

O 84: Poster Session - Solid-Liquid Interfaces: Reactions and Electrochemistry

Time: Wednesday 18:15–20:00

Location: P2/EG

O 84.1 Wed 18:15 P2/EG

Water-Based Electrolytes and Porous Tungsten Oxide in Electrochromic Cells — ●FLORIAN EBERHEIM, THI HAI QUYEN NGUYEN, and DERCK SCHLETTWEIN — Justus Liebig University Gießen, Institute of Applied Physics

Sputter-deposited tungsten oxide (WO_3) is commercially applied in light-managing devices (smart windows). The aim of this work consists in the preparation of porous WO_3 films and in the measurement of their electrochromic characteristics in contact to aqueous $LiCl$, $NaCl$, KCl and H_2SO_4 as alternatives to the established Li^+ -containing organic electrolytes. The films were prepared by spin-coating a precursor solution with *poly(ethylene glycole)* (PEG) of different molecular weight as additives and subsequent heating on a hot-plate at 250°C. Amorphous WO_3 was formed, shown by SEM and EDX. The transparent films were characterized by cyclic voltammetry and chronoamperometry while optical transmission was simultaneously monitored. It was shown that the films prepared with PEG as additive showed improved contrast of transmission compared to films prepared without additives. The water-based electrolytes led to the same blue coloration as the films in contact to Li^+ . Electrolytes with protons as ions reached the best coloration characteristics, but led to faster degradation of the films. It was shown in this study that porous WO_3 films reversibly switch their optical transmission by intercalation of ions from water-based electrolytes. Such combinations could be a healthy and inexpensive alternative to the established state-of-the-art.

O 84.2 Wed 18:15 P2/EG

Ab-initio studies of surface interactions on chevrel and spinel phases — ●KATHARINA HELMBRECHT — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

Due to substantial supply risks and safety issues associated with Li-ion batteries, there is a need for the development of post lithium batteries employing more abundant battery chemistries. However, this requires to identify new materials for electrodes and electrolytes. We will present first-principles electronic structure calculations based on density functional theory (DFT) to determine the most stable surface configuration of the chevrel phase (Mo_6S_8) which is regarded as a promising electrode material for Mg-ion batteries.

In order to estimate the Mg ion mobility in the chevrel phase, Mg bulk diffusion barriers were determined. Furthermore, the adsorption and intercalation of aluminum chlorides were studied, since aluminum is often used as a 'collector' for the chloride ions left on the surface after magnesium intercalation. In addition, a magnesium-lithium hybrid battery model was investigated by comparing the intercalation of lithium chloride and magnesium chloride into the chevrel phase. In order to model the electrode-electrolyte interface, the interaction of an organo-aluminum electrolyte proposed by Aurbach et al.[1] was determined, which also allows addressing desolvation processes and first steps of the formation of the solid electrolyte interphase (SEI). The results will be compared to corresponding studies for the spinel phase ($Mg(SSC_2)_2$).

[1] D.Aurbach et al., Nature **407**, 724-727 (2000).

O 84.3 Wed 18:15 P2/EG

Exploiting TEMPOL as redox mediator in water-based DSSCs — ●ROBERTO FANTIN, ANDREAS RINGLEB, RAFFAEL RUESS, DANIEL HOLZHACKER, and DERCK SCHLETTWEIN — Justus Liebig University Gießen, Institute of Applied Physics

In recent years, water-based dye-sensitized solar cells (DSSCs) emerged as a valid alternative to traditional organic solvent-based DSSCs, to improve stability and environmental compatibility, and reduce overall costs. Thus, all the other components of the device should be tailored to water. In this work, an aqueous solution of 4-*hydroxy*-2,2,6,6-tetramethylpiperidinyloxy (*TEMPOL*) was investigated as a study case in combination with photoanodes made of TiO_2 nanoparticles sensitized by a commercial dye, Y123. The multiple interactions occurring between electrolyte, photoanode, and cathode are highlighted. *TEMPOL* is a hydrophilic derivative of *TEMPO*, which is already known as a redox shuttle due to the fast and reversible charge-transfer kinetics. The interactions between *TEMPOL* and common additives in DSSCs such as 1-*methylbenzimidazole* and 4-*tert-butylpyridine*, needed to slow down recombination processes at the anode, dramati-

