

Short communication

## Soft X-ray absorption spectroscopy studies on the chemically delithiated commercial $\text{LiCoO}_2$ cathode material

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### Abstract

Variation of electronic structure for chemically delithiated  $\text{LiCoO}_2$  was investigated by X-ray absorption spectroscopy (XAS) at Co L-edge, K-edge and O K-edge. The commercial  $\text{LiCoO}_2$  powders were de-intercalated by an oxidizing agent,  $\text{Na}_2\text{S}_2\text{O}_8$ , in an aqueous solution. The soft XAS was performed at total electron yield as well as fluorescence modes. It was found that the changes in the spectral feature obtained from total electron yield mode are different from that obtained from fluorescence mode at the oxygen K-edge. The electronic transition from oxygen 1s state to 2p hole state (threshold energy) decreases at the surface region but not in the bulk. The shoulder absorption peak at the energy higher than the threshold energy contributed to the higher oxidation state of the oxygen site appears at total electron yield mode but does not appear at fluorescence mode, indicating the oxidation state of oxygen and the electronic transitions on the surface and in the bulk of the delithiated compounds are different. It implies that the chemically delithiated process takes place inhomogeneously and starts from the surface of the  $\text{Li}_x\text{CoO}_2$  compounds. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Soft X-ray absorption spectroscopy; Lithium ion battery;  $\text{LiCoO}_2$ ; Chemical delithiation

### 1. Introduction

Several lithium intercalation materials have been studied intensively during the past decade for use as cathodes in lithium-ion batteries, primarily for the application of portable electronic devices. A lot of researches on physical and electrochemical properties of  $\text{LiCoO}_2$  have been carried out for the applications of high-energy density electric vehicles [1–4]. However, the limitation of reversible capacity in  $\text{Li}_{1-x}\text{CoO}_2$  has been attributed to the phase transformation to the hexagonal from monoclinic if the delithiation value reaches  $x=0.5$ . Further, it leads to the non-uniform dimensional change which is mainly due to the significant change in the *c*-axis and it might cause a mechanical failure of the  $\text{LiCoO}_2$  particle [5]. For this reason, there are still

a lot of publications [6–19] reporting new methods to further understand its de-delithiation reactions and improve its electrochemical performance even though it has been widely used. In order to improve its electrochemical performance further, it is of great importance to understand the electronic structure of the delithiated  $\text{LiCoO}_2$  compounds. It is well known that the XAS is a versatile tool to probe the changes that occurred during electrochemical extraction and re-insertion processes. Recently first principle calculation on the electronic structure of  $\text{Li}_{1-x}\text{CoO}_2$  has been reported [20,21]. It indicates that the covalent interaction between cobalt and oxygen increases upon delithiation and the oxidation associated with deintercalation mainly takes place on oxygen. Since the interpretation of XAS results for a composite electrode (active particles, binder and conducting carbon) is always complicate, it is difficult to understand the variation of its electronic structure via an experimental approach. Fortunately, the delithiated  $\text{LiCoO}_2$  powders in the absence of binder and conducting carbon can be prepared by a chemical method. In this work, the changes of the electronic structure of commercial  $\text{LiCoO}_2$  powders chemically delithiated are investigated by X-

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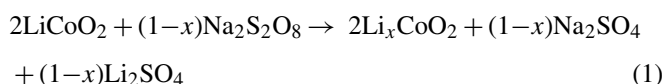
E-mail address: [bjh@mail.ntust.edu.tw](mailto:bjh@mail.ntust.edu.tw) (B.-J. Hwang).

ray absorption spectroscopy at O K-edge and Co L-edge. Both total electron yield and fluorescence modes at O K-edge are performed so that the electronic structure on the surface and bulk of the delithiated  $\text{LiCoO}_2$  powders can be differentiated.

