Research Report

In situ XAFS Study on Cathode Materials for Lithium Ion Batteries

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in situ XAFS

Abstract

The electronic states and local structures of cathode materials ($LiNi_{0.8}Co_{0.2}O_2$) for lithium ion batteries are studied by means of *in situ* XAFS (X-ray absorption fine structure) method. Ni and Co K-edge XAFS spectra of $LiNi_{0.8}Co_{0.2}O_2$ have been obtained using newly developed *in situ* coin cells. To investigate the electronic and structural changes that accompany capacity fading due to electrochemical cycling and keeping the batteries at high temperatures, cells with different cycling states and operating conditions (temperature, time) were prepared. Upon charging the cell, the Ni and Co K absorption edge shifted to a higher energy, and a good correlation between the range of chemical shifts upon charging and the capacity of the cell was observed. We have also performed first-principles molecular orbital calculations using a discrete variational Xα method to reproduce Ni-K XANES spectra. From quantitative analysis of EXAFS data and the results of molecular orbital calculations, capacity fading was found to be closely related to Jahn-Teller distortion of the NiO_6 octahedron.

($LiNi_{0.8}Co_{0.2}O_2$)   Ni

in situ XAFS   (X-ray   Co   X

absorption fine structure)

in situ   EXAFS

$LiNi_{0.8}Co_{0.2}O_2$ Ni   Co   K   XAFS   (NiO_6)

DV-Xα

Ni-K XANES

X

1. Introduction

$LiNi_{0.8}Co_{0.2}O_2$ is one of the current candidates as a cathode material for advanced rechargeable batteries having high capacities. It is known that the stability of $LiNi_{0.8}Co_{0.2}O_2$ is superior to that of $LiNiO_2$ because it exhibits a single-phase region upon oxidation from 3.0 V to 4.1 V.[1] However, capacity fading occurs not only during charge/discharge cycling but also when batteries are stored at high temperatures. Thus, capacity fading is the most important problem facing practical use. From the standpoint of overcoming capacity fading, it is essential to understand the electronic and structural changes that accompany capacity fading. For this purpose, *in situ* XAFS analysis is very useful, because it reveals information about the local structure around an absorber atom and its electronic structure without destroying the battery during measurement. Some studies applying *in situ* XAFS analysis to $LiNiO_2$ and $LiCoO_2$ have already been reported.[2, 3] However, an *in situ* XAFS study on capacity faded batteries has not yet been reported. Therefore, we prepared batteries having various capacities and measured *in situ* Ni and Co K-edge absorption spectra of $LiNi_{0.8}Co_{0.2}O_2$.

2. Experimental

2. 1 Sample preparation

Figure 1 shows a drawing of the coin cell newly developed for *in situ* XAFS measurements in transmission mode. By using 0.4 mm Beryllium windows, the X-rays can penetrate through the cell. XAFS data can be obtained at various voltages without taking the cathode material out of the cell. To investigate the changes resulting from cycling and keeping at high temperatures, cells having different cycling states and operating conditions (temperature, time) were prepared. The cells used in this study are listed in **Table 1**.

2. 2 XAFS measurements

Ni and Co K-edge XAFS data were collected using beamline BL16B2 at SPring-8 (Hyogo, Japan). Incident X-rays were monochromatized using a Si (111) double-crystal monochromator, and the harmonic content of the beam was minimized using a Rh-coated Si mirror inclined at 5 mrad. X-ray intensities were monitored using ionization chambers filled with nitrogen gas for the incident beam and a mixture of argon (25 %) and nitrogen (75 %) for the transmitted beam.

3. Results and discussion

3. 1 XANES

Figures 2(a) and (b) show the Ni K-edge and Co K-edge XANES spectra of $LiNi_{0.8}Co_{0.2}O_2$ for several samples. In both edges, chemical shifts of the edge peak energy were found. It should also be noted that some structures were observed in the energy region 8335-8340 eV (indicated by arrows in the figures), which are discussed later.

Graphical comparisons of the edge peak energies as a function of cell voltages are shown in **Fig. 3**(a)

Fig. 1 Schematic drawing of the *in situ* coin cell.

