X-ray diffraction (XRD) has become a widespread and powerful technique for characterizing the structure of active electrode materials in lithium-ion batteries. In situ XRD techniques have been used extensively to characterize structural changes in electrode materials during the charging or discharging of a battery cell. Alternatively, ex situ XRD of electrodes that have been harvested from aged or cycled cells is useful in the study of degradation mechanisms in batteries.

Presented here is a combined structural and thermodynamic examination of the degradation of active materials that are typically used in the positive electrodes (“cathodes”) of lithium-ion batteries. XRD analysis and thermodynamic measurements have been performed on electrodes following hundreds of lithiation-delithiation cycles. The main electrode materials of interest are lithium cobalt oxide (LiCoO$_2$, the most commonly commercialized cathode material in such batteries) and the state-of-the-art “NMC 532” oxide material (LiNi$_{1/2}$Mn$_{3/10}$Co$_{1/5}$O$_2$). NMC 532 has advantages over lithium cobalt oxide in terms of effective capacity and cost.

Following the collection of XRD spectra for the cycled electrodes, Rietveld refinement of the patterns was performed using the LiCoO$_2$ prototype lattice. Structural parameters refined for the structure were: $a$ and $c$ unit cell axes, oxygen ($z$) fractional coordinate, Li site occupancy as either Li or Co, and Co site occupancy as either Li or Co. While there were no major changes in lattice parameters with increased cycling of LiCoO$_2$, the NMC 532 material exhibited significant changes in unit cell dimensions and volume. Other characteristics determined from XRD refinements, such as site occupancies and their relation to interlayer cation mixing and disorder, will also be discussed.

In conjunction with structural studies, thermodynamics measurements (Gibbs free energy, enthalpy, and entropy) were performed on the cycled electrodes. The entropy of a lithium-ion electrode reaction varies significantly with state-of-charge, resulting in an “entropy profile” that is unique to a particular electrode material. The effects of extensive cycling on the entropy profiles of LiCoO$_2$ and NMC 532 will be presented here as an additional indication of fundamental changes experienced by these materials. Taken together, the complementary XRD and thermodynamics techniques provide insight into the degradation mechanisms of these electrode materials.

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