cally change the reaction mechanism at the counter electrode (CE). *Pt* and *PEDOT* were tested on the CE to improve the reduction of *TEMPOL*⁺. Both types of CE were modified with an ionomer (*Nafion*) in an attempt to accumulate *TEMPOL*⁺. Full DSSCs were characterized by I-V curves and electrochemical impedance spectroscopy (EIS), while the CEs were separately studied by cyclic voltammetry (CV) in a symmetrical two electrode setup.

O 84.4 Wed 18:15 P2/EG

Assembly and Characterization of Aqueous Dye-sensitized Solar Cells with Organic Nitroxides as Redox-mediators — ●DANIEL HOLZHACKER, RAFFAEL RUESS, and DERCK SCHLETTWEIN — Justus Liebig University Gießen, Institute of Applied Physics

Dye-sensitized solar cells (DSSCs) present a possible low-cost technology for the conversion of sunlight into electrical energy. The most efficient DSSCs are based on organic *cobalt* (II/III)-complexes in organic solvents, i.e. acetonitrile. Due to environmental reasons it is attractive to avoid the organic solvents. In view of the damage caused by water contamination in organic electrolytes, replacing acetonitrile by water seems to be a big challenge in DSSC research. Following tests on one or two components, complete aqueous DSSCs were assembled. Using cyclic voltammetry (CV) the diffusion coefficient and the redox-potential of the organic nitroxides in water were determined. For the investigation of the energy levels of the adsorbed dyes, CV and UV/vis-spectroscopy were performed. The cells were based on thin (2 – 3 μm) screen-printed and annealed *titania* films, sensitized with different organic dyes (*D51*, *D35* or *Y123*) overnight. J-V-curves and transient photocurrents of the different types of cells were measured. Power conversion efficiencies up to 4.4 %, which are among the highest reached for aqueous DSSCs so far, could be achieved using the molecule *TEMPO* as redox-mediator. Its derivatives *AZADO* and *TEMPOL* showed great potential in photocurrent and open circuit voltage but a limitation in the fill factor indicates the need for further investigations.

O 84.5 Wed 18:15 P2/EG

Characterization of Microelectrodes for Scanning Electrochemical Microscopy — ●LEON ROSENBECKER, RAFFAEL RUESS, and DERCK SCHLETTWEIN — Justus Liebig University Gießen, Institute of Applied Physics

Scanning electrochemical microscopy (SECM) can be used to investigate the dye regeneration process of dye-sensitized solar cells (DSSCs).[1] In the present work, we studied the performance and stability of different catalytic layers for the microelectrodes. The electrodes have been structured using photolithography on a polyethylene terephthalate (PET) substrate coated with indium tin oxide (ITO). However, as shown by cyclic voltammetry (CV), ITO does not provide sufficiently fast electrode kinetics. Therefore, PEDOT and gold have been coated onto the ITO microelectrodes. Sputtered gold has proven to be a suitable layer since it has shown high catalytic activity and high stability. Gold coated microelectrodes have then been used for SECM measurements in feedback mode using an actuator to press the microelectrodes against an insulator. A decrease in steady state current has been measured. However, the measured decrease is lower than expected. This is due to an imprecise landing of the microelectrode on the substrate. Presently, we are working on a more precise arrangement and progress will be discussed.

[1]. R. Ruess, S. Scarabino, A. Ringleb, K. Nonomura, N. Vlachopoulos, A. Hagfeldt, G. Wittstock, D. Schlettwein, *Phys.Chem.Chem.Phys.*, 2019, **21**, 13047-13057.

