

O 60: Solid-liquid interfaces: Structure, Spectroscopy II

Time: Wednesday 10:30–11:45

Location: MA 144

O 60.1 Wed 10:30 MA 144

Adlayer formation of water and (co-)adsorbed CO on Ru(0001) and Pt_{nML}/Ru(0001) – A low temperature STM model study — •MARTIN SCHILLING, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm

Understanding the processes occurring at the electrode | electrolyte interface is of fundamental interest to understand the electrochemical/-catalytic processes on a catalyst surface in an aqueous environment. The adsorption of water on monometallic single crystal surfaces can be considered as model system for the solid | electrolyte interface, and accordingly this has been studied intensely, including STM studies [1,2]. Here it is important to note, that for water adsorption adsorbate-adsorbate interactions play a pronounced, if not dominant role for the structure formation process. Here we report results of a low temperature STM study, where we investigated the adlayer formation of (co-)adsorbed water and CO on Pt_{nML}/Ru(0001) [3,4] and Ru(0001) surfaces under UHV conditions. We discuss first the observed structures, and the role of adsorbate-metal and adsorbate-adsorbate interactions. Next, we propose a kinetic model describing the adlayer formation, and finally we discuss the role of competing of different adsorbed species (H₂O, OH, CO, H) in the structure formation process. [1] J. Carrasco, A. Hodgson, A. Michaelides, *Nat. Mater.* **11** (2012) 667; [2] H.J. Yang, T. Minato, M. Kawai, Y. Kim, *J. Phys. Chem. C* **117** (2013) 16429; [3] M. Schilling, S. Brimaud, R.J. Behm, *PCCP* **19** (2017) 22434; [4] M. Schilling, S. Brimaud, R.J. Behm, *Surf. Sci.*, in press (2017).

O 60.2 Wed 10:45 MA 144

The Ionic Liquid|Graphite and Lithiated Graphite Interface – A Model Study for the Solid|Electrolyte Interphase in Li-ion Batteries — •FLORIAN BUCHNER^{1,2}, JIHYUN KIM², KATRIN FORSTER-TONIGOLD¹, ISABELLA WEBER², JOHANNES SCHNAIDT¹, JOACHIM BANSMANN², AXEL GROSS³, and R. JÜRGEN BEHM^{1,2} — ¹Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany — ²Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ³Ulm University, Institute of Theoretical Chemistry, D-89069 Ulm, Germany

Here we report results of a UHV study on the interaction of an Ionic Liquid (IL) with graphite(0001) as a model study for the solid|electrolyte interphase (SEI) in Li-ion batteries. The interaction of mono- and multilayers of the battery-relevant IL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BMP][TFSI] with pristine/lithiated graphite was investigated, employing X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) and dispersion corrected density functional calculations (DFT-D). The measurements reveal that intact ion pairs adsorb on graphite, while deposition on lithiated graphite at 300 K (>230 K) leads to instantaneous deintercalation of Li⁺. In general, contact of the IL with Li, either after deintercalation from lithiated graphite or after deposition from the vacuum side, results in the decomposition of the IL adlayer (Li₃N, Li₂S, etc.). The decomposition is different for multilayers. We will also compare the observed products with that in the electrochemical SEI in [Li][TFSI]/[BMP][TFSI].

O 60.3 Wed 11:00 MA 144

Potential-dependent distance-tunneling-current spectroscopy at the interface of gold(111) in an ionic liquid — •MARCEL LANG, STEFAN HERZOG, JEANNETE LINDNER, and ROLF SCHUSTER — Karlsruhe Institute of Technology, Karlsruhe, Germany

The behavior of ionic liquids at charged surfaces is fundamentally different from diluted electrolytes. For example ionic liquids form differ-

ent multi-layered structures depending on the polarization of the gold electrode.

We investigated the interface [BMP][TFSI] on gold(111) using an STM under inert gas atmosphere operating at room temperature. We could observe two distinctly different behaviours depending on the polarisation of the gold electrode. At potentials positive of -0.5 V vs Pt the barrier height steadily increases with distance. At potentials below -0.9 V vs Pt the barrier height shows local maxima and minima. The features in the measurements below -0.9 V vs Pt can be attributed to the structure of the first layer of the liquid.

O 60.4 Wed 11:15 MA 144

Time-resolved Electrochemical Surface Plasmon Resonance (SPR) Studies of the Aggregation of Surfactant Molecules at a Solid-liquid Interface — •KARIN SCHLAG, CHRISTIAN KÜHN, DETLEF NATTLAND, and ROLF SCHUSTER — Karlsruhe Institute of Technology, Karlsruhe, Germany

The potential induced adsorption and phase transitions of dodecyl sulfate molecules on Au(111) have been studied with time-resolved surface plasmon resonance spectroscopy (a full plasmon profile per millisecond). Plasmons are excited at a 50 nm thin gold film working electrode using the Kretschmann configuration for attenuated total reflection. Position and shape of the curve are highly sensitive to the dielectric properties at the interface. Thus, changes of the coverage by fractions of a monolayer or variations of the thickness of an adsorbed layer can be detected. A multilayer model is used to interpret the plasmon profiles in which each layer is characterized by its thickness and its complex refractive index. While cycling through the phase transition from a hemicylindrical to a compact phase of the sodium dodecyl sulfate (SDS) system we obtained a shift to higher resonance angles with increasing potential. On the reverse direction we observe a hysteresis in the shift of the resonance angle. This finding is in line with potential pulse experiments, which imply a nucleation and growth process along this first order phase transition on a timescale of several 100 milliseconds.

O 60.5 Wed 11:30 MA 144

Hydration of Concrete: The first steps — •PETER THISEN, NICOLAS GIRAUDO, CARSTEN NATZECK, and CHRISTOF WÖLL — Karlsruher Institut für Technologie (KIT), Institut für Funktionelle Grenzflächen (IFG), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Concrete is the most important construction material used by mankind and, at the same time, one of the most complex substances known in materials science. Since this mineral compound is highly porous, a better understanding of its surface chemistry, and in particular the reaction with water, is urgently required to understand and avoid corrosion of infrastructure. We have gained insight into proton transfer from concrete upon contact with water by applying the so-called Surface Science approach to a well-defined mineral, Wollastonite. Data from infrared spectroscopy reveal that exposure of this Calcium-Silicate (CS) substrate to water leads to dissociation and the formation of OH-species. This proton transfer is a chemical reaction of key importance, since on the one hand it triggers the conversion of cement into concrete (a CSH phase), but on the other hand also governs the corrosion of concrete. Interestingly, we find that no proton transfer takes place when the same surface is exposed to methanol. In order to understand this unexpected difference, the analysis of the spectroscopic data obtained was aided by a detailed, first-principles computational study employing density functional theory (DFT). The combined experimental and theoretical effort allows deriving a consistent picture of proton transfer reactions occurring on CS and CSH phases.