properties of the electrodes. [1] Schnaid, Beckord, Engstfeld, Klein, Brimaud, Behm, PCCP 19 (2017) 4166

O 13.7 Mon 16:30 H16

The Effect of DFT Functionals on First-principles Estimates of the Free Energy Barrier of Water Deprotonation on TiO₂(110) — ●AHMAD AGUNG, THOMAS STECHER,

KARSTEN REUTER, and HARALD OBERHOFER — Technische Universität München

Water splitting on TiO₂ is an important model reaction for photoelectrocatalytic processes in general. Recently, we calculated the kinetic barrier of the first deprotonation step on the rutile TiO₂(110) surface based on ab-initio molecular dynamics (AIMD) and utilizing QM-MM embedding, explicit solvation, and the HSE06 hybrid functional.[1] However, the high computational cost of hybrid DFT and the size of the system render such an approach infeasible e.g. for possible catalyst screening studies. In our contribution, we therefore investigate a different approach based on semi-local DFT dynamics and a statistical re-weighting of snapshots with HSE06. We show that, although semi-local DFT by itself would give qualitatively wrong results, the re-weighting procedure restores the correct shape of the free energy profile along the reaction coordinate. We discuss the reasons for the failure of semi-local DFT and highlight remaining sources of error in the re-weighting procedure, leading to still present over-estimation of the free energy barrier height. This work is an important step towards a computationally feasible simulation protocol for free energy barriers in photoelectrocatalytic processes.

[1] T. Stecher, K. Reuter and H. Oberhofer, Phys. Rev. Lett. 117, 276001 (2016).

O 13.8 Mon 16:45 H16

Hydration structures of brookite TiO₂ (210) before and after UV irradiation — •LEI YANG¹, EERO HOLMSTROM², TAKESHI FUKUMA³, and ADAM FOSTER² — ¹WPI Nano Life Science Institute, Kanazawa University, Kanazawa 920-1192, Japan — ²COMP, School of Science, Aalto University, P.O. Box 11100, FI-00076 Aalto, Finland — ³Division of Electrical Engineering and Computer Science, Kanazawa University, Kanazawa 920-1192, Japan

TiO₂/H₂O interface has attracted wide attention due to the photocatalytic capabilities of this system. While rutile and anatase have been intensively researched, the brookite phase remains to be much less explored, despite its significant potential applications in CO₂ reduction and water splitting. Targeting these photocatalytic applications, we carried out *ab initio* molecular dynamics (AIMD) simulations and atomic force microscopy (AFM) as well as attenuated total internal reflection (ATR-IR) spectroscopy measurements to elucidate the hydration structures of brookite (210) surface before and after ultraviolet irradiation. We show the surface to feature a higher hydrophilicity and the interface to present a different topography after irradiation in our experiments. Simulations were performed to provide a molecular-level explanation for the topographic difference between the hydration structures of surfaces with different hydrophilicities on the basis of hydrogen bonding. The difference in vibrational properties is predicted by AIMD as well, which needs to be further validated by ATR-IR

measurements.

O 13.9 Mon 17:00 H16

Interfacial water reorientation after UV irradiation of TiO₂ — •SHUMEI SUN¹, SAMAN HOSSEINPOUR¹, SIMON SCHLEGEL¹, MISCHA BONN¹, and ELLEN BACKUS^{1,2} — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany — ²Department of Physical Chemistry, University of Vienna

Clean energy like hydrogen can be generated on TiO₂ by photocatalytic water splitting with UV light, which was discovered more than 40 years ago. Since then, tremendous research efforts on TiO₂ have been driven by the potential benefits for renewable energy. However, the mechanism behind photocatalysis is still unclear. Sum frequency vibrational spectroscopy as a surface sensitive technique allows us to probe the interface of TiO₂/water. Here we use a femtosecond UV pulse as pump to excite TiO₂. Subsequently, sum frequency vibrational spectroscopy is used as probe to monitor the response of water molecules to UV excitation of TiO₂. Preliminary results show that electron and holes generated in the TiO₂ by UV excitation recombine on a few hundred picoseconds timescale. Moreover, the interfacial structure seems to change on a sub-ps timescale, showing differences depending on the pH of the solution. Our results show that UV pump-SFG probe is a powerful tool to unravel the mechanism of a photon induced surface reaction.

O 13.10 Mon 17:15 H16

Functionalisation of catalyst and electrocatalyst surfaces by means of a femtosecond laser process — •THOMAS GIMPEL¹, VIKTOR HOFFMANN¹, MATTHIAS KOJ², ANDREAS GABLER¹, LUISE F. HOFFMANN¹, MIA BÖRNER³, ANDERS NILSSON³, THOMAS TUREK², and WOLFGANG SCHADE^{1,4} — ¹EST, Clausthal University of Technology, Goslar, Germany — ²ICVT, Clausthal University of Technology, Clausthal-Zellerfeld, Germany — ³Chemical Physics Division, Stockholm University, Sweden — ⁴Fraunhofer Heinrich Hertz Institute, Goslar, Germany

Femtosecond laser ablation enables an increased surface and the formation of different structures up to the 100µm range on many materials. Simultaneously, elements from the process environment are incorporated into the substrate surface. The additional elements may stem from a gaseous, liquid or a solid phase. Thus, with a single process step important material properties are tailored to some extent. We address especially the catalytic activity, the wettability, the heat transfer and fluid transport mechanisms. This contribution shows selected results from the electrochemical CO₂ reduction reaction, a heterogeneous catalysis approach and in alkaline water electrolysis. This technique will help to develop tailored catalysts and electro catalysts beyond the mentioned applications.