## 2. Experimental

### 2.1. Sample preparation

99.5%  $\text{LiCoO}_2$  powders (CERAC) screened by a sieve with #325 mesh was used in this work. The  $\text{LiCoO}_2$  powders were delithiated chemically by an oxidizing agent,  $0.1 \text{ M Na}_2\text{S}_2\text{O}_8$ , in an aqueous solution. The degree of delithiation was controlled by adjusting the amount of the oxidant. The delithiation reaction would follow the following Equation:



The delithiated powders obtained were filtered, washed repeatedly with distilled water, and further washed with acetone. The samples were finally dried in a glove box in which the moisture and oxygen content are less than 1 ppm. The Li and Co contents in the resulting materials were analyzed using an inductively coupled plasma/atomic emission spectrometer (ICP/AES, Kontron S-35).

### 2.2. X-ray diffraction measurements

X-ray diffraction (XRD) measurements were carried out at the high-energy beam line 01C2 at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu. The beam line was operated at energy of 25 keV. The XRD pattern was recorded using the wavelength ( $\lambda$ ) =  $0.51667 \text{ \AA}$  for limited angular regions at room temperature. The optical design for the monochromatic beam is as follows: the first mirror focusing at the beam vertically and asymmetrically cut and horizontally bendable a perfect single crystal as the diffraction object monochromatically focused the beam. A single crystal of  $\text{Si}(111)$  with about 10% asymmetric cutting was used to deliver a monochromatic beam size 1 mm in diameter with a single spot at the sample, which is about 24 and 6 m away from the source and monochromatic, respectively, flat imaging plane was used as a 2D area detector, which can collect diffraction pattern of the  $2\theta$  scale up to  $40^\circ$ . The XRD pattern was read out by a MAC IPR420 off line imaging plate scanner.

### 2.3. X-ray absorption spectroscopy measurements

Hard X-ray absorption spectroscopy (XAS) measurements have been performed on the  $\text{LiCoO}_2$  cathode compound at room temperature. The Hard XAS data was collected in the transmission mode at the beam line BL17C at the National Synchrotron Radiation Research Center (NSRRC) at Hsinchu, Taiwan. The storage ring was operated with energy of 1.5 GeV and a current of 300 mA. A higher order harmonics were eliminated by adjusting the  $\text{Si}(111)$  double monochromatic crystal

and energy calibration was performed at each scan using the first inflection point of the Co (7709 eV) metal foil as a reference. Three gas-filled ionization chambers were used in series to measure the intensities of the incident beam ( $I_0$ ), the beam transmitted by the sample ( $I_t$ ), and the beam subsequently transmitted by the reference foil ( $I_r$ ). The control of parameters for EXAFS measurements, data collection modes and calculation of errors were all done as per the guidelines set by International XAFS Society Standards and Criteria Committee. The soft X-ray absorption measurements were made at the BL20A1 station and its measurements were done in the X-ray fluorescence mode for Co  $\text{L}_{\text{II,III}}$ -edge and total electron yield and fluorescence modes for O using an ultra high-vacuum (UHV) chamber with a base pressure of  $1 \times 10^{-10}$  Torr. The depth of fluorescence mode and total electron yield mode is more than  $50 \text{ \AA}$  and less than  $10 \text{ \AA}$ , respectively. Therefore, the information obtained by total electron yield mode and fluorescence mode is mainly contributed from the surface and the bulk of the particle, respectively.

