

Short communication

Electronic structural changes of the electrochemically Li-ion deintercalated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode material investigated by X-ray absorption spectroscopy

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Abstract

In situ hard X-ray absorption spectroscopy (XAS) at metal K-edges and soft XAS at O K-edge and metal L-edges have been carried out during the first charging process for the layered $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode material. The metal K-edge XAS results show that the major charge compensation at the metal site during Li-ion deintercalation is achieved by the oxidation of Ni ions, while the cobalt ions remain mostly unchanged in the Co^{3+} state. Ni L_{II,III}-edge and O K-edge XAS results in both the fluorescence yield (FY) and partial electron yield (PEY) modes show that substantial amount of Ni ions at the surface of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders exist as Ni^{2+} , whereas most of Ni ions in the bulk are in the form of Ni^{3+} . Therefore, if the PEY mode, which is a surface-sensitive technique, is used alone, the interpretation of the results is limited to the surface structures only. In order to get the full picture of both the surface and the bulk, the FY mode and PEY mode should be used simultaneously.

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1. Introduction

Extensive research on the electronic structure of Li-ion intercalated cathode materials has been carried out to elucidate the reaction mechanism of the electrochemical process in the cathode material during cycling. Hard X-ray absorption spectroscopy (XAS) has been employed in order to examine the electronic and local structure of transition metal ions in the electrode materials for use in Li rechargeable batteries [1–5]. The absorption peak features of the transition metal K-edge XAS provide useful structural information such as the oxidation state of chemical species, their site symmetries, and covalent bond strength. Soft XAS (200–1000 eV), using synchrotron radiation, has been applied to investigate the electronic structure of specific ions in the electrode materials for Li rechargeable batteries, especially, low *z* elements like oxygen and fluorine that cannot be directly investigated by hard XAS (above 1000 eV) [6–10]. Soft

XAS spectra can be obtained in both the electron yield (EY) and fluorescence yield (FY) modes. The electron yield mode is surface sensitive, with the total electron yield (TEY) mode probing a depth of ~ 100 Å and the partial electron yield (PEY) probing a depth of ~ 50 Å. The fluorescence yield mode probes the bulk to a depth of more than ~ 2000 Å [11,12]. Unfortunately, most of the soft XAS results reported in the literature on lithium battery materials have been obtained by the electron yield method only [6–8]. Although soft XAS, using electron yield method, gives useful information about the electronic structure of the transition metal and oxygen ions, the results are limited only to probing the surface or near surface, which may not reflect what is happening in the bulk. In contrast, our previous soft XAS study using both the FY and PEY modes clearly showed that the surface of nickel-based compounds has a different electronic structure from the bulk [10].

A great deal of research efforts have been carried out aimed at the development of alternative non-toxic cathode materials with higher capacity, lower cost, and increased safety characteristics, to replace LiCoO_2 . Among the new cathode materials developed, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ has demonstrated some promising

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advantages in high power applications such as power tools and hybrid electric vehicles (HEV). The significant improvement in safety characteristics and cycleability in large size lithium batteries over the LiNiO_2 cathode material was reported by Broussely [13] at SAFT and other researchers. This material was also thoroughly studied as one of the benchmark materials (assigned as Gen 2 material) by researchers from several US national labs under the Advanced Technology Development Program (ATD) supported by the FreedomCAR & Vehicle Technologies Program of US Department of Energy.

In this work, the electronic structure in the electrochemically Li-ion deintercalated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode system were studied using the combination of hard and soft XAS techniques, together with the simultaneous data collection with both PEY and FY modes in soft XAS. By doing this, a more complete picture of the electronic structure, both at the surface and in the bulk, was obtained for the electrochemically deintercalated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.

