

O 18: Solid-Liquid Interfaces I: Structure and Spectroscopy

Time: Monday 15:00–18:00

Location: H 1012

O 18.1 Mon 15:00 H 1012

Reporting activity and stability for the oxygen evolution reaction — ●MARCEL RISCH — Helmholtz-Zentrum Berlin, Berlin, Germany

The oxygen evolution reaction (OER) is a key enabler of sustainable chemical energy storage. It occurs on the anode of a fuel-producing device such as electrolyzers or photoelectrochemical cells and provides the protonated ions for the formation of the fuel molecule. The OER has been studied for more than 230 years. Yet, there is no consensus how to report the key performance parameters of electrocatalytic activity and stability [1,2], which thwarts, e.g., correlating these parameters to materials properties for systematic mechanistic insight [3]. The author assesses the current sore spots when reporting activity and stability and touches on the related topic of determining the electrochemical surface area [4]. Ideas are presented to improve upon the current sore spots.

[1] M. Risch, *Commun Chem* 6, 221 (2023) [2] M. Risch, *Cur. Op. Electrochem.* 38, 101247 (2023) [3] D. Antipin, M. Risch, *JPhys Energy* 2, 032003 (2020) [4] D.M. Morales, M. Risch, *JPhys Energy* 3, 034013 (2021)

O 18.2 Mon 15:15 H 1012

Interfacial water structure effects during CO₂ electroreduction — ●YA-WEI ZHOU^{1,2}, BEATRIZ ROLDAN CUENYA², and CHRISTOPHER SEIJI KLEY^{1,2} — ¹Helmholtz Young Investigator Group Nanoscale Operando CO₂ Photo-Electrocatalysis, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany — ²Department of Interface Science, Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany

We combine on-line differential electrochemical mass spectroscopy (DEMS), *in situ* attenuated total reflection surface enhanced Infrared spectroscopy (ATR-SEIRAS), operando shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) and density functional theory (DFT) to investigate the structure and dynamic process of interfacial water on Au and Cu surfaces during CO₂ electroreduction reaction (CO₂RR). Direct ATR-SEIRAS evidence and D₂O labelling DEMS data reveals that H₂O is the proton donor of CO₂RR and HER, while bicarbonate is solely involved in the Heyrovsky step. We reveal that hydrated CO₃²⁻ increases the ordering of the hydration water network, with shorter H-bond leading to rapid delivery of electrons and protons at the electrode-electrolyte interface. This, in turn, suppresses the CO₂RR due to promoted H^{*} formation through the increased connectivity of the CO₃²⁻ induced interfacial water network in the high current density region. We observe a carbonate anion radical (CO₃^{•-}) on both Au and Cu surfaces that we propose to originate from hydrated CO₃²⁻, acting as additional carbon source under reducing condition.

O 18.3 Mon 15:30 H 1012

Cu/Au(111) Surfaces and AuCu Intermetallics for Electrocatalytic Reduction of CO₂ in Ionic Liquid Electrolytes — ●BJÖRN RATSCHMEIER¹, CHRISTIAN PAULSEN¹, KLAUS STALLBERG², GINA ROSS¹, WINFRIED DAUM², RAINER PÖTTGEN¹, and BJÖRN BRAUNSCHWEIG¹ — ¹University of Münster, Germany — ²TU Clausthal, Germany

Room-temperature ionic liquids (RTIL) are important alternatives for reducing high overpotentials and modifying product selectivities in CO₂ reduction reactions (CO₂RR). The activity of Au(111), Cu(111), Cu-modified Au(111) electrodes, and AuCu intermetallics in contact with 1-butyl-3-methylimidazolium trifluorosulfonylimide [BMIM][NTf₂] electrolytes was investigated in terms of CO₂RR. *In operando* IR absorption spectroscopy (IRAS) of the bulk electrolyte reveals the formation of a 2-imidazolium carboxylic acid intermediate that can lower the overpotential for CO₂RR and does not require stabilization of the CO₂ radical anion as an alternative intermediate at the interface. On Au(111) we observe the formation of H₂ and mainly CO, while on Cu(111) the only reduction product is H₂. By systematically varying the copper content at the catalyst surfaces, we are able to tune the H₂/CO syngas ratio to a maximum of 1.8 for Cu-modified Au(111) electrodes and 3.2 for AuCu₃ catalysts, demonstrating a large tunability of the syngas ratio with electrode potential. The observed H₂/CO ratios approach the ideal value of 2 needed for the Fischer-Tropsch process and a ratio of 3 required for methanation.