## 3. Result and discussion

Fig. 1 shows the XRD pattern for the commercial  $\text{LiCoO}_2$  powder. All diffraction peaks can be indexed using the hexagonal axes option for the rhombohedral space group of  $R\bar{3}m$ . The XRD patterns for the  $\text{LiCoO}_2$  powders show good separation of (006)/(012) and the (108)/(110) couples of diffraction lines, indicating that this material consists of a well-developed layered  $\text{LiCoO}_2$  [22]. The oxygen octahedral of the central Co atom is edge-shared each other within the octahedral layer and the Li atoms are placed in the lattice channel between interlayer planes. The Co  $\text{L}_{\text{II}}$ - and  $\text{L}_{\text{III}}$ -edge X-ray absorption spectra of the  $\text{Li}_x\text{CoO}_2$  compounds were shown in Fig. 2. Two main peaks of Co  $\text{L}_{\text{III}}$ - and  $\text{L}_{\text{II}}$ - edges result from the electronic transitions of Co  $2p_{3/2}$  and  $2p_{1/2}$  core level to an unoccupied 3d level highly hybridized with oxygen 2p orbital. For the  $\text{Co}^{3+}$  state in  $\text{LiCoO}_2$ , the corresponding electronic final states represent  $[\text{Co } 2p^5 3d^7 (t_{2g}^6 e_g^1)]$ , where c represents the hole of the Co 2p core level.

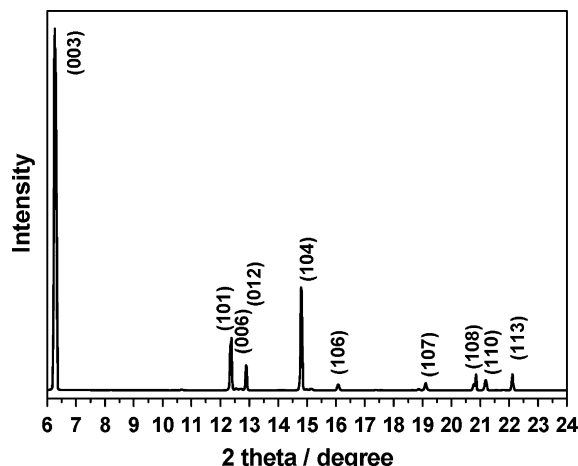


Fig. 1. XRD pattern of  $\text{LiCoO}_2$  powder based on the wavelength equal to  $0.0517 \text{ nm}$ .

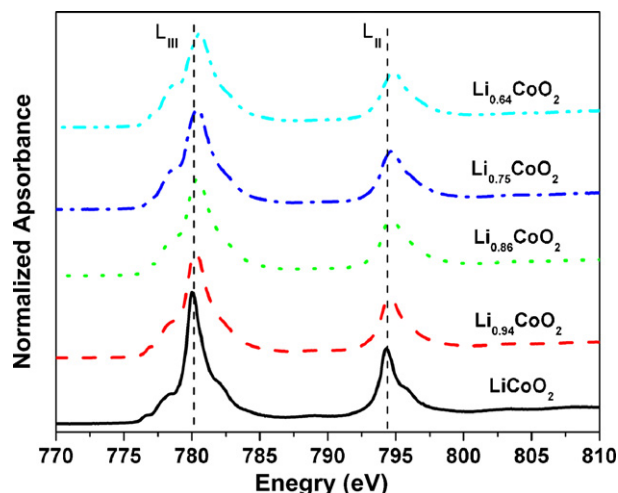


Fig. 2. Normalized Co L<sub>II,III</sub>-edge X-ray absorption spectra of LiCoO<sub>2</sub> system with respect to the various time intervals of oxidation.

The absorption peaks are relatively intense by the electric dipole-allowed 2p to 3d transition and are very sensitive to the oxidation state, spin state, and bond covalency. Therefore, the electronic structures of the Co ions in the Li<sub>x</sub>CoO<sub>2</sub> compounds can be investigated qualitatively with peak features of the Co L<sub>II</sub>- and L<sub>III</sub>-edge spectra. As shown in Fig. 2, the L<sub>II</sub> and L<sub>III</sub> peaks are shifted toward higher energy and the peak width is broadened. The main peak intensity decreases with an increase in the degree of delithiation. Fig. 3 illustrates the relationship between the peak position and the Li-ion content. It was found that the peak positions shift to higher energy with a decrease in the *x* value of the Li<sub>x</sub>CoO<sub>2</sub> compounds. The charge compensation is closely associated with the rehybridization of Co and O molecular orbitals which results in the change of the effective nuclear charge of Co ions. The rehybridization of Co and O molecular orbital is due to the minimization of the chemical perturbation upon delithiation which causes the charge transfers to Co sites [23]. The charge compensation can be accomplished by the local structural rearrangement of CoO<sub>6</sub> octahedral. The *k*<sup>3</sup>-weighed Fourier transform spectra at the Co K-edge for different Li-ion contents of the Li<sub>x</sub>CoO<sub>2</sub> compounds are shown in Fig. 4. As can

