# Industrial Applications

### IN SITU XAFS STUDY ON CATHODE MATERIALS FOR LITHIUM-ION BATTERIES FROM THE STANDPOINT OF INDUSTRIAL USE

LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> is one of the current candidates for a cathode material of advanced rechargeable batteries with high capacity. The stability of LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> is superior to LiNiO<sub>2</sub>, exhibiting a single-phase region upon oxidation from 3.0 V to 4.1 V. The capacity fading, however, occurs not only during charge/discharge cycling but also when batteries are kept at high temperatures, creating difficult problems for practical use. To overcome the problems of capacity fading, it is essential to understand the electronic and structural changes accompanied by the capacity fading. For this purpose, *in situ* XAFS analysis is very useful, because it gives information on both the local and

electronic structure surrounding an absorbing atom without disassembly of the battery for a measurement. Some studies applying *in situ* XAFS analysis to  $LiNiO_2$  or  $LiNi_{0.5}Co_{0.5}O_2$  have been already reported [1-3]. Nakai *et al.* revealed that the oxidation of the Ni ion occurred and the Jahn-Teller distortion of the  $NiO_6$  octahedron decreased with Li deintercalation. The *in situ* XAFS analysis of the capacity faded battery, however, has not been reported. In this study we prepared the batteries with various capacities to measure the *in situ* Ni and Co *K*-edge absorption spectra of LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> [4].

Figure 1 shows a drawing of the coin cell newly developed for *in situ* XAFS measurements in a transmission mode. The use of 0.4 mm Beryllium windows allow X-rays to penetrate the cell. XAFS data can therefore be obtained at various voltages without removing the cathode material from the 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 1 mA/cm <sup>2</sup> in the		

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

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

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To investigate the changes resulting from cycling and keeping at high temperatures, we prepared cells at different cycling states, and keeping temperature and time conditions. The cells used in this study are summarized in Table 1.

Ni and Co *K*-edge XAFS data were collected using beamline **BL16B2**. Incident X-rays were monochromatized using a Si (111) double-crystal monochromator. The harmonic content of the beam was minimized utilizing a Rh-coated Si mirror, inclined to 5 mrad. The 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.

Figure 2 shows the Ni *K*-edge XANES spectra of LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> for several samples. In both edges,



Fig. 2. Ni K-edge XANES spectra of LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>



Fig. 3. Graphical comparison of the edge peak energies  $(E_p)$  as a function of the voltages.

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chemical shifts of the edge peak energy were found. A graphical comparisons of the edge peak energies as a function of the cell voltages are shown in Fig. 3. The edge peak energy (Ep) is defined here as the energy at maximum height of the edge jump. Continuous shifts toward higher energies indicate the increases in the average oxidation states of Ni upon lithium removal [2]. For capacity faded samples, the ranges of chemical shifts upon charging are less than that in "after one cycle". A good correlation between the range of chemical shift and the capacity of the cell was found.

Fourier-transformation of the Ni *K*-edge EXAFS spectra for several samples are demonstrated in Fig. 4. The first peak at approximately 1.5 Å corresponds to Ni-O interactions, and the second

peak at approximately 2.5 Å corresponds to Ni-Ni interactions. The Ni-O peak height of the sample in its initial state is lower than that of the capacity faded samples. This phenomenon is explained by the local Jahn-Teller distortion of the NiO<sub>6</sub> octahedron, due to the low spin Ni<sup>3+</sup>. The distorted NiO<sub>6</sub> octahedral coordination, such as 4(shorter) + 2(longer) Ni-O bonds, causes the apparent decrease in the Ni-O peak height resulting from interference of the imaginary and real part of the FT [2]. The graph of the heights of the Ni-O peak plotted as a function of the cell voltage (Fig. 5), reveals that, upon charging, the extent of the local distortion is reduced, and the distorted NiO<sub>6</sub> octahedron becomes a regular octahedron.

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This phenomenon results from the gradual changes of the average valence of Ni from 3+ to 4+, making the shape of Fig. 5 similar to that of Fig. 3.

The averages of the Ni-O distances deduced from quantitative analysis of EXAFS data are shown in Fig. 6. The curve-fitting were performed with the coordination numbers of oxygen fixed to 6. "After one cycle", the Ni-O distance obviously decreases upon charging, while in "after 515 cycles", the distance changes only slightly. The change of the Ni-O distance originates mainly from the change in the ionradii accompanied by the change in oxidation from Ni<sup>3+</sup> to Ni<sup>4+</sup>.



#### References

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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.* 



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