

## O 65: Poster Session V: Solid-liquid interfaces: Reactions and electrochemistry II

Time: Wednesday 10:30–12:30

Location: P

O 65.1 Wed 10:30 P

**Modelling of Lithium Whisker Dissolution** — ●MARTIN WERRES<sup>1,2</sup>, ARNULF LATZ<sup>1,2,3</sup>, and BIRGER HORSTMANN<sup>1,2,3</sup> — <sup>1</sup>Helmholtz Institute Ulm for Electrochemical Energy Storage, Ulm, Germany — <sup>2</sup>German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Stuttgart, Germany — <sup>3</sup>Ulm University, Institute of Electrochemistry, Ulm, Germany

In the search for next generation batteries, lithium metal anode research experiences a refreshed attention due to its high theoretical energy density. Focus lies on enhancing the durability of lithium metal anode batteries and eliminating safety concerns. The battery capacity fades over cycling due to continuous SEI buildup, consuming lithium and electrolyte, and the formation of inactive lithium, which is electrically disconnected from the anode. As the surface of the anode is highly irregular and tends to form whisker during charging, experiments show that during discharge, the tip of the whisker is not dissolved and a droplet stays behind inside the SEI shell. We developed a generalized phase-field model of the dissolution in order to gain insights in the droplet formation process.

Utilizing non-equilibrium thermodynamics, our phase-field model describes the dissolution of a single lithium whisker by taking the surface tension of lithium metal into account, and the interaction between lithium and the SEI. We are able to predict the nucleation of a Rayleigh instability behind the tip, leading to the formation of an electronically isolated lithium metal droplet.

O 65.2 Wed 10:30 P

**Nanostructuring Cu tunes CO(2)R selectivity through the mass transport of products: the example of acetate** — ●HENDRIK H. HEENEN<sup>1</sup>, GEORG KASTLUNGER<sup>1</sup>, HAEUN SHIN<sup>2</sup>, SEAN OVERA<sup>2</sup>, JOSEPH A. GAUTHIER<sup>3</sup>, FENG JIAO<sup>2</sup>, and KAREN CHAN<sup>1</sup> — <sup>1</sup>Department of Physics, Technical University of Denmark — <sup>2</sup>Department of Chemical and Biomolecular Engineering, University of Delaware — <sup>3</sup>Department of Chemical Engineering, Stanford University

Nanostructured Cu catalysts have increased the yield of and lowered the overpotential for high value C-C coupled (C<sub>2+</sub>) products in electrochemical CO reduction (CORR). With this type of catalyst also the selectivity among C<sub>2+</sub> products has changed where acetate has emerged as a major product depending strongly on alkalinity and catalyst structure. This striking selectivity dependence is far from being understood. In this work, we elucidate the mechanism towards acetate using an *ab-initio* derived microkinetic model coupled to mass transport as well as loading experiments. We find that acetate selectivity is only dependent on local mass transport properties of the catalyst and not founded in changes of the intrinsic activity of Cu. The selectivity mechanism originates in the transport of ketene away from the catalyst surface. This unprecedented mechanism may also explain similar selectivity fluctuations observed for other saturated intermediates like CO and acetaldehyde. Our proposed mechanism explains changes in selectivity of acetate with potential, pH, and catalyst roughness which are the basis for design principles of a selective CORR operation.

O 65.3 Wed 10:30 P

**Surface pH estimation during electrochemical CO<sub>2</sub> reduction in a non-RDE setup** — ●DAVID EGGER, KARSTEN REUTER, and CHRISTOPH SCHEURER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The electro-chemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) represents a promising route to renewable fuels. CO<sub>2</sub>RR in aqueous electrolyte solutions is hampered by the loss of faradaic efficiency due to the competing hydrogen evolution reaction (HER) either by the reduction of hydronium ions or water. The latter lead to a pH increase towards the electrode surface under high current operating conditions. This shift in electrode pH can significantly influence the active catalytic state and stability of the electrode. Yet, the crucial surface pH is neither experimentally easily accessible, nor can it be simply obtained from bulk equilibrium thermodynamics.

Here, we present a semi-empirical approach to estimate the surface pH at a planar electrode from experimental electrode currents at a range of different nominal bulk pHs. By solving a 1-D simplified Poisson-Nernst-Planck equation to account for mass transport and

chemical kinetics, the current approach works even outside a rotating disc electrode setup. We apply it to corresponding CO<sub>2</sub>RR data at molybdenum carbide provided alongside *in situ* XPS measurements and show that only after surface pH correction the XPS compositional information can be brought into agreement with the Pourbaix diagram obtained from *ab initio* thermodynamics.

O 65.4 Wed 10:30 P

**Anodic Polarization of Electrodes at High Potentials in Alkaline Electrolytes** — ●EVELYN ARTMANN, LUKAS FORSCHNER, VINCENT PRAMOD MENEZES, MOHAMED ELNAGAR, LUDWIG KIBLER, TIMO JACOB, and ALBERT K. ENGSTFELD — Institute of Electrochemistry, University of Ulm, Germany

Polarization of electrodes in aqueous electrolytes at anodic potentials in the range of a few to several hundred volts has a significant impact on the structural properties of the electrodes as well as on the products formed in the solution [1-2]. This opens up interesting opportunities for applications, e.g. electrocatalyst design.

In this work we report on the I-U characteristics and the structural properties of Pt, Au and Cu wire electrodes during anodic polarization between the stability region of water and anodic Contact Glow Discharge Electrolysis (aCGDE) in alkaline electrolyte. The structural changes of the electrodes were characterized by means of scanning electron microscopy (SEM) and electrochemical measurements. The latter suggest potential dependent oxide formation on Au and Cu. The nature of the formed oxides is discussed based on X-ray photoelectron spectroscopy (XPS) measurements.