Table 1 The conditions of cells.

Cell no.	Condition	Capacity (relative value)
1	Initial state (no treatment)	NA
2	After one charge/discharge cycle*	100
3	After 515 charge/discharge cycles*	9.5
4	After keeping at 80°C for 3 days**	64.3
5	After keeping at 60°C for 25 days**	14.7

* The charge/discharge cycling have been done at rate of $1mA/cm^2$ in the range of voltage from 3.0 V to 4.1 V.

** Kept at charged state which corresponds to a voltage of 4.1V.

12

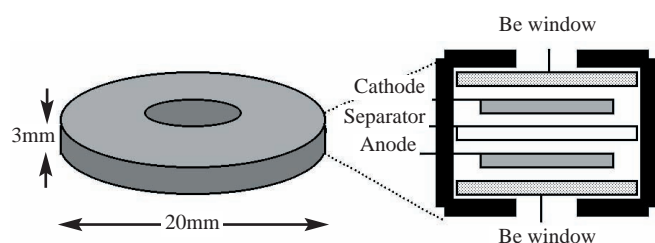and (b). The edge peak energy E_p is defined here as the energy at the maximum height of the edge jump. Continuous shifts toward higher energies are thought to indicate increases in the average oxidation states of Ni upon lithium removal.[3] In capacity faded samples, the degree of chemical shift upon charging was less than that in "after one cycle". A good correlation between the degree of chemical shift and cell capacity was found. It is also worth noting that chemical shifts of Co and Ni K-edge occur in the same way in spite of differences in electronic structure between Ni and Co. The reason for this phenomenon is not clear at present.

3. 2 EXAFS

Fourier-transforms of the Ni K-edge EXAFS spectra of several samples are shown in **Fig. 4**. The first peak at around 1.5 Å corresponds to Ni-O interactions and the second one at around 2.5 Å corresponds to Ni-Ni interactions. The Ni-O peak height of a sample in its initial state is lower than that of capacity faded samples. This phenomenon is explained by local Jahn-Teller distortion of the NiO_6
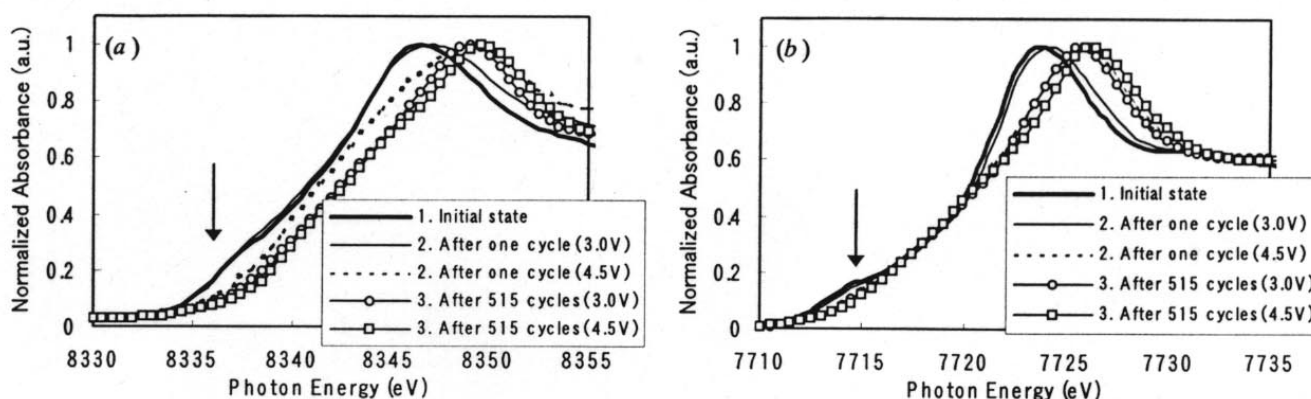
Fig. 2   (a) Ni K-edge and (b) Co K-edge XANES spectra of $LiNi_{0.8}Co_{0.2}O_2$.
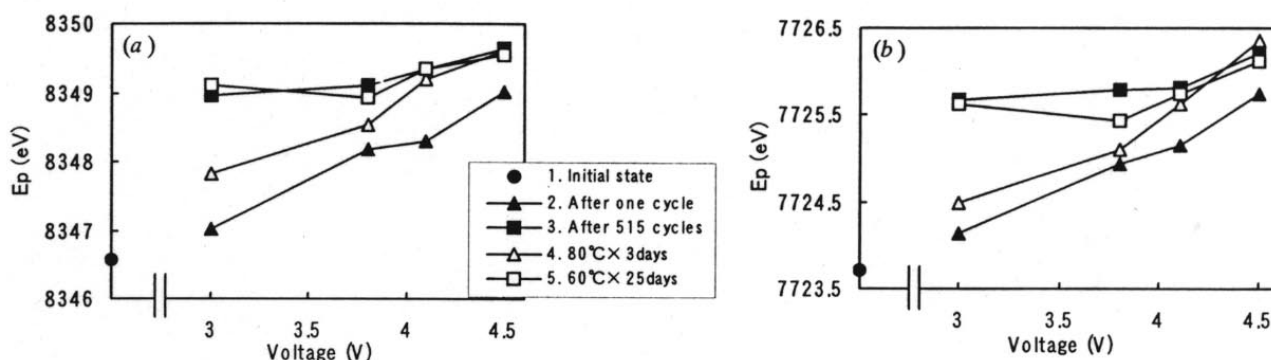
Fig. 3   Graphical comparisons of the edge peak energies (E_p) as a function of the voltages for (a) Ni K-edge and (b) Co K-edge.

