

O 33: Solid-Liquid Interfaces III

Time: Tuesday 14:00–16:15

Location: H10

O 33.1 Tue 14:00 H10

Interaction of ethylene carbonate and lithium on thin cobalt oxide films - A model of the electrode|electrolyte interphase in Li-ion batteries — ●JIHYUN KIM¹, FLORIAN BUCHNER¹, and R. JÜRGEN BEHM^{1,2} — ¹Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — ²Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany

In this model study, we aim to get a molecular scale understanding of the initial stages of the formation of the electrolyte interphase (SEI) at the electrode|electrolyte interface, which plays a critical role in the performance of Li ion batteries (LIBs). Here, we report on the interaction of ethylene carbonate (EC, main electrolyte component in LIBs) with a thin film of CoO(111) grown on Ru(0001), which was investigated by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIRS) under UHV conditions. EC adsorbs molecularly intact on CoO(111) at 80 K and is stable below 200 K, while above 240 K EC decomposition is initiated. To mimic the electrolyte, 0.5 - 2 ML of Li was stepwise post-deposited on an EC adlayer at 80 K, which leads to EC decomposition most likely into Li-containing -C=O, -C-O-C-, -C-H species as well as Li₂O₂ or LiOH. For CoO anodes in LIBs, lithiation leads to a conversion reaction of CoO into Co⁰ as well as Li₂O. However, for Li doses on EC adlayer at 80 K, we hardly observe such a reaction, indicating that Li directly interacts with EC. Only for Li doses on pristine CoO at 300 K, Co⁰ forms in the near surface regime. The results demonstrate the initial stage of the chemical SEI formation as well as the conversion of CoO.

O 33.2 Tue 14:15 H10

The ionic liquid|cobalt oxide interface and interaction with lithium - A model study for the solid|electrolyte interphase in Li-ion batteries — ●FLORIAN BUCHNER¹, JIHYUN KIM¹, and R. JÜRGEN BEHM^{1,2} — ¹Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — ²Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany

Here we report results of a UHV study on the interaction of an Ionic Liquid (IL) with lithium on different cobalt oxide thin films as a model study for the solid|electrolyte interphase (SEI) in Li-ion batteries (LIBs). After characterization of CoO(111) and Co₃O₄(111) by X-ray photoelectron spectroscopy (XPS) and scanning probe microscopy, the interaction of ultrathin films of the battery-relevant IL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BMP][TFSI] with Li on CoO and Co₃O₄(111) was investigated, employing mainly XPS. The measurements reveal that intact ion pairs adsorb on both CoO_x surfaces and that postdeposition of Li results in the decomposition of the cations and anions (Li₃N, LiC_xH_yN_z, LiF, etc.). In addition, the measurements reveal that Li deposition (both in the presence and absence of an IL adlayer) leads to the conversion of Co²⁺ to Co⁰ on CoO and the transformation from Co³⁺ to Co²⁺ on Co₃O₄(111) in the near surface region, due to charge transfer from Li to the surface together with the formation of Li₂O. Hence, the XP spectra resolve the initial stages of the chemical SEI formation (IL decomposition) (in the absence of an applied potential) as well as the reduction of CoO_x, which both play an essential role in the function of LIBs.

O 33.3 Tue 14:30 H10

Trapped electrons and their impact on oxygen reactivity near DMSO/Cu(111) interfaces — ●ANGELIKA DEMLING¹, SARAH B. KING², KATHARINA BROCH³, and JULIA STÄHLER¹ — ¹Department of Physical Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany — ²Department of Chemistry and James Franck Institute, University of Chicago, 929 E 57th Street, Chicago, IL 60637, USA — ³Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany

DMSO is a common non-aqueous solvent with the potential to be used in lithium-oxygen batteries due to its ability to catalyze superoxide formation [1]. In this study we investigate the electron dynamics in DMSO films on Cu(111) using time- and angle-resolved two-photon photoemission and disentangle the individual steps of charge transfer prior to superoxide formation: Electrons are injected from the metal to the DMSO where they form small polarons on sub-picosecond time scales. The subsequent trapping extends the electronic lifetimes to several seconds [2]. Electron attachment to co-adsorbed O₂ reduces

these lifetimes significantly and leads to negative surface charging.

These results highlight the complexity of a standard electrochemical process like superoxide formation.

