

KFM 24: Focus Session: Battery Materials – Ion Transport, Impurity Effects and Modelling (joint session KFM/MM)

The focus session is dedicated to the characterization of microstructure, electrochemical, thermal and safety properties of Lithium-ion and Post-Lithium cells and their individual active and passive materials. This is required to obtain quantitative and reliable data, which are necessary to improve the current understanding in order to design and develop better and safer materials and cells. Potential topics include, but are not limited to electrochemical characterization techniques, thermal characterisation techniques, safety testing, development of safer materials and cell designs, thermodynamic modelling of materials, modelling of thermal runaway and propagation.

Chair: Ilyas Mohsin (KIT Karlsruhe)

Time: Thursday 9:30–13:35

Location: EMH 225

Invited Talk KFM 24.1 Thu 9:30 EMH 225
Ion transport in battery electrolytes and related interphases
 — ●JELENA POPOVIC-NEUBER — University of Stavanger, Norway

The development of next generation batteries depends heavily on the capability of electrolytes to quickly and selectively transport alkali and alkaline earth metal cations, and form stable electrochemical interfaces. In the first part of my talk, current understanding of ion transport mechanisms and related electrochemical measurement techniques (impedance spectroscopy, galvanostatic polarization) in soft matter battery electrolytes including liquids, polymers and hybrid materials will be discussed. According to this discussion, I will give guidelines and examples of improvements of the relevant electrochemical properties including ionic conductivity and the cationic transference number. In the second part of my talk, I will show recent findings related to the electrochemical and chemical growth and transport in SEIs on several alkali and alkaline earth metal anodes in contact with liquid and solid-state electrolytes. The multitechnique approach involving the measurement of activation energy for ion transport showed that such SEIs are complex composite liquid/solid materials, with sometimes predominant ionic pathways in the liquid phase. The relevance of the native passive layer on alkali and alkaline earth metals, possibility of forming artificial SEIs and electrodeposition through porous SEI will be discussed. Finally, I will show a new modelling approach for treatment of impedance spectroscopy data of symmetric alkaline and alkaline earth metal cells.

KFM 24.2 Thu 10:00 EMH 225
NASICON as solid electrolyte for Mg- and Ca-ion batteries
 — ●KATHARINA HELMRECHT¹ and AXEL GROSS^{1,2} — ¹Institute of Theoretical Chemistry, Ulm University, Ulm, Germany — ²Helmholtz-Institute Ulm (HIU) for Electrochemical Energy Storage, Ulm, Germany

In Na-ion batteries, NASICON has been used as a solid-electrolyte material. Here we present a density functional theory study in which we investigate whether NASICON can also be a suitable solid electrolyte for bivalent charge carriers such as Mg and Ca. We have in particular chosen $\text{Ca}_{0.5}\text{Ti}_2(\text{PO}_4)_3$, $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$, $\text{Mg}_{0.5}\text{Sn}_2(\text{PO}_4)_3$, and $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ for our investigation. We find that these phases indeed show promise as solid electrolytes.

Unlike the classic NASICON phase, which often undergoes a phase transition from rhombohedral to monoclinic within the battery's operating range, this issue does not arise with Ca and Mg. However, only half of the sites occupied by Na (specifically, the Na1 sites) become occupied by the bivalent carriers. We investigate the energetic ordering of the occupied positions inside and the diffusion mechanism inside the phase as well as bottleneck sizes and compare this to the classic NASICON phase.

KFM 24.3 Thu 10:20 EMH 225
Rhombohedral (R-3) Prussian white cathode material: An ab-initio study — ●SEBASTIAN BAUMGART¹, MOHSEN SOTOUDEH¹, and AXEL GROSS^{1,2} — ¹Institute of Theoretical Chemistry, Ulm University, Ulm, Germany — ²Helmholtz-Institute Ulm (HIU) for Electrochemical Energy Storage, Ulm, Germany

The demand for efficient and sustainable cathode materials for alternative battery chemistries is ever more increasing. Prussian Blue analogues (PBAs) exhibit a long cycling life and a high rate capability, which makes them a promising cathode material for next-generation battery technologies. Notably, Prussian White (PW) exhibits a phase transition at high sodium and low vacancy content, transitioning to a

rhombohedral (R-3) phase.

