

MM 5: Materials in Energy Conversion: Mechanical Properties and Solid State Batteries

Time: Monday 10:15–13:00

Location: SCH A 215

MM 5.1 Mon 10:15 SCH A 215

Interplay between mechanics and electrochemistry in Li-Si anodes by atomistic simulation — ●DANIEL MUTTER¹, MANISHA POUDEL^{1,2}, DANIEL PFALZGRAF¹, and LEONHARD MAYRHOFER¹ — ¹Fraunhofer IWM, 79108 Freiburg — ²Institute of Physics, University of Freiburg, 79104 Freiburg

Silicon is a promising anode material for Li-ion batteries due to its high capacity, which considerably exceeds that of commonly used graphite. Its direct applicability however is hampered by the huge volume change the material undergoes during loading and unloading with Li, concomitant with mechanical stresses arising in the microstructure. In this work, we provide a deeper understanding on the interplay of mechanics and electrochemistry by analyzing the effect of deformation on the electrochemical potential. Using atomistic first principles calculations, we studied crystalline as well as amorphous Li-Si phases with different Li concentrations. We present results of elastic moduli, and the change of voltage during charging and discharging cycles under various characteristic mechanical loading scenarios. The results are essential input for continuum models acting on the nanoparticle scale to correctly describe the microstructural evolution.

MM 5.2 Mon 10:30 SCH A 215

Design of zero strain cathode materials based on colquiriite-type $\text{Li}_x\text{Ca}(\text{M},\text{M}')\text{F}_6$ — ●ALJOSCHA FELIX BAUMANN^{1,2}, DANIEL MUTTER², DANIEL URBAN^{1,2}, and CHRISTIAN ELSÄSSER^{1,2} — ¹Freiburger Materialforschungszentrum, Stefan-Meier-Straße 21, 79104 Freiburg im Breisgau — ²Fraunhofer-Institut für Werkstoffmechanik IWM, Wöhlerstr. 11, 79108 Freiburg

The long-term stability of Li ion batteries can be negatively affected by mechanical stresses in the microstructure of the cathode material during charge/discharge cycles. Therefore, materials are of great interest which show a zero-strain (ZS) behavior, i.e. a negligible volume change during insertion or extraction of Li ions. For specific compounds of the material class of colquiriites, $\text{Li}_x\text{A}^{\text{II}}\text{M}^{\text{III}}\text{F}_6$, ZS behavior was predicted theoretically and measured experimentally for different Li concentration ranges. In this work we investigate the effect of the electrochemically active cation M^{III} ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) on the volume change during (de-)lithiation. Using density-functional theory we calculated the equilibrium volumes at different Li concentrations. The analysis of the electronic and magnetic structures and the calculation of local structural parameters indicate that the total volume change depends mainly on the counteracting effects of expanding fluorine octahedra around the M ions due to the changing oxidation state, and a decrease of repulsion between fluorine anions due to the inserted Li ions. The trends in the properties along the period of the 3d transition metals provide a guideline for a design of new ZS cathode materials in solid solutions of type $\text{Li}_x\text{Ca}(\text{M},\text{M}')\text{F}_6$.

MM 5.3 Mon 10:45 SCH A 215

Planar gliding and vacancy condensation: The role of dislocations in the chemomechanical degradation of layered transition metal oxides — ●MARCEL SADOWSKI¹, KARSTEN ALBE¹, and SABRINA SICOLÒ² — ¹Technical University of Darmstadt, Darmstadt, Germany — ²BASF SE, Ludwigshafen, Germany

Stacking faults driven by dislocations have been observed in layered transition metal oxides cathodes both in cycled and uncycled materials. The reversibility of stacking-sequence changes directly impacts the material performance. Irreversible glide due to lattice invariance or local compositional changes can initiate a catastrophic sequence of degradation mechanisms. In this study we compare the chemomechanical properties of LiCoO_2 and LiNiO_2 by combining density functional theory (DFT) and anisotropic linear elasticity theory. We calculate stacking fault energies as a function of Li content and quantify the “pillar effect” of excess Ni in hindering stacking-sequence changes. We then characterize screw dislocations, which mediate stacking-sequence changes, and find a peculiarly compliant behavior of LiNiO_2 due to the interaction of Jahn-Teller distortions with the dislocation strain field. Finally, we analyze the tendency of vacancies to segregate along dislocation lines. This study represents the first instance of explicit ab-initio atomistic dislocation models in layered oxides and paves the way for the understanding and optimization of the chemomechanical behavior of cathode active materials during battery operation.