O 84.6 Wed 18:15 P2/EG

Effects of H₂O on CO₂ Electroreduction Reactions at Platinum/Imidazolium Based Ionic Liquid Interfaces — ●BJÖRN RATSCHMEIER, ANDRE KEMNA, and BJÖRN BRAUNSCHWEIG — Institute of Physical Chemistry, Münster, Germany

CO₂ reduction reactions (CO₂RR), which are interesting for power-to-x applications, have been studied on polycrystalline Pt electrodes in the following room-temperature ionic liquids (RTIL): [EMIM][DCA], [EMIM][BF₄] and [OMIM][BF₄]. Because water can play an important role as cosolvent and coreactant, we have addressed CO₂RR as a function of water concentration. Cyclic voltammetry (CV) indicates a

strong rise of activity for CO₂RR when the water concentration was increased. In order to provide molecular-level details, we have additionally applied *in operando* IR Absorption spectroscopy (IRAS) to reveal reaction products in the bulk electrolyte and *in situ* vibrational sum-frequency generation (SFG) to address surface-adsorbed species. From IRAS, we show that the formation of a imidazolium-COOH intermediate takes place at electrode potentials of -0.9 V vs SHE when the water concentration was as low as 31 mM, but is shifted to lower overpotentials at 1 M H₂O for all studied ionic liquids. In addition, SFG spectroscopy provides clear evidence for the formation of CO on Pt atop surface sites, which was used to determine the onset potential for the formation of CO. While in [OMIM][BF₄] no CO is formed even at very low potentials of -1.5 V, a significant decrease of the onset potential for CO formation with increasing water concentration is seen for the other RTIL.

O 84.7 Wed 18:15 P2/EG

Sum-Frequency Generation Spectroscopy of Water at [EMIM][BF₄]/Platinum Electrolyte/Electrode interfaces — ●ANDRE KEMNA and BJÖRN BRAUNSCHWEIG — Institute of Physical Chemistry, WWU Münster, 48149 Münster, Germany

In room-temperature ionic liquids (RTIL), the presence of water can heavily influence reactions at the electrode/electrolyte interface. In case of CO₂ reduction reactions, water influences the catalysis of CO₂ substantially. In order to gain a detailed molecular-level understanding, *in situ* studies of the interfacial water structure as a function of electrode potential are desirable. Using vibrational sum-frequency generation (SFG), we have now revealed the presence and structure of water at platinum interfaces in contact with a RTIL and as a function of electrode potential. At the [EMIM][BF₄]/Pt interface, the addition of water leads first to negligible O-H contributions to the SFG spectra at open circuit potentials, but to broad bands at 3200 and 3450 cm⁻¹ when the potential control is established. These bands are attributable to O-H stretching bands from hydrogen bonded interfacial molecules. Because the SFG intensity of the O-H bands increases during a cathodic sweep of the electrode potential, we propose that the interfacial layer of [EMIM][BF₄] in contact with a Pt electrode can be enriched with water molecules at low electrode potentials. In order to investigate the interaction of water at RTIL interfaces in more detail, we have applied SFG to the liquid/gas interface as an easily accessible model system. Here we demonstrate that the enrichment of water at RTIL interfaces strongly depends on the chemical identity of the cation.

O 84.8 Wed 18:15 P2/EG

Analysis of the electrochemical properties of Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_{2-δ} (NCM) thin film model cathodes — ●JULIUS K. DINTER, HENDRIK HEMMELMANN, and MATTHIAS T. ELM — Center for Materials Research, Gießen, Germany

Lithium ion batteries often suffer from capacity fading due to undesired side reaction occurring at the cathode surface. To get a deeper understanding of these side reactions, 2D model system are necessary. For this purpose, thin film NCM thin films were prepared via spin coating and annealing at high temperatures. A homogenous distribution of Ni, Co and Mn could be confirmed by EDX and SIMS measurements. The structural characteristics were analysed using Raman spectroscopy and XRD. Electrochemical properties were measured via cyclic voltammetry and cyclopotentiometry, confirming structural changes of the surface and an increase of the cell resistance, which indicates the formation of a solid electrolyte interface (SEI). Furthermore, the thin films were coated with Al₂O₃ using atomic layer deposition (ALD). Due to the coating of the NCM-thin film the long-term cycling stability could be improved and surface reactions were suppressed.

