

# X-ray absorption fine structure and neutron diffraction analyses of de-intercalation behavior in the $\text{LiCoO}_2$ and $\text{LiNiO}_2$ systems

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Accepted 6 January 1997

## Abstract

Variations of electronic and local structures of Ni and Co in  $\text{Li}_{1-x}\text{NiO}_2$  and  $\text{Li}_{1-x}\text{CoO}_2$  as a function of  $x$  were clarified for the first time by in situ X-ray absorption fine structure analysis (XAFS). Chemical shifts of the X-ray absorption near edge structure spectra of the Ni K-edge in  $\text{Li}_{1-x}\text{NiO}_2$  as a function of  $x$  were continuous while an abrupt change was observed for the Co K-edge spectra of  $\text{Li}_{1-x}\text{CoO}_2$ . Radial structure functions obtained by Fourier-transform of the Ni K-edge EXAFS of  $\text{LiNiO}_2$  exhibited abnormally low height of the Ni–O peak. This phenomenon is explained by the Jahn–Teller distortion of the  $\text{NiO}_6$  octahedron due to the low spin  $\text{Ni}^{3+}$  ( $d^7$ ) ion. De-intercalation of the Li ion caused oxidation of  $\text{Ni}^{3+}$  ( $d^7$ ) to  $\text{Ni}^{4+}$  ( $d^6$ ) and reduced the distortion, hence the Ni–O peak increased with increasing  $x$  value. The crystal structures of  $\text{LiNiO}_2$  treated with  $\text{D}_2\text{O}$ , and electrochemically de-intercalated  $\text{Li}_{0.44}\text{NiO}_2$  were solved by Rietveld analysis of neutron diffraction data. © 1997 Elsevier Science S.A.

**Keywords:** Lithium nickel oxide; Lithium cobalt oxide; Jahn–Teller distortion; X-ray absorption spectroscopy; Neutron diffraction; X-ray absorption fine structure analysis

## 1. Introduction

Recently,  $\text{LiNiO}_2$  has received particular attention as a possible candidate for next electrode materials for 4 V rechargeable lithium batteries [1,2]. However, a rather complicated phase transition appears in  $\text{Li}_{1-x}\text{NiO}_2$  during the course of the electrochemical intercalation and de-intercalation processes required a detailed structural study of these phases [3–6]. Though de-intercalated phases of  $\text{LiNiO}_2$  are obtained as fine crystalline powder, X-ray powder diffraction analysis gives little information on the Li position because of the low X-ray scattering power of the Li atom. It is also difficult to determine the structure of an unknown phase by powder diffraction techniques.

We have applied XAFS (X-ray absorption fine structure) analysis to this system to examine the de-intercalation process

of  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$ . This technique gives information on the local structure of an X-ray absorber atom, that is, Ni and Co in this case, and its electronic structure even from a powder specimen of an unknown structure. Just recently we have developed an in situ cell, from which XAFS data can be obtained at various voltages without taking out the sample from the cell. Preliminary results obtained using this in situ XAFS cell will be reported.

We have also applied the neutron diffraction technique to obtain structural information about the Li atom in a de-intercalated  $\text{Li}_{1-x}\text{NiO}_2$  sample. In addition, we have examined the possibility of Li-ion exchange with hydrogen by washing the sample with deuterated ( $\text{D}_2\text{O}$ ) water and by undertaking neutron diffraction analysis of the sample.

## 2. Experimental

The starting samples for de-intercalation experiments were obtained by conventional sintering method. The electrochem-

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ical de-intercalation was carried out by using lithium cells. Chemical de-intercalation was done by a treatment of the sample with 1 N HCl solution. Co and Ni K-edge XAFS data of the samples were measured at Photon Factory, National Laboratory for High Energy Physics, Tsukuba using 2.5 GeV synchrotron radiation and an Si(111) double-crystal monochromator. XAFS data were collected in a transmission mode using ionization chambers as X-ray detectors. A sample was spread on an Al foil. It was taken from a cell after the electrochemical de-intercalation or was kept in the in situ cell and was subjected to the XAFS measurements. Neutron diffraction data were obtained by high resolution powder diffractometer (HRPD) at JAERI (wave length: 1.823 Å, 0.05°/step,  $2\theta=5\text{--}165^\circ$ ). The samples used were D<sub>2</sub>O-treated LiNiO<sub>2</sub> and electrochemically de-intercalated Li<sub>1-x</sub>NiO<sub>2</sub> with  $x=0.66$ . The structures were solved by Rietveld analysis using application software 'RIETAN-94' [7].

