XAFS Characterization of Li Deintercalation in Rechargeable Lithium Battery Materials, LiCoO_2 - LiNiO_2

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Abstract *In situ* measurements of the Ni and Co K-edge XAFS spectra of $\text{Li}_{1-x}\text{NiO}_2$ and $\text{Li}_{1-x}\text{CoO}_2$ as a function of x were successfully carried out for the first time using an electrochemical cell. It is observed that a local Jahn-Teller distortion of the NiO_6 octahedron in LiNiO_2 was reduced with deintercalation of Li which caused oxidation of the Jahn-Teller $d^7 \text{Ni}^{3+}$ ion to $d^6 \text{Ni}^{4+}$ ion. A substitution of Co for Ni in LiNiO_2 also reduced the local distortion of the NiO_6 octahedron. XANES spectra of LiNiO_2 shifted to higher energy side with increasing x while an abrupt shape change was observed in the XANES spectra of $\text{Li}_{1-x}\text{CoO}_2$ corresponding to phase transition.

1. Introduction

LiNiO_2 is one of the promising candidates for next electrode material for rechargeable lithium battery subsequent to LiCoO_2 [1]. However, a rather complicated phase transition appeared in $\text{Li}_{1-x}\text{NiO}_2$ during the electrochemical deintercalation and intercalation process[2], which requires detailed structural characterization of these phases by XAFS technique. This paper reports results of the first *in situ* measurements of the XAFS spectra of LiNiO_2 and LiCoO_2 during electrochemical deintercalation. Rougier et al.[3] reported XAFS analysis of LiNiO_2 and found a local distortion of the NiO_6 octahedron due to the Jahn-Teller effect of the Ni^{3+} ion in the low spin state.

2. Experimental

Samples used were $\text{Li}_{1-x}\text{NiO}_2$ and $\text{Li}_{1-x}\text{CoO}_2$ with various x values and $\text{Li}(\text{Ni},\text{Co})\text{O}_2$. They were prepared by sintering method. The electrochemical deintercalation of Li was carried out by using a lithium cell. Ni and Co K-edge XAFS data were measured in transmission mode at BL-7C, Photon Factory, KEK, Japan using Si(111) double-crystal monochromator. Low temperature experiments were also carried out using a tape sample and CTI Model 22C CRYODYNE cryocooler at temperatures of 200, 110 and 20K. *In situ* measurements were made at room temperature using a XAFS cell for electrochemical deintercalation and intercalation newly developed for this experiment. Li ion was electrochemically deintercalated from the cathode material at a certain voltage and the XAFS data were measured without taking out the sample from the cell. LiNiO_2 and LiCoO_2 were used as the cathode and Li metal was used as the anode with suitable thickness for the transmission XAFS experiment.

3. Results and Discussion

Figure 1 shows the Ni K-edge XANES spectra of LiNiO_2 measured at 20, 110, 200 and 290K. Fourier transforms (FT) of k^3 weighted Ni and Co K-edge EXAFS are given in Fig. 2. Figure 1 shows that the spectra measured at different temperature are all equal to each other and the electronic structure of Ni were not significantly affected by their temperature. The first peak at around $1.5\text{\AA}$ in Fig. 2 corresponds to metal-oxygen interaction in the first coordination sphere, the second one at $2.4\text{\AA}$ is metal-metal interaction in the second coordination sphere. Simulated data calculated with the FEFF6 code [4] disclosed that the peaks at 4.6 and $5.4\text{\AA}$ are contribution mainly from metal-metal interactions and the focusing effect due to the multiple scattering is found in the latter peak. A comparison of the Ni-O peak in FT with that of the Co-O peak indicates that the former peak is abnormally lower than that of the latter. The low temperature experiments showed that the peak height did not increase even at 20 K precluding an effect of thermal vibration as a reason for the low peak height.

Figure 3 indicates XANES spectra measured using the *in situ* cell. As the Li ion is electrochemically deintercalated, the Ni K-edge of LiNiO_2 shifts to higher energy side indicating an increase in the positive charge of the Ni

Figure 1: Ni K-XANES spectra at various temperatures

Figure 2: Fourier transforms of the $k^3 \chi(k)$ of (a) LiNiO_2 , Ni K-edge (b) LiCoO_2 , Co K-edge

Figure 3: In situ XANES spectra (a) $\text{Li}_{1-x}\text{NiO}_2$, Ni K-edge (b) $\text{Li}_{1-x}\text{CoO}_2$, Co K-edge

Figure 4: Fourier transforms of the $k^3 \chi(k)$ of (a) $\text{Li}_{1-x}\text{NiO}_2$, Ni K-edge (b) $\text{Li}_{1-x}\text{CoO}_2$, Co K-edge

ion. On the other hand, the spectra of LiCoO_2 showed an abrupt change in the edge shape at $x=0.39$ indicating change of the local structure, which corresponds to trigonal to monoclinic transition known for $\text{Li}_{1-x}\text{CoO}_2$ at $x \approx 0.5$ [5]. FT of Ni and Co K-edge EXAFS measured using the *in situ* data are given in Fig. 4 (a) and (b), respectively. It is remarkable that the Ni-O peak height increases with deintercalation of Li, while the Co-O peak height remains almost constant. Rougier et al [3] reported that there is a local Jahn-Teller distortion in LiNiO_2 . Crystallographically, the Ni atom is located at the 3b site of $R\bar{3}m$ lattice with octahedral coordination with 6 O atoms at an equal distance. Therefore, a distortion from the octahedron could not occur in long range but it should be a local effect. The abnormally low peak height could be ascribed to the Jahn-Teller distortion from the true octahedral coordination yielding such as four short and two long Ni-O distances. This results in much lower peak in the FT than that of regular octahedral Ni-O distance due to the interaction of the imaginary and real parts of FT. Low spin Ni^{3+} is d^7 Jahn-Teller ion which has an electronic configuration of $t_{2g}^6 e_g^1$. Deintercalation of Li cause oxidation of Ni^{3+} to Ni^{4+} resulting in $t_{2g}^6 e_g^0$ state, which does not present a Jahn-Teller distortion. A substitution of Co for Ni in LiNiO_2 causes increase in the peak heights (Fig. 5). This phenomena also could be explained by the Jahn-Teller effect that the substitution of Co^{3+} , which is d^6 ion, may reduce the local distortion of the Ni ion.

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Figure 5: FT of the k^3 weighted Ni K-edge EXAFS of $\text{Li}(\text{Ni},\text{Co})\text{O}_2$