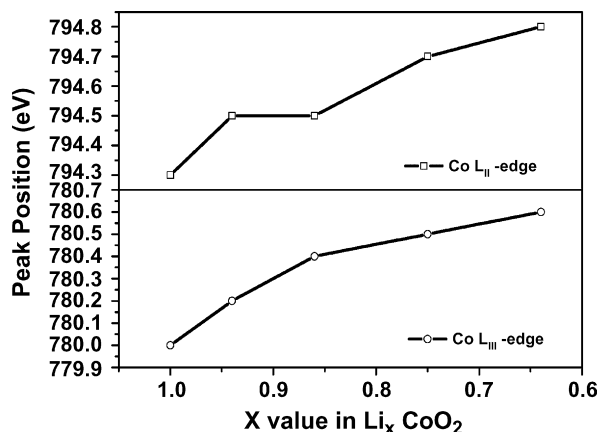


Fig. 3. Relationship between the peak positions of Co L<sub>II,III</sub>-edge X-ray absorption spectra and the Li-ion content.

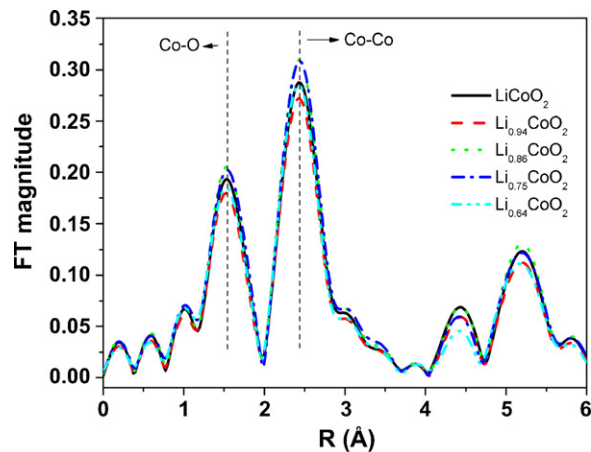


Fig. 4. The *k*<sup>3</sup>-weighed Fourier transform spectra in Co K-edge for different Li-ion contents.

be seen, two main peaks correspond to Co–O bond and Co–Co bond, respectively. Both the magnitudes of the Co–O bond and the Co–Co bond change at different delithiated states due to the local structure distortion of CoO<sub>6</sub> [24]. The observation is also responding to the rehybridization of Co and O molecular orbital. The change in the effective nuclear charge of the Co ions is due to the generation of positive charge upon delithiation. The higher absorption energy is necessary for the Co ions under the higher oxidative environment in order to excite the 2p core electron, which is strongly bounded to the less screened nucleus. It indicates that the contribution of Co ions is not negligible on the charge compensation process upon Li deintercalation.

The O K-edge X-ray absorption spectra in total electron yield mode for the chemically delithiated Li<sub>x</sub>CoO<sub>2</sub> compounds are shown in Fig. 5. The total electron yield mode is surface sensitive while the fluorescence yield mode is suitable for bulk study. The oxygen K-edge XAS is very sensitive to its chemical environment and its electronic structure is strongly dependent of Li-ion content in the Li<sub>x</sub>CoO<sub>2</sub> compounds. Therefore, the XAS spectra of oxygen K-edge for the Li<sub>x</sub>CoO<sub>2</sub> compounds can provide useful information about the electronic structure of the oxy-

