

## O 67: Solid-Liquid Interfaces III: OER, ORR, CO2RR, etc.

Time: Wednesday 10:30–13:30

Location: WIL C107

## Invited Talk

O 67.1 Wed 10:30 WIL C107

**The shiniest gold (111) surface** — WERONICA LINPE<sup>1</sup>, JONAS EVERTSSON<sup>1</sup>, GIUSEPPE ABBONDANZA<sup>1</sup>, ALFRED LARSSON<sup>1</sup>, GARY HARLOW<sup>1</sup>, JOHAN ZETTERBERG<sup>2</sup>, LISA RÄMISCH<sup>2</sup>, SEBASTIAN PFÄFF<sup>2</sup>, and EDVIN LUNDGREN<sup>1</sup> — <sup>1</sup>Division of Synchrotron Radiation Research, Lund University, Box 118, S-221 00, Sweden — <sup>2</sup>Division of Combustion Physics, Lund University, SE-22100 Lund, Sweden

We have studied in situ the development of the Au(111) surface during electrochemical Cyclic Voltammetry (CV) measurements using 2D Surface Optical Reflectance (SOR) and High Energy Surface X-Ray Diffraction (HESXRD) with high temporal resolution. We demonstrate that the famous Herring Bone (HB) reconstruction of Au(111) appears in HESXRD at voltages close to the hydrogen evolution reaction signature in the CV and is lifted close to the oxide formation signature. The 2D maximum SOR intensity is shown to coincide with the maximum of the HB intensity, demonstrating that the shiniest gold (111) surface is due to the presence of the HB. On the contrary, the crystal truncation rods exhibit a strong decrease in intensity in conjunction with the appearance of the HB reconstruction. The decrease in intensity of the CTRs can be attributed to the mixed fcc and hcp sites at the Au(111) surface in the HB structure.

O 67.2 Wed 11:00 WIL C107

**ORR and OER on Ni-modified Co<sub>3</sub>O<sub>4</sub>(111) - a combined surface science and electrochemical model study for Zn-Air batteries** — FLORIAN BUCHNER<sup>1</sup>, MARKUS ECKARDT<sup>1,2</sup>, TIMO BÖHLER<sup>1</sup>, JIHYUN KIM<sup>1</sup>, JOHANNES SCHNAIDT<sup>2</sup>, and R. JÜRGEN BEHM<sup>1,2</sup> — <sup>1</sup>Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — <sup>2</sup>Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11, D-89081 Ulm, Germany

We report results of a combined surface science and electrochemistry study on the oxygen reduction and oxygen evolution reactions (ORR and OER) on structurally well-defined Ni-free and Ni-modified single crystalline Co<sub>3</sub>O<sub>4</sub>(111) thin films. These films, which serve as model for the air cathode in Zn-air batteries, were grown on a Ir(100)-(2x1)O surface under ultrahigh vacuum (UHV) conditions. Co<sub>3</sub>O<sub>4</sub>(111) and their Ni-modified derivatives were first characterized by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) under UHV conditions. Post-deposition of Ni on a Co<sub>3</sub>O<sub>4</sub>(111) reveals a Ni<sup>0</sup> state in XPS, while simultaneous vapor deposition of Ni, Co and O<sub>2</sub> results in mixed metal oxides such as Ni<sub>x</sub>Co<sub>1-x</sub>O or Ni<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> (Ni<sup>2+</sup> and Ni<sup>3+</sup> states). STM images show extended flat island structures both for Co<sub>3</sub>O<sub>4</sub>(111) and mixed metal oxides, while post-deposited Ni forms clusters. The thin films revealed an up-shifted ORR onset for Co<sub>3</sub>O<sub>4</sub> compared to pure Ni and Ir. Nickel doping improves the ORR current densities, while hardly influencing the ORR and OER onsets.

O 67.3 Wed 11:15 WIL C107

**Ni-doped Fe<sub>3</sub>O<sub>4</sub>(001) surface as simple model to understand oxygen evolution reaction** — FRANCESCA MIRABELLA, MATTHIAS MÜLLNER, FLORIAN KRAUSHOFER, MICHAEL SCHMID, GARETH PARKINSON, and ULRIKE DIEBOLD — Technische Universität Wien, Vienna, Austria

Electrochemical water splitting is an environmentally friendly technology to convert renewable energy into H<sub>2</sub>-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. However, the synergistic role of Fe and Ni cations on the OER mechanism is yet unclear. The goal of this study is to develop a well-defined model system for understanding the OER and establishing the structure-reactivity relation on mixed Fe/Ni oxides. Reconstructed Fe<sub>3</sub>O<sub>4</sub>(001) provides well-defined sites for the adsorption or incorporation of various metal atoms including Ni. We combine UHV surface science techniques (LEED, XPS, ISS, STM) with exposure to ultrapure liquid water as well as cyclic voltammetry (CV) on UHV-prepared surfaces in alkaline media. When adding Ni, we observed a significant improvement in the OER activity compared to the clean Fe<sub>3</sub>O<sub>4</sub>(001). An optimum Fe:Ni ratio of 1:9 is found, in good agreement with what was

observed in powder catalysts. This observation makes our model system well suited to study the OER in alkaline media and gain further insight based on the high level of control of the surface and near-surface region, robustness and simplicity.