octahedron due to low spin Ni^{3+}. Distorted NiO_6 octahedral coordination such as 4(shorter) + 2(longer) Ni-O bonds causes an apparent decrease in the height of the Ni-O peak due to interference of the imaginary and real parts of the FT[3]. **Figure 5** shows the heights of the Ni-O peak as a function of cell voltage. Upon charging, the extent of the local distortion is reduced, and the distorted NiO_6 octahedron turns into a regular octahedron. This phenomenon results from gradual changes in the average valence of Ni from 3+ to 4+; and therefore, the shape of Fig. 5 is very similar to that of Fig. 3(a).

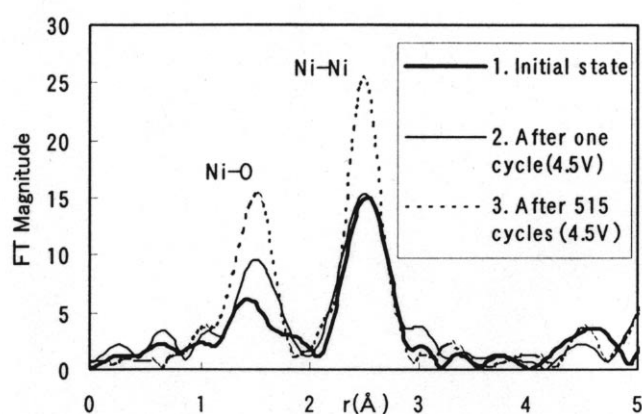Averages of Ni-O distances deduced from quantitative analysis of EXAFS data are shown in

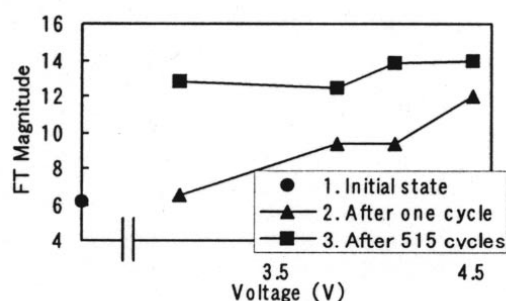**Fig. 4** Fourier-transforms of Ni K-EXAFS spectra for $LiNi_{0.8}Co_{0.2}O_2$.

Fig. 6. Single-shell curve-fitting was performed with the coordination numbers of oxygen fixed at 6. Phase shifts and backscattering amplitudes were obtained from the tabulated functions calculated by McKale et al.[4]. Estimated errors in distances (~ 0.02) are also shown in the figure.

