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Electronic states in oxidized Na_xCoO_2 as revealed by X-ray absorption spectroscopy coupled with *ab initio* calculation

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HIGHLIGHTS

- A combined study of the O K-edge XAS and *ab initio* calculation are performed on the electronic state of Na_xCoO_2.
- The calculation qualitatively reproduces the variation of the O K-edge spectra between O3-$Na_{0.91}CoO_2$ and P2-$Na_{0.66}CoO_2$.
- The study revealed that the electrons are partially removed from the O 2*p* state with oxidization of the Na_xCoO_2 (CoO_2 sheet).

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ABSTRACT

Layered cobalt oxides are promising cathode materials for sodium ion secondary batteries (SIBs). By combined study of the X-ray absorption spectroscopy (XAS) around the O K-edge and *ab initio* calculation, we investigated the electronic state of the Na_xCoO_2 with different oxidization state, *i.e*, in O3-$Na_{0.91}CoO_2$ ($CoO_2^{-0.91}$) and P2-$Na_{0.66}CoO_2$ ($CoO_2^{-0.66}$). The O K-edge spectra in the pre-edge (529–536 eV) region shows significant change with oxidization of Na_xCoO_2. In O3-$Na_{0.91}CoO_2$, the spectra shows an intense band (B band) at 531 eV. In P2-$Na_{0.66}CoO_2$, the spectral weight of the B band increases and a new band (A band) appears at 530 eV. These spectral changes are qualitatively reproduced by the calculated partial density of states (pDOSs) of O3-$NaCoO_2$ and P2-$Na_{1/2}CoO_2$. These results indicate that the electrons are partially removed from the O 2*p* state with oxidization of Na_xCoO_2.

1. Introduction

Sodium ion secondary batteries (SIBs) have attracted much attention as promising candidates for next-generation batteries beyond lithium ion secondary batteries [1–6]. Due to the abundancy and low cost of sodium, SIBs are applicable to large-scale electrical energy storage systems and electric vehicles. Among several types of cathode materials for SIBs, layered cobalt oxides with O3- and P2-type structures show promising electrochemical properties [7,8]. Both the O3- and P2-type structures consist of the CoO_2 sheet of edge-sharing CoO_6 octahedra. In the charge process, Na^+ is extracted between the neighboring CoO_2 sheets and electrons are removed from the CoO_2 sheet. Up to now, it is considered that electrons are removed from Co in the CoO_2 sheet. However, several groups proposed that the electrons are partly removed from the O 2*p* state [9–11].

XAS is a powerful tool to investigate the electronic states of the battery materials. Especially, soft XAS provides element-specific information sensitive to valence states of 3*d* transition metals (Ms) and ligand oxygens, because the energy range covers dipole-allowed transitions at the M L-edge and O K-edge. For O K-edge XAS, the *ab initio* calculation is considered to be a good approach because the spectra is nearly free from the multiplet and charge-transfer effects [12]. Recently, *in situ/operando* soft X-ray spectroscopy is becoming a powerful tool to investigate the variation of the electronic state of the battery materials during electrochemical reactions [13,14]. There, however, exist few reports [15,16] on the battery materials, since the *in situ/operando* soft X-ray spectroscopy needs a vacuum compatible batteries cell. On the other hand, the number of *ex situ* O K-edge XAS researches on binary or ternary transition metal layered oxides have been increasing [9–11,17,18].

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In this paper, variation of the electronic state of the Na_xCoO_2 (CoO_2 sheet) with oxidization was investigated by combined study of the O K-edge XAS and *ab initio* calculation. The O K-edge spectra in the pre-edge (529–536 eV) region show significant change between O3-$Na_{0.91}CoO_2$ ($CoO_2{}^{-0.91}$) and P2-$Na_{0.66}CoO_2$ ($CoO_2{}^{-0.66}$). The spectral changes are qualitatively reproduced by the pDOSs of O3-$NaCoO_2$ and P2-$Na_{1/2}CoO_2$. These results indicate that the electrons are partially removed from the O 2*p* state with oxidization of the Na_xCoO_2.