O 67.4 Wed 11:30 WIL C107

**Stable and cost-efficient core-shell catalysts for the electrochemical oxygen evolution reaction—a first-principles approach** — YONGHYUK LEE, CHRISTOPH SCHEURER, and KARSTEN REUTER — Technical University Munich, Germany

Most commercial oxygen evolution reaction (OER) catalysts in proton exchange membrane electrolyzers contain expensive IrO<sub>2</sub> due to its high catalytic activity and favorable stability in acidic electrolytes. Layer-coated IrO<sub>2</sub> on rutile TiO<sub>2</sub> has typically been utilized in order to reduce the price without sacrificing activity. However, thin IrO<sub>2</sub> films are not thermally stable on titania and a gradual dewetting of the film takes place.

In the present work, we use density-functional theory (DFT) calculations to explore alternative core-shell systems. We assess IrO<sub>2</sub> or RuO<sub>2</sub> thin films on lattice-matched rutile oxides as potentially highly active, relatively inexpensive, and long-term stable catalyst materials for water electrolysis. We calculate interface energy, interface formation energy, and the work of adhesion to quantify the stability of the oxide interfaces and compare to the dewetting behavior of IrO<sub>2</sub>(110) films on TiO<sub>2</sub>(110). *Ab initio* thermodynamics and the computational hydrogen electrode model are employed to determine relative stabilities of the core-shell systems compared to pure rutile catalysts at OER operating conditions [1]. Finally, we present thermodynamic reaction barriers for potential anodic OER pathways at surfaces of these core-shell materials and discuss design strategies for next-generation electrocatalysts. [1] D. Opalka *et al.*, ACS Catal. 9, 4944 (2019).

O 67.5 Wed 11:45 WIL C107

**Effect of electric field on oxygen reduction kinetics at the Pt(111), Au(111) and Au(100) electrodes** — SARA KELLY<sup>1</sup>, CHARLOTTE KIRK<sup>1</sup>, KAREN CHAN<sup>2</sup>, and JENS NØRSKOV<sup>2</sup> — <sup>1</sup>SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States — <sup>2</sup>Department of Physics, Technical University of Denmark, Building 311, DK-2800 Lyngby, Denmark

Microkinetic modeling of the oxygen reduction reaction (ORR) has thus far failed to predict dependence of this reaction on pH on several important catalysts. In this work, we create a new microkinetic model for the ORR which incorporates field effects into the established computational hydrogen electrode (CHE) model. We find that field can significantly alter the binding energy of the \*O<sub>2</sub>, \*OOH, and \*H<sub>2</sub>O<sub>2</sub> adsorbates. By considering these effects, we find that we can accurately reproduce experimental polarization curves and rotating ring disk electrode (RRDE) currents on Pt(111), Au(111), and Au(100) electrodes, allowing us to predict both overall ORR activity and selectivity toward hydrogen peroxide. We then use these predictions to better understand activity and selectivity of ORR catalysts and how each of these depends on pH. We show that hydrogen peroxide selectivity depends mainly on the binding energy of \*H<sub>2</sub>O<sub>2</sub> relative to that of \*OOH. Finally, we argue that considering field effects can expand the search for improved ORR catalysts by allowing us to deconvolute the activity dependence of catalysts on the standard hydrogen electrode (SHE) and the reversible hydrogen electrode (RHE).

O 67.6 Wed 12:00 WIL C107

**DFT+U investigation of the OER activity at LaCoO<sub>3</sub>(001) and (110) surfaces** — ACHIM FÜNGERLINGS, HAMIDREZA HAJYANI, and ROSSITZA PENTCHEVA — Department of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 47057 Duisburg

Using density functional theory calculations including an on-site Hubbard term we explore the oxygen evolution reaction at LaCoO<sub>3</sub> surfaces with different crystallographic orientations. For Co- and La-rich synthesis conditions respectively, the surface phase diagram is dominated by the (001) CoO<sub>2</sub>- and LaO- termination over a wide range of oxygen partial pressures. The OER overpotential calculated from the binding energies of the adsorbed intermediates for a Co-reaction site at the

CoO<sub>2</sub>-terminated (001) surface is 0.70V. To gain more insight, we analyze the changes of electronic structure during the reaction. Thereby, the cobalt's oxidation state, which is 3+ in the bulk structure and 2+ at the clean surface, becomes 3+ for an adsorbed OH-group and 4+ for the O intermediate. We furthermore explore the effect of A- and B-site substitution on the catalytic activity.

