X-ray Absorption Spectroscopic Studies of Li[Ni$_x$Co$_{1-2x}$Mn$_x$]O$_2$ for Li Rechargeable Batteries

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Recently, layer-structured lithium cobalt nickel manganese oxides (Li[Ni$_x$Co$_{1-2x}$Mn$_x$]O$_2$) have been considered as one of the most promising alternative materials to replace LiCoO$_2$ as cathode materials in lithium batteries. The electrochemical and safety characteristics of these new materials are comparable or better than LiCoO$_2$.[1,2] These materials contain alternating predominantly lithium layers, and layers containing Mn^{4+}, Ni^{2+}, and Co^{3+}. Metal K-edge X-ray absorption spectroscopy (hard XAS) has been employed to examine the electronic and local structure of transition metal in these electrode materials during cycling for Li rechargeable batteries. Soft XAS (200 eV to 1000 eV) is also well suited to probe the electronic structure of specific ions in the electrode materials, especially, low z element that cannot be directly investigated by hard XAS (above 1000 eV). Recently, Ceder et al.[3] reported based on theoretical calculations that electron exchange in cathode materials (i.e., oxidation and reduction) may involve the participation of oxygen 2p band, in addition to charge compensation by the metal ions. Soft XAS (200 eV to 1000 eV) results at O K-edge have provided experimental evidence for this oxygen contribution to charge compensation in the Li-ion intercalation-deintercalation process.[4] In this work, we apply both hard and soft XAS to shed light on the reaction mechanism of the electrochemical process in this cathode material.

Hard XAS measurements were performed in transmission mode at beamline X11A and X18B of the National Synchrotron Light Source (NSLS) using a Si(111) double-crystal monochromator detuned to 35 - 45% of its original intensity to eliminate the high order harmonics. The *in situ* Mn and Ni K-edge XAS data were obtained in two separate cells. Energy calibration was carried out by using the first inflection point of the spectrum of Mn and Ni metal foil as a reference (*i.e.*, Mn K-edge = 6539 eV, Co K-edge = 7709 eV, and Ni K-edge = 8333 eV). Reference spectra were simultaneously collected for each *in situ* spectrum by using Mn, Co, or Ni metal foils. Soft XAS measurements were carried out at beamline U7A of NSLS. The beam size was 1 mm in diameter. The estimated incident X-ray energy resolution was ~ 0.2 eV. Data were obtained in fluorescence yield (FY) modes. The FY data were recorded using a windowless energy dispersive Si (Li) detector.

Because of the electric dipole-allowed 2p →3d transition, the absorption peaks for the metal L$_{II,III}$-edge XAS are relatively intense and are very sensitive to the oxidation state, spin state, and bond covalency. The electronic structure of the Co ions in Li$_{1-x}$Co$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ can be investigated qualitatively through peak features in the XAS spectra. The Co L-edge XAS of electrochemically Li-ion deintercalated Li$_{1-x}$Co$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ system is shown in Figure 1. The Co L$_{II,III}$-edge XAS spectra of Li$_{1-x}$Co$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$, obtained in the FY mode remain mostly unchanged during charge, suggesting that Co ions in the electrode remain as Co^{3+} during charge.

Fourier transform magnitudes of the Co K-edge EXAFS spectra of electrochemically Li-ion deintercalated Li$_{1-x}$Co$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ system are shown in Figure 2. The first peak at ~1.5 Å in Fig. 2 is due to Co-O correlation. Co-O bond distance decreases during charge. Our previous O K-edge study showed the experimental evidence for oxygen contribution to charge compensation process during charge.[5] The decrease of Co-O bond length could be ascribed to be the increase of hole state of oxygen site during charge. Therefore, Co K-edge EXAFS results show that the oxygen contribution to charge compensation is strongly related to Co ions around O. More detailed discussion will be presented at the meeting.

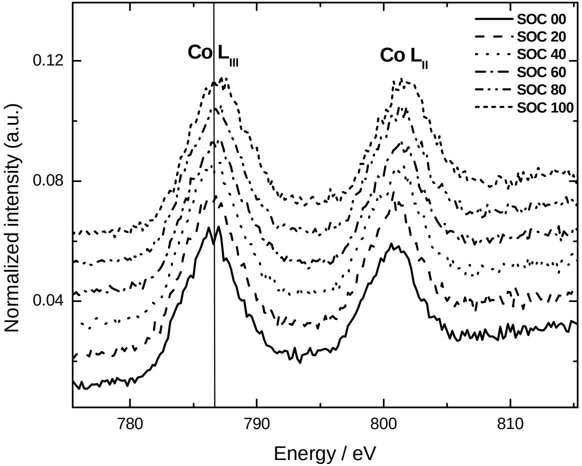

Figure 1. The Co L-edge XAS of electrochemically Li-ion deintercalated Li$_{1-x}$Co$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ electrode during charge.

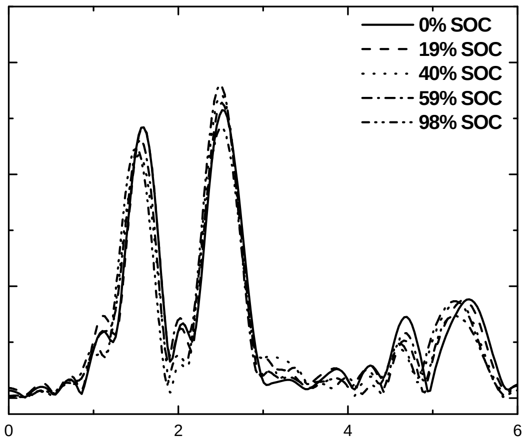

Figure 2. Fourier transform magnitudes of the Co K-edge EXAFS of electrochemically Li-ion deintercalated Li$_{1-x}$Co$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ electrode during charge.

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