

## MM 57: Topical Session Battery Materials III

Time: Thursday 14:00–15:30

Location: H6

**Topical Talk**

MM 57.1 Thu 14:00 H6

**Physical properties and synthesis of thin film materials for batteries** — •NANCY DUDNEY — Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

Thin film batteries prepared by vapor deposition processes are being manufactured for a variety of devices. These small power sources offer extended cycle life and stability under extremes in temperature and charging conditions. With a planar structure and chemistry free of side reactions and SEI formation, the thin film batteries can also be used as a model test cell for exploring the transport and physical properties of battery materials and interfaces. Examples will be described as well as recent efforts focused on developing processing for 3D architectures.

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MM 57.2 Thu 14:30 H6

**Li ion transport in sputter deposited LiCoO<sub>2</sub> thin films and glassy borate membranes** — •TOBIAS STOCKHOFF, TOBIAS GALLASCH, and GUIDO SCHMITZ — Westfälische Wilhelms-Universität Münster, Institut für Materialphysik, Münster (Westf.), Germany

LiCoO<sub>2</sub> membranes are key components of current battery technology. We investigate sputter-deposited thin films of these materials aiming at the application in all-solid-state thin film batteries. For this, LiCoO<sub>2</sub> films (10 - 200 nm) were deposited onto ITO-coated glass substrates by ion beam sputtering. In addition, a part of these films are coated by an ion-conductive membrane of Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> glasses in the thickness range of 50 to 300 nm. Structural, chemical and electrical properties of the layers are studied by means of TEM (EELS) and various electrical methods (cyclic voltammetry, chrono-amperometry / -potentiometry).

Since the color of the LiCoO<sub>2</sub> films changes from red-brown to grey during de-intercalation of Li and the substrate as well as the glassy membrane deposited on top are optical transparent, reversible Li de- and intercalation can be directly demonstrated and quantified by a measurement of light transmission through the layered system. Samples coated with an ion-conductive membrane reveal a characteristic delay in switching optical transparency which is due to the slower transport across the membrane. Varying the thickness of the glassy membrane, the d.c. ion-conductivity and permeation through the membrane is determined quantitatively. Using thin membranes in the range of a few tens of nanometers the critical current densities are way sufficient for battery applications.

MM 57.3 Thu 14:45 H6

**Electron energy loss spectroscopy of thin film electrodes and membranes in all-solid-state batteries** — •TOBIAS GALLASCH, DIETMAR BAITHER, and GUIDO SCHMITZ — Institut für Materialphysik, Westf. Wilhelms-Universität Münster, Wilhelm-Klemm-Str.10, 48149 Münster, Germany

Electron energy loss spectroscopy (EELS) is based on inelastic scattering of electrons in the TEM. The technique allows evaluating the chemical composition, the oxidation states and therefore, also the bonding characteristics of layered samples with a spatial resolution in the nanometer range.

For the experiments, model batteries comprising of layers of LiCoO<sub>2</sub>, Li-Borate glasses and V<sub>2</sub>O<sub>5</sub> are deposited onto ITO-coated glass substrates. Single layer thickness ranges from 50 to 400 nm. Electron transparent cross section samples are prepared by conventional ion milling and FIB technique. Measuring the observed chemical shift in the absorption edges of the energy loss spectra and comparing these

to appropriate reference materials, different charge states of the electrodes can be distinguished and the amount of Li intercalated in the structure is quantified. The talk demonstrates how these data are used to optimize the conditions of sputter deposition and to achieve suitable functional properties of the thin films.

Reversible Li-intercalation in the model thin film battery with active layers of 200 nm thickness and 50 nm thick membranes is demonstrated by cyclic voltametry.

