

Short communication

# Investigation of inorganic compounds on the surface of cathode materials using Li and O K-edge XANES

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## Abstract

Inorganic compounds on the surfaces of the cathode materials  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{LiCoO}_2$  were studied using Li and O K-edge X-ray absorption near edge structure (XANES) measurements. Rietveld analysis revealed that the  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  sample contained 2%  $\text{Li}_2\text{CO}_3$ , while the  $\text{LiCoO}_2$  sample was single-phase. The Li and O K-edge XANES spectra indicated that the surface of  $\text{LiCoO}_2$  was almost free of residual  $\text{Li}_2\text{CO}_3$ . In contrast, the presence of both residual  $\text{Li}_2\text{CO}_3$  and an additional cubic phase were observed, respectively, on and near the surface of  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ . These results demonstrate that the XANES technique, using a combination of the total electron yield and fluorescence methods, is an effective tool for probing the surfaces of cathode materials.

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**Keywords:** Layered oxides; Cathode materials for lithium secondary batteries; Synchrotron radiation; XANES method

## 1. Introduction

Lithium batteries have attracted interest for applications such as hybrid electric vehicles (HEV) and fuel cell vehicles (FCV) due to their promise as high-power sources. However, a target calendar life of at least 15 years has been set for batteries designed for use in HEV and FCV applications. Currently available cells experience a significant rise in impedance and loss of power after accelerated calendar life and cycle life testing at elevated temperatures. It is thought that the interfacial resistance at the positive electrode is the main reason behind the increase in impedance of high-power cells [1,2]. Therefore, the inorganic compounds found on the surfaces of cathode materials have become the focus of attention, being probed by several techniques including X-ray photoelectron spectroscopy (XPS) [3], Fourier transform infrared spectrometry (FT-IR) [4], and X-ray absorption near edge structure (XANES) measurements [5].

Andersson et al. have reported on  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -based positive electrode samples obtained from 18650-type cells subjected to accelerated calendar-life testing at temperatures ranging from 25 to 70 °C and at states-of-charge from 40 to 80%. XPS measurements demonstrated that a mixture of organic species such as polycarbonates, LiF,  $\text{Li}_x\text{PF}_y$ -type and  $\text{Li}_x\text{PF}_y\text{O}_z$ -type compounds were present in the form of a surface film on the positive electrodes regardless of the test temperature or duration, or the state-of-charge [3]. Zhuang et al. showed using attenuated total reflectance (ATR) FT-IR measurements that the long-term exposure of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  electrodes to air produced a dense  $\text{Li}_2\text{CO}_3$  coating of approximately 10 nm in thickness that severely reduced both the accessible capacity and the rate at which the electrodes could be cycled [4]. Balasubramanian et al. used soft X-ray absorption spectroscopy (XAS) in the total electron yield mode, which is surface sensitive, to demonstrate the formation of a solid electrolyte interface (SEI) on  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  cathodes from lithium-ion cells cycled at 40 °C and 70 °C when probing to a depth of ~5 nm [5]. In this study, fluorine K-edge XAS was used to demonstrate the presence of poly-vinylidene fluoride (PVdF) and LiF on the surfaces of cycled electrodes. Furthermore, this technique has indicated that the PVdF in the cycled electrodes is largely intact and

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that the LiF originates from the decomposition of  $\text{LiPF}_6$  in the electrolyte.

There has thus far been little focus on the electronic structure of Li-containing cathode materials, even though Li is a key element in these types of batteries. Graetz et al. probed the Li K-edge for the  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  system using the transmission electron energy-loss spectroscopy (EELS) method, and the bulk lithium concentration of the region under analysis could be determined by making use of its linear relationship with the Li K-edge intensity [6]. Tsuji et al. measured the Li K-edge XANES spectra of a variety of Li-containing compounds using the total electron yield (TEY) mode, and suggested that the spectrum of each compound could be classified according to the shape of the core exciton peak, namely either a sharp (LiF) or shoulder-like feature ( $\text{Li}_2\text{O}$ ) [7]. Handa et al. measured the Li K-edge XANES spectra of lithium halides (LiX) using the TEY mode and demonstrated that the energy of the first resonance peak of an atom shifts according to the difference in electronegativity with the neighboring atoms [8].