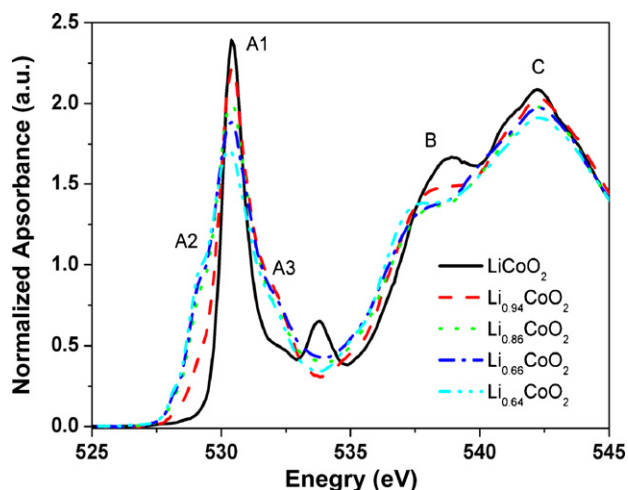


Fig. 5. Normalized oxygen K-edge X-ray absorption spectra of the LiCoO<sub>2</sub> with respect to the various time intervals of oxidation in the total electron yield mode.

gen ion and its bonding character with the Co metal ions. From the localized nature of the oxygen 1s orbital, a symmetric and intense absorption peak A1 in the pristine LiCoO<sub>2</sub> represents the transition of the oxygen 1s electron to the hole state in the oxygen 2p level has been called as threshold energy. The two broad peaks B and C at energy above 536 eV can be assigned to the transitions from oxygen 1s orbital to the hybridized states of oxygen 2p and Co 4sp orbitals. The A1 peak at the pristine state corresponds to the transition to an unoccupied molecular level which includes [Co 3d(e<sub>g</sub>)–O 2p] character since the oxygen 2p orbital is highly hybridized with the 3d orbital of the Co<sup>3+</sup> ion with low spin (t<sub>2g</sub><sup>6</sup>, e<sub>g</sub><sup>0</sup>) electronic configuration under octahedral symmetry. As we know that the oxygen 1s to Co 3d transition is forbidden by the electric-dipole approximation. Thus, the appearance of the absorption peak is due to the hybridization of Co 3d and oxygen 2p orbitals. The A1 peak at the final state corresponds to the electronic configuration of [O 1s<sup>1c</sup>+Co 3d<sup>7</sup> (t<sub>2g</sub><sup>6</sup>, e<sub>g</sub><sup>1</sup>)], where c is the oxygen 1s core hole.

As can be seen that the spectral changes of the O K-edge XAS are relatively more significant than those of the Co L<sub>II,III</sub>-edge XAS with respect to the Li-ion content. It was found that the delithiation process has much larger influence on the electronic structure of the oxygen ions than that of the Co ions based on the variation of their spectroscopic features. It was found that the electron exchange for charge compensation takes place in the oxygen sites as well as the Co sites in the chemically delithiated process. It is consistent with the observation in the electrochemically delithiated process [25]. It suggests that the oxygen 2p bond takes part in the electron exchange. For this result, the O K-edge XAS shows the direct responsibility of the oxygen 2p state on the bound state in the Li<sub>x</sub>CoO<sub>2</sub> compounds. As the degree of delithiation increases (the *x* value decrease), the A1 peak intensity decreases gradually and an additional broad peak A3 evolves as a shoulder peak in the energy higher around 1.2 eV than that of the peak A1. In our understanding, the chemical shift in the ligand 1s core energy is related to the effective charge on the ligand. The ligand pre-edge peak position shifts to the higher energy with an increase in its effective nuclear charge since the higher absorption energy is necessary for the oxygen ions with higher degree of oxidation in order to excite the oxygen 1s core electron, which is strongly bound to the less screened nucleus. Therefore, the shoulder absorption peak in the energy region higher than the threshold energy can be assigned to the oxygen sites with higher degree of oxidation upon delithiation process [25]. It indicates that the charge compensation for the electron exchange in the Li-ion deintercalation process could be achieved in the oxygen site on the surface of the compounds. Furthermore, the Li-ion deintercalation gives rise to the gradual formation of an additional well-resolved absorption peak A2 in the energy region lower than the threshold energy and its intensity increases systematically with the degree of Li-ion deintercalation. Hedman et al. [26] reported that the ligand pre-edge peak position shifts to the lower energy region due to both the local structural distortion and the increase of effective nuclear charge of the metal ion so that the peak intensity would change with the bond covalency. The A1 peak intensity decreases with