Support by the DFG within the CRC TRR 247, project B4, and a computational grant at the Leibniz-Rechenzentrum are gratefully acknowledged.

O 67.7 Wed 12:15 WIL C107

**Improvement of OER performance by Fe and Ni doping at the Co<sub>3</sub>O<sub>4</sub>(001) surface** — ●YUMAN PENG, HAMIDREZA HAJIYANI, and ROSSITZA PENTCHEVA — Department of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 47057 Duisburg

Using density functional theory (DFT)+*U* method, we study the oxygen evolution reaction (OER) at the Co<sub>3</sub>O<sub>4</sub>(001) surface. The stability of different surface terminations as a function of oxygen partial pressure, as well as of pH and applied voltage (Pourbaix diagram) were investigated. The termination with octahedral Co and O ions is found to have the lowest overpotential of 0.46 V for an octahedral Co reaction site. Furthermore, we systematically investigated the effect of Fe and Ni doping on the overpotential. Our results indicate that Ni doping at octahedral site in the surface layer reduces the overpotential from 0.46 to 0.36 V and Fe doping at octahedral site at the tetrahedral Co termination reduces the overpotential from 0.63 to 0.37 V, with the octahedral Co site being the active site. The scaling relationship of  $\Delta G_{*OOH}$  and  $\Delta G_{*OH}$  binding energies is overall reproduced, the Ni-doped system lying close to the top of the volcano of the overpotentials versus ( $\Delta G_{*O} - \Delta G_{*OH}$ ). Further insight was gained into the oxidation states of surface ions and in particular the Co active site during OER, by analyzing the magnetic and electronic properties. Support by the DFG, CRC TRR247, IMPRS-Surmat and a computational grant at the magnetUDE of the Center of Computer Science and Simulation are gratefully acknowledged.

O 67.8 Wed 12:30 WIL C107

**Oxygen reduction by doped graphene in Li-air batteries** — ●ELMAR KATAEV<sup>1</sup>, DANIL ITKIS<sup>2</sup>, ALINA BELOVA<sup>2</sup>, CARLOS ESCUDERO<sup>3</sup>, VIRGINIA PÉREZ-DIESTE<sup>3</sup>, AXEL KNOP-GERICKE<sup>4</sup>, and LADA YASHINA<sup>2</sup> — <sup>1</sup>Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Erlangen, Germany — <sup>2</sup>Department of Chemistry, Moscow State University, Moscow, Russia — <sup>3</sup>ALBA Synchrotron Light Source, Barcelona, Spain — <sup>4</sup>Fritz-Haber Institute of the Max Planck Society, Berlin, Germany

Oxygen reduction reaction (ORR) plays a key role in lithium-air batteries (LABs) that attract great attention thanks to their high theoretical specific energy. Because of high surface area and electric conductivity, various carbons are often materials of choice for applications as the LAB cathode. Unfortunately, the practical applications of LAB batteries are impeded by poor rechargeability, associated with ORR side reactions. Recently it was shown that doping of carbon materials could change its catalytic activity and potentially reduce reactivity towards ORR products. However, the mechanisms of doped-carbon reactivity in LAB are still unclear. Here we report a direct photoemission study of ORR pathway on pure, nitrogen-, boron- and oxygen-doped graphene. We designed the electrochemical cell with two-layer graphene transferred on glass-ceramics electrolyte to avoid side reactions of ORR products with liquid electrolyte. Combining operando photoemission data with in situ observation of superoxide anion attack on graphene in model chemical systems, we reveal the impact of impurities in carbon on its reactivity in ORR.

