# Lithium K-edge X-ray Absorption Analysis of Lithium-ion Battery Cathodes

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Cathode materials for lithium-ion batteries utilize oxidation/reduction reaction of metal-ion for charge storage. However, little analysis of the electronic state of lithium carrier ions has been performed. This is because there are not many methods for observing the light element lithium, and some surface films on active materials deposited after charging and discharging make the analysis of bulk structure difficult. In this study, the electronic structure change of lithium was analyzed by soft X-ray absorption spectroscopy which can directly observe the electronic state of lithium. To prevent the surface film formation, lithium was chemically extracted from $LiCoO_2$, $LiMn_2O_4$, $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$ of representative electrode materials

## 1. Introduction

For charge/discharge of cathodes in lithium-ion batteries, topochemical reaction utilizing insertion/extraction reaction of lithium-ions accompanying oxidation/reduction of transition metal ions proceeds, and electronic structure of electrode materials changes during the reaction [1]. Because the electronic structure affects the electrochemical potential and the electronic conductivity, understanding of the electronic structure is useful to improve charge/discharge properties of electrode materials. There are many reports on the electronic structure analysis of transition metals such as cobalt and nickel in oxides for electrode materials [2-8]. However, the contribution of lithium which is a carrier to the electronic structure change has not been sufficiently analyzed. This is because the carrier-ion itself does not change on charge/discharge and the observation techniques detecting the light element lithium are insufficient. Furthermore, the surface products that were formed on charge/discharge reaction make the analysis of lithium in electrode materials difficult.

X-ray absorption spectroscopy (XAS) is one of the powerful methods observing the electronic structure and the several Li *K*-edge XAS studies have been reported [9-12]. However, these studies did not discuss whether the spectrum derived from electrode materials changes with charge/discharge reaction. In this study, the electronic structure change of lithium caused by charge reaction was examined using the typical active materials of $LiCoO_2$, $LiMn_2O_4$ and Li-excess oxide($Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$). In order to suppress the influence of the surface products, the charged samples are prepared by the chemical delithiation.

## 2. Experiments

$LiCoO_2$ was prepared by solid state reaction. $Li_2CO_3$ and $Co_3O_4$ were mixed in a stoichiometric ratio using an agate mortar. The pelletized mixture was calcined at 550 °C for 5 h in the air, and then further calcined at 850 °C for 24 h in the air. $LiMn_2O_4$ was also synthesized by solid state reaction from $Li_2CO_3$ and $Mn_2O_3$. $MnCO_3$ was calcined at 600 °C for 20 h in the air to synthesize $Mn_2O_3$. After mixing at a stoichiometric ratio, the pellet of the mixture was calcined at 800 °C for 48 h in the air. $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$ purchased from Toshima Manufacturing Co. Ltd., which was prepared by sol-gel method, was used.

$LiCoO_2$, $LiMn_2O_4$, and $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$ were chemically delithiated. Each powder and the oxidizing agent $Br_2$ or $NO_2BF_4$ were stirred in acetonitrile for 48 h. The molar ratio active material: $Br_2$ was 1: 9, and active material: $NO_2BF_4$ was 1: 1. The precipitate was filtered, washed with acetonitrile, and dried under vacuum. These procedures were carried out in an argon atmosphere glove box.

X-ray diffraction patterns of the powder samples were measured by Ultima-IV (Rigaku) with 0.02° step at 40 kV and 40 mA. XAS measurements were performed at BL-2 in SR Center, Ritsumeikan University. XAS spectra at Li *K*-edge and O *K*-edge were measured in a total electron yield mode.