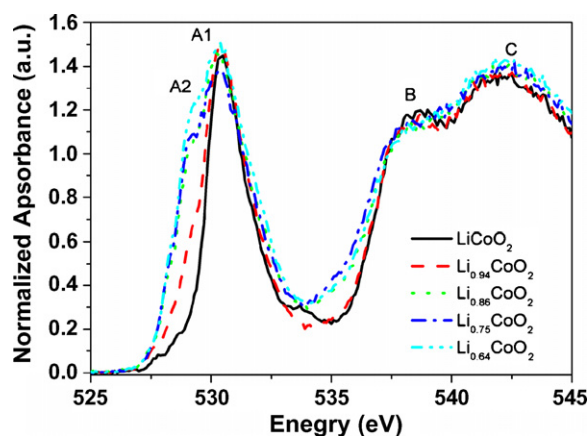


Fig. 6. Normalized oxygen K-edge X-ray absorption spectra of the LiCoO<sub>2</sub> with respect to the various time intervals of oxidation in the fluorescence mode.

an increase in the degree of delithiation, while the relative intensity of the A2 peak increases. The variation of the peak intensity with the chemical deintercalation can give important information about the hole state distribution and the effective charge on the oxygen atom since the density of the empty bond state in the molecular energy level is related to the hybridization of Co 3d–O 2p orbitals. It was also found that the weak absorption A2 peak of Li<sub>0.64</sub>CoO<sub>2</sub> compound appeared at around 528 eV due to the rehybridization between the oxygen and the Co ions with the greater effective nuclear charge in the local distorted Co–O bond. The bond covalency decreases due to the molecular rehybridization resulting from the local structural distortion around the Co ions. Therefore, the gradual increase of A2 peak intensity with the Li-ion deintercalation shows the systematic increase of the molecular rehybridization and then decrease of bond covalency on the surface of the compounds.

Fig. 6 shows the O K-edge X-ray absorption spectra in fluorescence mode for the chemically delithiated Li<sub>x</sub>CoO<sub>2</sub> compounds. Combination of the spectra obtained in both total electron yield and fluorescence modes can distinguish the difference between the surface and bulk properties of the delithiated Li<sub>x</sub>CoO<sub>2</sub> compounds. The A1 peak intensity changes insignificantly in Fig. 6, indicating that the transition of the oxygen 1s electron to the hole state in the oxygen 2p level remains unchanged. It was found that the A2 peak intensity increases dramatically but the peak A3 would not appear with an increase in the degree of delithiation. The shoulder absorption peak (A3) at the energy higher than the threshold energy contributed to the higher oxidation state of the oxygen site appears at total electron yield mode but does not appear at fluorescence mode, indicating the oxidation state of oxygen on the surface and in the bulk of the delithiated compounds is different. The molecular rehybridization due to the local distortion of CoO<sub>6</sub> octahedral symmetry and the oxidation of the oxygen sites would not change the A1 and A3 transitions in the bulk region of the compounds during the delithiation process. All the observations indicated that the oxidation state of oxygen and the electronic transitions occurring in the bulk region are different from on the surface region of the chemically delithiated Li<sub>x</sub>CoO<sub>2</sub> compounds. It implies that the chemically delithiated process takes place inhomogeneously