### 3. Results and discussion

Figs. 1 and 2 are the XANES (X-ray absorption near edge structure) spectra of Li<sub>1-x</sub>NiO<sub>2</sub> measured in non-in-situ condition and those measured by the in situ cell, respectively. It is found that the in situ data (Fig. 2) of the Ni system basically corresponds with the non-in-situ data (Fig. 1). However, a significant difference was observed in the Co K-edge XAFS spectra of Li<sub>1-x</sub>CoO<sub>2</sub> between the non-in-situ data and in situ data, which indicates a necessity for the in situ measurement especially in the Co system. Fig. 3 shows the Co K-edge XANES spectra measured by the in situ cell. The Ni K-edge spectra of Li<sub>1-x</sub>NiO<sub>2</sub> remained unchanged between  $x=0$  and 0.13, then they showed a continuous shift of the absorption edges as a function of  $x$  indicating a gradual

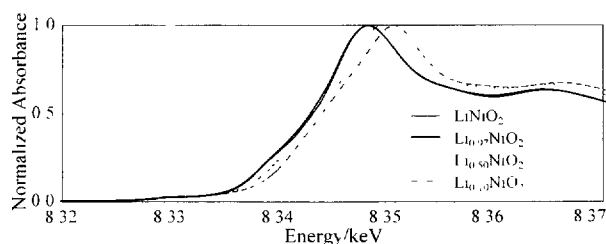


Fig. 1. Ni K-edge XANES spectra of Li<sub>1-x</sub>NiO<sub>2</sub> as a function of  $x$

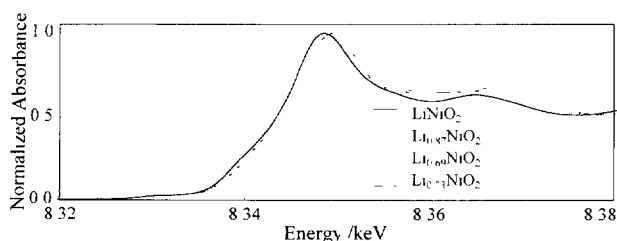


Fig. 2. Ni K-edge XANES spectra of Li<sub>1-x</sub>NiO<sub>2</sub> obtained by the in situ measurement.

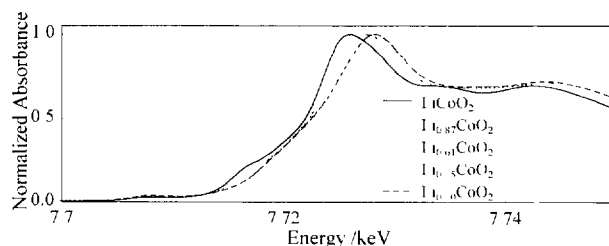


Fig. 3. Co K-edge XANES spectra of Li<sub>1-x</sub>CoO<sub>2</sub> obtained by the in situ measurement.

increase in the oxidation state of Ni. The Co K-edge spectra of Li<sub>1-x</sub>CoO<sub>2</sub> (Fig. 2) remained unchanged from  $x=0$  to  $x=0.13$ , then they changed their shape abruptly to  $x=0.65$ , and remained unchanged to  $x=0.9$ . It is found that the present spectral changes correspond well with the structural changes reported by the in situ X-ray diffraction analyses [4,5]. Li<sub>1-x</sub>NiO<sub>2</sub> exhibited trigonal to monoclinic transition at  $0.15 < x < 0.25$  and monoclinic to second trigonal transition at  $0.50 < x < 0.57$  [4]. On the other hand, Li<sub>1-x</sub>CoO<sub>2</sub> exhibited a first-order transition at  $0.07 < x < 0.25$  and lattice distortion from trigonal to monoclinic near at  $x=0.5$  [5]. Both Ni and Co K-XANES spectra showed spectral shifts when the phase transitions occurred. However, Ni showed continuous shift while Co showed an abrupt change in their shape indicating that the Li de-intercalation caused more significant change in the electronic structure of the Co atoms than in that of the Ni atoms. A detailed analysis and comparison of the two data are now underway and will be reported elsewhere in the near future.