However, the detailed exploration of the rhombohedral modification and its electronic structure remains incomplete. In this study, we provide insights into why the rhombohedral structure manifests itself only at high sodium contents, employing atomistic first-principles calculations.

Our findings reveal the stabilization of the rhombohedral structure by sodium atoms. Additionally, we elucidate the changes in the sodium ion minimum energy position during the phase transition and analyze the sodium migration barrier within the cubic and rhombohedral phases, offering a comprehensive theoretical assessment of its viability as a battery material.

KFM 24.4 Thu 10:40 EMH 225
Advancing Post-Lithium Batteries: Insights into Cathode Material Design and Electrochemical Stability — ●MOHSEN SOTOUDEH¹ and AXEL GROSS^{1,2} — ¹Institute of Theoretical Chemistry, Ulm University, Oberberghof 7, 89081 Ulm — ²Helmholtz Institute Ulm, Helmholtzstraße 11, 89081 Ulm

In the search for sustainable alternatives to the prevailing Li-ion batteries, key features that influence the activation energy barrier and electrochemical stability are investigated using periodic density functional theory calculations. The study employs a novel descriptor to determine the ionic mobility and highlights the critical role of ionic radii, oxidation state, and electronegativity on the mobility as well as the stability of crystalline materials, providing practical guidelines for the selection of promising solid materials. At the same time, the potential of Mg batteries with oxide cathodes is explored, recognizing the challenges posed by the sluggish kinetics of Mg^{2+} migration. Promising candidates, guided by theoretical insights, have been synthesized and structurally characterized, paving the way for the exploitation of functional cathode materials with improved Mg^{2+} transport properties. In addition, the electrochemical stability of binary and ternary spinel compounds is investigated, with potential applications as protective coatings, and solid electrolytes in batteries. This comprehensive study provides critical insights into the development of new battery technology for high-performance energy storage solutions.

The work has been supported by the DFG through Excellence Cluster EXC-2154, project No. 422053626.

KFM 24.5 Thu 11:00 EMH 225
Remodeling interfacial electrical field for superhigh capacity and ultralong lifespan aqueous zinc-ion batteries — ●YAN RAN¹, YUDE WANG², HUAPING ZHAO¹, and YONG LEI¹ — ¹Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany — ²Yunnan Key Laboratory of Carbon Neutrality and Green Low-carbon Technologies, Yunnan University, 650091 Kunming, China

Herein, density functional theory (DFT) calculations studied the $\text{NH}_4\text{V}_4\text{O}_{10}$ @carbon cloth (NVO@CC) as a high-performance cathode material at the heterostructure interface for AZIBs. The electronic structure, adsorption energy, and migration energy barrier prove there are additional active sites at the interface due to the built-in electric field between NVO and CC, which improves the conductivity and stability of the NVO@CC electrode material. Accordingly, the designed binder-free NVO@CC cathode exhibits high specific capacity (607.1 mAh/g at 0.1 A/g), an outstanding energy density (443.6 Wh/kg at 0.3 A/g), and an excellent long-term cyclability (the capacity retention rate is 81.24% after 10,000 ultra-long cycles at 5 A/g). This excellent electrochemical performance is attributed to enhanced conductivity

and fast electrochemical kinetics by a series of ex-situ characterizations. This work reveals a binder-free self-grown flexible cathode on carbon cloth, which is promising for high-performance aqueous zinc ion batteries.

15 min. break

KFM 24.6 Thu 11:35 EMH 225

Computational Screening of Chloride Perovskites as Cl^- -Ion Solid Electrolyte — •JOHANNES DÖHN¹ and AXEL GROSS^{1,2} — ¹Institute of Theoretical Chemistry, Ulm University, Germany — ²Helmholtz Institute Ulm, Germany

The intermittency of wind and solar power - the solely sustainable energy sources which are considered to be abundantly available - leaves only one consequence: For the transition towards renewable energy systems, efficient and reliable storage technologies are needed. Batteries are one of the most widely used storage devices but current technology based on the transfer of Li-ions faces several challenges including their dependence on critical materials with respect to both, scarcity and toxicity.