2. Experimental

The cathodes used in this study were supplied by Quallion Corp. (Sylmar, CA). The cathode coated on aluminum foil consists of 84% $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (Fuji Chemical), 4% carbon black (Chevron), 4% SFG-6 (Timical), and 8% PVdF (Kureha). The cathodes were incorporated into cells with a Li foil anode, a Celgard separator, and a 1 M LiPF_6 electrolyte in a 1:1 EC:DMC solvent (LP 30 from EM Industries, Inc.). The cell was assembled in an argon-filled glove box. The detailed design of the spectroelectrochemical cell used in the *in situ* XAS measurement has been described elsewhere [14]. Hard XAS measurements were performed in the transmission mode at beamline X18B of the National Synchrotron Light Source (NSLS) using a Si(1 1 1) channel cut monochromator. The monochromator was detuned to 35–45% of its original intensity to eliminate the high order harmonics. Energy calibration was carried out using the first inflection point of the spectrum of Ni metal foil as a reference (Ni K-edge = 8333 eV). Reference spectra were simultaneously collected for each *in situ* spectrum using Ni metal foil.

Soft-XAS measurements were performed at Beam Line U7A of NSLS. The beam size was 1 mm in diameter. The estimated incident X-ray energy resolution was ~ 0.2 eV. Data were obtained both in PEY and FY modes. The PEY mode collects more of the auger electrons and less of the inelastic secondary electrons than the TEY mode. Therefore, the surface sensitivity of PEY is higher than TEY. The PEY data were recorded using a channel electron multiplier while the FY data were recorded using a windowless energy dispersive Si (Li) detector.

3. Results and discussion

Co and Ni K-edges XAS experiments were conducted to monitor the evolution of the electronic structure of each transition metal atom under *in situ* conditions. The voltage profiles of the cell during the first charge for experiments performed at the Co and Ni K-edges are shown in Fig. 1. The *in situ* cell was charged with a constant current rate of $C/10$, calculated based

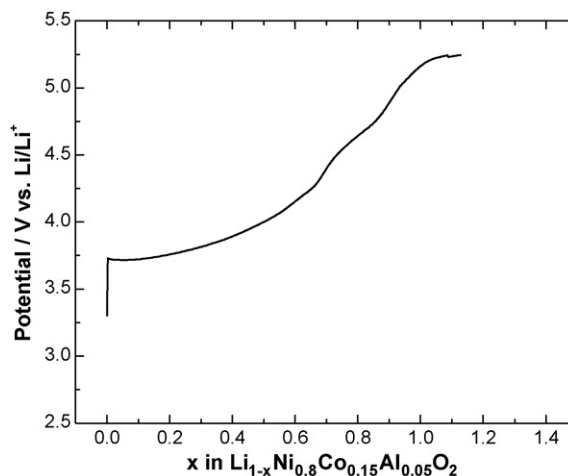


Fig. 1. First charge curve of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode for *in situ* metal K-edge XAS experiments.

on the theoretical capacity. The specific capacity was calculated from the elapsed time, current, and mass of the active material in the cathode, by assuming that all the current passed was due to lithium intercalation/deintercalation reaction.

Fig. 2 shows some selected normalized Co and Ni K-edge XANES spectra of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode during charge. As the Li ion is deintercalated, the Co K-edge XANES spectrum exhibits some changes in the shape of the edge due to changes in the Co local environment but does not show a rigid shift to higher energy values. The energy position and the shape of these spectra are very similar to those of the $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode material, in which cobalt remains as Co^{3+} throughout charge and discharge [15]. This provides clear evidence that most of Co ions in pristine $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ are in the Co^{3+} oxidation state and are not oxidized as a result of the Li deintercalation. Unlike the Co K-edge XANES spectra, the Ni K-edge XANES spectra shift to higher energy regions during charge. The entire edge shift to the higher energies indicates that the average oxidation state of nickel ions increases during charge.

Fig. 3 shows Fourier transform magnitudes of the Co and Ni K-edge EXAFS spectra during charge. The first coordination shell consists of oxygen, while the peak feature due to the second coordination shell is dominated by the transition metal ions. The most significant change during charge is observed in the first coordination shell around central Ni atoms (Fig. 3(b)). The dramatic changes of the first coordination peaks during charge indicate that the charge compensation mainly occurs at the Ni sites and results in a significant decrease in the average Ni–O bond length. The large changes seen for the first Ni–O shell are similar to those observed for the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ systems in our previous study [4]. In that work, by detailed quantitative analysis of the EXAFS data we had shown that the large changes seen in the first coordination shell around Ni is caused by the oxidation of Ni^{3+} ions to Ni^{4+} ions.