An important finding is that the structural properties of the electrodes also depend on how quickly the electrodes were removed from the electrolysis solution. We will discuss in how far the electrolysis products affect the structure formation after the anodic treatment.

[1] G. Saito, T. Akiyama, J. Nanomater., 10 (2015) 1.

[2] A. Allagui et. al., Electrochim. Acta, 93 (2013) 137.

O 65.5 Wed 10:30 P

**Increasing stability, efficiency, and fundamental understanding of lithium-mediated electrochemical nitrogen reduction** — ●VANESSA J. BUKAS<sup>1</sup>, SUZANNE Z. ANDERSEN<sup>1</sup>, MICHAEL J. STATT<sup>2</sup>, SARAH G. SHAPEL<sup>1</sup>, JAKOB B. PEDERSEN<sup>1</sup>, KEVIN KREMPLE<sup>1</sup>, MATTIA SACCOCCIO<sup>1</sup>, DEBASISH CHAKRABORTY<sup>1</sup>, JAKOB KIBSGAARD<sup>1</sup>, PETER C. K. VESBORG<sup>1</sup>, JENS K. NØRSKOV<sup>1</sup>, and IB CHORKENDORFF<sup>1</sup> — <sup>1</sup>Technical University of Denmark — <sup>2</sup>Stanford University, USA

Lithium-mediated nitrogen reduction is a proven method to electrochemically synthesize ammonia; yet the instability and low efficiency of this process have so far limited its practical application. One major obstacle against improving the Li-mediated approach is that very little is understood about the mechanism. We develop here a kinetic model that highlights mass transport limitations as a very important factor to the resulting faradaic efficiency. Our results reproduce experimental trends for varying conditions of N<sub>2</sub> pressure or H<sup>+</sup> availability and show that the relative diffusion rates of reacting Li<sup>+</sup>, N<sub>2</sub>, and H<sup>+</sup> species are key to selectively forming ammonia. On the basis of this understanding, we develop a potential-cycling strategy which can recover 'catalytic' high-energy electrons from unused metallic Li that was deposited at the electrode surface. This is shown experimentally to improve the stability of the system, alleviate the need for continuously replenishing the electrolyte with Li salts, and lead to a significant increase in both faradaic and energy efficiency [1].

[1] Andersen *et al.*, Energy Environ. Sci. **13**, 4291 (2020)

O 65.6 Wed 10:30 P

**Light assisted electrodeposition of Ni catalysts on p-doped Si(111) for photoelectrochemical water reduction** — ●DAVID OSTHEIMER<sup>1</sup>, MARIO KURNIAWAN<sup>2</sup>, LARA EGGERT<sup>2</sup>, THOMAS HANNAPPEL<sup>1</sup>, and ANDREAS BUND<sup>2</sup> — <sup>1</sup>Fundamentals of Energy Materials, Ilmenau University of Technology, Germany — <sup>2</sup>Electrochemistry and Electroplating, Ilmenau University of Technology, Germany

The development of efficient and inexpensive (photo-)electrocatalysts plays an important role to enhance the hydrogen evolution reaction for photoelectrochemical water-splitting. In the present work, nickel par-

ticles were electrochemically deposited on a p-type Si-(111) substrate under illumination. Different parameters have been varied to obtain beneficial morphologies and particle sizes. We show that they can be tailored by using either a potentiostatic method (resulting in large particles) or a galvanostatic deposition method (small particles), while the distribution of the particles on the surface is strongly influenced by the electrodeposition time. The particles size and the coverage including the surface roughness were investigated using atomic force microscopy. A relation between the surface morphology and catalytic activity was analyzed by comparing photocurrents of various samples. A dense particle coverage can block the incident light and thus limit the photoabsorption of the p-Si. This can be observed especially for samples with large catalyst particle sizes. Specimens with smaller nickel particles show a significant improvement of the photoactivity compared to samples with larger particles.

O 65.7 Wed 10:30 P

**Quantum Chemical Assessment of well-defined Catalysts for the Oxygen Reduction Reaction** — •CHRISTOPHER EHLERT<sup>1,2</sup>, ANNA PIRAS<sup>1,2</sup>, and GANNA GRYN'OVA<sup>1,2</sup> — <sup>1</sup>Heidelberg Insti-

tute for Theoretical Studies (HITS gGmbH), Heidelberg, Germany — <sup>2</sup>Interdisciplinary Center for Scientific Computing, Heidelberg University, Heidelberg, Germany

The Oxygen Reduction Reaction (ORR) is an important electrochemical process taking place at the negatively charged cathode with applications in fuel cells and metal-air batteries. The bare reduction shows a rather sluggish reaction kinetics requiring catalysts to achieve larger electrical currents. Precious metal Pt-alloys show good performance and serve as a reference, however their rareness, high prices and poor long-term durability inhibit large-scale applications.

In a recent study, Kahan et. al. (doi:10.1021/acs.chemmater.8b04027) investigated six well defined (co)doped polyaromatic hydrocarbons (PAHs), or nanographene sheets. In this study, we investigate the catalytic reaction pathways of the proposed PAHs from the physisorbed oxygen towards the chemisorbed minimum by density functional theory. For the neutral catalysts, the potential energy surface scans show fully repulsive or energetically unfavorable situations. We therefore suggest that the initial chemisorption occurs via negatively charged catalysts, which is confirmed by exergonic reaction energetics.