O 84.9 Wed 18:15 P2/EG

Characterization of the surface properties of coated and uncoated Ni-rich NCM cathodes by conductive atomic force microscopy — ●MIGUEL WICHE, RAJENDRA S. NEGI, and MATTHIAS T. ELM — Center for Materials Research, Gießen, Germany

One possibility to improve the cell performance of Lithium-ion batteries is coating of the cathode with a protective layer. The protective layer is typically an electronically insulating oxide, which suppresses side reactions at the electrode-electrolyte interface. However, a detailed understanding of the beneficial effect of the coating is still missing. Here, we present the coating of Ni-rich Li(Ni,Mn,Co)O₂ (NCM) powder with Al₂O₃ using an atomic-layer-deposition like solution based wet-chemical process. Energy dispersive X-ray spectroscopy images confirm a homogeneous Al₂O₃ coating on the NCM particles.

From the powders cathodes were prepared using binder and carbon as conductive additive. C-Rate and cycling tests indicate an improved electrochemical performance in comparison to cells with cathodes prepared from uncoated NCM powder. The surface of the cathodes of coated and uncoated NCM particles were investigated by conductive atomic force microscopy before and after cycling.

O 84.10 Wed 18:15 P2/EG

Surface plasmon resonance spectroscopy for surface reactions in aggressive organic solvents — ●ADRIAN JOE URBAN¹, DANIEL NÜRENBERG¹, DEB KUMAR BHOWMICK², and HELMUT ZACHARIAS¹ — ¹Center for Soft Nanoscience, Busso-Peuss-Straße 10, Münster — ²Faculty of Chemistry, Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel

Surface plasmon resonance (SPR) spectrometry in the Kretschmann configuration is a well established method to probe the gold-liquid interface. Commercially available devices typically work with aqueous solutions as the liquid phase while devices for more challenging solvents are rare. We have constructed an SPR spectrometer suitable for aggressive organic solvents and air-sensitive reagents in order to investigate the self-assembly of catalytically active, gold-based systems in organic solution. As a proof of concept, we have studied the self-assembly kinetics of alkanethiolen monolayers on a gold-surface. In these experiments, we obtained angle resolutions of up to $\Delta\theta = 0.01^\circ$, corresponding to $\Delta n \leq 10^{-3}$. Formation of the monolayers was complete after fifteen minutes.

O 84.11 Wed 18:15 P2/EG

In situ X-ray studies of electrodeposition at electrolyte-liquid metal interface — ●ANDREA SARTORI¹, OLAF MAGNUSSEN^{1,2}, and BRIDGET MURPHY^{1,2} — ¹University of Kiel — ²Ruprecht Haensel Laboratory, Kiel

We investigate nucleation and growth by *in situ* x-ray reflectivity and diffraction at liquid-liquid interfaces, focusing on Hg as liquid metal substrate in an electrochemical environment. By changing the electrolyte concentration, species and potential we can control the deposition mechanism. Liquid electrodes provide a stresses and defects-free template for nucleation and growth and ensure high mobility of reagent and products leading to high quality crystals. In previous studies of electrolyte containing NaF+NaBr+PbBr₂ the growth of a monolayer followed by 3D nanocrystal formation of PbBrF was observed. In the current experiments electrolytes were employed, which contain only a single halide anion species, namely NaBr+PbBr₂, NaCl+PbCl₂ NaF+PbF₂. Growth of Pb halide compounds is initiated by changing the potential from the amalgamation region, where the Pb²⁺ ions dissolve in the Hg, to a more positive potential, where the lead ions are dealumated. In all cases, a defined ultrathin adlayers are formed, followed by quasi-epitaxial growth of Pb-halides bulk crystals. These observations indicate that this growth behaviour is a general phenomenon. It may be explained by considering that for a potential positive of the amalgamation potential, the halide ions adsorb onto the Hg surface. When the Pb²⁺ is released from the Hg bulk, they coadsorb on top of the halide adsorbate, resulting in adlayer formation.