Because of the electric dipole-allowed $2p \rightarrow 3d$ transition, the absorption peaks for the metal $L_{II,III}$ -edge XAS are relatively intense and are very sensitive to the empty

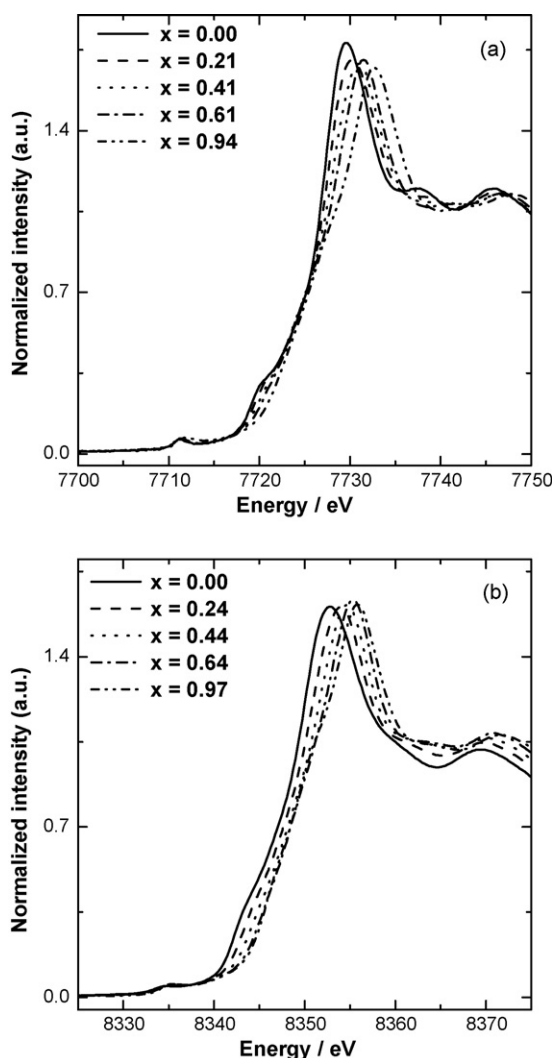


Fig. 2. Normalized *in situ* (a) Co K-edge and (b) Ni K-edge XANES spectra of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode during first charge.

d orbitals. The electronic structure of the Co and Ni ions in $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ can be investigated qualitatively through peak features in the metal L-edge XAS spectra. There are two main peaks at the L_{III} and L_{II} edges which are due to the respective electronic transitions from the metal $2p_{3/2}$ and $2p_{1/2}$ core levels, which are split by the spin-orbit interaction of the metal $2p$ core level, to an unoccupied $3d$ level. For the Co^{3+} , and Ni^{3+} states in pristine $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, the corresponding initial states in pristine $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ are $\text{Ni } 2p^6 3d^7 (t_{2g}^6 e_g^1)$ and $\text{Co } 2p^6 3d^6 (t_{2g}^6 e_g^0)$ state, and the corresponding electronic final states represent $\text{Ni } 2p^5 3d^8 (t_{2g}^6 e_g^2)$ and $\text{Co } 2p^5 3d^7 (t_{2g}^6 e_g^1)$. The FY data is distorted by self-absorption effects, which will diminish the intensity of peaks/features with high intrinsic intensity. However, the positions of the peaks are not significantly changed. Furthermore, the amount of self-absorption will be largely independent of Li-content.

Therefore, a comparison of FY data obtained at various states of charge can be performed. Fig. 4 shows the Co $L_{\text{II,III}}$ -edge XAS $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, at different x values, in both the PEY and FY modes. There is no substantial difference between