In our contribution, we will present atomic-scale investigations of potential future battery materials carried out using density functional theory (DFT). We employed a high-throughput approach in order to screen the well known materials' class of chloride perovskites as solid electrolyte material for chloride ion batteries and we derived several properties as electrochemical stability and diffusion barrier for in total 148 compounds. Our screening focusses on the highly symmetric cubic perovskite structure but for the most promising candidates also the less symmetric distorted phases are investigated, additionally shedding some light on potential property-structure relationships.

Such in silico investigations significantly narrow down the potential materials space for our experimental coworkers and, thereby, contribute to finding green, cheap and reliable devices for energy storage.

KFM 24.7 Thu 11:55 EMH 225

The role of the SEI for lithium whiskers in lithium metal batteries — •MARTIN WERRES^{1,2}, ARNULF LATZ^{1,2,3}, and BIRGER HORSTMANN^{1,2,3} — ¹Deutsches Zentrum für Luft- und Raumfahrt e.V. (DLR), Ulm, Deutschland — ²Helmholtz Institut Ulm (HIU), Ulm, Deutschland — ³Universität Ulm, Ulm, Deutschland

Lithium metal (Li) batteries are promising due to their high specific energy. However, safety concerns and non-optimal cycle stability hold back Li anodes paired with liquid electrolytes.[1] A major challenge is the growth of Li whiskers. Li whiskers come with cycling inefficiencies, e.g., enhanced formation of isolated Li.[2] Understanding why Li whiskers emerge can help find design rules for safer Li batteries. We study plating/stripping of Li under the aspect of the mechanical properties of Li and the role of the covering solid-electrolyte interphase (SEI).[3] We consider a Li nucleus covered by SEI, which grows continuously during plating. Once the stress in the SEI exceeds a threshold, the SEI breaks. Due to the softness of Li and significant creep under the expected stress conditions, Li can extrude through the hole in the SEI. We model this by approximating Li as a Herschel-Bulkley liquid. Our predicted shapes and growth rates are consistent with the experimental observation of Li whiskers. We deduce that the SEI is the most important design parameter to achieve safe Li batteries.

[1] B. Horstmann et al., *Energy Environ. Sci.* 2021, 14(10), 5289-5314. [2] M. Werres et al., *ACS Nano* 2023, 17(11), 10218-10228. [3] L. von Kolzenberg et al., *Phys. Chem. Chem. Phys.* 2022, 24(31), 18469-18476.

KFM 24.8 Thu 12:15 EMH 225

Elucidating the Silicon Voltage Hysteresis by Mechanical Coupling of Anode Particles and SEI — •LUKAS KÖBBING^{1,2}, ARNULF LATZ^{1,2,3}, and BIRGER HORSTMANN^{1,2,3} — ¹German Aerospace Center (DLR), Ulm, Germany — ²Helmholtz Institute Ulm (HIU), Ulm, Germany — ³Ulm University, Ulm, Germany

Silicon promises to be a superior next-generation anode material. However, a major challenge of silicon anodes is the significant voltage hysteresis reducing efficiency and leading to detrimental heat generation. Additionally, the hysteresis hinders precise state-of-charge estimation. Our recent research identifies the chemo-mechanical coupling of silicon and the Solid-Electrolyte Interphase (SEI) as the reason for the substantial voltage hysteresis. The SEI is a thin passivating film that grows on negative electrode particles due to electrolyte decomposition [1]. For silicon particles, volume changes lead to significant strains

and plastic deformation within the SEI [2]. As anode particle and SEI are mechanically coupled, the stress generated inside the SEI impacts the stress inside the anode, affecting its potential. Our chemo-mechanical model reproduces the observed open-circuit voltage hysteresis [3]. Furthermore, our visco-elastoplastic SEI model reproduces the voltage difference between slow cycling and the relaxed voltage. This detailed physical understanding can improve the performance of silicon anodes. [1] L. Köbbing et al. *J. Power Sources* 2023, DOI: 10.1016/j.jpowsour.2023.232651. [2] L. Kolzenberg et al. *Batter. Supercaps* 2022, 5, DOI: 10.1002/batt.202100216. [3] L. Köbbing et al. *Adv. Funct. Mater.* 2023, DOI: 10.1002/adfm.202308818.