O 84.12 Wed 18:15 P2/EG

Magnesium intercalation in layered MoS₂ - Fast kinetics by Mg²⁺ complexation with DME ligands and MoS₂ phase transition upon intercalation — ZHENYOU LI^{1,2}, XIAOKE MU², ZHIRONG ZHAO-KARGER^{1,2}, ●THOMAS DIEMANT³, R. JÜRGEN BEHM^{1,3}, CHRISTIAN KÜBEL^{1,2,4}, and MAX FICHTNER^{1,2} — ¹Helmholtz Institute Ulm (HIU), Helmholtzstr. 11, D-89081 Ulm, Germany — ²Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany — ³Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm, Germany — ⁴Karlsruhe Nano Micro Facility, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

Rechargeable magnesium batteries are one of the most promising candidates for next-generation battery technology. Despite recent significant progress, it remains a challenge to overcome the sluggish kinetics caused by the strong interaction between double charged Mg²⁺ ions and the intercalation host. Herein, we report that fast intercalation kinetics in layered MoS₂ can be achieved when using solvated Mg(DME)_x²⁺. The high charge density of Mg²⁺ is mitigated by DME complexation, reducing the trapping force of the cathode lattice to the Mg²⁺ cations. We also studied the intercalation process by various

spectroscopic and microscopic methods and found a phase transition of the MoS₂ host from the semi-conductive 2H to the metallic 1T phase upon intercalation.

O 84.13 Wed 18:15 P2/EG

DFT study of the effect of Br co-adsorbates on the adsorption energy and diffusion energy barrier of S ad-atoms on Ag(100) — ●SÖNKE BUTTENSCHÖN and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

Halides affect adsorption and diffusion of ad-atoms on coinage metal surfaces (see the work of O. Magnussen and his group, e.g. Ref. [1]). We have carried through density-functional total-energy calculations using the code PWscf and PWneb from the Quantum Espresso package [2] to quantify the effect of a single or few Br co-adsorbates on the adsorption energy and diffusion energy barrier of a sulfur ad-atom on the Ag(100) surface. We find a repulsive S–Br interaction, which amounts to a decrease of the absolute value of the sulfur adsorption energy by about 0.06 eV if S and Br occupy next-nearest neighbor positions on the p(1×1) substrate lattice. The repulsion decreases rapidly with separation. The S–Br interaction is compared with a superposition of the interaction energies of individual S–Br pairs. The energy of the transition state for sulfur surface diffusion varies less. We discuss the correlation with the adsorption energies of the respective initial and final S-adsorption configurations.

[1] B. Rahn, O. M. Magnussen, *ChemElectroChem* **5**, 3073 (2018).

[2] P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **21**, 395502 (2009), *ibid.* **29**, 465901 (2017).

O 84.14 Wed 18:15 P2/EG

Au (111)-water interface under external electric fields: An ab initio molecular dynamics study — ●AZADE YAZDANYAR, YUKI NAGAT, and KATRIN DOMKE — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Metal-water interfaces are present in many experimental settings and are of great relevance to various fields of study including electrochemistry. Therefore, a thorough understanding of water structure on the surface is essential and yet missing for many systems. Due to the exceptional properties of water and its complex behavior, computational methods can be great assets in providing unique insights to the metal-water interfaces, which may not be easily accessible via experiment.

Here, we study the Au (111)-water interface in the presence of an electric field using ab initio molecular dynamics simulations. The effect of the presence of the electric field and its strength on the interfacial water is studied. To be able to distinguish the effect of hydrogen bonding on the extent of re-orientation of water molecules due to the applied electric field, we compare the system containing a single water molecule with another system containing several layers of water, where the properties of bulk water are recovered. Our results so far show that upon applying the electric field the interfacial water seems to re-orient very weakly and may be dominated by the hydrogen bonding.