

Electronic and local structures of chemically-delithiated Li (Mn, Ni, Co, Li) O_{2-δ}

Yasushi Idemoto*, Naoya Ishida and Naoto Kitamura

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

1 Introduction

Recently, the lithium-ion battery has been expected to be applied for hybrid electric vehicles (HEV), electric vehicles (EV), power storage, and emergency power supplies as well as cellphones and laptops. In order to realize these applications, a development of a novel cathode material with higher energy density and safety is required. Li-rich layered rock-salt transition-metal oxides Li(Mn,Ni,Co,Li)O₂ – in which Mn, Ni and Co are tetravalent, divalent and trivalent, respectively – can be regarded as a promising candidate, because the materials show higher discharge capacity than commercialized cathodes, such as LiCoO₂. At the moment, however, the lower safety due to irreversible oxygen release at initial delithiation (charge) in the battery prohibits the commercialization [1]. In order to suppress the oxygen release, we have performed heat-treatments under reducing atmosphere for Li(Mn,Ni,Co,Li)O₂, and then found that the reduction process can improve the irreversibility [2]. From the X-ray absorption fine structure (XAFS) measurements, it was also suggested that the improvement was originated from oxygen vacancy around Mn in the reduced samples.

In this work, we performed a chemical delithiation using NO₂BF₄ for Li(Mn_{0.54}Ni_{0.13}Co_{0.13}Li_{0.2})O₂, *i.e.* Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂, and tried to prepare Li_xMn_{0.54}Ni_{0.13}Co_{0.13}O_{2-δ} which corresponds to the material after an initial irreversible charge process. This Li_xMn_{0.54}Ni_{0.13}Co_{0.13}O_{2-δ} are expected to be show both the high capacity and high safely. For the samples, we measured the XAFS spectra, and then discuss the electronic and local structures.

2 Experiment

Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ was synthesized by a coprecipitation method. Obtained precursors were calcined at 600 °C for 15 h, and the fired at 950 °C in air for 15 h. For the sample, chemical delithiations were carried out by immersing it into NO₂BF₄-containing acetonitrile at room temperature for 1-24 hours. The delithiation amount was controlled by the immersing time. The obtained products were characterized by X-ray diffraction measurements and inductively coupled plasma analyses (ICP).

Electronic and local structures around the transition metals of the samples were investigated by recording XAFS spectra of the Mn, Ni and Co *K*-edges. The measurements were performed with a transition mode by BL9A installed at Photon Factory in KEK. The obtained XAFS spectra were analyzed by the REX-2000 program.

3 Results and Discussion

X-ray diffraction measurements demonstrated that both the pristine Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ and chemically-delithiated Li_xMn_{0.54}Ni_{0.13}Co_{0.13}O_{2-δ} had a single phase of the layered rock-salt structure and there was no impurity phase. From the ICP analysis, it was confirmed that the lithium content decreased with the delithiation-treatment time although the transition-metal compositions were essentially the same as the nominal compositions.

In order to investigate the electronic and local structures of the Li_xMn_{0.54}Ni_{0.13}Co_{0.13}O_{2-δ}, we performed XAFS measurements for the Mn, Ni and Co *K*-edges. Figure 1 shows XANES spectra at the Mn *K*-edge of the samples as an example. In the delithiation process from *x*=0.766 to *x*=0.313, the electronic structure was almost independent of the lithium amount regardless of the transition metals. This implies that the charge change during the delithiation is compensated by not the transition-metal valences but oxygen release from the Li_xMn_{0.54}Ni_{0.13}Co_{0.13}O_{2-δ} in the same way as the initial charge process in the battery. We also analyzed the EXAFS oscillations, and a part of the results are given in Fig. 2. It was found that the chemical delithiation affected the local structure around Mn significantly: that is, the first coordination peak of Mn-O shell became lower after the delithiation from *x*=0.766 to *x*=0.313. This might be due to the oxygen release from around Mn because there was no drastic change in the electronic structure of Mn as mentioned above. Such a tendency was also observed in the cathode after the initial irreversible charging process. From these results, it is expected that the chemically-delithiated Li_xMn_{0.54}Ni_{0.13}Co_{0.13}O_{2-δ} shows high discharge capacity without any irreversible process in the battery.

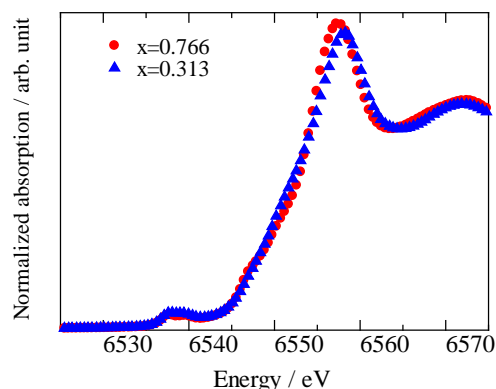


Fig. 1: XANES spectra of Mn *K*-edge of Li_xMn_{0.54}Ni_{0.13}Co_{0.13}O_{2-δ}.

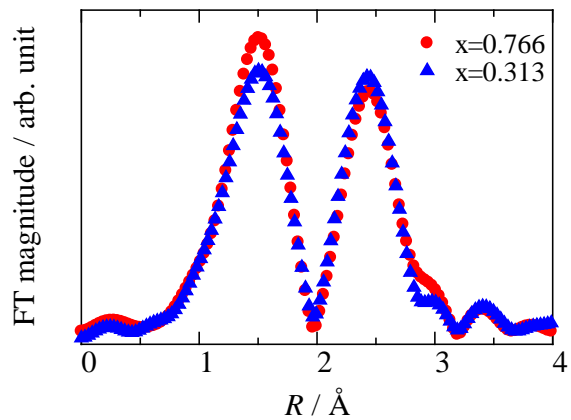


Fig. 2: Fourier transformations of EXAFS spectra of Mn K -edge of $\text{Li}_x\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_{2.6}$.

References

- [1] M.M. Thackeray et al., *J. Mater. Chem.* **17**, 3112 (2007).
- [2] Y. Idemoto et al., *Electrochemistry*, **80**, 791(2012).

* idemoto@rs.noda.tus.ac.jp