

## O 20: Solid-Liquid Interfaces: Reactions and Electrochemistry - Experiment I

Time: Monday 16:30–18:15

Location: WIL B321

O 20.1 Mon 16:30 WIL B321

**Novel Quantitative Approach for Characterizing the Buried Metal/Coating Interfacial Kinetics Using Hydrogen Permeation Based Potentiometry** — •DANDAPANI VIJAYSHANKAR and MICHAEL ROHWERDER — Max-Planck -Institut für Eisenforschung GmbH

Electrochemical integrity of the buried metal/organic coating interface is crucially governed by the extent to which the cathodic oxygen reduction reaction (ORR) is curtailed. Current electrochemical techniques are unable to quantitatively probe such hidden interfaces due to the restricted ionic transport through the organic coating. Recently, a new non-destructive approach based on using hydrogen permeation as a tool to measure this ORR rate has been introduced. By correlating the dynamic equilibrium potential established between the oxygen reduction and hydrogen oxidation reactions on the coated exit side with the hydrogen uptake rate on the entry side, a full current-potential curve  $I(U)$ . Good concurrence between the  $I(U)$  curves derived from this permeation based potentiometry approach to that from standard three-electrode setup for the uncoated palladium, proved the correct measurement of the ORR rate. Underneath coatings, owing to interfacial charge transfer processes free of ion mobility, true ORR rate could be measured. Further, interfacial reaction kinetic mechanisms of the electrochemical ORR investigated by prolonged cathodic polarization experiments were found to destroy the interface similar to cathodic delamination process.

O 20.2 Mon 16:45 WIL B321

**Photoelectrochemical CO<sub>2</sub> reduction at nanostructured gold/copper structures on Si** — •SIMON FILSER<sup>1</sup>, THOMAS L. MAIER<sup>1</sup>, ROBIN NAGEL<sup>2</sup>, TIANYUE ZHANG<sup>3</sup>, WERNER SCHINDLER<sup>1</sup>, JOSEF ZIMMERMANN<sup>1</sup>, QI LI<sup>1</sup>, PAOLO LUGLI<sup>2</sup>, and KATHARINA KRISCHER<sup>1</sup> — <sup>1</sup>Non-equilibrium chemical physics, TU Munich, Germany — <sup>2</sup>Chair for Nanoelectronics, TU Munich, Germany — <sup>3</sup>Photonics and Optoelectronics Group, LMU Munich, Germany

Due to its unique properties copper is the most promising electrode material for the electrochemical reduction of CO<sub>2</sub> to CO, ethylene and methane; their distribution sensitively depends on the electrode surface and the reaction conditions [1].

Our aim is to integrate copper nanostructures into a photoelectrode to directly transform solar energy into chemical fuels. We approach such a system by structuring a silicon substrate with chessboard arrays of gold nanodisks which are electrochemically plated by copper.

In our work we examine how doping, illumination, structure size and copper coverage influence the electrochemical behavior and the product distribution.

Additionally, we show that our structures feature surface plasmon polaritons (SPPs) which are predicted to enhance the electric field close to the metal surface [2], strengthening the adsorption of reactants and to polarizing adsorbates leading to lower overpotentials and a higher selectivity.

[1] Y. Hori, et al., Chem. Lett., 1695-1698 (1985). [2] S. Sun et al., Cat. Comm. 11, 4, 290-293, (2009).

O 20.3 Mon 17:00 WIL B321

**Electro-oxidation of CO on model electrodes – Atomic scale level nanostructures and their impact on the catalyst performance** — •JENS KLEIN, SYLVAIN BRIMAUD, VALERIA CHESNYAK und R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

The performance of electrocatalytic reactions, such as the CO oxidation, on monometallic and bimetallic Pt-based electrodes is highly sensitive towards the surface structure and surface composition of the catalyst on the atomic scale level.<sup>[1]</sup> On Pt an increased activity for the CO oxidation was observed if the amount of monoatomic high Pt step edges increases, while on PtRu electrodes the appearance of adjacent Ru and Pt atoms in the surface were found to enhance the CO oxidation due to a bifunctional mechanism.<sup>[1]</sup> For a more detailed understanding of the structure-activity relationship on the atomic scale level we studied the CO oxidation on single crystal model electrodes with well-defined nanostructured surfaces. Employing a combined ultrahigh vacuum (UHV) – electrochemical flow cell setup we prepared and structurally characterized by scanning tunneling microscopy (STM) under

UHV conditions Pt(111) and Ru(0001), which were structurally modified on the atomic scale, e.g., by varying the Pt step edge density or the number of adjacent PtRu-sites followed by electrochemical characterization. The nature and abundance of specific structure elements was correlated with the CO oxidation activity to obtain information on the nature of different active sites and their relative activity.

[1] N.M. Marković et al., Surf. Sci. Rep. 45 (2002) 117.

O 20.4 Mon 17:15 WIL B321

**Investigation of the Electrode-Electrolyte Interface in Lithium Ion Batteries Studied by Surface Science Methods** — •THOMAS SPÄTH, DIRK BECKER, WOLFRAM JAEGERMANN, and RENÉ HAUSBRAND — Institute of Material Science, Darmstadt University of Technology, Jovanka-Bontschits-Str. 2, 64287 Darmstadt

Reactions and Solid-Electrolyte Interface (SEI) formation between electrodes and electrolytes play a key role for performance and lifetime of batteries. For a better understanding of the reactivity of solvents with Li-ion battery electrode materials, we perform adsorption experiments on model electrodes. In these experiments we use High Resolution Electron Energy Loss Spectroscopy (HREELS) and Photoemission Spectroscopy (PES) to study vibrational modes and chemical composition at the surface. As both techniques offer complementary information, HREELS data can support the PES measurements.