O 67.9 Wed 12:45 WIL C107

**Electroreduction of water on Mo<sub>2</sub>C film electrodes affected by the presence of CO<sub>2</sub>** — ●EVA-MARIA WERNIG, CHRISTOPH GRIESSER, DANIEL WINKLER, NIUSHA SHAKIBI NIA, and JULIA KUNZE-LIEBHÄUSER — Institute of Physical Chemistry, University of Innsbruck, 6020 Innsbruck, Austria

The materials class of transition metal carbides (TMCs) has gained

importance among electrocatalysts for reduction processes such as the hydrogen evolution reaction (HER) and the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). For a comprehensive understanding of the electrocatalytic properties of Mo<sub>2</sub>C towards the HER under CO<sub>2</sub>RR conditions in aqueous electrolytes, the present study merges materials science and interface analytics with electrochemistry. We report on the synthesis of Mo<sub>2</sub>C films using direct carburization of polycrystalline Mo substrates through carbothermal conversion. Cyclic voltammetry, complemented by rotating ring disc electrode (RRDE) measurements, was used to investigate the electrocatalytic activity of Mo<sub>2</sub>C films towards the HER in the absence and presence of CO<sub>2</sub>, while changes of the chemical composition at the surface were analyzed with ex-situ emission X-ray photoelectron spectroscopy (XPS). In-situ infrared spectroscopy (SNIFTIRS) enabled the determination of reaction intermediates at the solid/liquid interface. Product analysis was accomplished with differential electrochemical mass spectrometry (DEMS) to monitor the formation of gaseous products such as hydrogen. The activity of Mo<sub>2</sub>C film electrodes towards the HER was found to be significantly enhanced in the presence of CO<sub>2</sub>.

O 67.10 Wed 13:00 WIL C107

**In Operando Spectroscopy of CO<sub>2</sub> Reduction Reactions at Pt/Ionic Liquid Interfaces** — ●ANDRE KEMNA, BJÖRN RATSCHMEIER, and BJÖRN BRAUNSCHWEIG — Institute of Physical Chemistry, WWU Münster, 48149 Münster, Germany

CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR) at Pt(poly)/[BMIM][BF<sub>4</sub>] interfaces were studied with cyclic voltammetry and in operando with IR absorption (IRAS) as well as sum frequency generation (SFG) spectroscopy to get mechanistic insights into CO<sub>2</sub>RR. IRAS revealed a vibrational band centered at 1670 cm<sup>-1</sup> at an onset potential of -0.65V vs SHE. We attribute the latter to the carbonyl stretching mode of an imidazolium carboxylic acid, which is generated via a carbene intermediate, for which we also present spectroscopic evidence. Via SFG spectroscopy we demonstrate that CO is formed in addition to [BMIM]-COOH on the Pt catalyst surface, at an onset potentials of -1.05 V. We therefore assume that the [BMIM]-COOH species is one reactive intermediate that results in low overpotentials for CO<sub>2</sub>RRs. The [BMIM]-COOH species can be further catalyzed to formic acid during an anodic potential sweep. At an electrode potential of 1.6 V, a vibrational band at 1750 cm<sup>-1</sup> arises in the IR spectra and is accompanied by a decrease of the imidazolium carboxylate band. We tentatively assign the former vibrational modes to C=O vibrations of formic acid. This indicates that electrocatalysis of CO<sub>2</sub> to formic acid may be possible in a two-step reaction process.

A. Kemna, N. García Rey, B. Braunschweig, *ACS Catal.* **2019**, *9*, 7, 6284-6292.

O 67.11 Wed 13:15 WIL C107

**A refined view on broken scaling relations for electrochemical CO<sub>2</sub> reduction on transition metal carbides** — ●HAOBO LI and KARSTEN REUTER — Chair for Theoretical Chemistry, TU Munich, Germany

The electrochemical reduction of CO<sub>2</sub> (CO<sub>2</sub>RR) is a promising approach to generate chemical energy carriers from renewable electricity. Transition metal carbides (TMCs) are a promising non-noble material class to catalyze this reaction, with e.g. Mo<sub>2</sub>C recently reported to convert CO<sub>2</sub> into CH<sub>4</sub> at low overpotentials [1]. Here, we further assess the proposition that this performance results from a break of scaling relations known to limit CO<sub>2</sub>RR on transition metals (TMs) and their alloys [2]. Using density-functional theory, we systematically compute the adsorption energies of key reaction intermediates at multiple adsorption sites offered at low-index surfaces of molybdenum carbides of varying stoichiometry. The obtained data base provides a refined view, with certain scaling relations indeed broken, but others maintained. We can rationalize these findings by the simultaneous presence of metal and carbon active sites at the surface of TMC catalysts and the concomitant stabilization of varying adsorption modes. With this understanding we revisit mechanistic CO<sub>2</sub>RR models established for TMs and explore routes to optimize CO<sub>2</sub>RR for TMCs.

[1] S.K. Kim *et al.*, *ACS Catal.* **6**, 2003 (2016).

[2] R. Michalsky *et al.*, *J. Phys. Chem. C* **118**, 13026 (2014).