After one cycle, the Ni-O distance decreases obviously after charging, while after 515 cycles, the distance does not change. It is supposed that the change in Ni-O distance originates mainly from the change in ion-radii accompanied by oxidation of Ni^{3+} to Ni^{4+}.

3. 3 Molecular orbital calculations for XANES spectra

To assign the structures that were observed in the energy region 8335-8340 eV of XANES spectra, first-principles molecular orbital calculations were performed using the discrete variational (DV) Xα cluster method.[5] **Figure 7**(a) shows the model cluster used in the present calculations. To investigate the effects of the local distortion of NiO_6 octahedra, a model cluster with a regular octahedron and the one with a distorted octahedron (4 shorter Ni-O and 2 longer Ni-O) were used for comparison. The program SCAT[6] was used to calculate electronic states of the model clusters. Atomic orbitals used in the calculations are $1s$-$4p$ for Ni, and $1s$-$3p$ for O.

XANES spectra reproduced by the calculations are shown in Fig. 7(b). The absorption intensity at around 8337 eV in the spectrum calculated for the
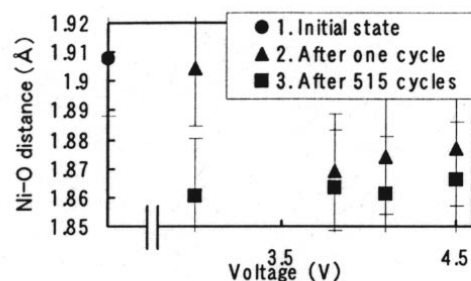

Fig. 5 A comparison of the heights of Ni-O peaks in FT spectra as a function of the voltages.

Fig. 6 A comparison of the averages of Ni-O distances as a function of the voltages.
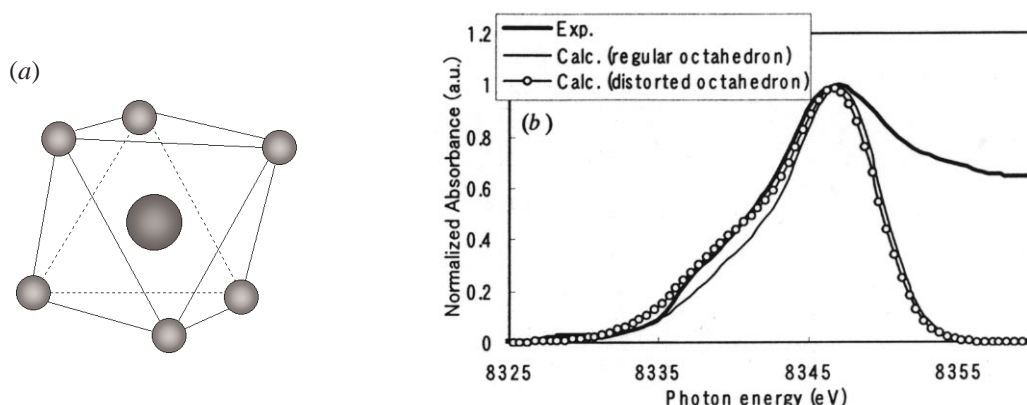
(*a*)

Fig. 7 (a) The model cluster used for calculations.
         (b) A comparison of experimental and calculated Ni K-edge XANES spectra.

distorted octahedron was larger than that of the regular octahedron. From these calculations, it is suggested that the observed structures originate from local Jahn-Teller distortion of NiO_6 octahedra.

As shown in Fig. 3(b), similar structures were found in Co K-edge XANES spectra. At present, however, we have no ideas about these structures.

4. Conclusion

Ni and Co K-edge XAFS spectra of $LiNi_{0.8}Co_{0.2}O_2$ were collected using newly developed *in situ* coin cells. The Ni and Co K absorption edges were found to shift to higher energies upon charging the cell, with good correlation between the degree of chemical shift upon charging and the capacity of the cell observed. From quantitative analysis of EXAFS data, capacity fading was found to be closely related to Jahn-Teller distortion of the NiO_6 octahedra. The present study clearly demonstrated that *in situ* XAFS methods are a powerful tool for investigating the electronic and local structures of cathode materials. To profoundly understand the mechanism of capacity fading, more studies using this method are needed.

References

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