

CPP 19: Energy Storage and Batteries II

Time: Tuesday 9:30–12:45

Location: H 0111

CPP 19.1 Tue 9:30 H 0111

Reactive molecular dynamics simulations of Lithium-ion battery electrolyte degradation — ●YOUSSEF MABROUK¹, DIDDO DIDDENS², and ANDREAS HEUER³ — ¹Forschungszentrum Jülich GmbH, Helmholtz-Institute Münster (IEK-12), Corrensstraße 46, 48149 Münster, Germany — ²Forschungszentrum Jülich GmbH, Helmholtz-Institute Münster (IEK-12), Corrensstraße 46, 48149 Münster, Germany — ³Institute of Physical Chemistry, University of Münster, Corrensstrasse 28/30, 48149 Münster, Germany

The development of reliable computational methods for novel battery materials has become essential due to the recently intensified research efforts on more sustainable energy storage materials. Here, we use a recently developed framework allowing to consistently incorporate quantum-mechanical activation barriers to classical molecular dynamics simulations to study the reductive solvent decomposition and formation of the solid electrolyte interphase for a graphite/carbonate electrolyte interface. We focus on deriving condensed-phase effective rates based on the elementary gas-phase reduction and decomposition energy barriers. After a short initial transient limited by the elementary barriers, we observe that the effective rate shows a transition to a kinetically slow regime influenced by the changing coordination environment and the ionic fluxes between the bulk electrolyte and the interface. We also discuss the impact of the decomposition on the ionic mobility. Thus, our work shows how elementary first-principles properties can be mechanistically leveraged to provide fundamental insights into electrochemical stability of battery electrolytes.

CPP 19.2 Tue 9:45 H 0111

Design, fabrication and nano-scale characterization of novel SEI layers — ●ZHUIJUN XU¹, GUANGJIU PAN¹, YAJUN CHENG², YONGGAO XIA², and PETER MÜLLER-BUSCHBAUM^{1,3} — ¹TUM School of Natural Sciences, Chair for Functional Materials, 85748 Garching, Germany — ²Ningbo Institute of Materials Technology and Engineering, CAS, Ningbo, 315201, China — ³TUM, MLZ, 85748 Garching, Germany

Lithium has a high specific capacity of 3860 mAh/g and a low electrochemical potential (-3.04 V), promising a high energy density lithium metal battery (LMB). However, the growth of lithium dendrites during charging and discharging would penetrate the separators in LMBs, which leads to short circuits. To inhibit the growth of lithium dendrites, we focus on optimizing the SEI layer through synergetic additives (FEC & LiNO₃) in commercial carbonate electrolytes.

In the traditional carbonate electrolytes consisting of ethylene carbonate, dimethyl carbonate, lithium hexafluorophosphate, lithium bis (fluorosulfonyl)imide, the types and contents of the additives (FEC & LiNO₃) are precisely regulated. We probe the electrochemical performance and morphology via gGalvanostatic tests and with scanning electron microscopy. Compared the control sample, Li-Li symmetrical cells, Li-Cu cells and Li-Ni₈₃(LiNi_{0.83}Co_{0.05}Mn_{0.12}O₂) with the synergetic additives display a better electrochemical performance with smoother surface of lithium metal.

CPP 19.3 Tue 10:00 H 0111

Maximizing utilization of n-type redox sites in polyaniline copolymer for stable non-aqueous sodium/potassium-ion batteries — ●CHENGZHAN YAN, HUAPING ZHAO, and YONG LEI — Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany.

Polyaniline (PANI) plays a multifaceted role in energy storage because of its tunable composition, structure and morphology. In non-aqueous sodium/potassium-ion batteries, PANI is a prime organic cathode with p-type anion storage. However, its specific capacity is limited owing to the partial utilization of the chain and is of ease decay in changeable electrochemical environments. Moreover, n-type redox sites that coexist with the p-type sites have not received much attention because they are difficult to introduce by in situ chemical oxidation. To this end, the elucidation of n-type reaction in PANI chain and its practice are urgently needed. Herein, a series of carboxylated polyaniline copolymers (named PA2A) are synthesized with a high proportion of quinoid nitrogen. PA2A delivers a high specific capacity of more than 300 mAh/g at a low current density. To further improve the rate per-

formance, PA2A is post-treated by ammonia to achieve a self-doped chain structure (named PA2A-de). This structure greatly accelerates the n-type reaction kinetics, and a low-carboxylated PA2A-de has a high capacity retention of over 70% as the current density increases 20 times from 0.1 A/g to 2 A/g. Besides, the long lifespan of PA2A-de is proven to be sustained in ether-based electrolytes.