To our knowledge, the presence of inorganic materials on the surface of cathode materials has thus far not been investigated using Li and O K-edge XANES measurements, even though detailed information on these inorganic materials is essential in order to determine the origin of the degradation of electrochemical performance in battery cells. We have previously reported that different aspects of the cathode material can be probed by soft and hard XAFS spectra and, therefore, that the combination of both measurements using synchrotron radiation is a powerful method for investigating changes in the surface structure [9,10]. We have studied the surfaces of  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  using Li and O K-edge XANES measurements. We present a schematic model to describe the surfaces of these cathode materials.

## 2. Experimental

We used  $\text{LiCoO}_2$  (Nippon Chemical Industrial Co., Ltd.; C5N) and  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (Toda Industrial Co., Ltd.; NCA-01) powder samples in this study. Synchrotron X-ray diffraction (XRD) data were collected at room temperature using the powder diffractometer on the BL02B2 beamline at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2005A0467-ND1a-np). The samples were contained in soda glass capillaries of inner diameter 0.3 mm and wall thickness 0.01 mm. The wavelength of the incident synchrotron radiation was fixed at 0.5 Å. The structural parameters were refined by Rietveld analysis using the computer program RIETAN2000 [11].

The O K-edge XANES spectra of the samples were measured on the BL4B beamline of the UVSOR Facility at the Institute for Molecular Science (Proposal No. 17-239). Data were obtained in the total electron yield (TEY) and fluorescence yield (FY) modes. The Li K-edge XANES spectra were measured on the BL2 beamline of the SR-center at Ritsumeikan Univ. as part of the Nanotechnology Support Project of the MEXT (Proposal no. H17-004). Data were obtained in the total electron yield (TEY) mode.

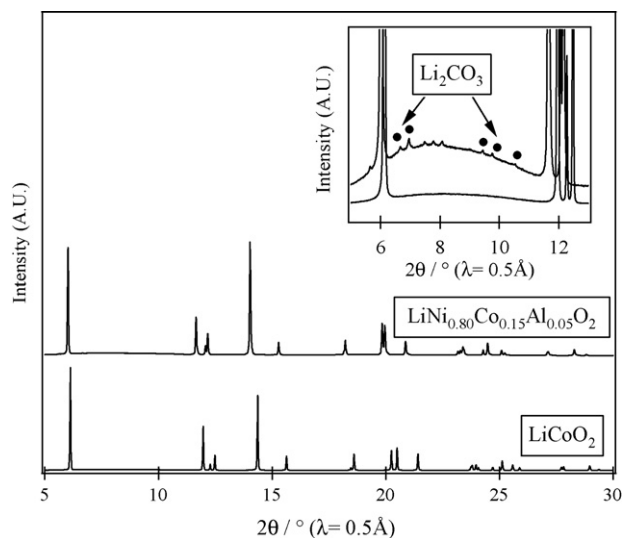


Fig. 1. Synchrotron XRD patterns of  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ .

## 3. Results and discussion

Fig. 1 shows the synchrotron XRD patterns of the  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  samples; the former is single-phase and the latter contains a  $\text{Li}_2\text{CO}_3$  impurity. The structures of both materials were refined using an initial  $\text{LiNiO}_2$  model [12], with space group  $R\bar{3}m$  and Li atomic positions at  $3a(0, 0, 0)$ , M (M = Ni, Co, Al) at  $3b(0, 0, 1/2)$ , and O at  $6c(0, 0, z)$ , where  $z \sim 0.25$ . For  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , the experimental XRD pattern was well fitted by a two-phase model consisting of  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{Li}_2\text{CO}_3$ . The lattice parameters of  $\text{LiCoO}_2$  were determined as  $a = 2.816$  Å and  $c = 14.05$  Å. The lattice parameters of  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  were determined as  $a = 2.892$  Å and  $c = 14.30$  Å, and this compound was present with a fraction of approximately 2%  $\text{Li}_2\text{CO}_3$ .

