Contribution ID: **16** Type: **not specified**

Positron Annihilation Spectrosopy for investigation of defect evolution of Li1-xNi1/3Mn1/3Co1/3O2 Lithium Ion Battery Electrodes

Tuesday 20 June 2017 16:34 (1 minute)

Understanding and controlling the aging behavior of lithium ion batteries is key for the successful application in various fields of interest. Especially when going from small handheld devices with short life times to electric vehicles or even energy in grid storage a limited lifetime and enhanced capacity losses have to be avoided. To achieve this, a fundamental understanding of the transport mechanisms and lithium trapping in the active materials is crucial. For example for the widely used Li1-xNi1/3Mn1/3Co1/3O2 (NMC-111) cathode material it is established that during the first charge-discharge cycle Li-ions can be removed from the NMC-111 structure but cannot be completely re-intercalated back into the material under standard conditions, resulting in a capacity loss (CL) corresponding to a value of x ~ 0.08. The underlying process is poorly understood. Prior studies utilizing electrochemical methods and in situ X-ray diffraction (XRD), showed that a slowing down or freezing of the Li mobility or kinetic hindrance or barrier grows as the fully intercalated state is being approached, so that the initial structure with x = 0 can only be recovered after an extended voltage hold at low potentials.
As such a kinetic limitation should be due to the type and concentration of atomistic defects in the material we applied Positron Annihilation Spectroscopy in combination with electrochemical methods and XRD to study the structure and evolution of vacancy type defects in NMC-111. The relation between positron annihilation and electronic structure is discussed in terms of structural dynamics during the lithiation process. Samples of NMC-111 electrodes with decreasing lithium content (x = 0 –0.7) covering the whole range of state of charge were electrochemically prepared for the non-destructive analysis using positron coincidence Doppler broadening spectroscopy (CDBS). The positron measurements allowed us to observe the evolution of the defect structure caused by the delithiation process in the NMC-111 electrodes. The combination of CDBS with X-ray diffraction for the characterization of the lattice structures enabled the analysis of the purported kinetic barrier effect in the first charge-discharge cycle and we discuss possible implications due to vacancy ordering. The usefulness of positrons to study such effects is not well known in the battery community as we also are the first group to report on the successful application of CDBS on NMC-111 electrodes yielding new insights in the important role of defects caused by the delithiation process and the kinetic barrier effect.

Summary

Positron Annihilation Spectrosopy is successfully established to investigate the defect evolution. New insights into the cause for the intrinsic NMC-111 1st cycle capacity loss are gained.

Author: SEIDLMAYER, Stefan

Co-authors: HUGENSCHMIDT, Christoph; GASTEIGER, Hubert (Chair of Technical Electrochemistry, Department of Chemistry and Catalysis Research Center, Technische Universität München, 85748 Garching, Germany); BUCHBERGER, Irmgard (Chair of Technical Electrochemistry, Department of Chemistry and Catalysis Research Center, Technische Universität München, 85748 Garching, Germany); REINER, Markus (Physik Department E21, Technische Universität München, 85748 Garching, Germany); GILLES, Ralph; GIGL, Thomas

Presenter: SEIDLMAYER, Stefan

Session Classification: Poster