[1] K. M. Abraham, *J. Electrochem. Soc.* 162, A3021 (2015)

[2] S. B. King et al., *J. Chem. Phys.* 150, 041702 (2019)

O 33.4 Tue 14:45 H10

DFT studies on the interface between an ionic liquid and inorganic substrates — ●KATRIN FORSTER-TONIGOLD¹ and AXEL GROSS^{1,2} — ¹Helmholtz Institute Ulm (HIU), Electrochemical Energy Storage, 89069 Ulm, Germany — ²Ulm University, Institute of Theoretical Chemistry, 89069 Ulm, Germany

In Li-ion batteries the so-called solid|electrolyte interphase (SEI) is formed at the electrode due to decomposition of the electrolyte. As it plays a crucial role for the function of the battery, a thorough understanding of the interface is needed. We employ density functional theory calculations to study the interface between the ionic liquid (IL) 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide used as electrolyte in Li-ion batteries and different inorganic substrates. First, the geometric and electronic adsorption properties of the IL at low coverages and within the monolayer structure at low temperature are discussed [1]. Furthermore, the impact of elevated temperature is taken into account by means of ab initio molecular dynamics simulations. In order to shed some light onto the initial steps of the SEI formation, interactions and reactions between the IL and Li atoms at the interface are considered as well [2].

[1] F. Buchner, K. Forster-Tonigold, M. Bozorgchenani, A. Groß and R. J. Behm. *J. Phys. Chem. Lett.* 7, 226 (2016).

[2] F. Buchner, K. Forster-Tonigold, J. Kim, C. Adler, J. Bansmann, A. Groß and R. J. Behm, *J. Phys. Chem. C* 122, 18968-18981 (2018).

O 33.5 Tue 15:00 H10

Ion Exchange at the Liquid/Solid Interface in Ultrathin Ionic Liquid Films on Ag(111) — ●MATTHIAS LEXOW, BETTINA HELLER, RADHA G. BHUIN, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

In the context of ionic liquid (IL) thin film applications, we studied mixed IL systems with respect to surface and interface ion distribution by angle-resolved X-ray photoelectron spectroscopy (ARXPS) as a function of anion, cation, composition, and temperature. By *in-situ* physical vapor deposition, ultrathin layers of two ILs were successively deposited on Ag(111) as model support. By temperature-dependent ARXPS, we found pronounced surface and interface enrichment effects due to rapid ion exchange processes that are proposed to be driven by the interplay of interface adsorption energy and surface free energy in these films.

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Lexow *et al.*, *ChemPhysChem*, **2018**, DOI: 10.1002/cphc.201800773.

Lexow *et al.*, *Langmuir*, **2018**, submitted.

O 33.6 Tue 15:15 H10

Charge transfer across the GaP(100) photoanode/electrolyte interface during direct, Au-catalysed photoelectrochemical water splitting — ●WAQAS SADDIQUE, GERHARD LILIENKAMP, and WINFRIED DAUM — IEPT, Technical University Clausthal, Clausthal-Zellerfeld, Germany

We have developed a procedure to stabilize n-GaP(100) for operation as a photoanode in hydrochloric acid electrolytes by a thin and dense surface layer of gallium oxide. Here, we report on direct photoelectrochemical water splitting achieved with stabilized photoanodes that, in addition, were functionalized with Au nanoparticles (NPs) as catalysts for water oxidation. The pronounced peaking of the photocurrent at a potential around 0 V vs RHE points to an indirect charge transfer of holes across the semiconductor/electrolyte interface, presumably via defect or interface states with energies in the band gap of GaP. To investigate the charge transfer processes at GaP photoanodes, Nyquist plots were measured for different applied potentials by electrochemical impedance spectroscopy, and reproduced by simulations with an appropriate equivalent electrical circuit. The plots reveal minimum impedance at a potential of -0.05 V vs RHE, which coincides with the

exact potential of maximum photocurrent in cyclic voltammetry. The Nyquist plots are composed of 6 (!) semi-circles, and their specific potential dependence reveals unprecedented details of a 6-step charge transfer process that includes all four steps of the water oxidation reaction. Our results highlight the favourable electrocatalytic properties of Au-NPs for all intermediate steps of the water oxidation reaction.