The O K-edge XANES spectra provide information on the surface and bulk when measured in the TEY and FY modes, respectively. Fig. 2 shows the O K-edge XANES spectra of  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  measured in TEY mode, together with those of the reference materials NiO and  $\text{Li}_2\text{CO}_3$ . The O K-edge spectrum of  $\text{LiCoO}_2$  contained one pre-edge peak at approximately 528 eV, originating from the layered structure, and no peaks corresponding to  $\text{Li}_2\text{CO}_3$  were visible. In contrast, the O K-edge spectrum of  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  contained three pre-edge peaks: peak A at approximately 529 eV, originating from the layered structure, peak B at approximately 533 eV, originating from a NiO-like cubic phase, and peak C at approximately 534 eV, originating from  $\text{Li}_2\text{CO}_3$ . Fig. 3 shows the O K-edge XANES spectra of  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and the reference material NiO measured in FY mode. For NiO, the spectra were essentially the same in both TEY and FY modes. For  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , peak A at  $\sim 529$  eV, originating from the layered structure, was clearly observed, but peak C at  $\sim 534$  eV, originating from  $\text{Li}_2\text{CO}_3$ , was absent. These results imply that the layered structure was retained in the bulk of the cathode, but that part of the layered structure was transformed to a cubic structure. Fur-

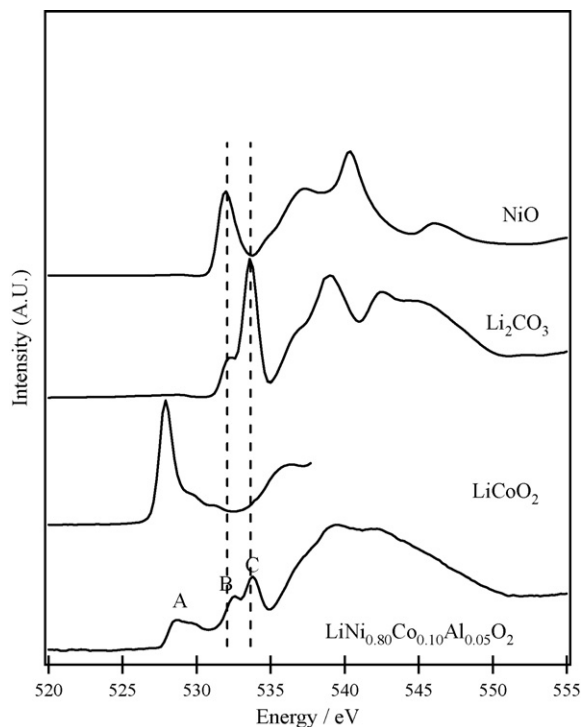


Fig. 2. O K-edge XANES spectra of LiCoO<sub>2</sub> and LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> together with those of reference materials NiO and Li<sub>2</sub>CO<sub>3</sub>, measured in TEY mode.

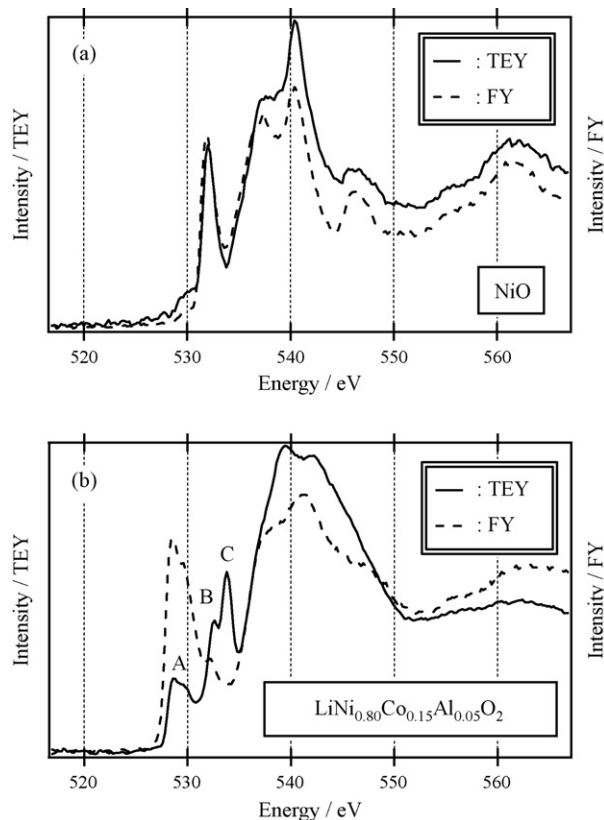


Fig. 3. O K-edge XANES spectra of LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> and reference material NiO, measured in both TEY and FY modes.

