

MM 14: Functional Materials III - Li ion batteries

Time: Monday 15:45–17:15

Location: IFW A

MM 14.1 Mon 15:45 IFW A

Studying the phase growth in LFP thin films — ●FABIAN WUNDE¹, FRANK BERKEMEIER¹, and GUIDO SCHMITZ² — ¹Institut für Materialphysik Universität Münster — ²Institut für Materialwissenschaft Universität Stuttgart

Lithium Iron Phosphate (LFP) is one of the state of the art cathode materials for lithium ion batteries. In this work, LFP thin films between 100 and 300 nm are deposited by ion beam sputtering. These films exhibit a reasonable electrochemical capacity and excellent cycle life stability, which makes them capable for fundamental research, like diffusion studies. Therefore, detailed cyclic voltammetry (CV) measurements are carried out on the films. According to Randles and Sevcik, the peak current of the CV diagrams is found to be proportional to the squareroot of the scan rate, but studies on LFP films of different thickness also show a proportionality to the film thickness. The latter differs from the theory of Randles and Sevcik and is expected to be due to the two-phase nature of LFP, forming a lithium-rich and a lithium-poor phase. Therefore, we numerically study the growth and descent of the two phases, by means of finite differences methods, using a discrete diffusion model and chemical potentials obtained from the regular solution. Within these studies, the time-dependence of the lithium content of the LFP is evaluated, and correlated to the experimental data.

MM 14.2 Mon 16:00 IFW A

The electrocapillary coupling in aprotic lithium electrolytes — ●TOBIAS KITZLER¹, JÜRGEN MARKMANN^{1,2}, and JÖRG WEISSMÜLLER^{1,2} — ¹Helmholtz-Zentrum Geesthacht — ²Technische Universität Hamburg-Harburg

During lithium loading and unloading into metal anodes, the electrodes undergo considerable volume change. Whenever there are gradients in composition, the volume change is accompanied by large internal stress. Depending on the mechanism of solution of Li into the electrode material, this results in different values for the electrocapillary coupling parameter (ECCP), which is here a change of apparent surface stress with apparent surface charge density and can be measured using the identity with change of electrode potential with elastic strain. Therefore the potential dependent ECCP can be used to analyse the Lithium solution mechanisms. In this talk, we present experimental results for the ECCP of a thin film gold electrode which was measured from the potential modulation when the electrode was cyclically strained in-situ during lithiation. We show supporting in-situ x-ray lattice parameter data, also measured on the films in-situ during lithiation. The underlying microscopic processes are discussed in relation to the observed ECCP.

MM 14.3 Mon 16:15 IFW A

All solid-state batteries using lithium iron phosphate and tin as electrodes — ●SUSANN NOWAK¹, FRANK BERKEMEIER², and GUIDO SCHMITZ¹ — ¹Institut für Materialwissenschaften, Heisenbergstr. 3, 70569 Stuttgart — ²Institut für Materialphysik, Wilhelm-Klemm-Str. 10, 48149 Münster

Thin-film all solid-state batteries have been prepared using lithium iron phosphate (LFP) as the cathode, lithium phosphoroxide oxynitride (LiPON) as a solid-state electrolyte, and tin as an anode. All layer preparations are carried out using ion beam sputtering which yields a battery of below 1 μm thickness on oxidized silicon. These all solid-state battery is characterized by means of electrochemical properties using chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS). Additionally the micro structure of the cells is investigated by transmission electron microscopy (TEM) and electron diffraction. It is found that in comparison to a system in liquid electrolyte (lithium perchlorate in EC/DEC) the all solid-state system gives very similar results and therefore presents an interesting and suitable model system for further studies of the behavior of lithium ion batteries, for example the investigation of the behavior at higher temperatures than possible in case of a liquid electrolyte.

