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Changes in Electronic Structure between Cobalt and Oxide Ions of Lithium Cobalt Phosphate as 4.8-V Positive Electrode Material

Masanobu Nakayama,[†] Satoshi Goto,[†]
Yoshiharu Uchimoto,[†] Masataka Wakihara,*,[†] and
Yoshinori Kitajima[‡]

Department of Applied Chemistry,
Tokyo Institute of Technology, Ookayama, Meguro-ku,
Tokyo 152-8552, Japan, and Photon Factory,
Institute of Materials Structure Science,
High Energy Accelerator Research Organization,
1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

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Rechargeable lithium ion battery is a device that meets certain crucial demands of our modern society, acting as the power source of various portable devices, future usage in electronic vehicles, and so on. The high-energy density, low-cost, long-life, and environmentally friendly electrode materials are urgently requested today. Thus, intensive work has been dedicated to the phosphate system, $LiMPO_4$ (M = Fe, Ni, Co),[1−3] with olivine-related structures as positive electrodes for rechargeable lithium ion batteries since the first report by Padhi et al.[1] This stems from the following: (1) These materials have relatively larger theoretical capacity, ca. 170 mA·h/g, and higher voltage ($LiCoPO_4$), over 4.5 V versus Li^+/Li, than $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ being the most representative. (2) Recent efforts in improving the electrolyte enabled an increase of the potential over 5 V.

These phosphate materials are classified as "polyanion" compounds containing compact tetrahedral structural units PO_4 with strong covalent bonding. As a result, the valence electrons of transition metals tend to be isolated from that of polyanion. Understanding of their unique electronic structure is the key to practical usage for the lithium ion battery. Although the isolated electronic structure of the transition metal would be the reason for the observed high-voltage properties,[1−3,5] it simultaneously leads to low electronic conductivities, causing technical difficulties for the battery construction.[4−7] To elucidate the origin of these electronic properties, the electronic structure of the $Li_{1-x}CoPO_4$ system, which shows the highest voltage, ~4.8 V, among $LiMPO_4$ (M = Fe, Ni, Co) systems has been investigated using X-ray absorption spectroscopy (XAS).[2]

The olivine-type $LiCoPO_4$ was synthesized by solid-state reaction. The stoichiometric reagents of Li_2CO_3, $Co(COO)_2·2H_2O$, and $(NH_4)_2HPO_4$ were used as starting materials. The mixtures were heated at 350 °C for 9 h in air, ground in agate motor, and heated again at 600 °C for 12 h. Electrochemical charge/discharge reaction was carried out in the 3.5−5.1 V range at 0.1 mA cm^{-2} using a three-electrode cell. Li foil (Aldrich) was used

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* Corresponding author. Tel.: +81-3-5734-2145. Fax: +81-3-5734-2146.

[†] Tokyo Institute of Technology.

[‡] High Energy Accelerator Research Organization.

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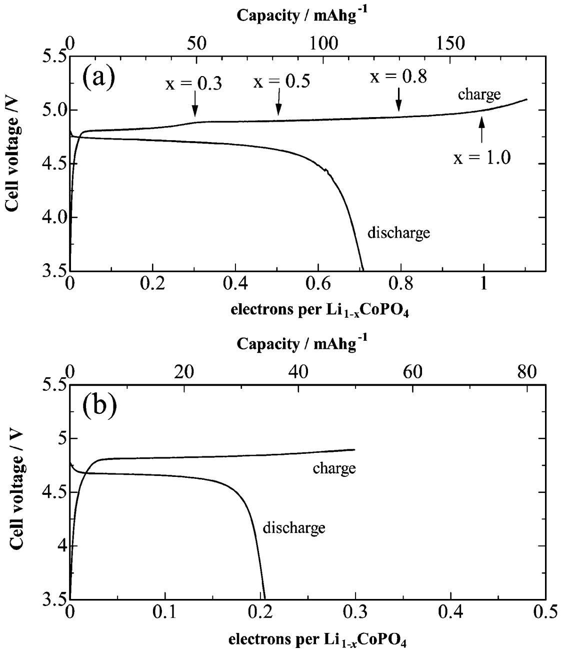

Figure 1. First charge and discharge profiles of $LiCoPO_4$. (a) Cut-off: 3.5−5.1 V. (b) Cut-off: $x = 0.3$ (charge), 3.5 V (discharge).

