

MM 6: Functional Materials I: Battery Materials

Time: Monday 10:15–11:45

Location: TC 010

MM 6.1 Mon 10:15 TC 010

Ultra-Thin All Solid-State Thin-Film Batteries — ●SUSANN NOWAK¹, FRANK BERKEMEIER², and GUIDO SCHMITZ¹ — ¹Lehrstuhl für Materialphysik, Universität Stuttgart — ²Institut für Materialphysik, Universität Münster

This talk focuses on ultra-thin all solid-state batteries with an overall thickness below 1 μm . They are prepared with a very good layer quality (roughness below 5 nm) via ion beam sputtering. The homogeneity and structure of the layers and interfaces is proven by cross-section TEM. The studied all solid-state batteries are composed of lithium iron phosphate as a cathode (LFP), lithium phosphorous oxynitride (LiPON) as an electrolyte and Sn or Si as an anode. Battery cells can be charged and discharged more than 100 cycles, still showing more than 50% of the initial capacity. The observed cycling behavior is strongly temperature dependent, exhibiting an increase of the capacity with elevated temperatures. The observed potential curve is compared to the expected one taking into account the charge-discharge behavior of the single electrodes. The influences of the balancing of the electrodes and the lithiation state of the anode on the energy density as well as the observed cell potentials are also discussed.

MM 6.2 Mon 10:30 TC 010

Electrically-induced interface reactions in lithium ion batteries — ●FRANK BERKEMEIER and FABIAN INKMANN — Universität Münster, Institut für Materialphysik, Wilhelm-Klemm-Str. 10, 48149 Münster

An unconventional type of thin film lithium ion battery will be presented, which consists of a lithium phosphorous oxynitride (LiPON) thin film that is embedded between a silver and a platinum layer. All layers are prepared by sputter deposition, resulting in a triple layer stack of a thickness well below 1 μm .

We demonstrate that it is possible to trigger an electrochemical reaction between LiPON and silver, when applying a negative voltage of about -3.8 V to the silver electrode. This interface reaction causes the growth of an interface reaction layer, which is capable to reversibly intercalate/deintercalate lithium.

To understand the properties of this layer in more detail, the structural and electrochemical properties of the overall layer stacks before and after electrochemical treatment have been investigated by e.g. impedance spectroscopy, cyclic voltammetry, and transmission electron microscopy. In course of these experiments it has been found that the cells exhibit a well-defined charge/discharge behavior and a promising cycling stability. Moreover, detailed informations about the morphology of the reaction layer have been obtained, as well as data about its growth kinetics and its lithium storage capacity.

MM 6.3 Mon 10:45 TC 010

Self-forming Lithium Ion Batteries: Optimization of Ag-LiPON Devices — ●LEILA RAAFAT, SUSANN NOWAK, and GUIDO SCHMITZ — Chair of Materials Physics, University of Stuttgart

Sandwiching the solid electrolyte lithium phosphorous oxynitride (LiPON) between two current collectors leads to a thin-film battery after initial charging (Liu et al., J. Electrochem. Soc. 155 (1), A8 (2008)). These electrochemically formed batteries are of particular interest, since the Li anode is internally electroplated without concern of its contamination. Three different devices of this design with a thickness of ca. 1 μm were electrochemically investigated. We discovered that employing an inert anode current collector towards LiPON like copper (Cu), will lead to Cu/LiPON/Ag-devices which can withstand over 500 cycles showing a stable discharge capacity. Since dendrite formation at the interfaces of such a device is inevitable, short circuits can occur. Extending a concept reported by Yourey et al. (Electrochim. Acta 66, 193 (2012)), the formation of short circuits can be prevented

by using a Li oxide based solid electrolyte interphase between the Li anode and LiPON. Therefore, we modified the devices by depositing a thin layer of lithium phosphate on the Cu current collector. This adjustment resulted in a significantly increased success rate and an improved cycle life; over 2000 cycles were measured. In order to understand the reactions happening within these batteries, the kinetics of the reaction layer are investigated depending on the cycle number.

MM 6.4 Mon 11:00 TC 010

LiCoO₂ and LiFePO₄ thin-films for application in lithium ion batteries — ●MARTIN FIEDLER¹, ANTONIA REYES JIMENEZ², FRANK BERKEMEIER¹, and GUIDO SCHMITZ³ — ¹Universität Münster, Institut für Materialphysik, Wilhelm-Klemm-Str. 10, 48149 Münster — ²Universität Münster, MEET - Batterieforschungszentrum, Corrensstr. 46, 48149 Münster — ³Universität Stuttgart, Institut für Materialwissenschaft, Heisenbergstraße 3, 70569 Stuttgart

In commercial lithium ion batteries, powders of Lithium Cobalt Oxide (LCO) or Lithium Iron Phosphate (LFP) are commonly used as cathode materials. Contrary to this common approach, in this work LCO and LFP electrodes are prepared by magnetron sputtering, resulting in films of a thickness between 120 and 5500 nm. After deposition, the layers are characterized by X-ray diffraction, electron microscopy, and different electrochemical techniques. In particular, the influence of post annealing and in situ heating of the films in a temperature range between 400 and 700°C is investigated, and it is found that the electrochemical performance of the layers significantly depends on both parameters. Moreover, it is demonstrated that, despite their large thickness, the cathodes are mechanically stable during cyclic lithiation/delithiation and thus allow detailed investigations of transport kinetics without being influenced by varying interface effects. In course of these measurements, the diffusion of lithium is investigated by means of electrochemical techniques, and is correlated to the microstructure of the layers. Finally, the technical relevance of the sputtered layers in functional full cells is presented.

MM 6.5 Mon 11:15 TC 010

Charging-induced defects in Li_{1-x}CoO₂ battery electrodes — ●GREGOR KLINSER¹, STEFAN TOPOLOVEC¹, PETER PARZ^{1,4}, HEINZ KRENN², HARALD KREN³, STEFAN KOLLER³, and ROLAND WÜRSCHUM¹ — ¹Institute of Materials Physics, Graz University of Technology, Austria — ²Institute of Physics, University of Graz, Austria — ³VARTA Micro Innovation GmbH, Graz, Austria — ⁴now at: Magna Steyr Battery Systems GmbH & Co OG, Zettling, Austria

Research in the field of modern battery materials demands characterization techniques which allow an inspection of atomistic processes during battery charging and discharging. In the present work, SQUID magnetometry is combined with positron annihilation spectroscopy to study the battery cathode material Li_{1-x}CoO₂ in dependence of the degree of charging.

Positron annihilation measurements reveal vacancy-type defects on the Li-sublattice the size of which increases with Li-extraction [1]. The concomitant increase of the magnetic moment with Li-extraction by SQUID magnetometry cannot exclusively be attributed to Co³⁺ → Co⁴⁺ oxidation, however, may also involve oxygen states. In the vicinity of the reversibility limit of charging, a sharp drop of the localized magnetic moment is observed, which may be linked to the Li vacancy reordering recorded by positron annihilation spectroscopy [1].

[1] P. Parz, B. Fuchsichler, S. Koller, B. Bitschnau, F. Mautner, W. Puff and R. Würschum, Appl. Phys. Lett. 102, 151901 (2013).

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