Fourier-transforms (FTs) of the Ni and Co K-edge EXAFS spectra obtained in the in situ condition are shown in Figs. 4 and 5, respectively. The FTs were not corrected for the phase shift. The first peak at around 1.5 Å in the FTs is due to the metal–oxygen (Ni–O or Co–O) interaction and that at around 2.5 Å corresponds to the metal–metal (Ni–Ni or Co–Co) contact. A comparison of Fig. 4 with Fig. 5 indicates that the height of the Ni–O peak is abnormally low in LiNiO<sub>2</sub> (Fig. 4) compared with that of the Co–O peak in LiCoO<sub>2</sub> (Fig. 5). It is noteworthy that de-intercalation of Li from Li<sub>1-x</sub>NiO<sub>2</sub> increased the height of the Ni–O peak with increasing the  $x$  value (Fig. 4). A chemical de-intercalation of Li by HCl treatment of LiNiO<sub>2</sub> also increased the height of the Ni–O peak. A similar phenomenon was observed when the Ni atom in LiNiO<sub>2</sub> was substituted by the Co atom. On the other hand,

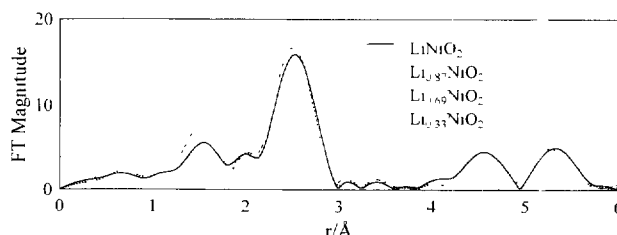


Fig. 4. Fourier-transform of the in situ Ni K-edge EXAFS spectra of Li<sub>1-x</sub>NiO<sub>2</sub>.

Table 1  
Summary of structural information determined by Rietveld analysis of the neutron diffraction data

	LiNiO <sub>2</sub> treated with D <sub>2</sub> O	Li <sub>0.34</sub> NiO <sub>2</sub>
Synthesis temperature (°C)	650	650
Space group	$R\bar{3}m$	$R\bar{3}m$
$R_{wp}$ , $R_i$ , S	8.25, 3.23, 2.29	8.02, 7.14, 3.61
Lattice parameter		
$a$ (Å)	2.8752(1)	2.8312(2)
$c$ (Å)	14.2255(2)	14.395(1)
Occupancy of 3a site	Li: 0.95(16) Ni: 0.03(fix)	Li 0.34(44)
$z$ of O atom	0.240(1)	0.235(2)
Li–O distance (Å)	2.12(1)	2.16(2)
Ni–O distance (Å)	1.97(1)	1.91(2)
Interlayer distance (Å)		
O–Li–O	2.63	2.80
O–Ni–O	2.10	1.98

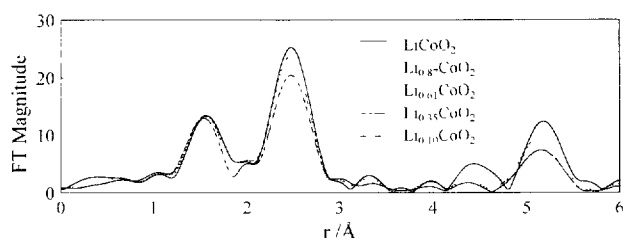


Fig. 5. Fourier-transform of the in situ Co K-edge EXAFS spectra of Li<sub>1-x</sub>CoO<sub>2</sub>.