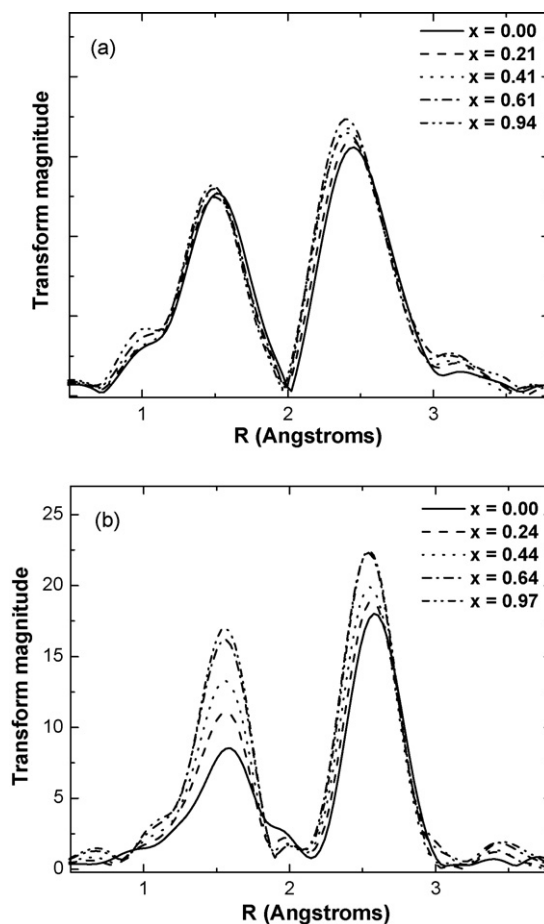


Fig. 3. k^3 -weighted Fourier transform magnitudes of the (a) Co and (b) Ni K-edge EXAFS spectra of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode during first charge.

Co $L_{\text{II,III}}$ -edge XAS spectra obtained using the PEY and FY methods. This indicates that the electronic structure and local geometry around Co ions are the same at surface and in the bulk for pristine $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. As shown in Fig. 4, as Li ions are deintercalated, the Co $2p$ spectra do not show any changes in shape or energy position in both the PEY and FY data, indicating that the Co ions in the surface and in the bulk remain mostly unchanged in the Co^{3+} state during charge. In contrast, Co K-edge XAS results in Fig. 2 did show notable changes in the shape of edge structure during charge due to changes in the Co local environment. Although the entire edge does not show a rigid shift, suggesting that the Co oxidation state remains unchanged, some ambiguity and questions could be raised because of changes in the edge shape. However, the identical Co $2p$ spectra at different charge states, shown in Fig. 4 provide unambiguous evidence to support the statement that the Co ions in this compound remain unchanged in Co^{3+} state during charge.

The Ni $L_{\text{II,III}}$ -edge X-ray absorption spectra of $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ system at different x values, obtained from PEY and FY methods, are shown in Fig. 5. These spectra correspond to Ni $2p \rightarrow \text{Ni } 3d$ transitions, split by the spin-orbit interaction of the Ni $2p$ core level. Based on the previous Ni L-edge XAS experimental results and calculations [6], Ni L-

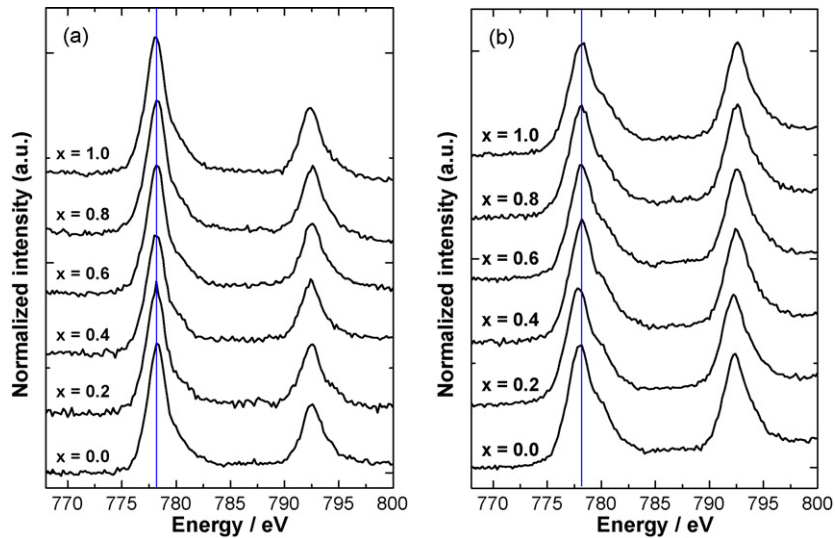


Fig. 4. Normalized Co L_{II,III}-edge XAS spectra of Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O₂ electrode at different x values using (a) PEY method and (b) FY method.

