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, 7wt.% carbon black as conducting agent, 5wt.% 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 (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 pprof [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.


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