

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

Shinichi KOMABA, Kazuyo YAMAMOTO, Kazuhiro YOSHII,  
Masae SUGANO, Saori TAKADA, Yoshinari ABE, Izumi NAKAI  
Department of Applied Chemistry, Tokyo University of Science,  
1-3 Kagurazaka, Shinjuku, Tokyo 162-8601

### Introduction

Recently, layered lithium manganese oxides are of interest as positive electrode materials for lithium ion batteries. Compared to conventional  $\text{Me}^{3+}/\text{Me}^{4+}$  one electron redox reaction, chromium ion shows  $\text{Cr}^{3+}/\text{Cr}^{6+}$  three electrons redox in the layered solid state matrix, leading the possible high energy materials.<sup>1)</sup> Therefore, we prepared the solid solution  $\text{Li}_2\text{MnO}_3\text{-LiCrO}_2\text{-LiCoO}_2$  and examined the electrochemical properties of these solid-solution compounds. In this study, we investigate the change in the electronic structures of the materials by X-ray absorption spectroscopy, and discuss the reaction mechanism during electrochemical reactions in the chromium ion containing solid-solution system.

### Experimental

To make the composite electrodes for the electrochemical testing, a slurry containing  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.2}\text{Co}_{0.2}\text{O}_2$ , 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  $\text{LiPF}_6$  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.  $\text{Li}/\text{Li}^+$  at a rate of 10 mA/g, and then discharged to 2.0 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 1a shows the Cr K-edge XANES spectra of  $\text{Li}_x\text{Mn}_{0.4}\text{Cr}_{0.2}\text{Co}_{0.2}\text{O}_2$  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  $\text{LiCrO}_2$ , 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  $\text{K}_2\text{CrO}_4$  exhibited an intense pre-edge absorption at 5992 eV. The increased intensity in the pre-edge peaks indicates an increase in  $\text{Cr}^{6+}$  component in the positive electrodes. After discharge to 2.0 V, intensity of the pre-edge peak decreased, indicating that the electrochemically oxidized  $\text{Cr}^{6+}$  was partly reduced to  $\text{Cr}^{3+}$ . Since the ionic radius of  $\text{Cr}^{6+}$  (0.44 Å) is much smaller than that of  $\text{Cr}^{3+}$  (0.61 Å),  $\text{Cr}^{6+}$  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  $\text{LiCoO}_2$ , 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  $\text{Co}^{3+/4+}$  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  $\text{Li}_2\text{MnO}_3$ , indicating that Mn ion is tetravalent state. The spectrum obtained after the 1st cycle is locating between  $\text{Li}_2\text{MnO}_3$  and  $\text{LiMn}_2\text{O}_4$ , suggesting that manganese ions are partly reduced to trivalent states. We conclude that  $\text{Cr}^{3+}/\text{Cr}^{6+}$  three electron redox reaction and reduction of manganese, which was originally electrochemically inactive, result in the high energy material.

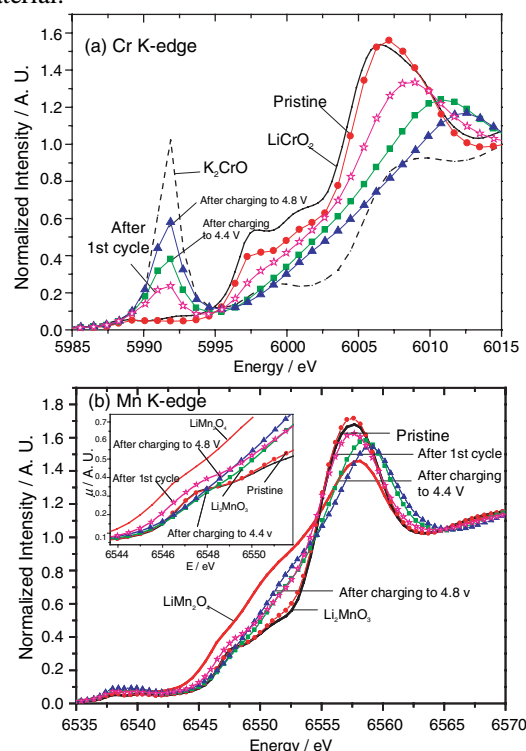


Figure 1 X-ray absorption near edge structure spectra for  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.2}\text{Co}_{0.2}\text{O}_2$ .

### Reference

1) Z. Lu *et al.*, *J. Electrochem. Soc.*, **150**, A1044 (2003).  
Mail: komaba@rs.kagu.tus.ac.jp