XAFS analyses of Cr-Mn based oxides for non-aqueous secondary battery materials.

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Introduction
Recently, layered lithium manganese oxides are of interest as positive electrode materials for lithium ion batteries. Compared to conventional Me$^{3+}$/Me$^{4+}$ one electron redox reaction, chromium ion shows Cr$^{3+}$/Cr$^{6+}$ three electrons redox in the layered solid state matrix, leading the possible high energy materials. Therefore, we prepared the solid solution Li$_2$MnO$_3$-LiCrO$_2$ for the first cycle in the range of 2.0 V vs. Li/Li$^+$. The Cr K-edge spectrum of the pristine sample is identical to that of LiCrO$_2$, indicating that Cr ion is trivalent. And the spectra shifted to high energy side with the extraction of Li from the cathode, suggesting that Co ion is oxidized to tetravalent for charging. After the 1st cycle, the spectrum shifts back to that of the pristine material, indicating that Co$^{3+/4+}$ redox is reversible reaction. Figure 1a shows the Cr K-edge XANES spectra during the first cycle. The spectra of the samples except the sample after the 1st cycle are identical to that of Li$_2$MnO$_3$, indicating that Mn ion is tetravalent state. The spectrum obtained after the 1st cycle is locating between Li$_2$MnO$_3$ and LiMn$_2$O$_4$, suggesting that manganese ions are partly reduced to trivalent states.

Experimental
To make the composite electrodes for the electrochemical testing, a slurry containing Li$_{1.2}$Mn$_{0.4}$Cr$_{0.2}$Co$_{0.2}$O$_2$. acetylene black, poly(vinylidene fluoride) in 80 : 10 : 10 weight ratio was coated by the doctor blade on an aluminum foil current collector. Positive electrodes were assembled in coin cells together with lithium metal foil as negative electrode, and 1 M LiPF$_6$ solution in 1:1 volume ratio of ethylene carbonate / dimethyl carbonate (DMC) as electrolyte solution. The K$_2$CrO$_4$ exhibited an intense pre-edge absorption at 5992 eV. The increased intensity in the pre-edge peaks indicates an increase in Cr$^{6+}$ component in the positive electrodes.

Results and Discussion
Figure 1a shows the Cr K-edge XANES spectra of Li$_{1.2}$Mn$_{0.4}$Cr$_{0.2}$Co$_{0.2}$O$_2$ for the first cycle in the range of 2.0 V-4.8 V. The Cr K-edge spectrum of the pristine sample is identical to that of LiCrO$_2$, indicating that the Cr ion exists as trivalent state. The intensity of pre-edge at 5992 eV increases by the extraction of Li from the positive electrodes. The K$_2$CrO$_4$ exhibited an intense pre-edge absorption at 5992 eV. The increased intensity in the pre-edge peaks indicates an increase in Cr$^{6+}$ component in the positive electrodes. After discharge to 2.0 V, intensity of the pre-edge peak decreased, indicating that the electrochemically oxidized Cr$^{6+}$ was partly reduced to Cr$^{3+}$. Since the ionic radius of Cr$^{3+}$ (0.44Å) is much smaller than that of Cr$^{6+}$ (0.61Å), Cr$^{6+}$ would migrate to the tetrahedral site in the lithium layer. Moreover, it has been found that chromium ions migrates reversibly from the tetrahedral sites to the original octahedral sites during discharge process. The Co K-edge spectrum (not shown) of the pristine materials is also identical to that of LiCoO$_2$, indicating that Co ion is trivalent. And the spectra shifted to high energy side with the extraction of Li from the cathode, suggesting that Co ion is oxidized to tetravalent for charging. After the 1st cycle, the spectrum shifts back to that of the pristine material, indicating that Co$^{3+/4+}$ redox is reversible reaction. Figure 1b shows the Mn K-edge XANES spectra during the first cycle. The spectra of the samples except the sample after the 1st cycle are identical to that of Li$_2$MnO$_3$, indicating that Mn ion is tetravalent state. The spectrum obtained after the 1st cycle is locating between Li$_2$MnO$_3$ and LiMn$_2$O$_4$, suggesting that manganese ions are partly reduced to trivalent states. We conclude that Cr$^{3+/6+}$ three electron redox reaction and reduction of manganese, which was originally electrochemically inactive, result in the high energy material.

Reference
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