Poster Presentation

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Charge-Induced Defect Formation in LixCoO2 Battery Cathodes: XRD and PA Spectroscopy Study

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Lithium-ion batteries have developed into most advanced battery systems, e.g. laptops and mobile phones. LiCoO2 is a typical intercalation battery cathode material. However, reversible charge-discharge cycling of LiCoO2 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-K⍰ 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 (22NaCl) was sandwiched between two identical LiCoO2 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 ⍰-line in the detector system corresponds to ca. 0.88keV (FWHM). Both the Doppler broadening S parameter as well as the positron lifetime component ⍰1 exhibit a characteristic variation with increasing amount of Li+-extraction; the S-parameter and ⍰1 first increases upon decreasing x from 1 to 0.6. Further Li+-extraction causes a decrease of S and ⍰1 (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.

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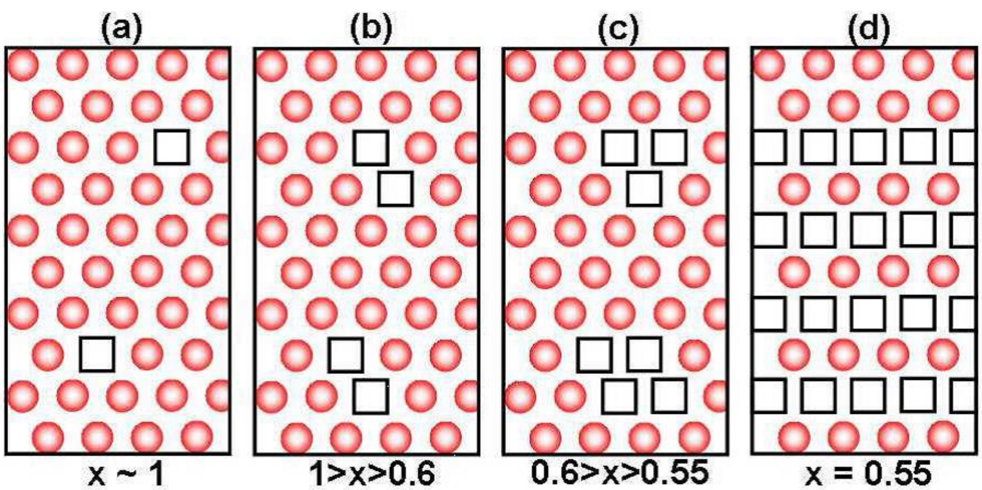

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