2. Experimental and calculation details

2.1. Sample preparation

O3- and P2-type Na_xCoO_2 were prepared by solid state reaction. In the O3-type compound, Na_2O_2 and Co_3O_4 were mixed in a 1.25: 1 atomic ratio and calcined at 823 K for 16 h in O_2. Then, the product was finely ground, and again calcined in the same condition. In the P2-type compound, Na_2CO_3 and Co_3O_4 were mixed in a 0.7:1 atomic ratio and calcined at 1073 K for 12 h in air. The Na concentrations (*x*) were determined by the Rietveld analyses of the synchrotron-radiation X-ray powder diffraction pattern.

2.2. X-ray diffraction and Rietveld analysis

Synchrotron-radiation X-ray powder diffraction (XRD) measurements were performed at the BL-8A beamline of the Photon Factory, KEK. The samples were finely ground and placed in ϕ0.3 mm glass capillaries. The capillaries were sealed and mounted on the Debye-Scherrer camera. The powder diffraction patterns were detected with an imaging plate. The exposure time was 5 min. The wavelength (= 0.68903 Å) of the X-ray was calibrated by the lattice constant of standard CeO_2 powders. The XRD patterns of the O3-type compound was analyzed by the Rietveld method with a trigonal model ($R\bar{3}m$; $Z = 3$, hexagonal setting). The XRD patterns of the P2-type compound was analyzed by the Rietveld method with a hexagonal model ($P6_3/mmc$; $Z = 2$). X-ray diffraction patterns and Rietveld refinement profiles are shown in Figure S1 and S2 in the Supplementary Materials. In both compounds, no traces of impurities nor secondary phases were observed. The obtained structural parameters are listed in Tables 1 and 2.

2.3. X-ray absorption spectroscopy

O K-edge and Co L-edge XAS recorded in the total electron yield (TEY) mode were measured at soft X-ray beam line BL12 of the SAGA Light Source, Japan. The spectra were obtained at room temperature in a vacuum of 2×10^{-8} Torr. The TEY-XAS spectra were obtained by dividing the sample drain current by the gold mesh current of the incident X-ray intensity. The energy resolution ($E/\Delta E$) was over 2000. The O K-edge XAS recorded in the partial fluorescence yield (PFY) mode were conducted at TLS BL08B1 beamline at the NSRRC in Taiwan. The PFY-XAS spectra were obtained using a silicon drift detector (SDD, Amptek) at room temperature. The energy resolution was over 2000.

Table 1

Structural parameters of O3-$Na_{0.91}CoO_2$ at 300 K refined by the Rietveld method ($R\bar{3}m$, $Z = 3$). *g* and *B* are occupancy and atomic displacement parameter, respectively. Lattice constants are $a = 2.88795(5)$ Å, $c = 15.59923(32)$ Å. Reliable parameters are $R_{wp} = 5.15\%$, $R_I = 5.26\%$, and $S = 5.54$.

atom	site	*g*	*x*	*y*	*z*	*B*
Na	3a	0.905(4)	0	0	0	0.09(4)
Co	3b	1	0	0	0.5	0.17(1)
O	6c	1	0	0	0.2281(1)	0.37(4)

Table 2

Structural parameters of P2-$Na_{0.66}CoO_2$ at 300K refined by the Rietveld method ($P6_3/mmc$; $Z = 2$). *g* and *B* are occupancy and atomic displacement parameter, respectively. Lattice constants are $a = 2.82842(11)$ Å, $c = 10.94605(65)$ Å. Reliable parameters are $R_{wp} = 5.90\%$, $R_I = 7.46\%$, and $S = 6.12$.

atom	site	*g*	*x*	*y*	*z*	*B*
Na1	2b	0.246(7)	0	0	0.25	3.88(37)
Na2	2d	0.418(9)	1/3	2/3	0.75	3.88
Co	2a	1	0	0	0	0.30(3)
O	4f	1	1/3	2/3	0.0840(4)	0.66(9)