In this contribution we present the results of our investigations of the electrode-electrolyte interface performing a stepwise adsorption of diethyl carbonate and dimethyl carbonate both on sputtered thin films of *LiCoO<sub>2</sub>* and lithiated silicon surfaces. We discuss the assignment of the different features in the pristine spectra and present HREELS and PES spectra of the electrolyte adsorbed samples. For both techniques several new features can be observed, which are assigned to physically adsorbed species as well as chemisorbed or chemically reacted species. From this data we are able to conclude on the chemical reactions at the interfaces. This information allows us to obtain a deeper understanding of the SEI formation mechanisms in Lithium Ion Batteries.

O 20.5 Mon 17:30 WIL B321

**Li-Ion Battery Anodes: Electrochemical Model Studies at the Electrode|Electrolyte Interphase** — •ISABELLA WEBER<sup>1</sup>, JOHANNES SCHNAIDT<sup>2</sup>, CARINA BODIRSKY<sup>1</sup>, THOMAS DIEMANT<sup>1</sup>, and R. JÜRGEN BEHM<sup>1,2</sup> — <sup>1</sup>Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — <sup>2</sup>Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany

State-of-the-art Lithium-ion batteries (LIBs) consist of Li-intercalating electrode structures and blends of organic solvents mixed with Li-salts. During the charge/discharge process, a protective film forms at the electrode|electrolyte interface which is referred to as the solid-electrolyte interphase (SEI). Due to the complex composition of the electrodes (active material, binder, etc.) and the electrolyte, however, the processes leading to SEI formation are still a matter of discussion. For a more detailed understanding, we systematically studied model systems by varying the anode material (different graphite powders with or without binder) and electrolyte solvents (ethylene carbonate with LiPF<sub>6</sub>). Cyclic voltammetry was applied to characterize the electrolyte decomposition. Post-mortem XPS allowed the elemental analysis of the reduction products, as well as a depth-profiling of the SEI formed at different scan rates. In-situ infrared spectroscopy, finally, provided additional information on the adsorbed intermediates accumulated during SEI formation. The influence of the different LIB components on the formation, composition and product distribution of the SEI and the implications of our model studies on the understanding of the SEI formation in LIBs will be discussed.

O 20.6 Mon 17:45 WIL B321

**Model Studies on the Electrochemical Decomposition of BMP TFSI on Gold and Glassy Carbon Electrodes** — •DOROTHEA ALWAST<sup>1</sup>, JOHANNES SCHNAIDT<sup>2</sup>, KURTUS HANCOCK<sup>1</sup>, and R. JÜRGEN BEHM<sup>1,2</sup> — <sup>1</sup>Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — <sup>2</sup>Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany

Ionic liquids (ILs) have shown promise as possible electrolytes for batteries. Therefore, the electrochemical stability of these ILs plays a key

role for the use in batteries. In order to better understand the catalytic effect of different electrode materials on the electrochemical decomposition of ILs, we investigated the formation of volatile products of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (BMP TFSI) formed during linear potential sweeps on polycrystalline Au and GC electrodes. For the online analysis of the volatile decomposition products we used a differential electrochemical mass spectrometry (DEMS) setup specifically designed for studying ILs. On both gold and glassy carbon electrodes decomposition products of the TFSI anion ( $m/z = 69$ ,  $\text{CF}_3^+$ ;  $m/z = 64$ ,  $\text{SO}_2^+$ ) are mainly detected at positive potentials, while decomposition products of both ions are formed at negative potentials. The similarities and differences in the products' distribution on the two electrode materials and the implications of these findings on the mechanism of the IL's electrochemical decomposition will be discussed.

O 20.7 Mon 18:00 WIL B321

**Live, in situ STM observation of the oxidative roughening of Pt(111)** — ●LEON JACOBSE<sup>1</sup>, YI-FAN HUANG<sup>1</sup>, MARCEL J. ROST<sup>2</sup>, and MARC T.M. KOPER<sup>1</sup> — <sup>1</sup>Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands — <sup>2</sup>Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands

Platinum nanoparticles are used in a wide variety of catalytic processes. In many of these applications, e.g. the anodes of fuel cells, the platinum surface is (partly) oxidized. It is known that by oxidizing and reducing platinum electrochemically, its surface structure is altered, which plays a role in the degradation of the catalyst. However, even for well-defined single crystal surfaces, over thirty years of research did not yet yield a conclusive description of this process on the atomic level.

Using our high-speed, electrochemical scanning tunneling microscope (EC-STM) we continuously oxidized and reduced the surface while simultaneously imaging the surface on the atomic level during the full potential sweep. This provides us with unique information, from which we directly can correlate the changes in surface structure to the changes in the cyclic voltammetry. The formation of nanoscale islands, upon oxidizing and reducing the surface, goes hand in hand with an increase in the current related to hydrogen desorption from step edges. Surprisingly, the development of these islands seems to continue on much longer timescales than suggested in literature, where the evolution of the surface structure was studied in great detail by cyclic voltammetry.[1]

[1] e.g. *Electrochim. Acta* 2012, 82 (0), 558-569.