

Changes in electronic structure by Li ion deintercalation in LiCoO_2 from cobalt L -edge and oxygen K -edge XANES

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Cobalt L -edge and oxygen K -edge X-ray Absorption Near Edge Structure (XANES) investigated change in electronic structure by electrochemical lithium ion de-intercalation in LiCoO_2 . The Co L -edge XANES of $\text{Li}_{1-x}\text{CoO}_2$ did not show any chemical shift even at high x value. The oxygen K -edge XANES of $\text{Li}_{1-x}\text{CoO}_2$ indicated that the holes compensating the lithium ion de-intercalation are located primarily in the oxygen 2p states rather than in the Co 3d states.

Keywords: XANES, electronic structure, lithium battery.

1. Introduction

Lithium cobalt oxide, LiCoO_2 , is used as the cathode active material in commercially available 4V-type lithium secondary battery because of its high theoretical energy density and good cycle performance (Mizushima *et al.*, 1980; Ozawa, 1994; Thomas *et al.*, 1985). In the lithium secondary batteries, which are called 'Rocking-chair' batteries, graphite is used as the negative electrode. During the charge and discharge process, lithium ions are transferred from one electrode to the other electrode through an intercalation and/or de-intercalation process. It is important to clarify the change of electronic structure during the charge and discharge process in order to understand the electrochemical properties. Recently first principle molecular orbital calculation studies of the electronic structure of the $\text{Li}_{1-x}\text{CoO}_2$ have been reported (Koyama *et al.*, 1999; Aydiol *et al.*, 1997; van der Ven *et al.*, 1998). These calculation results indicate that the lithium ion deintercalation increases the covalent interaction between cobalt and oxygen and that the oxidation associated with the deintercalation mainly takes place on oxygen. However experimental information about the electronic structure change during the lithium ion deintercalation is insufficient. To our knowledge, X-ray Absorption Near Edge Structure (XANES) measurement for LiCoO_2 (de Groot *et al.*, 1993; Montoro *et al.*, 1999) and chemically de-intercalated Li_xCoO_2 (Montoro *et al.*, 2000) has been reported, but the detailed electronic structure change during electrochemically intercalation and/or de-intercalation process has not yet been reported.

In this study, a measurement of cobalt L_{23} -edge and oxygen K -edge XANES was used to determine the electronic structure changes of LiCoO_2 during the electrochemical lithium ion deintercalation.

2. Experimental

LiCoO_2 powder was prepared by conventional solid state reaction starting with lithium hydroxide (Wako Chemical Co. Inc., 99.9%) and cobalt hydroxide (Wako Chemical Co. Inc., 99.9%).

A mixture of $\text{Li}(\text{OH})$ and $\text{Co}(\text{OH})_2$ in a mole ratio of 1:1 was heated at 700°C for 13 h in air atmosphere. The crystal structure of the product was determined by XRD using Mo-K α radiation. $\text{Li}_{1-x}\text{CoO}_2$ oxides were prepared by electrochemical lithium de-intercalation. A mixture of 82.5 wt% LiCoO_2 , 15 wt% acetylene black, and 2.5 wt% polytetrafluoropropylene binder was used as working electrode. Lithium metal was used as counter and reference electrode. The electrolyte was 1M lithium perchlorate in propylene carbonate solution.

Co L_{23} -edge XANES and oxygen K -edge XANES were measured on BL-8B1 beam line at UVSOR (Okazaki, Japan) with ring energy of 750 MeV in a mode of total electron yield at room temperature, respectively.

3. Results and Discussion

The XRD pattern of LiCoO_2 was indexed to a rhombohedral lattice and is in good agreement of that of LiCoO_2 ($R\bar{3}m$). Figure 1 shows the electrode potential change during the electrochemical extraction of lithium from LiCoO_2 in the region from $x = 0$ to $x = 0.8$ of $\text{Li}_{1-x}\text{CoO}_2$. The electrode potential change is in good agreement with the open circuit voltage curve of $\text{Li}_{1-x}\text{CoO}_2$ reported by Mizushima *et al.* (Mizushima *et al.*, 1980).

Figure 2 shows the Co L -edge XANES of $\text{Li}_{1-x}\text{CoO}_2$ at various x values together with that of LaCoO_3 as model compounds of Co^{3+} oxidation state. The Co L -edge XANES shows two strong absorption features due to the spin-orbit splitting of the Co 2p core hole (Abbate *et al.*, 1993). The absorption about 779 eV is $2p_{3/2}$ (L_3) edge and that about 794 eV is $2p_{1/2}$ (L_2) edge. The Co L -edge XANES of LiCoO_2 is in good agreement that reported by Montoro *et al.* (Montoro *et al.*, 1999). The shape of the Co L -edge XANES of LiCoO_2 and LaCoO_3 close similarity of low-spin Co^{3+} (Montoro *et al.*, 1999; Abbate *et al.*, 1993). The Co L -edge spectra of $\text{Li}_{1-x}\text{CoO}_2$ ($x=0.2, 0.4, 0.5, 0.6, 0.8, 1.0$) do not exhibit chemical shift and the changes of the shape are small. The result that the XANES did not show any chemical shift indicates the Co ion in the $\text{Li}_{1-x}\text{CoO}_2$ is still trivalent Co^{3+} cations even at low x value of 0.2. This result is in good agreement with that of chemically de-intercalated sample (Montoro *et al.*, 1999).