MM 5.4 Mon 11:00 SCH A 215

Modification of iron-based oxide anodes for potassium ion storage — ●ZIDONG WANG, HUAPING ZHAO, and YONG LEI — Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany

Due to the abundance of potassium and its easy accessibility, potassium-based electrochemical energy storage technology has attracted extensive research interests and significant progress of it has been made in recent years. Among different anode materials for anodes of potassium-ion storage devices, transition metal oxides especially of iron-based oxides have high potential due to their high capacity and low cost. However, their poor electrical conductivity and weak structure impede their development. In this work, adjustment of the anionic and cationic composition of iron oxides is achieved. This adjustment can effectively result in a high-performance anode for potassium ion storage. In brief, the synergistic effect of multivalent metal cations will result in excellent potassium storage properties. And the conductivity can be further improved by the replacement of anions. Our results indicate that the adjusted iron-based compound can be used as a promising high-performance anode material for potassium ion storage devices.

MM 5.5 Mon 11:15 SCH A 215

Construction of V5S8/Sb2S3@C Heterostructures as High-Performance Anode Materials for Potassium-ion Batteries — ●VINCENT HARTMANN, YULIAN DONG, HUAPING ZHAO, and YONG LEI — Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany

Transition metal sulfides (TMSs) have been studied widely and deeply as anode materials for potassium ion batteries (PIBs) owing to their relatively high theoretical capacities. However, poor electrical conductivity, large volume expansion, and slow diffusion kinetics hinder their further applications. Herein, a unique hierarchical structure of V5S8/Sb2S3@C is fabricated by a concise solvothermal method and subsequently annealing. Such a well-designed architecture affords fast K^+ diffusion kinetics and improved charge transfer at the heterointerfaces due to the metallicity of the internal V5S8. In addition, the synergistic coupling interaction among the interior V5S8, interlayer Sb2S3, and external C layer generates a stable nanostructure, which extremely accelerates the electronic/ion transport and effectively alleviates the volume expansion upon long cyclic performance. As a result, it exhibits a high initial capacity of 525.19 mAh/g at 100 mA/g and excellent cyclic stability with 95% capacity retention after 500 cycles at 1 A/g. Our results reveal that the combination of heterostructures construction and interfacial interaction enables optimizing electronic structures and macroscopic mechanical properties of TMSs, thus achieving high-performance anodes for PIBs with high energy density.

15 min. break

MM 5.6 Mon 11:45 SCH A 215

Influence of interstitial Li on the electronic properties of $\text{Li}_x\text{CsPbI}_3$ for photovoltaic and battery applications — ●WEI WEI^{1,2}, JULIAN GEBHARDT^{1,2}, DANIEL URBAN^{2,3}, and CHRISTIAN ELSÄSSER^{1,2,3} — ¹Cluster of Excellence livMatS, University of Freiburg, Germany — ²Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany — ³Freiburg Materials Research Center (FMF), University of Freiburg, Germany

The stability of crystalline CsPbI_3 with interstitial Li ions is investigated together with the effect that Li has on the electronic structure of the resulting compound $\text{Li}_x\text{CsPbI}_3$. We analyze this by two structural models for CsPbI_3 at room temperature, the cubic α phase and a distorted structure analogous to the γ phase (γ' structure). The hypothetical α phase does thermodynamically not allow Li uptake and is likely to be structurally unstable for $x > 1/4$, while adding Li up to $x=1$ in the γ' structure is possible. In all cases, Li promotes structural distortions, namely tilting of bond angles $\Delta_{\text{Pb-I-Pb}}$ and Cs off-center displacements Δ_{rCS} , which are increasing with the Li concentration.

Interstitial Li has the following effects on the electronic structure of CsPbI_3 : i) the induced structural distortion leads to a significant increase of the band gap; ii) the screening of additional electrons in the conduction band leads to a small increase of the band gap; iii) the

effect of Li 2s states on the band edges and band gap is negligible. Altogether, the change of the band gap is dominated by the tilting of $\Delta_{\text{Pb-I-Pb}}$ angles: stronger distortion caused by increasing Li content is accompanied by an increased band gap.

MM 5.7 Mon 12:00 SCH A 215

Design for Dual-Functional Electrode Promoting Dendrite-free and CO₂ Utilization Enabled High-Reversible Symmetrical Na-CO₂ batteries — •CHANGFAN XU, HUAPING ZHAO, and YONG LEI — Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany

A one stone two-birds strategy is presented by using carbon paper embedded with Ru nanoparticles (RuCP) as dual-functional electrodes for both the Na anode and CO₂ cathode. As an anode host, the RuCP with remarkable sodiophilicity can dominate Na nucleation behavior and achieve a uniform Na ion flux for the inhibition of dendrite formation, meanwhile, the RuCP affords high catalytic activity for catalyzing the formation/decomposition of Na₂CO₃ in CO₂ cathode. As a result, the Na was homogeneously deposited on the RuCP anode without Na dendrite formation, showing a high Coulombic efficiency of over 99% and a long cycle lifetime, and the RuCP cathode demonstrates low overpotentials and excellent cycling stability (>300 cycles). Implementation of the RuCP@Na anode and RuCP cathode allows for the construction of a symmetrical Na-CO₂ battery with long-duration cyclability because of the dendrite-free sodium morphology and numerous Ru catalytic sites. Such electrodes and battery designs offer an effective method for the tailoring and optimization of sodium metal batteries with high energy density.