KFM 24.9 Thu 12:35 EMH 225

Understanding SEI formation in Alkali Metal Batteries — •DANIEL STOTTMEISTER¹ and AXEL GROSS^{1,2} — ¹Institut für Theoretische Chemie, Ulm University, Ulm, Germany — ²Helmholtz Institute Ulm, Ulm, Germany

Batteries have established themselves as one of the prime energy storage devices in modern times. Due to the relative scarcity of lithium and the ever-increasing demand for safe, efficient, and affordable energy storage solutions, post-lithium battery systems have emerged as promising future energy storage solutions. Other more common alkali metals like sodium and potassium are of particular interest. However, like their lithium predecessors, sodium and potassium batteries suffer from various issues, some of which originate from the formation of an instable solid electrolyte interphase (SEI). The formation mechanisms of said SEI are yet to be fully understood. Density Functional Theory (DFT) is a well-established method for the description of systems at the atomic level and can help to unravel some of the reaction mechanisms relevant to the formation of the SEI. This contribution uses ab initio molecular dynamics (AIMD) and DFT simulations to investigate and compare the electrolyte decomposition and the resulting SEI formation mechanisms of lithium, sodium, and potassium metal batteries at the atomistic level.

KFM 24.10 Thu 12:55 EMH 225

Effects of Aluminum trifluoride impurities on NMC811 /Graphite Lithium-ion battery performance. — •SLAHEDDINE JABRI — Institute of Applied Physics, Technische Universität Braunschweig, 38106 Braunschweig, Germany

The effects of aluminum trifluoride (AlF_3) impurities in the electrolyte of full cell lithium-ion batteries has been studied using NMC811/Graphite electrodes. A strong decline of the retention capacity is observed when the cells are cycled at 50 °C in the presence of AlF_3 impurities in the electrolyte. The AlF_3 accelerates the cell degradation by the generation of various compounds during battery operation. The NMC811 cathode and the Graphite anode are characterized with different techniques. Scanning electron microscopy SEM, including cross-section- Focus Ion Beam FIB, Raman spectroscopy and X-ray photoelectron spectroscopy XPS methods are employed to investigate the effect of the degradation on the electrolyte due to the AlF_3 impurities. We found modified chemical components and morphology of the surface electrolyte interface (SEI) and cathode electrolyte interface (CEI) layers of anode and cathode after cell aging with polymer layers on the both surfaces. Pathways to understand the AlF_3 impact are proposed.

KFM 24.11 Thu 13:15 EMH 225

Impurity Effects of AlCl_3 on the Performance of Polyamide-Ionic-Liquid-based Polymer Electrolytes for Aluminium Batteries — •MOHAMMAD MOSTAFIZAR RAHMAN, AMIR MOHAMMAD, SHUVRODEV BISWAS, HARTMUT STÖCKER, and DIRK C. MEYER — Institute of Experimental Physics, TU Bergakademie Freiberg

The AlCl_3 - Et_3NHCl ionic liquid (IL) has emerged as a promising and cost-effective option for the rechargeable Al-ion battery system. The polyamide-based solid polymer electrolyte (SPE) derived from this IL was utilized for the present investigation. Six different purities of AlCl_3 salts (ranging from 98 % to 99.999 %) with variable prices were used to prepare the SPEs and their performance was evaluated using various electrochemical characterization techniques. The results indicate good reversibility and Al stripping/plating behavior without impurity effects. Conductivities range from 0.19 mS/cm to 0.21 mS/cm, while stability windows span 2.70 V to 2.83 V. In addition, specific capacities range from 28 mAh/g to 39 mAh/g with no systematic effect of impurities. Overall, the electrochemical analysis shows that impurities in AlCl_3 salts have minimal impact on the SPE electrochemical properties. A cost-benefit analysis indicates that utilizing a low-cost

AlCl_3 salt (0.027 €/g) yields comparable electrolyte performance as a higher-priced (6.198 €/g) high-purity salt. This discovery enables a reduction in electrolyte cost by approximately a factor of 17, consequently leading to a decrease in the overall cost of Al batteries.