O 18.4 Mon 15:45 H 1012

The Influence of Mesoscopic Surface Structure on the Electrocatalytic Selectivity of CO₂ Reduction with UHV-Prepared Cu(111) Single Crystals — ●KHANH-LY NGUYEN, JARED P. BRUCE, ARAM YOON, JUAN NAVARRO, FABIAN SCHOLTEN, FELIX LANDWEHR, CLARA RETTENMAIER, MARKUS HEYDE, and BEATRIZ ROLDAN CUENYA — Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

Electrocatalytic conversion of CO₂ to higher order hydrocarbons has been proposed as a promising approach to re-utilize the greenhouse CO₂. The only pure metal that is capable of reducing CO₂ to C₂+ hydrocarbons is copper although it suffers from low selectivity. Cu(111) single crystal surfaces prepared under ultra-high vacuum (UHV) conditions were found to display different product selectivity during CO₂RR despite similar chemical and local microscopic surface features. In particular, changes in selectivity from hydrogen-dominant to hydrocarbon-dominant product distributions were observed based on the number of CO₂RR electrolysis and subsequent UHV treatments. Significant mesostructural changes were observed through a micron scale microscopic analysis, including a higher density of irregular steps on the samples producing hydrocarbons. Thus, our findings highlight that step edges are key for C-C coupling in CO₂RR and that not only atomistic but also mesoscale characterization of electrocatalytic materials is needed in order to comprehend complex selectivity trends.

O 18.5 Mon 16:00 H 1012

Oxygen reduction reaction on adlayer covered surfaces: A case study on Ru(0001) in acid — ●ALBERT K. ENGSTFELD^{1,2}, STEPHAN BECKORD¹, STEFAN FUCHS¹, and R.JÜRGEN BEHM^{1,3} — ¹Institute of Surface Chemistry and Catalysis, Ulm, DE — ²Institute of Electrochemistry, Ulm, DE — ³Institute of Theoretical, Chemistry, Ulm, DE

On bare Ruthenium (Ru) electrodes, the oxygen reduction reaction (ORR) primarily leads to the formation of water. Depending on the electrode structure and availability of surface (hydr)oxides, in certain potential regions also H₂O₂ can be formed. Recently we have shown that the electrode surface is never free from adsorbates.[1] In this work, we will show how such adlayers influence the ORR activity and discuss the limitations of the commonly accepted reaction pathway, which involves free surface sites. The electrodes are prepared under ultra-high vacuum conditions and their structural integrity is determined by scanning tunnelling (STM) measurements performed before and after the electrocatalytic investigation. The electrocatalytic measurements are performed in O₂-free and O₂-saturated acid electrolytes (HClO₄ and H₂SO₄). We will discuss the impact of bisulfate on the reactivity, which almost completely inhibits the reactivity of the surface. Furthermore, we illustrate that adsorbed OH plays a major role in the formation of H₂O₂ on such surfaces. Additional differential electrochemical mass spectrometry (DEMS) measurements allow disentangling the ORR from the hydrogen evolution reaction at high overpotentials.

[1] A.K. Engstfeld *et al.*, *Electrochimica Acta*, **389** (2021) 138350

O 18.6 Mon 16:15 H 1012

Initial Stages of Alkali Metal Deposition on Au(111) from [MPPip][TFSI] — ●MAREN-KATHRIN HEUBACH¹, FABIAN M. SCHUETT¹, AREEG ABDELRAHMAN¹, LUDWIG A. KIBLER¹, TONI MOSER², JULIA KUNZE-LIEBHÄUSER², and TIMO JACOB^{1,3,4} — ¹Institute of Electrochemistry, Ulm University, Ulm, Germany — ²Institute of Physical Chemistry, University of Innsbruck, Innrain 52c, Innsbruck, 6020 Austria — ³Helmholtz-Institute-Ulm (HIU), Ulm, Germany — ⁴Karlsruhe Institute of Technology, Karlsruhe, Germany

The cycling stability of alkali metal batteries using a metal anode is often limited by dendritic growth.^{1,2} Hereby, the initial stages of metal deposition and dissolution play a key role since they have a huge impact on the macroscopic morphology of the deposits.³

In this study, the initial stages of sodium and lithium deposition on Au(111) from the ionic liquid *N*-methyl-*N*-propylpiperidinium bis(trifluoromethane-sulfonyl)imide ([MPPip][TFSI]) are investigated by cyclic voltammetry and *in situ* scanning tunnelling microscopy. The deposition of both alkali metals starts at underpotentials of approximately 1 V with island formation and the following underpotential deposition includes more than two monolayers.⁴

[1] A. Jana, R. E. García, *Nano Energy* **2017**, *41*, 552–565. [2] B. Lee, E. Paek, D. Mitlin, S. W. Lee, *Chemical Reviews* **2019**, *119*, 5416–5460. [3] C. A. Berger, M. U. Cebelin, T. Jacob, *ChemElectroChem* **2017**, *4*, 261–265. [4] M.-K. Heubach, F. M. Schuett, L. A. Kibler, A. Abdelrahman, T. Jacob, *ChemElectroChem* **2022**, *9*, e202200722.

