

MM 37: Materials for Energy Storage and Conversion - Structure of Battery Materials

Time: Wednesday 11:45–13:00

Location: IFW D

MM 37.1 Wed 11:45 IFW D

Analytical TEM studies of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$, LiCoO_2 , and Si electrodes for Li-ion batteries — ●ARDAVAN MAKVANDI¹, MARTIN PETERLECHNER¹, SIMONE CASINO², TOBIAS GALLASCH², MARTIN WINTER², and GERHARD WILDE¹ — ¹Institute of Materials Physics, University of Münster, Münster, Germany — ²MEET Battery Research Center, University of Münster, Münster, Germany

The modification of state-of-the-art electrodes by nanostructured coatings is one approach to optimize crucial parameters for applications, such as the electronic conductivity or mechanical stability. In general, interfaces (e.g. active material/coating; electrode surface/electrolyte) determine the local Li-ion transport kinetics and finally the electrochemical performance in terms of cycling stability or capacity retention. Therefore, it is necessary to study the structure and chemistry of electrodes and electrode/electrolyte interfaces. In this work, the structure and chemistry of the bulk and surface regions of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC-622), LiCoO_2 (LCO), and Si electrodes after cycling are studied using transmission electron microscopy (TEM). In the case of NMC-622 and LCO electrodes, the effect of an Al doped ZnO-coating layer on the stability of the surface upon cycling is studied. Moreover, in the case of a Si electrode, the effect of a carbon-coating layer on the strain evolution caused by the volume expansion during cycling is studied.

MM 37.2 Wed 12:00 IFW D

Creating an NCM thin film cathode model system for the interface analysis of liquid electrolyte batteries — ●HENDRIK HEMMELMANN^{1,2}, JULIUS K. DINTER^{1,2}, JURI E. BECKER^{1,2}, ANGELIKA POLITY², and MATTHIAS T. ELM^{1,2} — ¹Center for Materials Research, Justus-Liebig-University Giessen, Germany — ²I. Physikalisches Institut, Justus-Liebig-University Giessen, Germany

Coating the active cathode material (CAM) with a chemically inactive layer can significantly improve the performance of lithium ion batteries (LIBs). However, the reason for the beneficial effect of the coating is lacking a deeper understanding. Here, we present the preparation of lithium nickel cobalt manganese layered oxide (NCM) thin films, which were subsequently coated with Al_2O_3 of different thicknesses using atomic layer deposition (ALD). Such thin films are ideal model systems to characterize the interface properties using surface-sensitive techniques. To investigate the influence of the coating, electrochemical measurements were performed using metallic Li as anode and the interface properties were characterized using XRD, SEM, AFM, Raman and XPS.

MM 37.3 Wed 12:15 IFW D

Highly stable and highly conductive LiCoPO_4 olivine-based thin film 5V cathode material. — ●GENNADY CHERKASHIN¹, ROBERT EILHARDT¹, SILVIA NAPPINI², IGOR PIŠ², FEDERICA BONDINO², SIMONE DAL ZILIO², ELENA MAGNANO², MATTEO COCCIONI³, and LAMBERT ALFF¹ — ¹Technische Universität Darmstadt, Germany — ²IOM CNR Laboratorio TASC, Basovizza, TS, Italy — ³Physics Department, University of Pavia, Italy

Recently, we have discovered high electronic conductivity of the LiCoPO_4 olivine 5V cathode thin film material tailored with $\text{LiCo}_2\text{P}_3\text{O}_{10}$. The crystal structure of the compound remains stable even if all Li-ions leave the olivine structure, which corresponds to $\sim 5.1\text{V}$ vs. Li^+/Li . Here we explore the intrinsic stability of the novel thin film cathode material and the stability of cathode/electrolyte interface upon the charging/discharging potential in the 3.0-5.1V range. We apply the comprehensive in-situ electron spectroscopy approach (XPS and XAS) combined with first principle calculations to study

