Electronic and local structures of Li(Mn,Ni,Co,Li)O$_{2\text{-}\delta}$ during electrochemical charge and discharge processes

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1 Introduction

In the last few decades, lithium-ion battery has been used widely as an energy source of cellphones and laptops and so on. More recently, their application has been extended to hybrid electric vehicles (HEV), electric vehicles (EV), power storage, and emergency power supplies, and then a development of a novel cathode material with higher energy density is highly expected. As a candidate of the new cathode, Li-rich layered rock-salt transition-metal oxides Li(Mn,Ni,Co,Li)O$_2$ – in which Mn, Ni and Co are tetravalent, divalent and trivalent, respectively – have drawn much attention, because these materials exhibit higher discharge capacity than commercialized cathodes. According to previous work [1], such a high capacity can be induced by an activation of Mn due to an oxygen loss during initial charge-discharge process. However, this process deteriorated a safety of the battery at the same time. In our recent study, it was demonstrated that heat-treatments under vacuum reducing conditions could suppress the oxygen loss, while keeping the high discharge capacity [2]. But effects of the heat-treatments on electronic states and local structures of Li(Mn,Ni,Co,Li)O$_2$ are still ambiguous at the moment. In order to make the effects clearer, we prepared Li(Mn,Ni,Co,Li)O$_2$, and then measured X-ray absorption fine structure (XAFS) spectra of the samples.

2 Experiment

Li(Mn,Ni,Co,Li)O$_2$ with various metal compositions were synthesized by a coprecipitation method. Obtained precursors were calcined in air at 650 $^{\circ}$C for 15 h, and the fired at 950 $^{\circ}$C for 15 h. As a post heat-treatment process, a part of the samples were annealed at 800 $^{\circ}$C for 6 h under a reducing condition: i.e., $P=10^{-4}\sim10^{-2}$ Pa. These obtained products were characterized by X-ray diffraction measurements, inductively coupled plasma analyses (ICP), and charge-discharge cycle tests.

In order to clarify their electronic and local structures around the transition metals, X-ray absorption fine structure (XAFS) spectra of the Mn, Ni and Co K-edges were measured with BL7C installed at Photon Factory in KEK. We performed these measurements with a transition mode for cathodes after electrochemical charging and discharging, and then analyzed the XAFS spectra by using REX-2000 program.

3 Results and Discussion

From X-ray diffraction patterns, it was confirmed that both the pristine Li(Mn,Ni,Co,Li)O$_2$ and reduced Li(Mn,Ni,Co,Li)O$_{2\text{-}\delta}$ had a single phase of the layered rock-salt structure and there was no impurity phase. It was also found by ICP that the metal compositions were essentially the same as the nominal compositions. Charge-discharge cycle tests clarified that the irreversible capacity was improved by the heat-treatments.

In order to investigate the heat-treatment effect on the local structures, we performed XAFS measurements and then analyzed the EXAFS oscillations. As a result, it was suggested that the reducing treatment made a significant influence on the local structure around Mn: that is, the first coordination peak of Mn-O shell became lower by the treatment. Similar change was also observed in the cathode after an initial charge process. Taking the previous work into account [1], the reducing treatment might remove oxygen around Mn and then activate Mn as well as the electrochemical charging.

We also investigated the local-structure change during the discharge process. In order to eliminate the oxygen-loss effect, the measurements were carried out for the cathodes at the second discharging with various cut-off voltages. Figure 1 shows Fourier transformations of k^2-weighted EXAFS spectra at the Mn K-edge of Li$_x$(Mn$_{1/2}$Ni$_{1/6}$Co$_{1/6}$Li$_{1/6}$)O$_2$. As shown in this figure, the first coordination peaks (the Mn-O shell) became weaker by the discharge, indicating higher distortion around Mn. One of the reasons may be due to a reduction from Mn^{4+} to Mn^{3+} which exhibits the Jahn-Teller effect. Such a reduction was also indicated by XANES spectra presented in Fig. 2. Because the structure distortion should be related with the decay of the cathode property, effects of the vacuum reducing treatments on the local structure in the discharge process will be discussed.
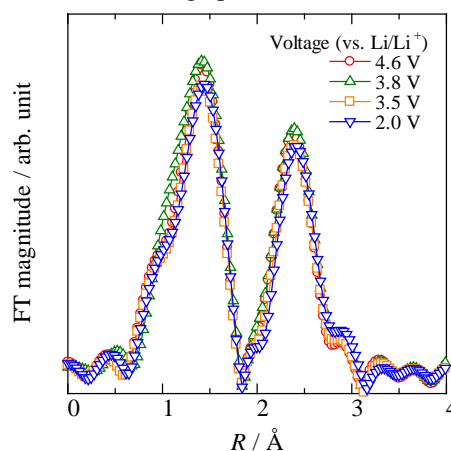

Fig. 1: Fourier transformations of EXAFS spectra of Mn K-edge of Li$_x$(Mn$_{1/2}$Ni$_{1/6}$Co$_{1/6}$Li$_{1/6}$)O$_2$.
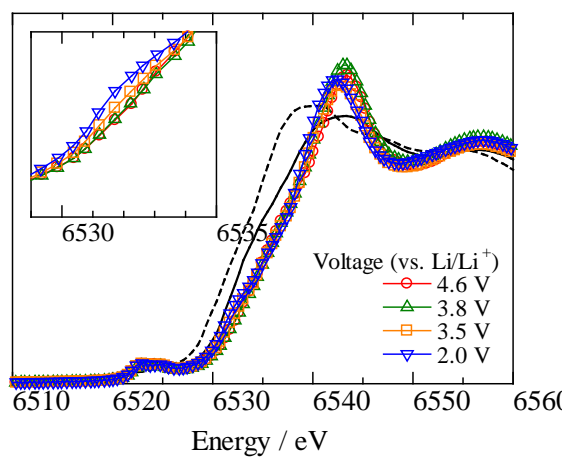
Fig. 2: XANES spectra of Mn *K*-edge of
$Li_x(Mn_{1/2}Ni_{1/6}Co_{1/6}Li_{1/6})O_2$. The solid and broken lines
represent spectra of MnO_2 and Mn_2O_3, respectively.

References
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