O 18.7 Mon 16:30 H 1012

Self-organized structures of carboxylic acids on the Au (111) electrode surface — ●KRISTIN GRATZFELD¹, ANNA J. KNY¹, TOMASZ KOSMALA², RADOSŁAW WASIELEWSKI², MAREK NOWICKI², KLAUS WANDEL¹, and MORITZ SOKOŁOWSKI¹ — ¹Clausius-Institute of Physical and Theoretical Chemistry, University of Bonn, Germany — ²Institute of Experimental Physics, University of Wrocław, Poland

We investigated the self-ordered structures of 3,4,9,10-perylene-tetracarboxylic acid (PTCA) and 1,4,5,8-naphthalene-tetracarboxylic acid (NTCA) on the Au(111) electrode interface in an aqueous electrolyte. Electrochemical studies of PTCA were performed before [1], however no structural data was reported, yet. We used cyclic voltammetry (CV) with in situ electrochemical STM (EC-STM): By tuning the electrode potential, we can observe different ordered phases of both molecules on the Au(111) electrode surface. We will discuss the geometrical differences of the ordered phases and why we observe the transitions between phases at different electrode potentials on the Au(111) surface. When shifting to more positive electrode potentials, we observe that the PTCA molecules in the ordered phases change from an upright to a tilted and finally to a flat orientation. In contrast, for NTCA we observe only ordered phases of tilted molecules.

This work was supported by the DFG through the research training group 2591, the DAAD (Deutscher Akademischer Austauschdienst) program Ostpartnerschaften and the NAWA (National Agency for Academic Exchange) program.

[1] *Journal of American Society*, 138, 1490–1493, 2016.

O 18.8 Mon 16:45 H 1012

In situ electrochemical atomic force microscopy studies of a copper surface during lithium plating and dissolution — ●LUCA KAUFER¹, RONJA HAAS², THOMAS GÖDDENHENNRICH¹, DANIEL EBELING¹, JÜRGEN JANEK², and ANDRÉ SCHIRMEISEN¹ — ¹Institute of Applied Physics, Justus-Liebig-University, Gießen, Germany — ²Institute of Physical Chemistry, Justus-Liebig-University, Gießen, Germany

The increasing concern about climate change and the transition to sustainable energy sources has led to an increased demand for high energy density batteries for energy storage. Lithium is considered a favourable anode material [1]. However, challenges like dendrite growth when used in batteries are still present [2]. This investigation focuses on the processes involved in dendrite formation and growth and upcoming side reactions in a lithium-copper system with in situ electrochemical atomic force microscopy as a method. We will cover two topics. Firstly, the technical development of an appropriate measurement setup for in situ investigation of cells in atomic force microscopy. Secondly, the presentation of initial findings on the processes of formation and growth of dendrites within a lithium-copper cell system.

[1] Yan, K.; Lu, Z.; Lee, H.-W.; Xiong, F.; Hsu, P.-C.; Li, Y.; Zhao, J.; Chu, S.; Cui, Y. *Nat Energy* 2016, DOI: 10.1038/nenergy.2016.10

[2] TAKEDA, Y.; YAMAMOTO, O.; IMANISHI, N. *Electrochemistry* 2016, DOI: 10.5796/electrochemistry.84.210

O 18.9 Mon 17:00 H 1012

Size Effects and Active State Formation in Cobalt Oxide Nanoparticles during Oxygen Evolution Reaction — ●ARNO BERGMANN¹, FELIX T. HAASE¹, TRAVIS E. JONES², JANNIS TIMOSHENKO¹, and BEATRIZ ROLDAN CUENYA¹ — ¹Department of Interface Science, Fritz-Haber-Institut, Berlin, Deutschland — ²Department of Inorganic Chemistry, Fritz-Haber-Institut, Berlin, Deutschland

Water electrolysis for a CO₂-neutral H₂ production remains challenging due to the large overpotential required for the anodic oxygen evolution reaction (OER). Cobalt oxides exhibit high catalytic activity for OER but the underlying principles of the oxygen-evolving surface is unknown. Thus, we investigated size-selected CoO_x(OH)_y nanoparticle (NP) catalysts down to 1 nm using operando X-ray absorption spectroscopy (XAS) combined with DFT calculations. [1] The mass-based activity showed an increasing OER current with decreasing NP size which correlates with a larger accessible surface area. XAS revealed reversible changes in charge density at the Co-O ligand system during OER, being more pronounced with decreasing NP size. Size-dependent

changes in the Co-O distance during OER were correlated to charge-transfer between Co and O ligand determined by DFT suggesting electrophilic O sites and allow to extract quantitative information on the near-surface atomic and electronic structure of the oxygen evolving CoO_x(OH)_y NP near-surface. [1] F.T. Haase et al, *Nat Energy* 7, 765 (2022).

