

MM 23: Methods in Computational Materials Modelling: Battery Materials

Time: Tuesday 11:45–12:45

Location: H 0106

MM 23.1 Tue 11:45 H 0106

Electronic structure of oxygen-deficient $\text{Li}_4\text{Ti}_5\text{O}_{12-\delta}$ — SASKIA STEGMAIER, CHRISTOPH SCHEURER, and KARSTEN REUTER — Technische Universität München, Germany

The lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is a promising alternative anode material for rechargeable lithium-ion batteries which offers advantageous materials properties in terms of safety and stability. The low electronic conductivity of pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$, however, is a drawback. LTO samples with an increased electronic conductivity have been prepared, for example, via routes including thermal treatment in reducing atmosphere. Under these conditions, oxygen vacancies are formed and Ti^{4+} ions are reduced. Experimental XPS and EPR data indicate the presence of discrete Ti^{3+} and Ti^{4+} ions rather than a full delocalization of the extra electrons.[1,2] Such oxygen-deficient materials with mixed-valent metal cations pose a challenge to computational materials modeling with density-functional theory (DFT) methods since calculations with standard LDA or GGA functionals only lead to a delocalized picture of the charge distribution. DFT+U calculations can be employed to capture spatial localization of excess electrons on transition metal sites but the choice of the Hubbard U parameter introduces some ambiguity. We thus performed DFT calculations with hybrid functionals in order to gain a more reliable first principles based insight into the defect chemistry and electronic structure of oxygen-deficient $\text{Li}_4\text{Ti}_5\text{O}_{12-\delta}$.

[1] J. Wolfenstine, J. L. Allen, *J. Power Sources* **2008**, 180, 582.

[2] H. Song et al., *Sci. Rep.* **2014**, 4, 4350.

MM 23.2 Tue 12:00 H 0106

Assessing PAW pseudopotentials for solid-state NMR calculations — ARY FERREIRA, KARSTEN REUTER, and CHRISTOPH SCHEURER — Technische Universität München

The Gauge-Including (GI) Projector Augmented Wave (PAW) method [1] allows for an efficient simulation of solid-state Nuclear Magnetic Resonance (NMR) spectra within a density-functional theory framework. It derives its efficiency by calculating the all-electron magnetic response with frozen-core PAW pseudopotentials. The accuracy of GI-PAW calculated nuclear magnetic shieldings and electric field gradients is correspondingly critically determined by the quality of these PAW potentials. Here we assess this quality for a range of metal oxides of differing covalency in the metal-O bond by comparing to reference full-potential calculations performed within the LAPW/APW+lo method. We compute correlations between NMR parameters and isotropic changes in each MO_n coordination environment [2] to propose the use a single number to systematically express the difference between results obtained with the two methods. [1] C.J. Pickard and F. Mauri, *Phys. Rev. B* **63**, 245101 (2001). [2] K. Lejaeghere et al.,

Crit. Rev. Solid State Mater. Sci. **39**, 1 (2014).

MM 23.3 Tue 12:15 H 0106

DFT-based reference parameters for solid-state NMR on Li-ion batteries — SIMONE KÖCHER^{1,2}, RÜDIGER EICHEL¹, KARSTEN REUTER², and CHRISTOPH SCHEURER² — ¹IEK-9, Forschungszentrum Jülich — ²Technische Universität München

In-operando Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful tool to gain a detailed understanding of the fundamental dynamical processes inside an operating battery cell [1]. Notwithstanding, the experimental spectra are complex and their unambiguous interpretation has to rely on independent first-principles based simulations. For studies of the ionic charge carrier mobility in Li-ion batteries by ^{6,7}Li solid-state NMR, corresponding simulations require an accurate reference scale of different lithium compounds. We establish these NMR parameters through density-functional theory (DFT) calculations for ideal periodic lithium salts as well as for some organolithium compounds [2]. We specifically explore the influence of geometry, symmetry and computational method on the calculated chemical shieldings and address the challenges involved in simulating disordered materials.

[1] B. Key et al., *J. Am. Chem. Soc.* **131**, 9239 (2009); [2] C. Bonhomme et al., *Chem. Rev.* **112**, 5733 (2012).

MM 23.4 Tue 12:30 H 0106

Phase field modeling of Li-insertion kinetics in single LiFePO_4 - nano-particles for rechargeable Li-ion battery application — MICHAEL FLECK, HOLGER FEDERMANN, PHILIPP AMENDT, and HEIKE EMMERICH — Materials and Processsimulation, University of Bayreuth

LiFePO_4 is widely considered to be a promising cathode material for Li-ion rechargeable batteries. The lithiation process in LiFePO_4 nano-particles proceeds via a coherent solid-solid phase transformation between the LiFePO_4 (LFP-phase) and FePO_4 (FP-phase). We develop a continuum phase field model for solid-solid phase transformations in single- LiFePO_4 -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. Here, with the inclusion of the elastically soft electrolyte-phase, we consider also non-rectangular shaped LiFePO_4 - 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.