

In situ X-ray absorption spectroscopy of Li rich Mn-Ni-Fe oxide cathode.

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Cobalt free, lithium rich manganese, nickel and iron composite oxides are promising cathode materials as they show attractive initial cycle electrochemical performance and can reduce the cost and toxicity of a lithium ion battery. However, Li-rich cathodes suffer from capacity and voltage fading on long term cycling. The structural changes, such as deformation of crystallographic phase, cationic mixing, and amorphization of electrode material during cycling are reported as the main reasons behind the performance degradation. To better understand how the structural changes in this material are related to the composition and electrochemical performance we have synthesized and systematically studied a series of $\text{Li}_{1.2}\text{Mn}_{0.40+x}\text{Ni}_{0.30-x}\text{Fe}_{0.10}\text{O}_2$ materials with $x = 0, 0.05, 0.10,$ and 0.15 . Change in the ratio between Mn and Ni elements affects fractions of the monoclinic and rhombohedral phases (higher fraction of monoclinic phase with increase in Mn content), as well as cationic mixing within rhombohedral phase (more cation mixing at higher Ni content). The results of this study demonstrate synergistic effect of the two phase composition enabling stable electrochemical cycling performance. The series of cathode materials was studied with X-ray absorption spectroscopy (XAS) before and after cycling. For the first time we report EXAFS data analysis at all three K-edges: Mn, Ni and Fe. The results from X-ray diffraction and in-situ XAS provide information on changes in atomic distances and near neighbors with composition and during electrode cycling, which allowed proposing comprehensive voltage and capacity fading mechanisms.