O 18.10 Mon 17:15 H 1012

Tuning the HER activity by using ion confinement in layered MoS₂ — ●MARCO SCHÖNIG¹, SIMON FLEISCHMANN², and MARC KOPER¹ — ¹Leiden University, Leiden, The Netherlands — ²HIU, Ulm, Germany

The optimization of energy storage and conversion materials caused a decrease of the pore size in these materials to the nanometer scale. On this length scale the ions can not simply enter the pores but are forced to (partially) shed their solvation shell [1]. This so called "ion confinement" was shown to be promising way to increase the storage capacity of supercapacitors [2]. However, this effect is scarcely exploited in electrocatalysis, although ions close to the surface play an important role in several electrocatalytic reactions, including the HER [3]. In this contribution, we study the effect of the confinement of different ions on the activity of the HER at MoS₂. This is achieved by tuning the ion confinement via the interlayer distance of the layered MoS₂, as well as the ion diameter.

[1] Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P.-L. *Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer* *Science*, 2006, 313, 1760–1763. [2] Fleischmann, S.; Spencer, M. A.; Augustyn, V. *Electrochemical Reactivity under Confinement Enabled by Molecularly Pillared 2D and Layered Materials* *Chem. Mater.*, 2020, 32, 3325–3334. [3] Monteiro, M. C. O.; Goyal, A.; Moerland, P.; Koper, M. T. M. *Understanding Cation Trends for Hydrogen Evolution on Platinum and Gold Electrodes in Alkaline Media* *ACS Catal.*, 2021, 11, 14328–14335.

O 18.11 Mon 17:30 H 1012

Impedance Spectroscopy with Microscopic Reference Electrodes as a Technique to Study Electrode Kinetics in Dye-Sensitized Solar Cells — ●DANIEL HOLZHACKER and DERCK SCHLETTWEIN — Institut für Angewandte Physik, Justus-Liebig-Universität Gießen

A detailed impedance analysis of dye-sensitized solar cells (DSSC) is essential to precisely optimize performance-limiting steps in these cells. Two-electrode impedance measurements as typically used, however, often do not allow a separate analysis of charge transfer reactions at different electrodes that occur with similar time constants. The use of a microscopic quasi-reference electrode (μ RE) offers the possibility to separately record impedance spectra of the photoanode (WE) and the counter electrode (CE) of a DSSC under operating conditions in one experiment. In three-electrode experiments, the potential was modulated between the μ RE and WE. The respective impedance (Z_{WE}) and, simultaneously, the impedance between μ RE and CE (Z_{CE}) were recorded and the overall cell impedance Z calculated. The latter was identical to Z determined in a two-electrode measurement, proving the validity of the experimental approach. Thus, one experiment yielded spectra for the full cell and both respective half-cells, which allowed to simultaneously study the interactions of novel redox mediators with photoanodes and counter electrode materials in detail.

O 18.12 Mon 17:45 H 1012

Arrhenius follows Frumkin to describe Atomic Diffusion involved Peaks in Cyclic Voltammograms: the Reversible Place-Exchange on Pt(111) — JON BJARKE VALBAEK MYGIND¹, FRANCESC VALLS MASCARÓ², and ●MARCEL J. ROST³ — ¹Department of Physics, Technical University of Denmark, 2800 Kongens Lyngby, Denmark — ²Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands — ³Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands

CVs are one of the most powerful tools for the experimental investigation and characterization of electron transfer processes in electrochemistry. Determined by the driving force, thus the potential of the working electrode, electrochemical interfaces can be assessed on their structure as well as activity. As the unique electrochemical fingerprint of a particular system is given by specific (current) peaks in the CV, it is not surprising that great effort is done to understand, describe, and model these peaks analytically. However, the underlying involved thermodynamic and kinetic processes makes this a difficult task, even if specific changes in the fingerprint occur upon change of the voltam-

mogram's sweep rate. Here we show on the example of the reversible Place-Exchange peak, a precursor in the electrochemical oxidation of the Pt(111) surface, that a combination of a Frumkin isotherm followed by an Arrhenius (atomic) diffusion process delivers a rather good de-

scription. All peaks of all CVs, measured with different sweep rates, are simultaneously fitted together with only three (basic description) or six (extended description) fit variables.