as the counter and reference electrodes, and 1 M solution of $LiPF_6$ in anhydrous ethylene carbonate, diethyl carbonate (EC:DEC, 1:1 volume ratio) was used as the electrolyte. The working electrode was a mixture of 70 wt % olivine powders, 25 wt % acetylene black current collector, and 5 wt % poly(tetrafluoroethylene) (PTFE) binder. The phase identification was carried out by powder X-ray diffraction technique using Cu Kα radiation (RINT-2500V, Rigaku Co. Ltd), and the observed diffraction patterns showed that the host structure remained in its olivine-type arrangement before and after Li extraction reaction. The Co K-edge and O K-edge XAS measurements were carried out using synchorotron radiation at the beam line BL-7C and BL-11A, Photon Factory (PF), High Energy Accelerator Research Organization in Tsukuba, Japan. The XAS measurement of Co K-edge was performed by transmission method, and Cu metal foil was used for the calibration of the absorption energy scale. The absorbance of O K-edge spectra was determined by the total-electron-yield method, and the absolute energy was calibrated using O K-edge XAS of the NiO powder. For the samples after electrochemical treatment, all installation operations were performed under an Ar or N_2 atomosphere.

Figure 1a shows voltage profiles of the first charge/discharge reaction in the $Li_{1-x}CoPO_4$ system, and it was confirmed that the Li insertion/extraction reaction occurred reversibly up to 120 mA·h/g. The discharge profile with one voltage plateau and its specific capacity (∼120 mA·h/g) was observed and was consistent with the reported one.[2] In addition, two plateaus were observed in the charge process, ∼4.8 V ($0 \leq x \leq \sim 0.3$) and ∼4.9 V ($x > \sim 0.3$), respectively. Similar behavior was reported quite recently.[8] Since the charge/discharge reaction at the first plateau (∼4.8 V) was performed reversibly as shown in Figure 1b, it was confirmed that the reaction at the first plateau could not be ascribed to the irreversible side reaction. One of the conceivable reasons is the fact that the surface structure due to low-temperature synthesis leads to an increase in electrochemical polarization around $x \sim 0.3$. The arrows in Figure 1 indicate the samples used for XAS measurements. Hereinafter the samples for the XAS measurement was referred by the composition x in $Li_{1-x}CoPO_4$ under the assumption that all the passed current via the outer circuit was consumed for the Li extraction reaction. (Note that the total charge capacity (>180 mA·h/g) exceeded the theoretical one (=167 mA·h/g), indicating that the reaction includes side reactions to a certain extent.)

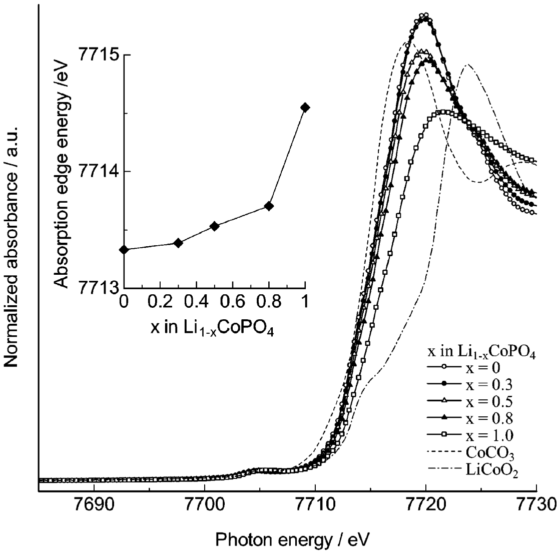

Figure 2. Co K-edge XAS of $Li_{1-x}CoPO_4$ during the lithium extraction process. Inset indicates the variation of the absorption edge energy E_A as a function of composition x.

The Co K-edge XAS for $Li_{1-x}CoPO_4$ is presented in Figure 2, and its threshold energy is also shown in the inset of Figure 2 as a function of composition x. The spectra of $CoCO_3$ and $LiCoO_2$ as the reference materials of Co^{2+} and Co^{3+} are also shown in Figure 2. Since the threshold energy of $LiCoPO_4$ is close to that of the divalent reference, $CoCO_3$, Co ions are almost 2+ in valence state in the $LiCoPO_4$. During the charge reaction, the threshold energy gradually shifted to the higher energy side. The results indicate that the Co ion is oxidized for the charge compensation in the entire region of the charge reaction (from $x = 0.0$ to $x = 1.0$). Similar results were also reported recently for the samples of the end composition (fully charged and discharged ones).[9]