MM 5.8 Mon 12:15 SCH A 215

Dynamic stability and *ab initio* free energy calculations of argyrodite Li₆PS₅Cl solid electrolyte — •YONGLIANG OU, YUJI IKEDA, PRASHANTH SRINIVASAN, and BLAZEJ GRABOWSKI — Institute for Materials Science, University of Stuttgart, 70569 Stuttgart, Germany

High ionic conductivity of argyrodite Li₆PS₅Cl, which was shown in both experiments and simulations, renders it a promising candidate for the solid electrolyte in all-solid-state lithium-ion batteries. Although the diffusion mechanism has been intensively investigated in previous studies, the dynamic and thermodynamic stability of Li₆PS₅Cl have not yet been fully understood. To address this issue, systematic investigations are carried out under the *ab initio* framework in this study. At 0 K, the dynamic instability of the ideal structure is revealed by the calculated imaginary phonon modes. Molecular dynamics simulations accelerated by machine-learning interatomic potentials show dynamic stabilization via vibrational entropy at finite temperatures. Further, *ab initio* free energy calculations are performed in wide temperature and pressure ranges utilizing a multistage thermodynamic integration technique. The calculated free energies provide important information for subsequent studies focusing on the energetic aspects, e.g., defect or grain boundary formation energy, of Li₆PS₅Cl. It can be expected that the present results benefit the research and application of all-solid-state

lithium-ion batteries.

MM 5.9 Mon 12:30 SCH A 215

Exploration of cathode-stable layered solid-state electrolytes — •SINA ZIEGLER, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin, Germany

Promising higher safety and capacity, all-solid-state lithium batteries are envisioned to replace standard lithium-ion batteries in the future. Lithium thiophosphates achieve the highest Li ion conductivities of all solid-state electrolytes (SSE) known to date but their instability towards high-performance electrodes remains a critical challenge. To address this issue, we investigate the concept of rare earth lithium halides as a material-efficient, nanometer thick cathode coating in contact with thiophosphate electrolytes. Halides provide wide electrochemical stability windows as well as good chemical and thermodynamic stability [1,2].

To determine a suitable halide/thiophosphate combination, an energetically feasible reaction pathway in the multidimensional phase diagram between the two materials needs to be identified. Consequently, the thermodynamic stabilities of the emerging SSE / halide interfaces are examined by *ab initio* thermodynamics to screen reaction free enthalpies of possible interface reactions. Next, an end member analysis is performed to analyze possible compositions of interface products and possible secondary phases.

[1] J. Liang *et al.*, *Acc. Chem. Res.* 2021, 54, 1023-1033 [2] K. Kim *et al.*, *Chem. Mater.* 2021, 33, 10, 3669-3677

MM 5.10 Mon 12:45 SCH A 215

Active Site Deactivation of the Air Electrode in High-Temperature Solid Oxide Cells — •HANNA TÜRK, THOMAS GÖTSCH, FRANZ-PHILIPP SCHMIDT, AXEL KNOP-GERICKE, ROBERT SCHLÖGL, THOMAS LUNKENBEIN, KARSTEN REUTER, and CHRISTOPH SCHEURER — Fritz-Haber-Institut der MPG, Berlin, Germany

Degradation of the air electrode in electrolysis mode severely limits the commercial adoption of solid oxide cells (SOCs). This degradation goes hand in hand with the oxygen evolution reaction (OER) taking place at the triple-phase boundary (TPB) between the anode, the solid electrolyte, and the gas phase. Up to now, the atomistic structure of this active catalyst region is essentially unknown, though, which prevents a detailed analysis of the actual degradation mechanisms.

Recently, we took the first step in elucidating the TPB structure by revealing a complex structure at the underlying solid/solid interface of the sintered anode[1], featuring partial amorphization and varying elemental distributions deviating from the confining bulk phases. Based on this finding, we now expand our force field based Monte-Carlo simulations to the OER active site. Our experimentally validated results show unexpected compositional changes with respect to the thermodynamic equilibrium, that combined with a spatially resolved diffusion study indicate a hitherto unknown mechanism underlying the deactivation of the anode[2].

[1] H. Türk *et al.*, *Adv. Mater. Interfaces* 8, 2100967 (2021).
[2] H. Türk *et al.*, *ChemCatChem* 14, e202200300 (2022).