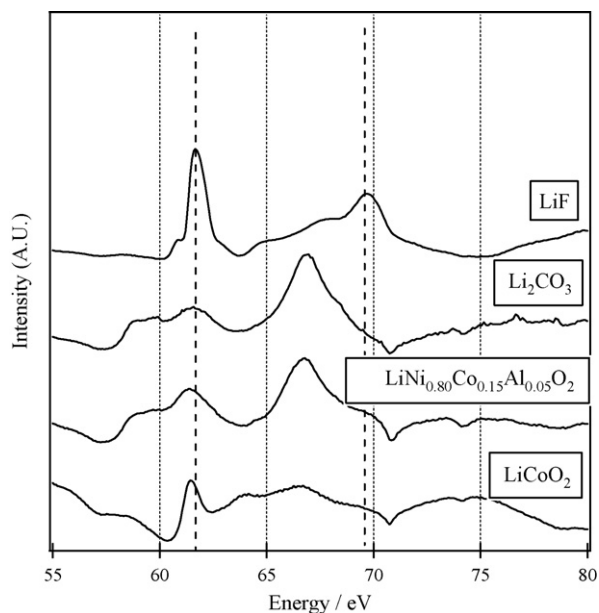


Fig. 4. Li K-edge XANES spectra of LiCoO<sub>2</sub> and LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, together with those of reference materials LiF and Li<sub>2</sub>CO<sub>3</sub>, measured in TEY mode.

thermore, Li<sub>2</sub>CO<sub>3</sub> was present as an impurity in the active materials.

The Li K-edge XANES spectra provide information on the surface when measured in TEY mode. Fig. 4 shows the Li K-edge XANES spectra of LiCoO<sub>2</sub> and LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> together with those of the reference materials LiF and Li<sub>2</sub>CO<sub>3</sub>. There is a sharp peak at 61.7 eV in the LiF spectrum, while there are two broad peaks in the region of 61.0 eV and one strong broad peak at 66.9 eV in the Li<sub>2</sub>CO<sub>3</sub> spectrum. The LiF and Li<sub>2</sub>CO<sub>3</sub> spectra are in good agreement with those previously reported [7,8]. The spectra of LiCoO<sub>2</sub> and LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> could be classified according to the shape of the core exciton peak, either a sharp (LiF) or a shoulder-like structure (Li<sub>2</sub>O). The Li K-edge spectrum of LiCoO<sub>2</sub> contained a sharp peak at 61.5 eV and weak shoulder-like peaks between 64.0 and 66.6 eV. We consider that the sharp peak of LiCoO<sub>2</sub> is characteristic of the layered structure and conclude that residual Li<sub>2</sub>CO<sub>3</sub> was almost absent from the surface of this sample. In contrast, the Li K-edge spectrum of LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> contained two broad peaks at 61.0 eV and one strong broad peak at 66.8 eV, without any strong peak in the region of 62.0 eV that would be expected for the layered structure. Graetz et al. performed EELS measurements on the Li<sub>1-x</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> system and reported that the onset of the Li K-edge occurs at 58 eV; the spectra also contained contributions from the Co and Ni M<sub>II,III</sub>-edges at ~60 and ~68 eV, respectively [6]. However, the spectrum of LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> observed in the present study is different to that of Li<sub>1-x</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> previously reported. We conclude that the residual Li<sub>2</sub>CO<sub>3</sub> almost covered the surface of the LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> sample.

Handa et al. reported that the energy of the first resonance peak for an atom in lithium halides (LiX) shifts according to the difference in electronegativity with the neighboring atoms