the evolution of the oxidation and valence states, the $\text{Co}3d\text{-O}2p$ hybridization, the work function, the density of occupied and unoccupied states near the Fermi level, the chemical composition, etc. as a function of the Li-content. We show that the electronic structure/properties of the compound are fully reversible; $\text{LiCo}_2\text{P}_3\text{O}_{10}$ stabilizes the olivine structure in its fully delithiated state. First-principles simulations predict $\sim 5.2\text{V}$ redox for $\text{LiCo}_2\text{P}_3\text{O}_{10}$. Thus, higher energy density via the involvement of $\text{LiCo}_2\text{P}_3\text{O}_{10}$ into the redox reaction is possible. A reason of enhanced conductivity at atomic level is analyzed.

MM 37.4 Wed 12:30 IFW D

First-principles investigation of a LISICON-to-LGPS phase transition in $\text{Li}_{10}\text{GeP}_2\text{O}_{12}$ — ●GIULIANA MATERZANINI and NICOLA MARZARI — Theory and Simulations of Materials (THEOS) and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Using ab-initio molecular dynamics, we have recently reported a remarkably high Li-ion conductivity ($\sigma \simeq 10^{-3}\text{S/cm}$ at 25°C , $E_a = 0.21\text{ eV}$) for the oxide analogue of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS, tetragonal $\text{P}4_2/\text{nmc}$). Though not being reported in the experimental literature so far, this system possesses the same density and stoichiometry of the LISICON $\text{Li}_{3.33}\text{Ge}_{0.33}\text{P}_{0.66}\text{O}_4$ (orthorhombic Pnma), that oppositely shows low conductivity ($\sigma \simeq 10^{-6}\text{S/cm}$ at 25°C , $E_a = 0.54\text{ eV}$). Aim of this work is shedding light on a possible phase transition from the existing orthorhombic phase to a tetragonal phase of $\text{Li}_{10}\text{GeP}_2\text{O}_{12}$ (LGPO). We use variable-cell (NPT) Car-Parrinello molecular dynamics (CP package of the QUANTUM ESPRESSO distribution) at 600K, 1200K and 1500K. Simulations are conducted starting from both the tetragonal ideal LGPS structure (t-LGPO) and the existing orthorhombic structure (o-LGPO). Although t-LGPO has higher enthalpy than o-LGPO at all temperatures, at 1200K o-LGPO undergoes phase transitions, possibly driven by the higher entropy and Li-ion conductivity of the phases formed during the dynamics. Structural similarities with t-LGPO of these phases are discussed, and their conductivities at 600K assessed through NPT and NVT simulations.

MM 37.5 Wed 12:45 IFW D

Graded electrodes for lithium-ion batteries — ●CHUAN CHENG¹, ROSS DRUMMOND², STEPHEN DUNCAN², and PATRICK GRANT³ — ¹Warwick Manufacturing Group (WMG), University of Warwick, Coventry CV4 7AL, UK — ²Department of Engineering Science, University of Oxford, Oxford OX1 3PJ, UK. — ³Department of Materials, University of Oxford, Oxford OX1 3PH, UK.

Homogeneous electrode structures used in conventional Li-ion batteries (LIB) lead to inhomogeneous active material utilization and gradients of overpotential and Li-ion concentration at the cell-scale, which are detrimental for both capacity retention at high charge-discharge rates and for battery lifetime. To account for these gradients, we demonstrate that heterogeneous electrode structures with engineered gradients in material distribution can improve LIB C-rate and long-term cycling performance when compared with conventional uniform electrodes in full-cell and half-cell LIBs. The improved performance of graded electrodes is shown to derive from a lower charge transfer resistance and reduced polarization at high C-rates, which suggests a more spatially homogeneous distribution of over-potential and hindering of the side reaction-induced battery degradation during long-term cycling.

References

- [1] C. Cheng, R. Drummond, S. R. Duncan, and P. S. Grant, *J. Power Sources* 413, 59 (2019).
- [2] C. Cheng, R. Drummond, S. R. Duncan, and P. S. Grant, *J. Power Sources*, In Press. <https://doi.org/10.1016/j.jpowsour.2019.227376>