Figure 3 represents the results of O K-edge XAS upon lithium extraction reaction in $Li_{1-x}CoPO_4$. As described in previous papers,[10] O K-edge XAS is very sensitive to the chemical bond in the transition metal ion. The peak position is related to the net formal charge variation of oxygen by the charge donation to the metal ion, and peak intensity corresponds to the number of "d" hole

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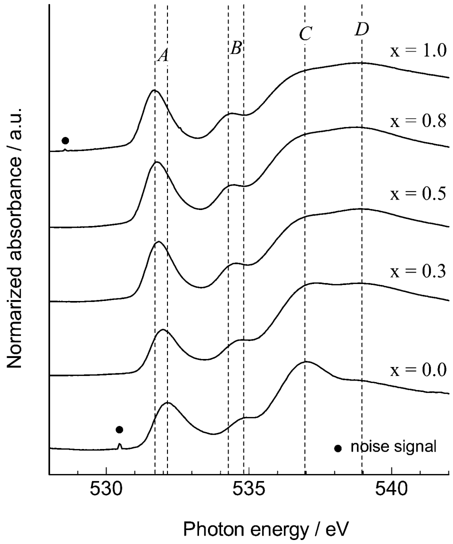

Figure 3. O K-edge XAS of $Li_{1-x}CoPO_4$ during the lithium extraction process.

states in the transition metal d orbital hybridized with the oxygen 2p orbital. The shape of the absorption peak depends on the bond nature of the oxygen−metal bond; for example, sharper peak indicates the localized hybridization and vice versa. Therefore, the spectral change of the O K-edge XAS upon lithium extraction would directly give us information on the electronic structure of the oxygen ion and the bonding nature with the transition metal ions. Four peaks labeled A−D were observed in the energy range of 530−540 eV. Referring to the literature,[10] the sharp XAS peaks on the lower energy side in transition metal oxides are usually ascribed to the hybrid unoccupied orbital between transition metal d and oxygen 2p orbitals. Hence, peak *A* in Figure 2 corresponds to the Co 3d−O 2p hybridized orbital. The broad peaks C and D would be ascribed to the unoccupied O 2p orbital hybridized with the s and/or p character orbital of P and Co ions. (The origin of peak B is uncertain. However, it is speculated that peak B is ascribed to the Co 3d−O 2p hybridized orbital since the spectral variation versus composition x is close to that of peak A, and the split in energy between peak A and peak B is about 3 eV, which is a typical value of the d orbital split in octahedral coordination.) According to the figure, the whole spectral feature preserved itself during lithium insertion, indicating that the crystal structure and local atomic arrangement remains unchanged during electrochemical lithium extraction. In addition, the sharp peak feature in peak A which indicates localized band nature of Co 3d−O 2p also does not vary during Li extraction. At the early stage of lithium extraction ($0 \leq x \leq \sim 0.5$), the peaks A and B shifted to the lower energy side. Moreover, the intensity of peak A increased with composition x, indicating an increase of hole state at the oxygen site. Such spectroscopic behavior signifies changes in the electronic configuration and would be ascribed to the electronic exchange via hybridized orbital in Co 3d and O 2p during the electrochemical reaction because the observed peak shift and increase in peak A intensity indicates a decrease in d electron donation from transition metal ion to hybridized orbital as mentioned above. In addition, only a little variation was observed at the O K-edge XAS in the region of $x > \sim 0.5$, indicating that the Co atom mainly contributes to electronic exchange for charge compensation. Furthermore, the intensity of peak D is significantly increased in the first plateau region (~4.8 V). The origin of this spectral change is uncertain yet, and further studies, such as ab initio calculation, are required to understand the electronic structural change during the lithium extraction at the first voltage plateau.

In conclusion, the mechanism of charge compensation during the lithium extraction in olivine $LiCoPO_4$ was qualitatively explored through XAS measurements. Although the valence electrons of the transition metal are considered to be isolated due to the strong covalent bonds of compact PO_4 tetrahedron, it was revealed that the electrochemical lithium insertion accompanies modifications of the electronic structure in the hybridized orbital of Co 3d and O 2p as revealed from the experimental study on Co K-edge and O K-edge XAS. In addition, the changes in electronic structure seemed to occur in a stepwise manner as a function of composition x.

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