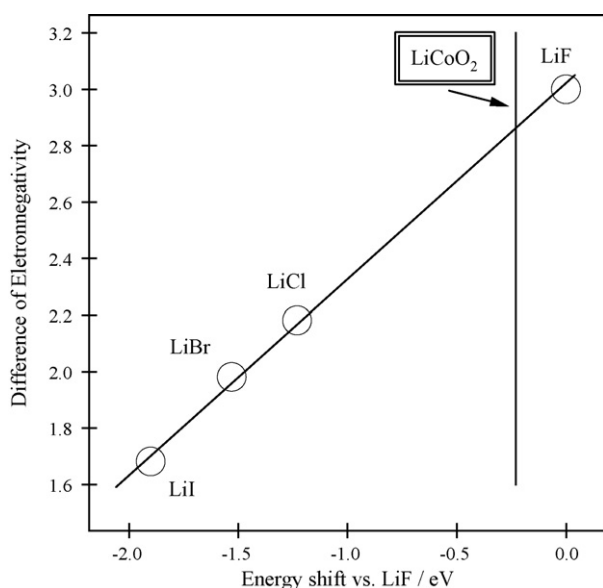


Fig. 5. Relationship between the energy of the first resonance peak and electronegativity difference in LiX and LiCoO<sub>2</sub>.

[8]. Fig. 5 shows the relationship between the energy of the first resonance peak and the electronegativity difference for LiX and LiCoO<sub>2</sub>. In our measurements, the difference in the energies of the LiF and LiCoO<sub>2</sub> peaks is approximately 0.3 eV, and thus LiCoO<sub>2</sub> lies between LiF and LiCl on the plot. This region of the spectrum also contains overlapping contributions from the Co M<sub>II,III</sub>-edges at 60 eV, but the contribution from Co is small enough that changes in the Li K-edge can still be resolved clearly. These results indicate that the Li in LiCoO<sub>2</sub> is ionically bonded to the host structure.

Fig. 6 shows a schematic model of the surfaces of LiCoO<sub>2</sub> and LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>. The Li and O K-edge spectra indicated

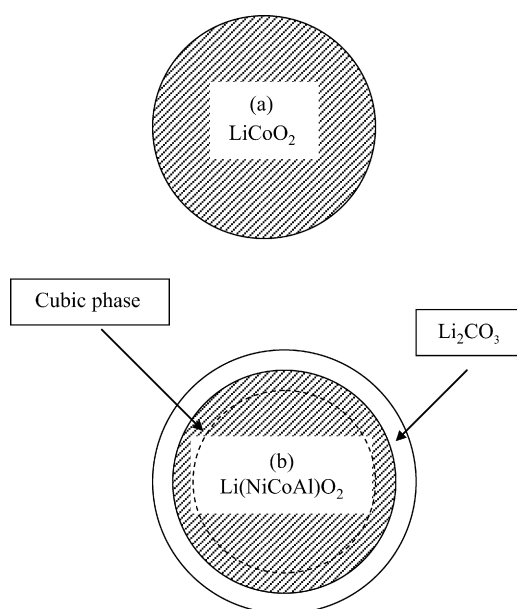


Fig. 6. Schematic representation surface structure for LiCoO<sub>2</sub> and LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>.

that LiCoO<sub>2</sub> had a surface structure free of Li<sub>2</sub>CO<sub>3</sub>. In contrast, the surface of LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> was covered with both Li<sub>2</sub>CO<sub>3</sub> and a cubic phase. The relationship between the surface of the cathode materials and the power fading of batteries has recently been discussed [4,13,14]. A combination of XRD and XPS measurements has shown that the formation of Li<sub>2</sub>CO<sub>3</sub> and a breakdown of the ordered layered structure at the surface of LiNiO<sub>2</sub> occur after extended exposure to air [13]. In addition, a surface reaction mechanism based on the interconversion of Ni<sup>3+</sup>/Ni<sup>2+</sup> and the evolution of active oxygen species has been proposed using the O<sub>2</sub> temperature-programmed desorption mass spectroscopy (TPD-MS) technique. It has been reported that the long-term exposure to air of LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> electrodes gives rise to a dense Li<sub>2</sub>CO<sub>3</sub> coating, approximately 10 nm in thickness, which severely reduces both the accessible capacity and the rate at which the electrodes could be cycled, as determined by FT-IR [4]. A combination of oxygen K-edge XAS, high resolution transmission electron microscopy (HRTEM), nanoprobe diffraction (ND), and electron energy loss spectroscopy (EELS) has shown the appearance of a cubic phase at the surface of particles of LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> electrodes after cycle tests had been performed, giving rise to a modified layer of less than 5 nm thickness [14]. This modified layer results from a loss of Ni and Li ordering in the layered *R* $\bar{3}m$  structure, caused by oxygen deficiency and a lowering of the Ni- and Co-oxidation states in the surface layer. Growth of this surface layer may contribute to the rise in impedance and loss of power observed during accelerated aging of these Li-ion cells.