MM 57.4 Thu 15:00 H6

**Grenzflächen-Untersuchungen an Festkörper-Batterien** — •SUSANNE JACKE, JIE SONG, GENNADY CHERKASHININ, RENÉ HAUSBRAND und WOLFRAM JAGERMANN — TU Darmstadt, Fachbereich Materialwissenschaft, Petersenstrasse 32, 64287 Darmstadt

Dünnschicht-Festkörperbatterien sind in letzter Zeit in den Fokus verschiedener Forschungsaktivitäten für Anwendungen in mobilen elektronischen Geräten sowie Mikroelektronik oder Solarzellen gerückt. Ein wichtiger Aspekt bei der Verbesserung der Eigenschaften dieser Batterien ist das Verständnis der Ermüdungserscheinungen. Bei dem Zyklieren der Batterien spielen die Grenzflächen zwischen Elektrolyt und Elektroden eine wichtige Rolle. In der vorliegenden Studie wurde die Entstehung von Festkörper-Festkörper Grenzflächen schon während des Aufwuchsprozesses der Batterie in der Herstellung untersucht. So wurde die Entstehung der Grenzschicht zwischen Kathode und Elektrolyt sowie die zwischen Anode und Elektrolyt untersucht, indem ihre Zusammensetzung nach kurzen Depositionsschritten mit Photoelektronenspektroskopie analysiert wurde. Die Kathode, bestehend aus LiCoO<sub>2</sub>, wurde mit Hilfe von Sputter-Deposition aufgebracht, ebenso wie der LiPON-Elektrolyt und die Lithium-Aluminium-Anode. Eine auf diese Weise hergestellte Batterie zeigte das charakteristische Zyklierungsverhalten einer Batterie. Einige interessante Abweichungen von der Festkörperstruktur wurden an der Grenzfläche gefunden: so entsteht z.B. an der Grenzfläche Elektrolyt-Kathode eine Zwischenschicht, die Nitrit- (NO<sub>2</sub>-), und Nitrat (NO<sub>3</sub>-) Produkte enthält.

MM 57.5 Thu 15:15 H6

**Valence states and surface/interface reactions in Li-ion battery cathodes** — •GENNADY CHERKASHININ<sup>1</sup>, DAVID ENSLING<sup>1</sup>, STEFAN SCHMID<sup>1</sup>, JIE SONG<sup>1</sup>, SUSANNE JACKE<sup>1</sup>, RENÉ HAUSBRAND<sup>1</sup>, KRISTIAN NIKOLOWSKI<sup>2</sup>, HELMUT EHRENBERG<sup>2</sup>, and WOLFRAM JAEGERMANN<sup>1</sup> — <sup>1</sup>Department of Materials Science, Surface Science Institute, Darmstadt University of Technology, Darmstadt 64283, Germany — <sup>2</sup>IFW Dresden, Institute for Complex Materials, Germany

Surface electronic properties of promising Li-Ion cathode materials such as LiMO<sub>2</sub> (Ni, Co, Mn) as well as evolution of electrolyte-cathode interfaces formed after contact to the electrolyte, due to electrochemical charging and after cycling were systematically studied using XPS, UPS and synchrotron photoelectron spectroscopy (SXPS, XAS). To study fundamental surface properties of the oxides we investigated both thin film cathodes in-situ, whose surfaces are not contaminated by impurities, and synthesized powder cathodes used in industry. For LiMO<sub>2</sub> (Ni, Co, Mn) cathodes, we have found that contact of the cathodes to the electrolyte results in the loss of lattice lithium and in the formation of a solid electrolyte interface (SEI) layer consisting of Li<sub>2</sub>CO<sub>3</sub>, Li<sub>x</sub>O<sub>y</sub>, LiF (if LiPF<sub>6</sub>-electrolyte is used) and other species. For oxides containing Ni<sup>3+</sup>, we observe a Ni<sup>3+</sup> to Ni<sup>2+</sup> reduction. Charging of Li<sub>x</sub>(M)O<sub>2</sub> (M=Co,Ni) does not only lead to Co<sup>3+</sup> to Co<sup>4+</sup> oxidation but also to oxygen deficiency. We detect no oxygen site participation in the charge compensation at the initial stage of the Li-de-intercalation.