CPP 19.4 Tue 10:15 H 0111

Composite Cathode Materials for Improved Iono-Polymer Aluminium Batteries — ●SHUVRODEV BISWAS, THOMAS KÖHLER, AMIR MOHAMMAD, HARTMUT STÖCKER, and DIRK C. MEYER — Institute of Experimental Physics, TU Bergakademie Freiberg

Aluminium batteries are one significant candidate for “post-lithium” batteries due to their exceptional performance in terms of theoretical capacity and cyclability, as well as the inherent advantages of aluminium metal, such as its good availability and low cost. Nevertheless, mass production is still hindered because of several challenges, such as lack of suitable cathode materials, and electrolytes. In search of a better cathode-electrolyte combination, this study investigates several composites based on 9, 10-phenanthrenequinone (PQ) and different graphite modifications synthesized by melt infiltration as novel cathode materials in combination with iono-polymer electrolytes based on triethylamine hydrochloride, polyamide, and aluminium chloride. The electrochemical analysis shows a significant performance boost of the specific capacity with superior rate capability and life cycle when compared to pure graphite or pure PQ. FTIR spectroscopy results also confirm better stability of the composite cathode than the pure PQ cathode. This research highlights the essential electrochemical features of aluminium batteries and serves as the foundation for a new research route using composite cathodes for improved aluminium battery systems.

CPP 19.5 Tue 10:30 H 0111

Dynamic Structure Evolution of Extensively Delithiated High Voltage Spinel — NICOLA JOBST¹, ●NEELIMA PAUL², PREM-SYL BERAN³, MARILENA MANCINI¹, RALPH GILLES², MARGRET WOHLFAHRT-MEHRENS¹, and PETER AXMANN¹ — ¹Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Ulm — ²Heinz Maier-Leibnitz Zentrum, Technische Universität München, Garching — ³Nuclear Physics Institute, Czech Republic & European Spallation Source, Lund

High voltage spinel is one of the most promising next-generation cobalt-free cathode materials for lithium ion battery applications. Besides the typically utilized compositional range of Li_xNi_{0.5}Mn_{1.5}O₄ (0 < x < 1, additional 1.5 mol of Li per formula unit can be introduced into the structure in an extended voltage range upto 1.50 V. Theoretically, this leads to significant increase of the specific energy from 690 to 1190 Wh/kg. However, utilization of the extended potential window leads to rapid capacity fading and voltage polarization that lack a comprehensive explanation. In this work, we conducted potentiostatic entropymetry, operando XRD and neutron diffraction on the ordered stoichiometric spinel Li_xNi_{0.5}Mn_{1.5}O₄ within 0 < x < 2.5 in order to understand the dynamic structure evolution and correlate it with the voltage profile. During the two-phase reaction from cubic (x < 1) to tetragonal (x > 1) phase at ~2.8 V, we identified the evolution of a second tetragonal phase with x > 2. Evaluation of neutron diffraction data reveal location of additional lithium ions.

CPP 19.6 Tue 10:45 H 0111

Investigation of Li depth profiles in Si/graphite anodes from Li-ion battery cells via NDP and GD-OES — ●IVANA PIVARNÍKOVÁ^{1,2}, MARIUS FLÜGEL³, NEELIMA PAUL¹, ANTONINO CANNAVO⁴, GIOVANNI CECCIO⁴, JIŘÍ VACÍK⁴, PETER MÜLLER-BUSCHBAUM^{1,2}, MARGRET WOHLFAHRT-MEHRENS^{3,5}, THOMAS WALDMANN^{3,5}, and RALPH GILLES¹ — ¹TUM, MLZ, Garching, Germany — ²TUM School of Natural Sciences, Chair for Functional Materials, Garching, Germany — ³ZSW, Ulm, Germany — ⁴NPI, CAS, Rez, Czech Republic — ⁵HIU, Ulm, Germany

The loss of Li inventory is a common aging mechanism in Li-ion batteries. To better understand the underlying reversible and irreversible degradation processes in Si/graphite electrodes, depth-resolved methods need to be used to obtain information on the decomposition prod-

ucts of the Li-containing electrolyte across the electrode thickness. In this work we present two Post-Mortem analytical methods, which can be used to obtain quantified Li depth profiles to depths bigger than 10 μm from the electrode surface, the neutron depth profiling (NDP) and glow discharge optical emission spectroscopy (GD-OES). The validation of GD-OES using NDP by examining the Si/graphite anodes from cylindrical 21700 cells is presented. These two methods are complementary to each other. It has been demonstrated that the preferential sputtering can occur on the anode surface during the GD-OES measurements. This phenomenon is caused by the higher sputter rate of Li, as it is mainly present in the Li plated layer or in the solid electrolyte interface (SEI).

