Characterization of the effects of Al-substitution in layered oxide cathode materials for Li-ion batteries

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Layered mixed transition metal oxide materials have been extensively investigated as replacements for $LiCoO_2$ in consumer electronics and, especially, for potential electric vehicle applications. NMC materials $LiNi_xCo_{1-2x}Mn_xO_2$ with x=0.33 and x=0.4 have proven commercially successful with improved performance, though a further reduction of the Co-content is desirable for cost and environmental reasons. Al-substitution for Co has been shown to improve both cost and safety aspects of the cathode materials and, notably, enhance the cycling stability for reasons that are not explicitly known (Fig. 1). This work explores the specific effects of Al-substitution in the $LiNi_{0.45}Co_{0.1-x}Al_xMn_{0.45}O_2$ ($0 \le x \le 0.1$) system, in which Co is decreased both by a relative increase of the amounts of Ni and Mn and direct replacement by Al. The structural and electronic effects of Al-substitution are probed using X-ray absorption spectroscopy (XAS). The near-edge structure (XANES) elucidates the charge compensation mechanisms and electronic structure changes during battery operation. Analysis of the extended fine structure (EXAFS) is used to determine element-specific local structure within the materials during charge, and the changes that occur as a result of prolonged cycling (Fig. 2). Additionally, both *in situ* and *ex situ* X-ray diffraction (XRD) are used to further characterize the structural evolution of the materials during the charge and discharge processes and cycle lifetimes.

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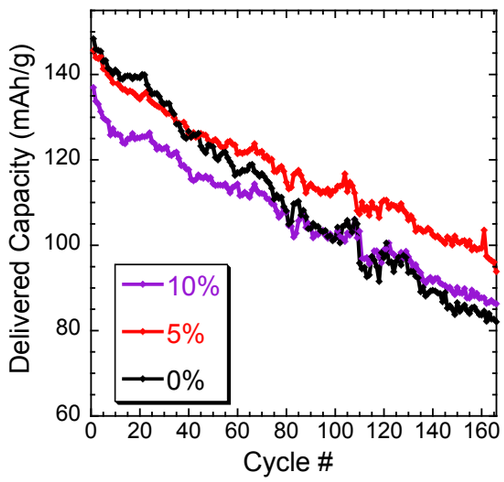

Figure 1: Discharge capacity vs. cycle for $LiNi_{0.45}Co_{0.1-x}Al_xMn_{0.45}O_2$ ($0 \le x \le 0.1$) materials cycled between 2-4.3 V at 12 mA/g.

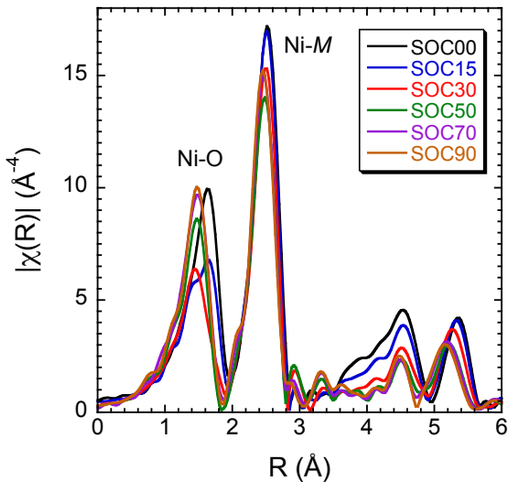

Figure 2: k^3-weighted Fourier transform of Ni EXAFS data at various states-of-charge (SOC) during Li extraction from $Li_xNi_{0.45}Co_{0.1}Mn_{0.45}O_2$. Marked peaks correspond to scattering between Ni-O and Ni-*M* where *M*=Ni, Mn, or Co.

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