XAFS Characterization of Li Deintercalation in Rechargeable Lithium Battery Materials, LiCoO2-LiNiO2
I. Nakai, K. Takahash, Y. Shiraishi, T. Nakagome

To cite this version:

HAL Id: jpa-00255287
https://hal.archives-ouvertes.fr/jpa-00255287
Submitted on 1 Jan 1997

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
XAFS Characterization of Li Deintercalation in Rechargeable Lithium Battery Materials, LiCoO$_2$-LiNiO$_2$

I. Nakai, K. Takahashi, Y. Shiraishi and T. Nakagome

Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku, Tokyo 162, Japan

Abstract In situ measurements of the Ni and Co K-edge XAFS spectra of Li$_{1-x}$NiO$_2$ and Li$_{1-x}$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 $d^9$ Ni$^{3+}$ ion to $d^6$ 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 Li$_{1-x}$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 Li$_{1-x}$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 Li$_{1-x}$NiO$_2$ and Li$_{1-x}$CoO$_2$ with various x values and Li(Ni,Co)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

Figures 1 shows the Ni K-edge XANES spectra of LiNiO$_2$ measured at 20, 110, 200 and 290K. Fourier transforms (FT) of $k^2$ 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 1.5Å in Fig. 2 corresponds to metal-oxygen interaction in the first coordination sphere, the second one at 2.4Å 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 5.4Å 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.
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 Li$_1$CoO$_2$ at $x=c.a.0.5$.[5] FT of Ni and Co K-edge EXAFS measured using the in situ cell 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 $R3m$ 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$^{II}$ is d$^9$ Jahn-Teller ion which has an electronic configuration of t$_2g^6e_g^3$. Deintercalation of Li cause oxidation of Ni$^{II}$ to Ni$^{III}$ resulting in t$_2g^6e_g^0$ 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$^7$ ion, may reduce the local distortion of the Ni ion.

**Acknowledgments**

The authors are grateful to Mrs. F. Nishikawa and T. Himeda for their kind help in the experiments.

**References**


---

**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) Li$_{1-x}$NiO$_2$, Ni K-edge (b) Li$_{1-x}$CoO$_2$, Co K-edge

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

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