

MM 10: Functional materials II: Battery Materials

Time: Monday 11:45–13:00

Location: TC 010

MM 10.1 Mon 11:45 TC 010

Towards an All-Solid-State Thin-Film Li-Ion Battery 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. Regarding fabrication, chemical vapor deposition (CVD) is a suitable method to grow functional thin-films for Li-ion batteries, since it allows for a homogeneous growth over large areas with high deposition rates and a very high purity. Unique is also the capability of conformal, directional deposition in order to realize three-dimensional architectures. In this contribution we report on our latest progress towards an all-solid-state thin-film Li-ion battery deposited by novel CO₂-laser assisted chemical vapor deposition (LA-CVD). The detailed characterization of (i) LiCoO₂ and (ii) Li₇La₃Zr₂O₁₂ thin-films includes results on microstructure, phase composition and electrochemical performance.

MM 10.2 Mon 12:00 TC 010

Modeling the structural stability during delithiation in Li-Mn-Ni oxides from first-principles — ●JAN-MICHAEL ALBINA, ANIKA MARUSCZYK, THOMAS HAMMERSCHMIDT, and RALF DRAUTZ — ICAMS, Ruhr-Universität Bochum, Germany

The gradual reduction in both the charge and discharge voltage upon cycling in lithium batteries (aka voltage fade) is related to phase transformations in the cathode material. Therefore a better understanding of the phase transformation sequences occurring during cycling is important for improved performance of cathode materials. In this work we present a first-principles approach for modeling and analyzing phase relationships in multi-component systems. In particular, we will study the effect of delithiation on the phase evolution, phase stability, and variation of the chemical potentials for a selection of cathode materials based on Li-Mn-Ni oxides. The open circuit voltage will be estimated and discussed.

MM 10.3 Mon 12:15 TC 010

Single crystal growth, magnetism and ionic conductivity of LiMn_{1-x}Fe_xPO₄ — ●CHRISTOPH NEEF¹, HUBERT WADEPOHL², HANS-PETER MEYER³, and RÜDIGER KLINGELER¹ — ¹Kirchhoff Institut für Physik, Universität Heidelberg, D-69120 Heidelberg — ²Anorganisch-Chemisches Institut, Universität Heidelberg, D-69120 Heidelberg — ³Institut für Geowissenschaften, Universität Heidelberg, D-69120 Heidelberg

Single crystals LiMn_{1-x}Fe_xPO₄ were grown using the optical floating zone technique at elevated argon pressure up to 30 bar. The resulting mm-sized single crystals were used to study the influence of Fe doping on the structural, magnetic and transport properties by means of single crystal XRD, thermal expansion, magnetometry, and impedance

spectroscopy. The resulting phase diagram illustrates the evolution of the long range antiferromagnetically ordered ground state for different doping levels. The ionic conductivity which is of particular interest for application of the material in Li-ion batteries is very low in the end member LiMnPO₄ but clearly increases upon Fe doping.

MM 10.4 Mon 12:30 TC 010

A Mn₃O₄@MWCNT composite as anode material for Li-ion batteries — ●ALEXANDER OTTMANN¹, PHILIP SCHNEIDER¹, ELISA THAUER¹, MAIK SCHOLZ², MARCEL HAFT², MARKUS GELLESCH², FRANZISKA HAMMERATH², BERND BÜCHNER², SILKE HAMPEL², and RÜDIGER KLINGELER¹ — ¹Kirchhoff-Institute for Physics, Heidelberg University, Germany — ²Leibniz Institute for Solid State and Materials Research (IFW), Dresden, Germany

Mn₃O₄ nano-sized particles have been incorporated into the inner hollow cavities of multi-walled carbon nanotubes (MWCNT) via a solution-based approach. The resulting composite material with about 40 wt% of incorporated Mn₃O₄ has been used for electrochemical half-cell studies against Li⁰/Li⁺ by means of cyclic voltammetry and galvanostatic cycling with potential limitation (GCPL). For electrode preparation, no additional carbon black has been used. Cyclic voltammetry shows well-performing working electrodes. The redox peaks during the first half-cycle indicate formation of MnO and subsequently its reversible conversion reaction to metallic Mn. This is confirmed, e.g., by our magnetic studies. In addition, the electrochemical data reveal the formation of a solid electrolyte interface (SEI) and reversible lithium de-/intercalation into the MWCNT. The GCPL data confirm complete conversion of Mn₃O₄ to MnO during the first half-cycle and full accessibility of the theoretical capacity of the MnO + 2Li⁺ + 2e⁻ ⇌ Li₂O + Mn conversion reaction (703 mAhg⁻¹). The composite material reaches a maximum discharge capacity of 461 mAhg⁻¹ at a current of 100 mA g⁻¹ and maintains 97% of it in the 30th cycle.

MM 10.5 Mon 12:45 TC 010

Separation of surface and bulk stress in a model lithium alloy electrode reveals grain boundary alloying at high electric potentials vs. Li/Li⁺. — ●TOBIAS KITZLER¹, JÜRGEN MARKMANN^{1,2}, EMAD MAAWAD³, DANIEL TÖBBENS⁴, and JÖRG WEISSMÜLLER^{1,2} — ¹Helmholtz-Zentrum Geesthacht, Department of Materials Reserch, Materials Mechanics — ²Hamburg University of Technology, Department of Materials Physics and Materials Technology — ³Helmholtz-Zentrum Geesthacht, Department of Materials Reserch, Materials Physics — ⁴Helmholtz-Zentrum Berlin, Department of crystallography

We present the results of a combined study using the potential strain coupling parameter and microstructural characterisation to separate surface and bulk contributions to the stress in gold thin film electrodes during electrochemical cycling in an organic lithium electrolyte.

The results were used to show, that grain boundary alloying is an important mechanism which appears long before intermetallic alloys appear, and that it induces a stress on a film electrode which can easily be mistaken as a surface stress. This is especially important, since the effect is in the same order of magnitude (apparent surface stress: -2.9 N/m) as the actual surface stress. Furthermore the separation allowed estimating the surface stress resulting from underpotential deposition of lithium on the gold surface of roughly -2.6 N/m, which is good agreement with DFT results of -2.8 N/m calculated by Tavessol et. al.