CPP 19.7 Tue 11:00 H 0111

Novel Current Collectors for Post-Lithium Energy Storage Systems using Thin-Film Coating — ●OLIVER SCHMIDT, AMIR MOHAMMAD, SHUVRODEV BISWAS, HARTMUT STÖCKER, and DIRK C. MEYER — TU Bergakademie Freiberg, Leipziger Straße 23, 09599 Freiberg, Germany

An often-overlooked component of batteries is the current collector, which provides the connection between the ionic charge carriers and the electronic current. For post-Lithium batteries like Aluminium-ion batteries the requirements are more demanding than for Lithium-ion batteries. The electrolytes in these batteries are highly acidic ionic liquids based on Aluminium chloride. They tend to corrode conventional current collectors such as Aluminium or Copper.

Stable materials for the current collector are refractory metals such as Mo, conductive TiN or amorphous Carbon. Instead of using these materials directly as foils, they are coated on top of a carrier foil (e.g. Aluminium, Polyimide). To reduce weight and price and to simplify handling, different coating systems are developed. To improve the adhesion and coating properties, a subsequent flash lamp annealing (FLA) is used. The FLA process provides a very rapid annealing step (pulse length of 1 to 10 milliseconds) without damaging the substrate. After an initial optimization of coating thickness and FLA treatment, the obtained coatings are found to be long-term stable and well applicable in Aluminium batteries.

15 min. break

CPP 19.8 Tue 11:30 H 0111

Coexistence of Cationic and Anionic Phosphate Moieties in the Solid Acid $\text{Cs}_7(\text{H}_4\text{PO}_4)(\text{H}_2\text{PO}_4)_8$ — ●CHRISTIAN DRESSLER¹, JONAS HÄNSEROTH², and DANIEL SEBASTIANI² — ¹Theoretical Solid State Physics, TU Ilmenau, Germany — ²Theoretical Chemistry, MLU Halle-Wittenberg, Germany

We have studied the proton distribution and proton mobility in the recently synthesized solid state proton conductor $\text{Cs}_7(\text{H}_4\text{PO}_4)(\text{H}_2\text{PO}_4)_8$ by ab initio molecular dynamics simulations.[1] In agreement with experimental observations [2], we can clearly distinguish in our simulations an unusual cationic H_4PO_4^+ and an anionic H_2PO_4^- form that coexist in this solid acid. This paradox situation is achieved by partial substitution of Cs^+ by H_4PO_4^+ in CsH_2PO_4 . Thus, H_nPO_4 act simultaneously as both the positive and the negative ion of the salt. We analyze the dynamical protonation pattern within the unusual hydrogen bond network that is established between the ions. Our AIMD simulations show that a conventional assignment of protonation states of the phosphate groups is not meaningful. Instead, a better description of the protonation situation is achieved by a fractional assignment of the strongly hydrogen-bonded protons to both its nearest and next-nearest oxygen neighbors. Furthermore, we also discuss the effect of the insertion of the cation H_4PO_4^+ on the proton mobility.

[1] Drekle, Hänseroth, Sebastiani, J. Phys. Chem. Lett. 2023, 14, 32, 7249-7255; [2] Wang, Patel, Sanghvi, Hu, Haile, J. Am. Chem. Soc. 2020, 142, 47, 19992-20001.

CPP 19.9 Tue 11:45 H 0111

Operando observation of lithium dendrite growth in polymer based batteries by nanofocus WAXS — ●FABIAN A.C. APFELBECK¹, GILLES E. WITTMANN², LYUYANG CHENG¹, YUXIN LIANG¹, YINGYING YAN¹, ANTON DAVYDOK³, and PETER MÜLLER-BUSCHBAUM^{1,2} — ¹TUM School of Natural Sciences, Chair for Functional Materials, Garching — ²MLZ, TUM, Garching — ³Institute of Material Physics, Helmholtz-Zentrum Hereon, Hamburg

Single-ion conducting polymers are a promising candidate as electrolyte in lithium metal batteries due to a theoretical transference

number of one, which is accompanied by the suppression of lithium dendrite growth. This can extend the cycle life and improve the overall safety of lithium metal batteries. However, the practical usage is still under debate since dendrite growth has also been reported in single-ion conducting polymer based cells. Here, we study operando the lithium dendrite growth in lithium symmetric cells with polymer electrolytes by nanofocus wide angle X-ray scattering (nano WAXS). With this technique, we can spatially resolve the crystalline behavior of the cell on a nanoscale by scanning the polymer during operation.