electrochemical de-intercalation of Li from Li<sub>1-x</sub>CoO<sub>2</sub> caused little change in the Co–O peak with increasing  $x$  (Fig. 5). Crystallographically, both Ni and Co atoms in trigonal  $R\bar{3}m$  lattices of LiNiO<sub>2</sub> and LiCoO<sub>2</sub> are respectively located at the 3b sites, which are coordinated by 6 oxygen atoms at an equal distance. However, the Ni<sup>3+</sup> ion is in the low spin d<sup>7</sup> state, which could exhibit the Jahn–Teller distortion while Co<sup>3+</sup> is in the d<sup>6</sup> state. Our simulated FT for LiNiO<sub>2</sub> calculated by ab initio XAFS code FEFF6 [8] indicated that a distorted NiO<sub>6</sub> octahedral coordination such as 4+2 causes an apparent decrease in the height of the metal–oxygen peak due to the interference of imaginary and real part of the FT. Therefore, the abnormally low peak height is due to the Jahn–Teller distortion of the Ni ion in LiNiO<sub>2</sub>. This is local distortion and could not be detected by diffraction technique. This distortion is reduced by oxidation of Ni<sup>3+</sup> (d<sup>7</sup>) ion to Ni<sup>4+</sup> (d<sup>6</sup>) ion caused by de-intercalation of Li<sup>+</sup> or by substitution of Ni<sup>3+</sup> by Co<sup>3+</sup> (d<sup>6</sup>) ion. The possibility of the Jahn–Teller distortion in the end-member LiNiO<sub>2</sub> phase is first reported by Rougier et al. [9]. The present paper confirms their interpretation and reports the first observation of the dynamic change of this effect during the de-intercalation process based on the in situ XAFS data. The existence of the Jahn–Teller distortion in LiNiO<sub>2</sub> may account for the instability of LiNiO<sub>2</sub> as a battery material.

Results of the Rietveld analysis of the neutron diffraction data are summarized in Table 1. The analysis of D<sub>2</sub>O-treated LiNiO<sub>2</sub> indicated that ~2% of Li at the 3a site could be vacancy indicating the possibility of substitution of D for Li. The X-ray Rietveld analysis using the same sample also indicated that 3% of the Li site was substituted by Ni. However, large errors were introduced in the determination of the site occupancy factor because of the strong correlation of the thermal parameters with the occupancy factors. In addition, the existence of a partial substitution of Ni for the Li site prevented from determining the occupancy factors unambiguously. Rietveld analyses of electrochemically de-intercalated Li<sub>1-x</sub>NiO<sub>2</sub> ( $x = 0.66$ ) showed an elongation of the Li–O distance (2.16 Å) and a shortening of the Ni–O distance (1.91 Å) resulting in a shrinking of the  $a$ -axis and an expansion of the  $c$ -axis of the structure (Table 1). This phenomenon is explained by coulombic repulsion of the two oxygen layers facing each other by loss of the interlayer Li atoms and shrinking of the Ni–O polyhedra due to an increase in the positive charge of Ni by the de-intercalation of Li.

A comparison of the results of our structure analysis of Li<sub>0.34</sub>NiO<sub>2</sub> with that of Li<sub>0.45</sub>NiO<sub>2</sub> [6] indicates that the former sample has a longer Li–O distance and a shorter Ni–O distance than those in the latter phase. This tendency is consistent with our interpretation mentioned above. It was reported from the in situ powder diffraction analysis that Li<sub>1-x</sub>NiO<sub>2</sub> with  $0.50 < x < 0.57$  was located at a two-phase region composed of a monoclinic phase and a new trigonal phase, and Li<sub>1-x</sub>NiO<sub>2</sub> with  $0.57 < x < 0.68$  was at single trigonal phase region [4]. Considering from the fact that XANES spectra of Li<sub>1-x</sub>NiO<sub>2</sub> exhibited a continuous shift to  $x = 0.1$  and that the structure of Li<sub>0.34</sub>NiO<sub>2</sub> was successfully solved with a space group  $R\bar{3}m$ , which is the same as that of the end member LiNiO<sub>2</sub>, the structural changes of LiNiO<sub>2</sub> with de-intercalation seems to be continuous but not to be destructive.

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