

CPP 53: Solid-liquid interfaces: Reactions and electrochemistry III (joint session O/CPP)

Time: Wednesday 15:00–16:15

Location: MA 144

CPP 53.1 Wed 15:00 MA 144

Atomically-Defined Pt/Co₃O₄(111) as Model Electrocatalyst — ●MANON BERTRAM, CORINNA STUMM, FIRAS FAISAL, YAROSLAVA LYKHACH, OLAF BRUMMEL, and JÖRG LIBUDA — Physikalische Chemie II, FAU Erlangen

The surface science approach, i.e. studying model catalysts in ultra-high vacuum (UHV), is well known in heterogeneous catalysis. We apply this approach to electrocatalysis and transfer complex, but well-defined catalysts from UHV to electrochemical (EC) conditions.

As a model system we prepared Pt nanoparticles (NPs) on ordered Co₃O₄(111) thin films on Ir(100). The oxide support and the complete catalyst were characterized by low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS) and other methods. We transferred the systems to EC environments under ultra-clean conditions. With a scanning flow cell coupled to an inductively coupled plasma mass spectrometer and EC infrared reflection-absorption spectroscopy (EC-IRRAS), LEED, and XPS we determined the stability window for the oxide support under EC conditions.

Using Pt/Co₃O₄(111) with different Pt loadings, we followed the CO electro-oxidation by EC-IRRAS and cyclic voltammetry. As reference, we studied CO adsorption under UHV conditions with infrared reflection absorption spectroscopy. We identify different adsorption sites, a suppression of bridging CO on small NPs, and electronic metal support interactions (EMSI) leading to formation of partially oxidized Pt. The EMSI influences the CO adsorption and, thus, the electrocatalytic properties.

CPP 53.2 Wed 15:15 MA 144

Real-Time Measurement of Silica Dissolution at the interface with water — ●JAN SCHAEFER, ELLEN H.G. BACKUS, and MISCHA BONN — Max Planck Institute for Polymer Research, Mainz, Germany

Dissolution processes of minerals in water are often studied on macroscopic scales by detecting dissolution products in bulk solution and inferring microscopic reaction rates using models that require assumptions. Here, we present a direct way to measure the dissolution rate of silica, a mineral of geological significance, in contact with water. We find that on a surprisingly short timescale of tens of hours, the interfacial concentration of dissolution products saturates at a level close to the solubility of silica (~ millimolar). As the bulk solution is known to be equilibrated only after several weeks, our results reveal that the macroscopic dissolution process is limited by diffusion. A comparison with a simple 1D reaction/diffusion model indicates that the diffusion coefficient of dissolved silica decays with progressing dissolution which suggests that the small silicic acid species polymerize next to the silica surface.

CPP 53.3 Wed 15:30 MA 144

Charge transfer across the n-GaP(100) photoanode/electrolyte interface during photoelectrochemical water splitting — ●WAQAS SADDIQUE, GERHARD LILIENKAMP, and WINFRIED DAUM — Institute of Energy Research and Physical Technologies, Technical University Clausthal, Clausthal-Zellerfeld, Germany

A detailed understanding of charge transfer across the electrode/electrolyte interface is required for the development of electrodes for efficient water splitting. We have studied the charge transfer processes across the n-GaP(100) photoanode/electrolyte interface at different photoelectrochemical (PEC) conditions. In a 0.02 M HCl electrolyte, high photoanodic currents from n-GaP(100) photoanodes related to photolytic water splitting were measured at low anodic potentials, these currents diminished at cathodic potentials as well as at high anodic potentials. Nyquist plots obtained from electrochemical impedance spectroscopy (EIS) results were analyzed with two differ-

ent equivalent electrical circuits (EECs) for the electrode/electrolyte charge transfer pathways. For both EECs, the potential dependence of resistances and constant phase elements were determined from fits to Nyquist plots and then compared with the potential variation of the current in the cyclic voltammogram. XPS measurements revealed that the surface oxide consists mainly of Ga₂O₃, while small concentrations of GaPO₄, P₂O₅ and metal-like Ga are also detected in the topmost layers. Our results suggest that energetically favorable absorption of hydroxide, presumably at metal-like surface Ga, and their subsequent oxidation at low anodic potentials lead to high currents.

CPP 53.4 Wed 15:45 MA 144

Epitaxial oxides as model electrodes for electrolyzer and fuel cell reactions at room temperature — ●MARCEL RISCH, JULIUS SCHOLZ, JANIS GEPPERT, LENNART KÖHLER, GARLEF WARTNER, and CHRISTIAN JOOSS — Georg-August-Universität Göttingen, Institut für Materialphysik,

Energy carriers based on sustainable hydrogen are highly desirable for storage of intermittent renewable energy. The performance of the required electrolyzer and fuel cell technology could be improved significantly by a fundamental understanding of the basic reaction steps of the oxygen electrodes, which present the current bottleneck for electrocatalysis at room temperature. The chemistry and correlation physics of perovskite oxides can be tuned by chemical substitution to derive property-activity relationships [1]. Epitaxial thin films with optimized composition are very active for both the evolution as well as reduction of oxygen [2]. Moreover, perovskite oxide films of conductive (La,Sr)MnO₃ showed terraces with unit cell step height and the perovskite structure was preserved after electrolysis in alkaline solution [3]. These properties make perovskite oxides ideal model surfaces to elucidate the catalytic mechanisms of oxygen evolution and reduction at room temperature. It will be discussed how the combination of materials physics, electrochemistry and spectroscopy leads to the desired mechanistic insight on selected perovskite oxides with defined surfaces.

References: [1] Risch et al., *Catalysts* 7, 139 (2017); [2] Risch et al., *J. Am. Chem. Soc.* 136, 5229 (2014); [3] Scholz et al., *J. Phys. Chem. C* 120, 27746 (2016), Scholz et al., *Catalysts* 7, 139 (2017).

CPP 53.5 Wed 16:00 MA 144

Operando Phonon Studies of the Protonation Mechanism in Highly Active Hydrogen Evolution Reaction Pentlandite Catalysts — ●IOANNIS ZEGKINOGLU¹, ALI ZENDEGANI², ILYA SINEV¹, ULF-PETER APFEL³, TILMANN HICKEL², and BEATRIZ ROLDAN CUENYA¹ — ¹Department of Physics, Ruhr-University Bochum, Germany — ²Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany — ³Inorganic Chemistry I, Ruhr-University Bochum, Germany

Synthetic pentlandite (Fe_{4.5}Ni_{4.5}S₈) is a promising electrocatalyst for hydrogen evolution, demonstrating high current densities, low overpotential, and remarkable stability in bulk form. The depletion of sulfur from the surface of this catalyst during the electrochemical reaction has been proposed to be beneficial for its catalytic performance. We have performed operando studies of the vibrational dynamics of pentlandite under hydrogen evolution reaction conditions using ⁵⁷Fe nuclear resonant inelastic X-ray scattering [1]. Comparing the measured Fe partial vibrational density of states with DFT calculations, we have demonstrated that hydrogen atoms preferentially occupy substitutional positions replacing pre-existing sulfur vacancies. Once all vacancies are filled, the protonation proceeds interstitially, which slows down the reaction. Our results highlight the beneficial role of sulfur vacancies in the electrocatalytic performance of pentlandite and give insights into the hydrogen adsorption mechanism during the reaction. [1] I. Zegkinoglou et al., *J. Am. Chem. Soc.* 139, 14360 (2017).