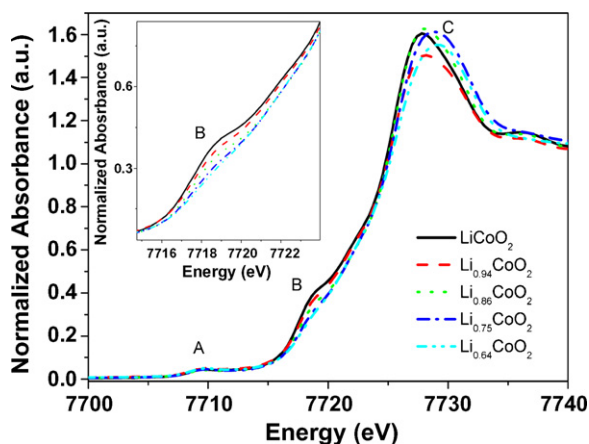


Fig. 7. X-ray near edge absorption spectra in Co K-edge for different Li-ion contents.

and the phase transition from monoclinic to hexagonal may be induced from the surface.

Fig. 7 shows the normalized Co K-edge XANES of the  $\text{Li}_x\text{CoO}_2$  compounds for the comparison with the O K-edge XANES. The weak absorption peak A at around 7710 eV represents the transition of the 1s electron to an unoccupied 3d orbital of  $\text{Co}^{3+}$  ion with low-spin ( $t_{2g}^6, e_g^0$ ) electronic configuration. In principle, the 1s to 3d transition is an electric dipole-forbidden transition in an ideal octahedral symmetry, the appearance of the weak absorption peak is due to pure electric quadrupole coupling and the noncentrosymmetric environment of the slightly distorted  $\text{CoO}_6$  octahedral site. Both B and C peaks appear by the electric dipole-allowed transition of a 1s core electron to an unoccupied 4p bound state. The B and C peaks correspond to two final states of a  $1s^1c3d^7L4p^1$  with the shakedown process by ligand to metal charge transfer and a  $1s^1c3d^64p^1$  without the shakedown process, respectively, where c and L are the 1s core hole and a ligand hole. From the disappearance of the peak B intensity, the Li-ion deintercalation leads to local structural distortion around the Co atom, which is in good agreement with the O K-edge results. The decrease of the transition (disappearance of peak B) is due to the mismatched Co 3d–O 2p orbital overlapped by the tilted arrangement of the  $\text{CoO}_6$  octahedra. Herein, the ligand to metal charge transfer process would be difficult to take place in the higher degree of delithiation. These observations suggest that the chemical Li-ion deintercalation leads to the local distortion of  $\text{CoO}_6$  octahedral symmetry and the main charge compensation for the electron exchange in the chemical Li-ion deintercalation process is accomplished at the oxygen sites as well as the Co sites.

#### 4. Conclusions

The electronic structure for the chemically Li-ion deintercalated  $\text{Li}_x\text{CoO}_2$  powders has been investigated intensively with hard and soft X-ray absorption spectroscopy at the O K-edge, Co  $L_{II,III}$ -edge, and Co K-edge. It was found that the charge compensation is closely associated with the rehybridization of Co and O molecular orbitals and the change of the effective

nuclear charge of Co ions from the variation of the Co  $L_{II,III}$ -edge. The contribution of Co ions is not negligible on the charge compensation process for Li-ion deintercalation. The electron exchange for charge compensation in a chemically delithiated process is same as in an electrochemically delithiated one. The shoulder absorption peak (A3) at the energy higher than the threshold energy contributed to the higher oxidation state of the oxygen site appears at total electron yield mode but does not appear at fluorescence mode, indicating the oxidation state of oxygen on the surface and in the bulk of the delithiated compounds is different. The chemical Li-ion deintercalation leads to the local distortion of  $\text{CoO}_6$  octahedral symmetry in both the surface and bulk region and the main charge compensation for the electron exchange in the chemical Li-ion deintercalation process is accomplished at the oxygen sites as well as the Co sites. These results indicate that the electronic transitions occurs in the bulk region is different from that of the surface region. It implies that the chemically delithiated process takes place inhomogeneously and starts from the surface of the  $\text{Li}_x\text{CoO}_2$  compounds.