MM 14.4 Mon 16:30 IFW A

Diffusion and Interface Transport in LCO Thin-Films — ●FRANK BERKEMEIER, TOBIAS STOCKHOFF, and GUIDO SCHMITZ — Universität Münster, Institut für Materialphysik, Wilhelm-Klemm-Str. 10, 48149 Münster

Lithium cobalt oxide (LCO) thin-films are prepared by ion-beam sputter deposition. The capability of the films to reversibly store and release lithium ions is proven by cyclic voltammetry and chronopotentiometry. It is demonstrated that the lithium concentration of the films can be reliably determined by electrochromic absorption technique using visible light, which even allows to measure the time-dependence of the lithiation/delithiation reaction. Using this electrochromic absorption technique, the intercalation of lithium into LCO is studied in case of films between 10 and 400 nm in thickness. To describe the intercalation reaction in a proper way, it is found that – apart from the volume diffusion – the interface transport of lithium has to be taken into account. Therefore, we suggest a diffusion model which includes an interface transport coefficient that considers the transfer of lithium ions from the liquid electrolyte into the LCO. Using this model, we are able to accurately describe the experimental data, and determine the interface transport coefficient to $\approx 10^{-7}$ cm/s.

MM 14.5 Mon 16:45 IFW A

Functional Thin-Films for Li-Ion Batteries Grown by Novel CO₂-Laser Assisted Chemical Vapor Deposition — ●CHRISTOPH LOHO¹, AZAD DARBANDI^{1,2}, RUZICA DJENADIC^{1,3}, OLIVER CLEMENS^{1,2}, and HORST HAHN^{1,2,3} — ¹Joint Research Laboratory Nanomaterials, Technical University of Darmstadt and Karlsruhe Institute of Technology, Germany — ²Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany — ³Helmholtz Institute Ulm, Germany

Over the last decades a progressive miniaturization of electronic components took place. As a result there is an increasing demand for micro-sized power sources, which drives the current research on thin-film batteries. Among the applications are RFID tags, pacemakers, energy harvesting and lab-on-a-chip devices. In this respect an all-solid-state thin-film battery is desirable, since its excellent safety properties and easy integration in microelectronics are outstanding advantages.

We report on the functional thin-film synthesis via CO₂-laser assisted chemical vapor deposition (LACVD). The use of a CO₂-laser as part of the precursor delivery system is unique in the field of thin-film deposition so far and thus will be introduced. Furthermore, the characterization of a cathode (LiCoO₂) as well as solid-state electrolyte (Li₇La₃Zr₂O₁₂) material for thin-film Li-ion batteries is presented. In addition to results on the microstructure and composition of these materials we give an account of their electrochemical performance.

MM 14.6 Mon 17:00 IFW A

Effect of Ni-doping on structural, magnetic and electrochemical properties of LiMn_{1-x}Ni_xPO₄ — ●ALEXANDER OTTMANN¹, CARSTEN JÄHNE¹, HANS-PETER MEYER², and RÜDIGER KLINGELER¹ — ¹Kirchhoff-Institute for Physics, University of Heidelberg, Germany — ²Institute of Earth Sciences, University of Heidelberg, Germany

Nanoscaled polycrystalline LiMn_{1-x}Ni_xPO₄ with a doping level of x up to 0.45 has been synthesized via a microwave-assisted hydrothermal route. Characterization of the materials by means of X-ray powder diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and SQUID-magnetometry confirm well controlled Ni-doping in LiMnPO₄. The data show solid solution behaviour with the lattice parameters linearly decreasing upon increasing the nickel concentration, corresponding to Vegard's law. Concomitantly, the room temperature magnetization decreases which implies substitution of Mn²⁺ by Ni²⁺ in the LiMnPO₄ host structure. Electrochemical characterization by means of cyclic voltammetry reveals an active Mn³⁺/Mn²⁺ redox couple. The redox potential depends on the nickel concentration in LiMn_{1-x}Ni_xPO₄ and increases with x . Quantitatively, the reduction potential vs. lithium increases from 3.97 V in LiMnPO₄ to 4.09 V in LiMn_{0.55}Ni_{0.45}PO₄.