MM 56: Materials for Energy Storage and Conversion - Intercalation

Time: Thursday 11:45–13:00 Location: IFW D

MM 56.1 Thu 11:45 IFW D

Modulation of the optical properties of LixCo2O via Li-ion transport — •Sanaz Banifarsi[1], Yug Joshi[2], Robert Lawitzki[3], and Guido Schmitz[4] — [1]Heisenbergstrasse 3, 70569 Stuttgart, Germany — [2]Heisenbergstrasse 3, 70569 Stuttgart, Germany — [3]Heisenbergstrasse 3, 70569 Stuttgart, Germany — [4]Heisenbergstrasse 3, 70569 Stuttgart, Germany

Modulation of the optical properties of LixCo2O via Li-ion transport

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Previous studies reveal that the electronic structure of Lithium cobalt oxide (LixCoO2, LCO) undergoes severe change upon lithium de-/intercalation. The present study probes this behavior by combining electrochemistry with Vis-NIR spectroscopy of the LCO during the battery cycling. To this aim, thin films of LCO serving as an active material were deposited on the platinum metallization (on oxidized silicon wafer, acting as current collector as well as a reflector), by ion beam sputtering. The structure of the active material is investigated by X-ray diffraction and transmission electron microscopy. The refractive index, derived from the Clausius-Mossotti dispersion equation, as a function of wavelength evolves upon lithium de-/intercalation. The study attempts at linking this evolution of the dispersion curves to the underlying electronic structure of the LCO. In addition, in situ electrochemical measurement proves electrochromic reversibility.

MM 56.2 Thu 12:00 IFW D

Laser-assisted atom probe tomography (APT) study on the lithiation behavior in the conversion reaction of CuO as an anode in lithium ion battery — •Jianshu Zheng, Patrick Stender, and Guido Schmitz — Chair of Materials Physics, Institute of Materials Science, University of Stuttgart, Heisenbergstr. 3, D-70569 Stuttgart, Germany

The lithiation behavior in conversion reaction of CuO as an anode in lithium ion battery is investigated by the laser-assisted atom probe tomography (APT). For this purpose, the CuO thin film is firstly prepared by ion beam sputtering, then lithiated to various conversion states via electrochemical techniques, afterwards lifted out and glued onto Tungsten post, and further shaped into sharp tip with diameter smaller than 100 nm by focus ion beam, before it is finally measured in laser-assisted APT. The following reconstruction on the resultant data provides the 3D coordinates of atoms in real space, enabling us to view the distribution of atoms and concentration profiles within certain volumes. Three conversion states in the first cycle of CuO are studied, where in the initial, intermediate, and fully conversion states, lithium clusters, a mixed compound CuOLix ($0<x<2$), and nanometer-scaled metallic Cu particles in Li2O matrix are observed, respectively. With the advantage of APT, the size distribution of Cu particles and the concentration profile across the Cu/Li2O interface are obtained, revealing the structure and concentration evolution of Cu particles in Li2O matrix. Based on the above results, a model on the diffusion pathway and kinetics of lithium ions is created.

MM 56.3 Thu 12:15 IFW D

Quantifying the intercalation process in graphite based anode materials using DFT — •Holger Euchner[1] and Axel Gross[1,2] — [1]Helmholtz Institute Ulm for Electrochemical Energy Storage, Helmholtzstraße 11, 89081 Ulm — [2]Institute of Theoretical Chemistry, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm

Carbon derivatives such as hard carbon are considered as anode materials for Li-ion and particularly post Li-ion technology. Despite its importance, the underlying storage mechanism in the different types of carbon based anodes and for different alkali metal cations is still debated and clear characterization strategies are missing.

In this contribution, we present lattice dynamics and band structure calculations for different stages of alkali metal intercalation in graphitic model structures as obtained from periodic denisty functional theory. An interpretation of these results with respect to Raman and double resonance Raman scattering – focussing on the G-band and D-band excitations – suggests D- and G-band as sensitive descriptors of the intercalation process [1]. Consequently, these insights may be used for distinguishing the exact insertion mechanism for different alkaline metals in carbon based materials.

[1] M. Anji Reddy, M. Helen, A. Groß, M. Fichtner, H. Euchner, ACS Energy Lett. **3**, 2851 (2018).

MM 56.4 Thu 12:30 IFW D

A new hop: a DFTB model for Li diffusion in low-SOC graphite anodes. — •Chiara Panosetti[1], Simon Annies[1], Cristina Grosu[1,2], Maria Voronenko[1], and Christoph Scheurer[1] — [1]T. U. München — [2]Forschungszentrum Jülich

Despite having been employed in consumer electronics for decades, Li-graphite anodes are not yet understood enough to *e.g.* upscale usage towards automotive applications. Many mechanisms involved in charging/discharging, ageing, and other key aspects, were never grasped in detail. Part of this difficulty is due to a structural complexity emerging particularly at low states of charge (SOC), which complicates both the interpretation of experiments and the computational modelling. From a computational standpoint, targeted system sizes compatible with the SOC range of interest are inaccessible to first-principles calculations, yet require first-principles treatment of key effects such as dispersion and long-range electrostatics. Density-Functional Tight Binding (DFTB), a semi-empirical approximation to DFT, offers a high-quality trade-off between accuracy and speed. With our recently developed parametrization [1], we are able for the first time to resolve the full Potential Energy Surface (PES) of Li motion in stage-I and stage-II LiC_{108} (SOC 5%). The PES contains information that enables us to implement, and hereby discuss, both kinetic Monte Carlo (kMC) models of Li-ion mobility in the graphite host, and free-energy sampling which ultimately yields the computed voltage profile of the anode.

[1] C. Panosetti *et al.*, arXiv:1904.13351 (2019).

MM 56.5 Thu 12:45 IFW D

The Electrostatic GAP: Machine-Learning Potentials for Battery Materials — •Carsten Staacke[1], Christoph Scheurer[1], Johannes Margraf[1], Gabor Csanyi[2], and Karsten Reuter[1] — [1]Chair of Theoretical Chemistry, TUM, Germany — [2]Engineering Department, Cambridge University, UK

All-solid-state Li-ion batteries promise gains in safety and durability by combining high Li-ion conductivity and mechanical ductility. In this respect, solid-state electrolytes (SSE) such as the $Li_7P_3S_{11}$ glass-ceramic have gained much attention.[1] From a modelling perspective, describing ionic conductivity and the role of crystalline/amorphous interfaces in such SSEs requires an accurate and efficient description of covalent and electrostatic interactions. To this end, we have combined short-ranged machine-learning potentials based on the Gaussian Approximation Potential (GAP)[2] approach with a classical electrostatic model in the long-range. We will present a first-principles validation of both, pure GAP potential and the new electrostatic GAP for the LPS SSE. In particular, the role of Coulomb interactions in SSE simulations will be shown and evaluated.

[1] A. Hayashi, A. Sakuda, M. Tatsumisago, *Front. Energy Res.,* ***2016****, 4, 25* [2] A. P. Bartók, M. C. Payne, R. Kondor, G. Csányi *Phys. Rev. Lett.,* ***2010****, 104, 136403*