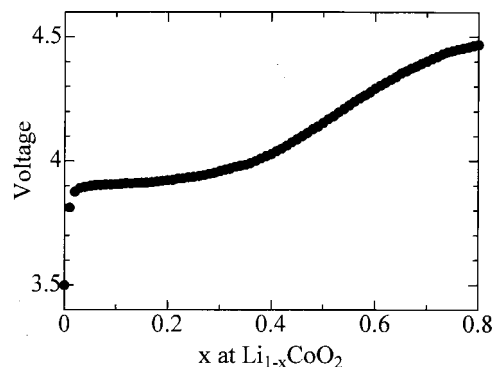


Fig. 1.

Electrode potential change of the $\text{Li}_{1-x}\text{CoO}_2$ electrode during the charge process.

Figure 3 shows the oxygen K -edge XANES of $\text{Li}_{1-x}\text{CoO}_2$ at various x values. A peak at about 528-530 eV is attributed to transition to the unoccupied band derived from the mixing of the Co 3d states with oxygen 2p states. The broad structure about 535-550 eV is attributed to band of Co 4s and/or 4p character. The peak is broad, so that the peak is difficult to divide two characters. Figure 4 shows a magnified part of Figure 3 between 525 and 535 eV. The peak at about 527 eV increases with decreasing lithium content. This result shows that oxidation also

takes place on oxygen 2p orbital and the ground state of $\text{Li}_{1-x}\text{CoO}_2$ is $\text{Co}^{3+}\underline{\text{L}}$, where $\underline{\text{L}}$ represents a ligand hole state. This phenomenon indicates that the oxidation by anode reaction of lithium deintercalation mainly takes place by using oxygen 2p orbital but Co 3d orbital. This is in good agreement with the result of First-Principles calculation for $\text{Li}_{1-x}\text{CoO}_2$ oxides (Koyama et al., 1999).

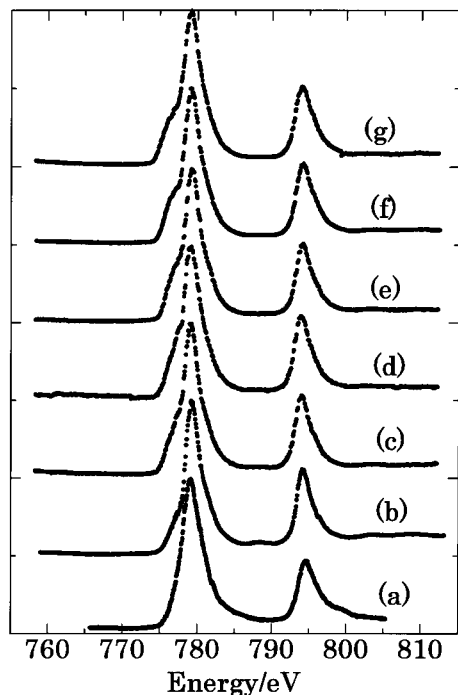


Fig. 2. Co 2p absorption spectra of LaCoO_3 (a) and $\text{Li}_{1-x}\text{CoO}_2$ (b-g). (b) 1.0, (c) 0.8, (d) 0.6, (e) 0.5, (f) 0.4, (g) 0.2

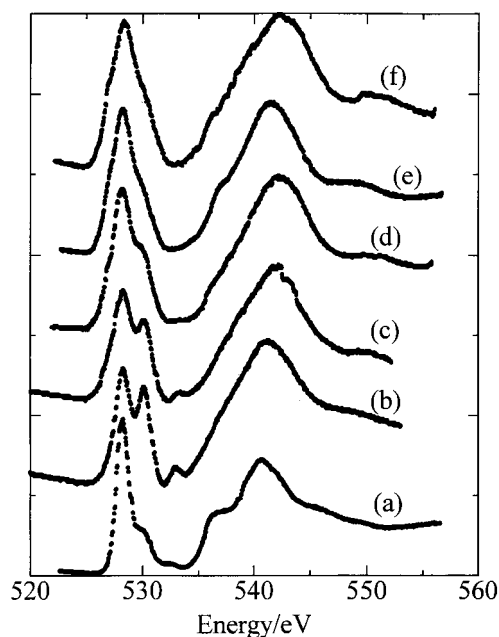


Fig. 3. O 1s absorption spectra of $\text{Li}_{1-x}\text{CoO}_2$. (a) 1.0, (b) 0.8, (c) 0.6, (d) 0.5, (e) 0.4, (f) 0.2

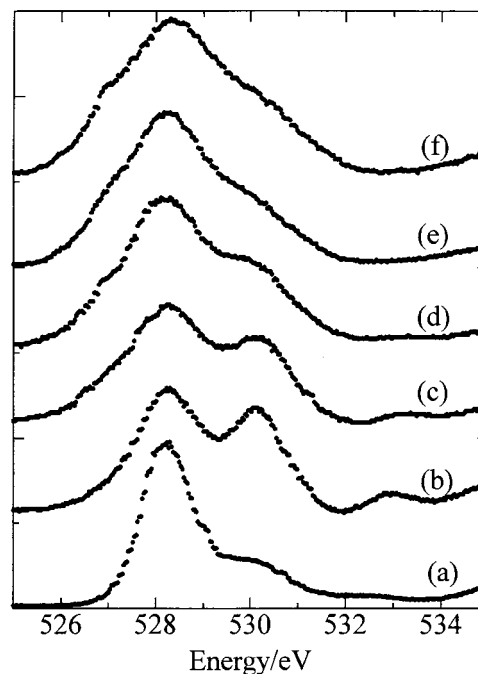


Fig. 4. O 1s absorption spectra of $\text{Li}_{1-x}\text{CoO}_2$ between 525 and 535 eV. (a) 1.0, (b) 0.8, (c) 0.6, (d) 0.5, (e) 0.4, (f) 0.2

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