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#### References

- [1] Y.M. Chiang, Y.I. Jang, H.F. Wang, B.Y. Huang, D.R. Sadoway, P.X. Ye, *J. Electrochem. Soc.* 145 (1998) 887.
- [2] P. Ganguly, T.N. Venkatraman, P.R. Rajanohanan, S. Ganapathy, *J. Phys. Chem. B* 72 (1997) 91.
- [3] P.N. Kumta, D. Gallet, A. Waghay, G.E. Blomgren, M.P. Setter, *J. Power Sources* 138 (1998) 2207.
- [4] H. Tukmoto, A.R. West, *J. Electrochem. Soc.* 144 (1997) 3164.
- [5] H. Wang, Y. Jang, B. Huang, D.R. Sadoway, Y. Chiang, *J. Electrochem. Soc.* 146 (1999) 473.
- [6] O.A. Brylev, O.A. Shlyakhtin, T.L. Kulova, et al., *Solid State Ionics* 156 (2003) 291.
- [7] A. Burukhin, O. Brylev, P. Hany, et al., *Solid State Ionics* 151 (2002) 259.
- [8] Y. Baba, S. Okada, J. Yamaki, *Solid State Ionics* 148 (2002) 311.
- [9] N. Imanishi, M. Fujii, A. Hirano, et al., *Solid State Ionics* 140 (2001) 45.
- [10] W.T. Jeong, K.S. Lee, J. Alloys Compd. 322 (2001) 205.
- [11] Z. Wang, C. Wu, L. Liu, et al., *J. Electrochem. Soc.* 149 (2002) A466.
- [12] M. Mladenov, R. Stoyanova, E. Zhecheva, et al., *Electrochem. Commun.* 3 (2001) 410.
- [13] Z. Wang, L. Liu, L. Chen, et al., *Solid State Ionics* 148 (2002) 335.
- [14] E. Endo, T. Yasuda, A. Kita, et al., *J. Electrochem. Soc.* 147 (2000) 1291.
- [15] C. Julien, *Solid State Ionics* 157 (2003) 57.
- [16] S. Yonezawa, T. Okayama, H. Tsuda, et al., *J. Fluorine Chem.* 87 (1998) 141.
- [17] S.T. Myung, N. Kumagai, S. Komaba, et al., *Solid State Ionics* 139 (2001) 47.
- [18] J.K. Hong, J.H. Lee, S.M. Oh, *J. Power Sources* 111 (2002) 90.
- [19] S. Madhavi, G.V.S. Rao, B.V.R. Chowdari, *Electrochim. Acta* 48 (2002) 219.

- [20] A. van der Ven, M.K. Aydiol, G. Cedar, G. Kresse, J. Hafner, *Phys. Rev. B* 58 (1998) 2975.
- [21] A. van der Ven, M.K. Aydiol, G. Cedar, *J. Electrochem. Soc.* 145 (1998) 2149.
- [22] R.J. Gummow, M.M. Thackeray, W.I.F. David, S. Hull, *Mater. Res. Bull.* 27 (1992) 317.
- [23] C. Wolverton, A. Zunger, *Phys. Rev. Lett.* 81 (1998) 606.
- [24] I. Nakai, K. Takahashi, Y. Shiraishi, T. Nakagome, F. Izumi, Y. Ishii, F. Nishikawa, T. Konishi, *J. Power Sources* 68 (1997) 536.
- [25] G. Ceder, Y.M. Ching, D.R. Sadoway, M.K. Aydinol, Y.I. Jang, B. Huang, *Nature* 392 (1998) 694.
- [26] B. Hedman, K.O. Hodgson, E.I. Solomon, *J. Am. Chem. Soc.* 112 (1990) 1643.