

MM 36: Functional materials II: Batteries II

Time: Wednesday 11:45–13:00

Location: H53

MM 36.1 Wed 11:45 H53

Phase field modeling of Li-insertion kinetics in single LiFePO₄– nano-particles for rechargeable Li-ion battery application — ●MICHAEL FLECK, PHILIPP AMENDT, HOLGER FEDERMANN, and HEIKE ENNERICH — Materials and Process Simulation, University of Bayreuth, Germany

LiFePO₄ is widely considered to be a promising cathode material for Li-ion rechargeable batteries. The lithiation process in LiFePO₄– nano-particles proceeds via a coherent solid-solid phase transformation between the LiFePO₄ (LFP-phase) and FePO₄ (FP-phase). We develop a continuum phase field model for solid-solid phase transformations in single-LiFePO₄– nano-particles, embedded in an elastically soft electrolyte-phase. The model-description explicitly includes anisotropic (orthorhombic) and inhomogeneous elastic effects, resulting from coherency strain, as well as anisotropic (1D) Li-diffusion insight the nano-particles. The moving LFP/FP-phase boundary is modeled as a diffuse interface of finite width. Here, with the inclusion of the elastically soft electrolyte-phase, we consider also non-rectangular shaped LiFePO₄– particles in a fully anisotropic 3D-framework. The resulting model is employed to investigate effects of the nano-particle's size and shape on the kinetics of FP to LFP phase transformations, relating to single particle charge rates. In respective model studies, we find that in flat particles the transformation velocity increases over more than two orders of magnitudes with decreasing particle-height. We show that in contrast to Cahn-Hilliard-type models this behavior can be regularized in Allen-Cahn-type phase-field formulations.

MM 36.2 Wed 12:00 H53

Charge localization and energetics of Li-ion batteries cathodes from Hubbard-corrected DFT functionals — MATTEO COCCIONI and ●NICOLA MARZARI — EPFL, Lausanne, Switzerland

An accurate modeling of the electronic, magnetic and structural properties of transition-metal (TM) compounds is essential for their deployment in many emerging technologies. Unfortunately, the importance of electronic correlations makes first-principles calculations on these systems very challenging. This is particularly true for Li-ion battery materials and for all the electrochemical energy conversion and storage applications based on mixed-valence TM ions. DFT functionals augmented with corrective terms based on the Hubbard model (DFT+U) improve significantly the description of these correlated materials and have proven themselves as the standard choice when high computational efficiency is required (e.g., for screening large numbers of compounds). This work shows how an extended formulation of DFT+U, including on-site (U) and inter-site (V) interactions, improves the description of mixed-valence materials. Focusing on LiFePO₄ and Li_xMnPO₄ we discuss their structural and electronic properties in dependence of Li content. Contradicting common practice, we also show that using computed interaction parameters is actually crucial to reliably compare the energy of different Li concentrations and, in particular, to assess the thermodynamic stability of various compositions and to evaluate the voltage of the resulting battery.

MM 36.3 Wed 12:15 H53

Ab-initio based continuum parameters for phase separating Li battery materials — ●NICOLAS G. HÖRMANN^{1,2} and AXEL GROSS^{1,3} — ¹Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11, 89069 Ulm — ²THEOS, EPFL, Switzerland — ³Universität Ulm, Institut für Theoretische Chemie, Albert-Einstein-Allee 11, 89069 Ulm

Modelling of battery materials is getting increasing attention due to the importance of understanding and improving electrochemical en-

ergy storage systems. Electrode properties have been studied widely both by ab-initio computations and within continuum models based on experimental parameters [1-3]. It would be desirable, however, to obtain continuum parameters based on ab-initio computations, firstly, to compare results on both scales and understand better the limitations of each approach, and secondly, to estimate the behavior of materials not yet known from experiment.

In this talk, we present a scheme to derive continuum parameters, in particular the mean field homogeneous free energy, from ab-initio calculations based on density functional theory (DFT) for the two phase separating materials LiFePO₄ and Li₂FeSiO₄. We will also test the quantitative accuracy against experimental results for properties such as the phase diagram and the expected voltage hysteresis.

[1] R. Malik et al., *J. Electrochem. Soc.*, **160**, 5, A3179-A3197 (2013)
[2] R. Malik et al., *Nat. Mater.*, **10**, 587-590 (2011) [3] D. A. Cogswell et al., *Nano Lett.*, **13**, 3036-3041 (2013)

MM 36.4 Wed 12:30 H53

Highly Conductive Interfaces: A Key Factor for Solid State Lithium Batteries — ●YASER HAMED JΟΥYBARI and FRANK BERKEMEIER — Institute of Materials Physics, Westfälische Wilhelms-Universität Münster, Germany

Thin film lithium ion batteries have been in focus during the last years, e.g. due to their prospective capability of carrying high energy densities. However, their development is facing some major challenges such as the synthesis of highly conductive solid state electrolytes and highly conductive interfaces between the electrolyte and the electrodes.

Hence, in this work lithium phosphorous oxynitride (LiPON) layers are prepared via rf magnetron sputtering, serving as a potential solid state electrolyte in future thin film batteries. First, the influence of different sputter parameters on the properties of the LiPON is investigated, to obtain optimized LiPON layers of highest achievable conductivity. Afterwards, the interface adhesion and conductivity between LiPON and different electrode materials is studied. Within these studies it is found that the lithium transport through the interface between LiPON and the electrode material strongly depends on the interface adhesion and the interface bonding conditions. These can be controlled by the sputter parameters during LiPON deposition. Therefore, the dependence of the morphological and electrochemical properties of the layer stacks on the processing parameters is characterized in detailed and explained, theoretically. Finally, by applying optimum processing parameters, LiPON coated electrodes are prepared which exhibit a high interface conductivity and excellent storage capacities.

MM 36.5 Wed 12:45 H53

Local Structure, Transport and Phase Transformation in Lithium Manganese Dioxide — ●CARSTEN NOWAK, JONAS ARLT, TORBEN ERICHSEN, JOHANNES MAIER, BJÖRN PFEIFFER, and CYNTHIA A. VOLKERT — Georg-August-Universität Göttingen, Institute for Materials Physics, Göttingen, Germany

Local structure, ionic and electronic transport, and phase transformations are crucial for the interconversion of electrical and chemical energy in Lithium Manganese Oxide (LMO). Although the material is widely used for electrochemical energy storage, transport and conversion mechanisms at the atomic scale are not fully understood.

Here, we present experimental results on the local characterization of structure, transport and phase transformations in LMO using transmission electron microscopy (TEM) and atom probe tomography (APT). Combining different analytical techniques and in-situ experiments, the Lithium content of LMO is changed and the response of the material is characterized on nanometer length scales. Results are discussed in view of electrochemical energy storage.