Poster Presentations

[MS28-06] Charge-Induced Defect Formation in LixCoO2 Battery Cathodes: XRD and PA Spectroscopy Study.

Brigitte Bitschnau,[a] Franz A. Mautner,[a] Peter Parz,[b], Werner Puff,[b] Roland Würschum,[b] Bernd Fuchsbichler,[c] Stefan Koller,[c],

[a] *Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, Graz, Austria;*
[b] *Institute of Materials Physics, Petersgasse 16, Graz, Austria,*
[c] *VARTA Micro Innovation GmbH, Stremayrgasse 9, Graz, Austria*
E-mail: bitschnau@tugraz.at

Lithium-ion batteries have developed into most advanced battery systems, e.g. laptops and mobile phones. $LiCoO_2$ is a typical intercalation battery cathode material. However, reversible charge-discharge cycling of $LiCoO_2$ is only possible down to 50% of the available Li-ions since further removal of Li-ions drastically reduces the capacity and cycle stability. The formation of vacancy-type defects during the charging process in LixCoO2 battery cathodes was investigated by XRD and position life-time spectroscopy and Doppler broadening of positron-electron annihilation (PA) radiation as defect specific techniques [1]. Li^+-extraction, which in a battery mode corresponds to charging, was performed at 293 K under electrochemical control in a 3-electrode test-cell with a Maccor Series 4000 battery tester. The composition of the lithium-ion electrode material used was: 88wt.% LiCoO2 particles, 7 wt.% carbon black as conducting agent, 5 wt.% binder material (polyvinylidene difluoride hexafluoropropylene copolymer). Structural analysis of the electrode samples was performed by means of X-Ray diffraction using a Bruker D8 Advance diffractometer in Bragg-Brentano geometry with Cu-Kα radiation. Diffractograms were measured in the 2-Theta angle range from 15° to 130° and were analysed by Rietveld refinement with the programs FULLPROF [2] and X'PertHighScorePlus (Panalytical). For positron annihilation measurements a positron source (^{22}NaCl) was sandwiched between two identical $LiCoO_2$ electrode samples. Positron lifetime measurements were performed with a fast-fast spectrometer with a time resolution of 221 ps. The spectra were analysed by using the program pfposfit [3]. Doppler broadening (DB) measurements were performed in a coincidence setup with two high purity Ge detectors.with energy resolution for the 511 keV annihilation γ-line in the detector system corresponds to ca. 0.88keV (FWHM). Both the Doppler broadening S parameter as well as the positron lifetime component τ1 exhibit a characteristic variation with increasing amount of Li^+-extraction; the S-parameter and τ1 first increases upon decreasing x from 1 to 0.6. Further Li^+-extraction causes a decrease of S and τ1 (x = 0.55), followed by a re-increase for x<0.55. Conclusions: The regime of reversible charging is dominated by vacancy-type defects on the Li^+-sublattice the size of which increases with increasing Li+-extraction. Indication is found that Li^+-reordering which occurs at the limit of reversible Li^+-extraction (x = 0.55) causes a transition from the two-dimensional agglomerates into one-dimensional vacancy chains. Degradation upon further Li^+-extraction is accompanied by the formation of vacancy complexes on the Co-and anion sublattice.

[1] Parz, P., Fuchsbichler, B., Koller, S., Bitschnau, B., Mautner, F.A., Puff, W., Würschum, R. (2013). *Appl. Phys. Lett.,* **102**, 151901.
[2] Rodriguez-Carvajal, J. (1993). *Physica B,* **192**, 55.
[3] Puff, W. (1983). *Comput. Phys. Commun.* **30**, 359.

Keywords: batteries; lithium compounds; positron annihiliation, powder X-Ray diffraction