Structural Investigation and Fading Mechanisms of Cathode Materials for Lithium-Ion Battery

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In situ XAS experiments of metal K-edge were performed in transmission mode at beam line BL-17C at the National Synchrotron Radiation Research Center (NSRRC) at Hsinchu, Taiwan. The metal foil (Ni, Co and Mn) was employed for energy calibration in each scan simultaneously. To analyze the in situ XAS data, all raw absorption spectra were normalized to compare the regions of pre-edge, near-edge and post-edge. For extended X-ray absorption fine structure (EXAFS) spectra, pre-edge background was subtracted, and then normalized with respect to the edge jump. The normalized $\chi(E)$ spectra were converted to $\chi(k)$ in k space. The $k3$-weighted $\chi(k)$ data ranged from 3.5 °A^{-1} to 13.65 °A^{-1} for Ni K-edge, 3.65 °A^{-1} to 11.4 °A^{-1} for Co K-edge, and 3.75 °A^{-1} to 12.4 °A^{-1} for Mn Kedge were Fourier transformed (FT) to r space by separating the EXAFS contributions according to different coordination shells.

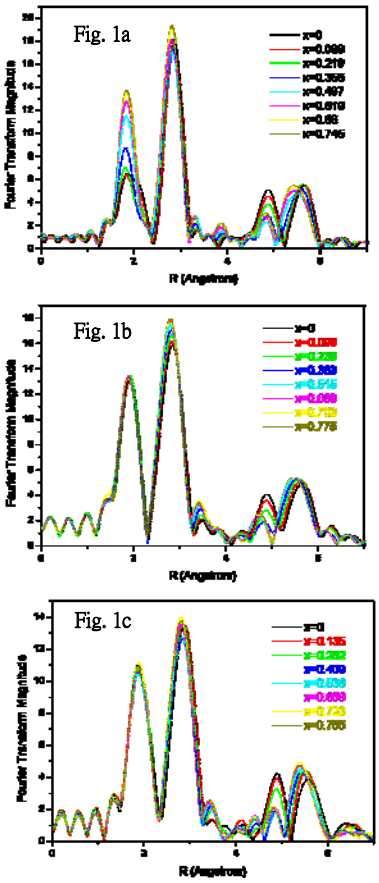

Figure 1. Fourier transformed spectra of the (a) Ni K-edge, (b) Co K-edge and (c) Mn K-edge for $Li_{1-x}Ni_{05}Co_{0.25}Mn_{0.25}O_2$ as a function of lithium content x during charge.

The local structure of selected absorbers Ni, Co and Mn are also investigated using each extended X-ray absorption fine structure (EXAFS) for $Li_{1-x}Ni_{0.5}Co_{0.25}Mn_{0.25}O_2$. Fig. 1 shows Fourier transform magnitudes of Ni, Co and Mn K-edge EXAFS spectra during charge. The first peak is attributed to Ni-O, Co-O and Mn-O, as shown in Figs. 1 (a), (b) and (c), respectively. It is revealed that on delithiation Ni-O distance varies dramatically, while the changes for Co-O and Mn-O distances are rather negligible. It is because that the charge compensation mainly occurs at the Ni atoms and Ni^{2+} is oxidized to Ni^{4+}, resulting in a significant decrease in the average Ni-O distance. The second peak at around 2.8 Å in Fig. 1 is assigned to the six-coordinated transition metal Ni/Co/Mn ions around the absorber atom in transition metal layer. The peaks shown up at 4.8 Å and 5.5 Å in the higher R region correspond to single M-M and multiple M-M-M scattering, respectively.

The EXAFS structural parameters were obtained by fitting the first two peaks of FT spectra. The first shell metal-oxygen (Ni-O, Co-O and Mn-O) distance as a function of x for $Li_{1-x}Ni_{0.5}Co_{0.25}Mn_{0.25}O_2$ is shown in Fig. 2. For the pristine state, bond lengths are 1.99 Å, 1.93 Å and 1.92 Å for Ni-O, Co-O and M-O, respectively. As referred to the literatures, the bond length of Co-O is the same as that in $LiCo_{0.85}Al_{0.15}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. Yabuuchi et al. stated that layer-structured $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ consisted of Co^{3+}, Ni^{2+} and Mn^{4+}. This indicates that Co is in the trivalent state for bare $LiNi_{0.5}Co_{0.25}Mn_{0.25}O_2$, which is consistent with XANES result. In addition, the distance of 1.99 Å for Ni-O is smaller than that in $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (2.03 Å) due to the co-existence of Ni^{2+} and Ni^{3+}. The distance of 1.92 Å for Mn-O is larger than that in $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (1.91 Å), suggesting that the compound in this study contained a small amount of Mn^{3+}. Fig. 2 clearly demonstrates that the variation in Mn-O distance is the least (only 0.01 Å), while that of the Ni-O distance is the most, i.e. 0.11 Å during the whole charge process. It is worth while to note that the bond distance of Ni-O decreases drastically from x=o to x=0.36 and then the change is relatively small as x > 0.5 for the $Li_{1-x}Ni_{0.5}Co_{0.25}Mn_{0.25}O_2$. Fig. 3 shows the second shell metal-metal distance (Ni-M, Co-M and Mn-M) as a function of Li concentration. It appears that on delithiation all the bond distances decrease, yet almost remain constant at the end of charge.