

MM 49: Topical Session Battery Materials I

Time: Thursday 10:15–11:45

Location: H6

Topical Talk MM 49.1 Thu 10:15 H6
Mechanisms of intercalation, ionic motion and new metastable cathode materials — ●STANLEY WHITTINGHAM — SUNY, Binghamton, NY, USA

Intercalation is the predominant reaction mechanism in rechargeable batteries in use today. Intercalation processes, unlike conversion reactions, allow for fast ionic motion both on lithium insertion and lithium removal. Moreover the structural maintenance during reaction permits essentially unlimited cycling of the material.

Intercalation can occur within a single phase as originally demonstrated in titanium disulfide, or with the formation of a second phase, as demonstrated in vanadium diselenide, the manganese oxide spinels and most recently in the lithium iron phosphate olivine. Although two-phase reactions were thought to be rate-limiting, such is not necessarily the case.

Ionic motion will be compared in materials with different intercalation mechanisms, and for thermodynamically stable as well as metastable compounds. This work is being supported by the United States Department of Energy, Energy Frontier Research Center.

Topical Talk MM 49.2 Thu 10:45 H6
Ion conductivity and effects of mechanical treatment — ●PAUL HEITJANS and MARTIN WILKENING — Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, D-30167 Hannover

A way to enhance the ionic conductivity of materials being suitable, e.g., for batteries is to reduce the crystallite size. The largely increased volume fraction of interfacial regions in nanocrystalline ceramics provides pathways for fast cation as well as anion diffusion. Nanostructuring can easily be achieved by high-energy ball milling. We will review studies on single- and two-phase ion conductors such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiTaO_3 , LiNbO_3 and $\text{Li}_2\text{O}:\text{Al}_2\text{O}_3$, $\text{BaF}_2:\text{CaF}_2$, respectively, serving as model substances to investigate the effect of mechanical treatment on the ionic diffusivity. As an example, ball milled nanocrystalline LiTaO_3 - even when treated in a shaker mill for only 30 min - exhibits an increase of the overall room temperature Li conductivity by about five orders of magnitude compared to that of the coarse grained source material. Mechanical treatment of BaF_2 and CaF_2 together for about 32 h in a shaker mill leads to a composite material where the anion conductivity is increased by a factor of 10^3 compared to that of single-phase nanocrystalline BaF_2 prepared under the same conditions. Besides conductivity measurements we used a variety of ^7Li and ^{19}F solid state NMR techniques to gain detailed information about the dynamics as well as first insights into the microstructure of these highly defective materials.

MM 49.3 Thu 11:15 H6
Determination of the lithium diffusion coefficient in novel

anode materials based on graphite/SiCN composites — ●ANDRZEJ P. NOWAK, MAGDALENA GRACZYK-ZAJAC, CLAUDIA FASEL, and RALF RIEDEL — Institute of Materials Science, Darmstadt University of Technology, Petersenstr. 23, 64287 Darmstadt, Germany
 Commercially available anode materials for lithium ion secondary batteries are based on graphite due to its cycle stability, low price, easy to handle and reversible capacity of 372 mAh/g. This type of anode material is suitable for high energy application. However, there is still a need for new materials for high power applications. Here, we report on novel graphite/SiCN composite materials which exhibit promising electrochemical performances for high energy and high power density batteries. For high energy application the ratio graphite to preceramic polymer is 3:1 and the capacity reaches a value of 600 mAh/g. For high power application the starting materials ratio is 1:1 and the capacity after 200 cycles has been determined to be about 200 mAh/g. The correlation between electrode capacity and the graphite/SiCN ratio, the pyrolysis temperature and materials composition has been established. The relation between these parameters as well as the lithium diffusion coefficient in the novel electrode materials was calculated from the results obtained from EIS, CV and GITT studies. The direct dependence between the lithium diffusion coefficient and the materials electrochemical properties is discussed.

MM 49.4 Thu 11:30 H6
Atom probe tomography of solid state ion-conductive membranes — ●GERD-HENDRIK GREIWE, GUIDO SCHMITZ, and FRANK BERKEMEIER — Institut für Materialphysik WWU Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Deutschland

Our group has long-termed interest in glassy ion-conductive membranes to be used in all solid state batteries. Using ion beam sputtering methods, we could demonstrate that thin film membranes of amorphous Li-borate glass reveal a conductivity even better than quenched bulk glasses and furthermore a finite-size effect was documented (1,2). However, the Li content of sputter deposited thin films could not be determined by conventional EDX or EELS analysis due to the low mass of Li.

In new experiments, we measure the Li content of the glass by means of laser-assisted atom probe tomography. For this, glass layers and suitable electrodes are deposited upon pre-shaped tungsten tips. Although quite complex, the obtained mass spectra are well understood in terms of various molecular species so that a quantitative analysis gets possible. It is indicated that the reported finite-size effect is due to indiffusion of Li from the electrode materials.

- (1) F. Berkemeier, M.R. Abouzari, and G. Schmitz, Phys. Rev. B 76, (2007) 024205.
- (2) F. Berkemeier, M.R. Abouzari, G. Schmitz, Ionics, DOI 10.1007/s11581-008-0266-4.