CPP 19.10 Tue 12:00 H 0111

"Corrections of Cation- π Interactions in Force Field with $1/\tau^4$ and Sigma (σ) Nonbonded Terms" — ●DIPTESH GAYEN¹, YANNIK SCHÜTZE², SEBASTIEN GROH¹, and JOACHIM DZUBIELLA¹ — ¹Applied Theoretical Physics - Computational Physics, Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany — ²Theoretical Chemistry, Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany

This study explores cation- π interactions in a poly(4-(thiophene-3-yl)benzenethiol) (PTBT) cathode for Li-S batteries using molecular dynamics (MD) simulations. MD often underestimates cation- π binding energies compared to quantum mechanics (QM). To address this, we enhance the MD force field for PTBT, introducing distance-dependent terms optimized for accurate cation- π representation. The study contributes insights into refining force fields for realistic simulations of polymer-ion interactions in Li-S batteries. Additionally, we construct an MD simulation model for representative PTBT-electrolyte-solvent systems, incorporating LiTFSI and LiNO₃ electrolytes in 1,2-dimethoxyethane and 1,3-dioxolane mixtures. Our work provides a pathway to improve the accuracy of MD simulations in studying ion dynamics in polymer-based cathodes, with implications for enhancing Li-S battery performance.

CPP 19.11 Tue 12:15 H 0111

The wavelength-dependent photoexcitation and mobility of holes in hematite for photoelectrochemical water splitting — ●YUKE YANG, FELIX ZERRES, YUJIN TONG, and RICHARD KRAMER CAMPEN — Faculty of Physics, University of Duisburg-Essen, 47057 Duisburg, Germany

Photoelectrochemical water splitting is a promising technique for converting solar energy into hydrogen fuel. It is well-established that a significant percentage of absorbed photons in common photoelectrodes do not contribute to chemical reactions. This effect in oxides is usually attributed to polaron formation and subsequent recombination of some fraction of the excited charge carriers. Methods to directly probe polaron populations are, therefore, an essential part of any materials optimization strategy. Most of these methods are suitable for application only by specialists: they require amplified laser systems and ultrasensitive detection schemes. Here we conduct chopped photocurrent measurements in a hematite ($\alpha\text{-Fe}_2\text{O}_3$) photoanode as a function of photon energy. The bias and wavelength dependence of the resulting kinetics, and their change when adding the hole scavenger H_2O_2 to the electrolyte, allow us to characterize electron polarons (that adversely affect device performance) and hole polarons that are OER intermediates. This straightforward way of characterizing polaron energies and relaxation time in this model oxide photoanode offers a useful complementary tool to more complicated experimental techniques that are well matched to high throughput anode creation to empirically changes in polaron stability with changes in catalyst or electrolyte composition.

CPP 19.12 Tue 12:30 H 0111

The Role of Oxygen in Phenazine-TCNQ Charge-Transfer Complex Regeneration — ●KIRILL GUBANOV¹, YANA REVA¹, DANIEL LANGFORD¹, FRANK HAMPEL¹, ANDREAS SPÄTH¹, EVANIE FRANZ¹, RYAN W. CRISP¹, SEBASTIAN BOCHMANN¹, BENJAMIN WATTS², JÖRG LIBUDA¹, DIRK M. GULD¹, and RAINER H. FINK¹ — ¹Department of Chemistry and Pharmacy, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany — ²Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland

Organic charge-transfer complexes (CTC) are promising candidates as electrode material in rechargeable lithium-ion batteries. Besides being renewable, non-toxic and affordable in contrast with their inorganic counterparts, the intrinsic features of the organic CTC, such as electrical conductivity or high cycle performance, are greatly enhanced in comparison with their single-moiety parent components. However, the charge-trap states, induced by the structural defects within the CTC crystal lattice lower the initial degree of charge transferred from the

electron donor to acceptor molecules. Remarkably, oxygen-enriched environment regenerates the charge-transfer process in the complex of Phenazine (PNZ)/Tetracyanoquinodimethane (TCNQ) CTC crystal nanoaggregates. By means of the NEXAFS-based microspectroscopy and (spectro)electrochemical methods, we prove that the oxygen do-

nates electrons to fill the trap states and ultimately enhances the degree of charge-transfer from PNZ to TCNQ, improving the overall charge-transport properties of the material. The research is funded by the BMBF (contract 05K19WE2).