Recently, we reported that LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> has a surface structure free from Li<sub>2</sub>CO<sub>3</sub> [10]. We suppose that the surface structure of LiNiO<sub>2</sub>-related materials is sensitive to synthesis and storage conditions. Although the deterioration of lithium battery performance is at least partly due to the positive electrodes, the mechanism of the deterioration of the electrodes is still unclear. Detailed information on the changes in the surfaces of cathode electrodes is very important in order to determine the origin of the degradation of electrochemical performance of battery cells. We conclude that different aspects of cathode materials can be probed by soft and hard XAFS spectra and, therefore, that the combination of both measurements using synchrotron radiation is a powerful method for investigating changes in the surface structure.

#### 4. Conclusion

In this study, Li and O K-edge XANES analysis has clarified that the surface of particles of LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> was covered with Li<sub>2</sub>CO<sub>3</sub>. In addition, a change in crystal structure from rhombohedral to a lithium-deficient cubic phase was observed in the surface region of the positive electrode. When compared with the corresponding results for LiCoO<sub>2</sub>, we conclude that the surface structure of LiNiO<sub>2</sub>-related materials may be sensitive to synthesis and storage conditions. Soft XANES spectra using synchrotron radiation allows the analysis of information on particle surfaces to include more physical depth than XPS spectra. Therefore, we will further investigate the relationship between

surface structure and the degradation of battery cell performance using this powerful method in the near future.

## References

- [1] K. Amine, C.H. Chen, J. Liu, M. Hammond, A. Jansen, D. Dees, I. Bloom, D. Vissers, G. Henriksen, J. Power Sources 97–98 (2001) 684–687.
- [2] Y. Itou, Y. Ukyo, J. Power Sources 146 (2005) 39–44.
- [3] A.M. Andersson, D.P. Abraham, R. Haasch, S. MacLaren, J. Liu, K. Amine, J. Electrochem. Soc. 149 (2002) A1358–A1369.
- [4] G.V. Zhuang, G. Chen, J. Shim, X. Song, P.N. Ross, T.J. Richardson, J. Power Sources 134 (2004) 293–297.
- [5] M. Balasubramanian, H.S. Lee, X. Sun, X.Q. Yang, A.R. Moodenbaugh, J. McBreen, D.A. Fischer, Z. Fub, Electrochem. Solid State Lett. 5 (2002) A22–A25.
- [6] J. Graetz, C.C. Ahn, R. Yazami, B. Fultz, J. Phys. Chem. B 107 (2003) 2887–2891.
- [7] J. Tsuji, H. Nakamatsu, T. Mukoyama, K. Kojima, S. Ikeda, K. Taniguchi, X-ray Spectrom. 31 (2002) 319–326.
- [8] H. Handa, K. Kojima, K. Taniguchi, K. Ozutsumi, S. Ikeda, Memories Sr. Center Ritsumeikan Univ. 7 (2005) 3–6.
- [9] H. Kobayashi, Y. Arachi, S. Emura, H. Kageyama, K. Tatsumi, T. Kamiyama, J. Power Sources 146 (2005) 640–644.
- [10] H. Kobayashi, Y. Arachi, S. Emura, K. Hannda, K. Tatsumi, AIP Conference Proceedings of X-ray Absorption Fine Structure—XAFS-13, vol. 882, 2007, pp. 478–480.
- [11] F. Izumi, in: R.A. Young (Ed.), The Rietveld Method, Oxford University Press, Oxford, 1993 (Chapter 13).
- [12] A. Hirano, R. Kanno, Y. Kawamoto, Y. Nitta, K. Okamura, T. Kamiyama, F. Izumi, Solid State Ionics 78 (1995) 123–131.
- [13] H.S. Liu, Z.R. Zhang, Z.L. Gong, Y. Yang, Electrochem. Solid State Lett. 7 (2004) A190–A193.
- [14] D.P. Abraham, R.D. Twisten, M. Balasubramanian, J. Kropf, D. Fischer, J. McBreen, I. Petrov, K. Amine, J. Electrochem. Soc. 150 (2003) A1450–A1456.