O 33.7 Tue 15:30 H10

Semiconductor/water interfaces: ab initio molecular dynamics at constant electrode potential and spectroscopic signatures — ●STEFAN WIPPERMANN¹, LEI YANG², FANG NIU¹, MARC PANDER¹, ANDREAS ERBE³, MIRA TODOROVA¹, and JÖRG NEUGEBAUER¹ — ¹Max-Planck-Institut für Eisenforschung, Germany — ²Kanazawa University, Japan — ³NTNU Trondheim, Norway

Despite the importance of understanding the structural and bonding properties of solid-liquid interfaces for a wide range of (photo-)electrochemical applications, there are presently no experimental techniques available to directly probe the microscopic structure of solid-liquid interfaces. To develop robust strategies to interpret experiments and validate theory, we carried out attenuated total internal reflection (ATR-IR) spectroscopy measurements and ab initio molecular dynamics (AIMD) calculations for interfaces between liquid water and well-controlled prototypical semiconductor substrates. The calculations are performed at constant electrode potential, based on the approach recently suggested by S. Surendralal et al. [1]. We discuss interactions between commonly used thermostats and the potentiostat, and suggest to introduce temperature-induced dipole fluctuations directly into the potentiostat scheme. This new approach has been validated by extensive benchmarks and is shown to not affect the vibrational spectra at the solid-liquid interface. Support from BMBF NanoMatFutur grant No. 13N12972 is gratefully acknowledged.

[1] S. Surendralal, M. Todorova, M. Finnis, J. Neugebauer, Phys. Rev. Lett. 120 246801 (2018)

O 33.8 Tue 15:45 H10

Two-dimensional Polymer Structures for Energy Conversion — ●PATRICK ALEXA¹, DORIS GRUMELLI², JUAN LOMBARDI³, PAULA ABUFAGER³, HERIBERTO BUSNENGO³, VIJAY VYAS¹, FREDERIK HAASE¹, BETTINA LOTSCH^{1,4}, RICO GUTZLER¹, and KLAUS KERN^{1,5} — ¹Max Planck Institute for Solid State Research, Stuttgart, Germany — ²Universidad Nacional de La Plata, Argentina — ³Universidad Nacional de Rosario, Argentina — ⁴University of Munich (LMU), Germany — ⁵Ecole Polytechnique Fédérale de Lausanne,

Switzerland

During the last decade the necessity for clean and renewable energy sources has driven societal and political agendas. Progress in energy conversion chemistry can be achieved by the utilization of tailored nanomaterials created in a bottom-up approach, for example when used as efficient electrocatalysts. In this work we investigate two-dimensional networks for their propensity for the hydrogen evolution reaction. In particular, we synthesize two-dimensional polymers with varying amount of nitrogen heteroatoms on Au(111) and visualize their topography by scanning tunneling microscopy. The polymer decorated surface shows promising enhancement effects for the catalytic activity of the hydrogen evolution reaction. The influence of the electrochemical conditions on the organic structure is discussed as well as the varying nitrogen content on electrocatalytic activity. The experimental and theoretical results highlight the capability of single-layer functional two-dimensional polymers for electrocatalysis and provide a molecular picture that explains increased catalytic activity.

O 33.9 Tue 16:00 H10

Theoretical study of two-dimensional titanium carbide MXenes functionalization process — ●RINA IBRAGIMOVA, MARTTI PUSKA, and HANNU-PEKKA KOMSA — Aalto University, Espoo, Finland

MXene phases are a new rapidly developing class of two-dimensional materials with suitable electronic, optical and mechanical properties for different applications. These phases consist of transition metals such as Ti, Sc, Zr, Hf, V, Nb, Ta, Cr, Mo and carbon or nitrogen atoms, and can be produced through the etching of layered MAX phases. During the etching process, it is possible to terminate the surface by O, OH, and F functional groups in order to modify materials properties. In this work, we accurately describe the surface distribution of functional groups and its interaction with Ti-based two-dimensional carbides in the solution through the use of different approaches. The free Gibbs energies of formation for the distinctly terminated surfaces have studied by combining DFT, phonon calculations and implicit solvation model. Our results indicate the formation of O, OH and F mixture, which coincides with experimental data. Furthermore, DFT together with cluster expansion (CE), and Monte Carlo methods are employed to investigate the distribution of the functional groups on the surface. The proposed computational approach allows us to deeper understand a functionalization mechanism and introduce the range of experimental conditions for further tuning the MXenes properties.