edge XAS of pristine LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ obtained in PEY mode clearly shows that substantial amount of Ni ions at the surface of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ powders exist as Ni²⁺. As Li ions are deintercalated, Ni²⁺ ions at the surface are oxidized to higher oxidation state. In contrast, Ni L-edge XAS of pristine LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ in FY mode shows most of Ni ions in the bulk are in the form of Ni³⁺. The Ni ions in the bulk oxidized from Ni³⁺ to Ni⁴⁺ during Li deintercalation. A similar phenomenon about the difference between the surface and the bulk was seen in our previous soft XAS study on nickel-based cathode materials [10,15]. This difference in electronic structures during charge between the surface and bulk is a unique feature of the nickel-based cathode materials. Recent studies of LiNi_{0.8}Co_{0.2}O₂ reported by Abraham et al. also provided strong support for this statement [16]. In that work, by using a combination of high-resolution transmission electron microscopy (HRTEM) and nano-probe electron energy

loss spectroscopy (EELS), the authors showed that the surface structure of LiNi_{0.8}Co_{0.2}O₂ is distinctly different from the bulk. The modified surface layer in the cathode materials is believed to be a significant contributor to the cathode impedance rise observed during the electrochemical cycling process.

The O K-edge XAS spectra of electrochemically Li-ion deintercalated Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O₂ system is shown in Fig. 6. The O K-edge XAS spectrum collected by the PEY mode plotted in Fig. 6(a) is dramatically different from that collected by the FY mode shown in Fig. 6(b). The most significant differences are in the pre-edge peak features. Pre-edge peaks below ~534 eV in these spectra correspond to the transition of oxygen 1s electron to the hybridized state of the metal 3d and oxygen 2p orbitals, whereas the broad higher peaks above ~534 eV correspond to the transitions to hybridized states of oxygen 2p and metal 4sp orbitals. O K-edge XAS spectra of Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O₂ collected by the FY mode in Fig. 6(b) show a intense absorp-

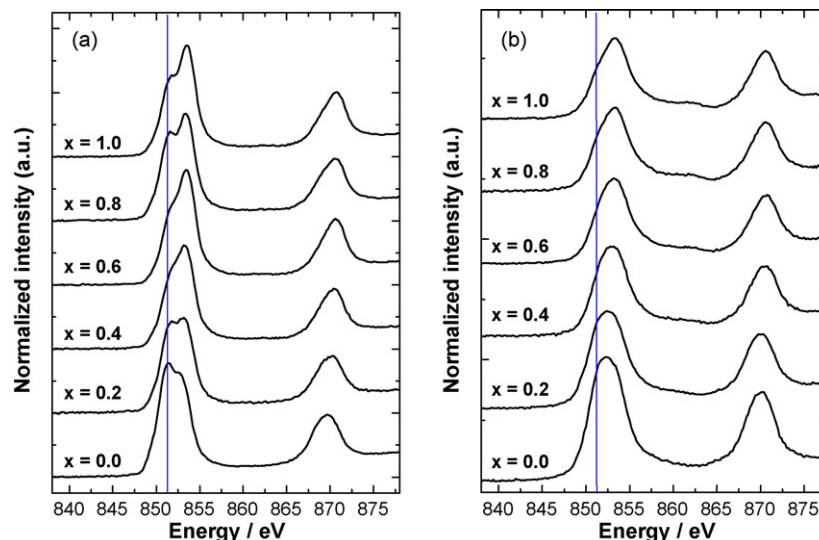


Fig. 5. Normalized Ni L_{II,III}-edge XAS spectra of Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O₂ electrode at different x values using (a) PEY method and (b) FY method.

