**Introduction**

Recently, lithium-excess layered lithium manganese oxides are of interest as positive electrode materials for large-scale lithium-ion batteries. Compared to conventional Me\(^{3+}/Me^{4+}\) one electron redox reaction, chromium ion allows Cr\(^{3+}/Cr^{6+}\) three electrons redox in the layered solid state matrix, leading the possible high energy materials.\(^1\) Recently, we have prepared the solid solution consisting of Li\(_2\)MnO\(_3\)-LiCrO\(_2\)-LiCoO\(_2\) and demonstrated those high-capacity performance as the positive electrode materials. In this study, we investigate the change in the electronic structures of the materials by X-ray absorption spectroscopy, and discuss the reaction mechanisms during the electrochemical cycling for the chromium ion containing solid-solution.

**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) (80 : 10 : 10 in weight ratio) was coated by the doctor blade on an aluminum current collector. The positive electrodes were assembled in coin cells together with lithium metal foil as negative electrodes, and 1 M LiPF\(_6\) solution in 1:1 volume ratio of ethylene carbonate / dimethyl carbonate (DMC) as electrolyte solution.

For the sample preparation of XAS measurements the coin cells were galvanostatically charged to 4.4 V or 4.8 V vs. Li/Li\(^+\) at a rate of 10 mA/g, and then discharged to 2.0 V or 1.5 V. Thus prepared electrodes were separated from the cells and were washed with DMC solvent, and then dried in vacuum. These electrodes were put into a film bag which was sealed in a glove box to prevent air contamination.

**Results and Discussion**

Figure 1 show 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 1.5 V – 4.8 V. Cr K-edge spectrum of the pristine sample is identical to that of LiCrO\(_2\), indicating that the Cr ion exists as the trivalent state. The intensity of pre-edge located at 5992 eV increases by the extraction of Li from the crystal lattice. K\(_2\)CrO\(_4\) exhibited an intense pre-edge absorption at 5993 eV. The increased intensity in the pre-edge peaks indicates increase in Cr\(^{6+}\) component during the charging process. After the discharging to 1.5 V, intensity of the pre-edge peak significantly weakened, indicating that the Cr\(^{6+}\) was electrochemically reduced to Cr\(^{3+}\). Since the ionic radius of Cr\(^{6+}\) (0.44Å) is much smaller than that of Cr\(^{3+}\) (0.61Å), Cr\(^{6+}\) would migrate to the tetrahedral site in the lithium layer. Moreover, it has been found that chromium ions migrate reversibly from the tetrahedral sites to the octahedral sites during discharge process. Note that EXAFS analysis suggested that trivalent chromium ions are located at both 3a and 3b octahedral sites, indicating that change in the cation distribution during the electrochemical cycling.

From the Mn K-edge XANES spectra of the samples (not shown), it is easily estimated that the sample is consisting of tetravalent manganese ions. After discharge to 1.5 V, manganese ions in the crystal lattice are partly reduced to trivalent states. Reversible change in the Co K-edge spectrum is also confirmed during the electrochemical cycling.

From these results, we conclude that the high-capacity property of Li\(_2\)MnO\(_3\)-LiCrO\(_2\)-LiCoO\(_2\) solid solution is originated by mainly Cr\(^{3+}/Cr^{6+}\) three electron redox and partly from cobalt and activated managanese ions.

**References**


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