2.4. First principles calculation

The pDOSs were calculated for O3-$NaCoO_2$, P2-$NaCoO_2$, and P2-$Na_{1/2}CoO_2$ using density functional theory with the plane-wave self-consistent field (PWscf) package [19]. A plane wave basis set with a cutoff energy of 612 eV was chosen, and the projector-augmented-wave potentials were used. We adopted the exchange-correlation functional of Perdew-Burke-Ernzerhof type within generalized gradient approximation. Local spin density approximation was used to take account of electron spin. In the calculation of O3-$NaCoO_2$, we used the lattice constant (*a* and *c*) and atomic coordinate (*z*) of O3-$Na_{0.91}CoO_2$ (Table 1) without structural optimization. In the calculation of P2-$NaCoO_2$, we used the lattice constant (*a* and *c*) and atomic coordinate (*z*) of P2-$Na_{0.66}CoO_2$ (Table 2) without structural optimization. The Na ions were placed in the Na(2) sites because the total energy is lower by 117 meV/FU than that for the Na(1) site. In the calculation of P2-$Na_{1/2}CoO_2$, 1 × 2 × 1 supercell was built based on the hexagonal unit cell. The Na ions were alternately placed in the Na(2) sites, as shown in the inset of Fig. 3(b). We used the lattice constant (*a* and *c*) and atomic coordinate (*z*) of P2-$Na_{0.66}CoO_2$ (Table 2) without structural optimization. Brillouin-zone sampling for the scf (DOS) calculations was made using the Monkhorst-Pack method with 12 × 12 × 12 (36 × 36 × 36) k points for P2-$NaCoO_2$, 12× 12 × 8 (36 × 36 × 24) for O3-$NaCoO_2$ and 12 × 6 × 12 (36 × 18 × 36) for P2-$Na_{1/2}CoO_2$. The calculation shows good convergence with respect to the cutoff energy and k point.

3. Results and discussion

3.1. Co L-edge XAS spectra

Fig. 1(a) shows Co L-edge spectra of O3-$Na_{0.91}CoO_2$ and P2-$Na_{0.66}CoO_2$. Two intense absorptions, L_2 and L_3, are observed. L_2 (L_3) is ascribed to the dipole-allowed transition from the Co $2p_{1/2}$ (Co $2p_{3/2}$) to Co 3*d* orbitals. Spectral feature of P2-$Na_{0.66}CoO_2$ is almost the same as that of O3-$Na_{0.91}CoO_{2,}$ except for slight blue-shift of the peak energies. The energy shift is consistent with Co L-edge XAS of Li_xCoO_2 reported by Mizokawa et al. [20]. As the concentration of Li decreases, the $2p_{3/2}$ (L_3) peak energy shifts to higher photon energy (blue shift). Therefore, the blue-shit suggests increases in the Co valence of the Na_xCoO_2.

3.2. O K-edge XAS spectra

Fig. 1(b) shows O K-edge spectra of O3-$Na_{0.91}CoO_2$ and P2-$Na_{0.66}CoO_2$. The spectra were normalized to have the same total area (526–550 eV). For the convenience of explanation, we divide the spectra into the pre-edge (529–536 eV) and main (> 536 eV) regions. In the pre-edge region (529–536 eV), an intense peak (labeled as peak B) is observed around 531 eV in both the compounds. In P2-$Na_{0.66}CoO_2$, an additional peak (labeled as peak A) and its shoulder peak A′ appears around 530 eV and 529 eV, respectively. The pre-edge peak profiles are similar to that of Li_xCoO_2 [20]. The peaks A′, A and B are ascribed to the transitions from the O 1*s* to O 2*p* orbital. The O 2*p* state is strongly hybridized with the Co 3*d* state. Several studies on $Na_{0.5}CoO_2$ [21] and $Na_xCo_{2/3}Mn_{1/3}O_2$ [10] have reported that O K-edge XAS spectra show