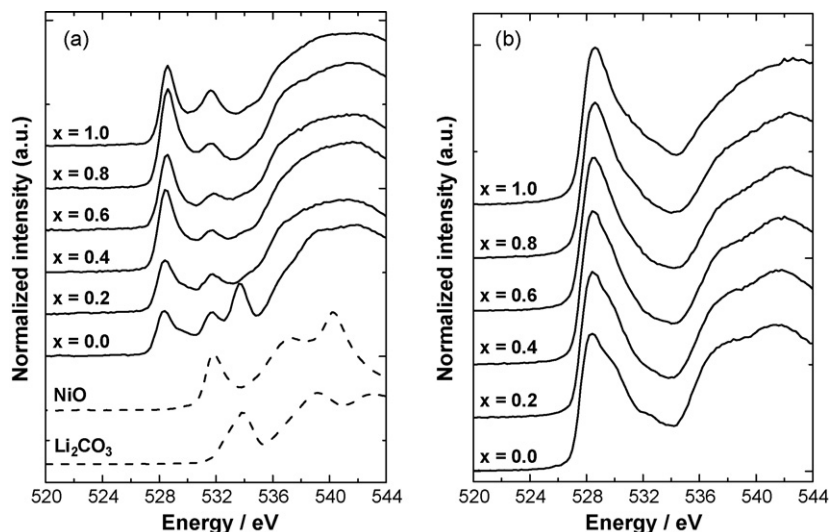


Fig. 6. Normalized O K-edge XAS spectra of $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode at different x values using (a) PEY method and (b) FY method.

tion peak at ~ 528.5 eV which corresponds to a transition to the hybridized state of $\text{Ni}^{3+,4+}$ 3d–O 2p orbitals. In contrast, in the O K-edge XAS spectra of $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ collected by the PEY mode in Fig. 6(a), an additional pre-edge peak at ~ 531.8 eV is observed, which corresponds to the hybridized state of Ni^{2+} 3d–O 2p orbitals. The assignment of Ni^{2+} state can be clearly verified by the reference spectrum of NiO plotted in dash line. The observation of this transition tells us that the substantial amount of Ni ions at the surface of $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ is in the form of Ni^{2+} . The reference spectrum of Li_2CO_3 is also plotted in dash line as marked in Fig. 6(a). Another pre-edge peak at ~ 533.8 eV could be due to the existence of Li_2CO_3 phase on the surface. Li_2CO_3 is a common contamination formed at the surface of cathode materials and gradually dissolved in the electrolyte during Li deintercalation. The effects of Li_2CO_3 are basically disappeared in the early stage of charge. As shown in Fig. 6(b), as the degree of electrochemical deintercalation increases (the x value increases), the integrated peak intensity at ~ 528.5 eV increases slightly in O K-edge XAS spectra of $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ in the FY mode. Compared to our earlier O K-edge absorption study of $\text{Li}_{1-x}\text{CoO}_2$ system [8,10], it is clear that changes in O K-edge XAS of $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ system during the charge process are very small. It is notable that this behavior is dramatically different from that of the electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{CoO}_2$ system where oxygen site makes large contribution for the charge compensation for the Li-ion deintercalation process, which is reflected in much larger changes in the integrated intensity of the corresponding transition. This results support our previous O K-edge XAS works suggesting the important role of cobalt atoms on the oxygen contribution to the charge compensation during Li-ion deintercalation.

4. Conclusion

The electronic structure for the electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ materials has been

investigated using X-ray absorption spectroscopy at O K-edge and metal $\text{L}_{\text{II,III}}$ -edge in the soft X-ray region, in combination with metal K-edge XAS spectra in hard X-ray region. From the observation of metal K-edge XAS results, we can conclude that the major charge compensation at the metal site during charge is achieved by the oxidation of nickel ions, while the cobalt ions remain mostly unchanged in the Co^{3+} state. Ni $\text{L}_{\text{II,III}}$ -edge and O K-edge XAS results of $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode, collected in both the FY and PEY modes, show that substantial amount of Ni ions at the surface of $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders exist as Ni^{2+} , whereas most of Ni ions in the bulk are in the form of Ni^{3+} . Therefore, if the PEY mode, which is a surface-sensitive technique, is used alone, the interpretation of the results is limited to the surface structures only. In order to get the full picture of both the surface and the bulk, the FY mode and PEY mode should be used simultaneously.

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