## 3. Results and discussion

Figure 1(a) shows the XRD patterns of the prepared $LiCoO_2$ and delithiated $Li_xCoO_2$. The diffraction peaks of $LiCoO_2$ can be indexed as trigonal *R*3/*m* space group without any impurity phase. The calculated lattice constant is $a = 2.8130$ Å and $c = 14.039$ Å, being in agreement with the reported values [13]. The chemical delithiation using $Br_2$ and $NO_2BF_4$ corresponds to the electrochemical potential of 4.1 V and 5.1 V vs. $Li/Li^+$ in the charged state, respectively [14]. The 003 diffraction of the chemical delithiation using $Br_2$ shifts towards lower angles, which indicates the expansion of *c*-axis lattice constant. Moreover, the 104 diffraction splits into the two peaks. These results well agree with the reported results where *in-situ* XRD measurement was performed under the charge reaction [15]. On the other hand, when the stronger oxidant $NO_2BF_4$ is used, broadening of the diffraction peak is observed. This may be due to the destabilization of

LiCoO₂ under high potential. The 003 diffraction peak is shifted towards higher angle compared with the sample of $Br_2$ chemical delithiation, which shows a decrease in the lattice constant of *c*-axis. This is also consistent with the reported behavior of crystal structure changes under high voltage charging [16]. Therefore, the $Li_xCoO_2$ samples prepared by chemical delithiation with $Br_2$ and $NO_2BF_4$ correspond to the different states of charge.

Figure 1(b) shows the XRD patterns of the prepared $LiMn_2O_4$ and the delithiated $Li_xMn_2O_4$. These diffraction peaks can be indexed at the cubic space group of $Fd3/m$, and no impurities are identified. The lattice constant of the prepared $LiMn_2O_4$ shows good agreement with the reported values [17]. The diffraction peaks of the chemically delithiated $Li_xMn_2O_4$ using $Br_2$ are shifted towards higher angle, showing the lattice volume shrinking. Furthermore, the chemical delithiation of $NO_2BF_4$ results in a much higher shift.
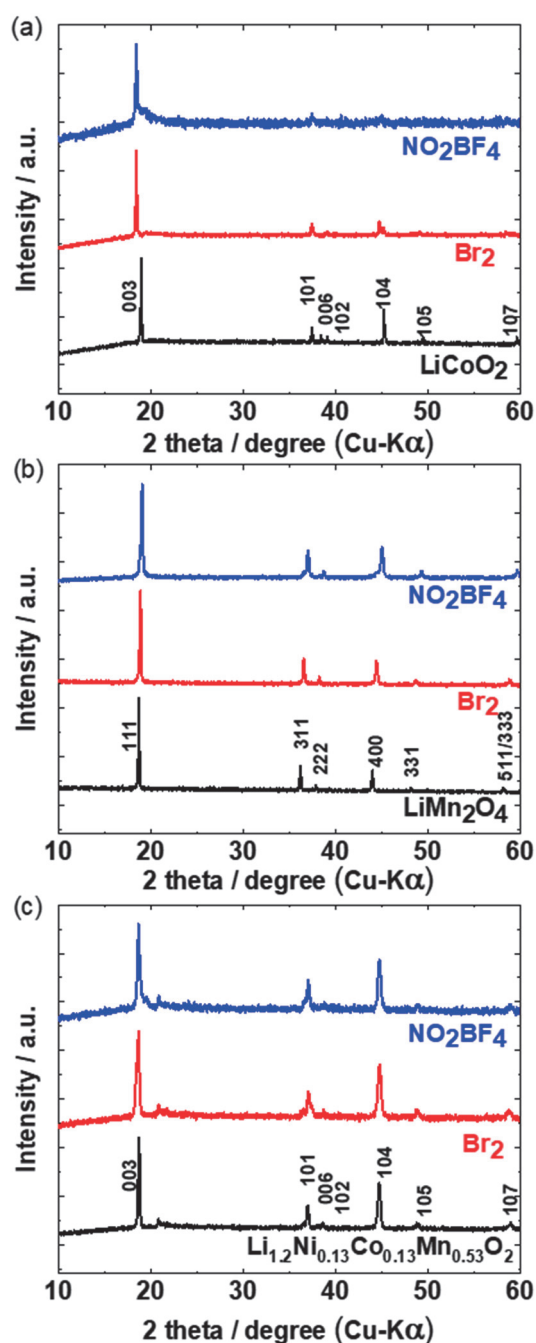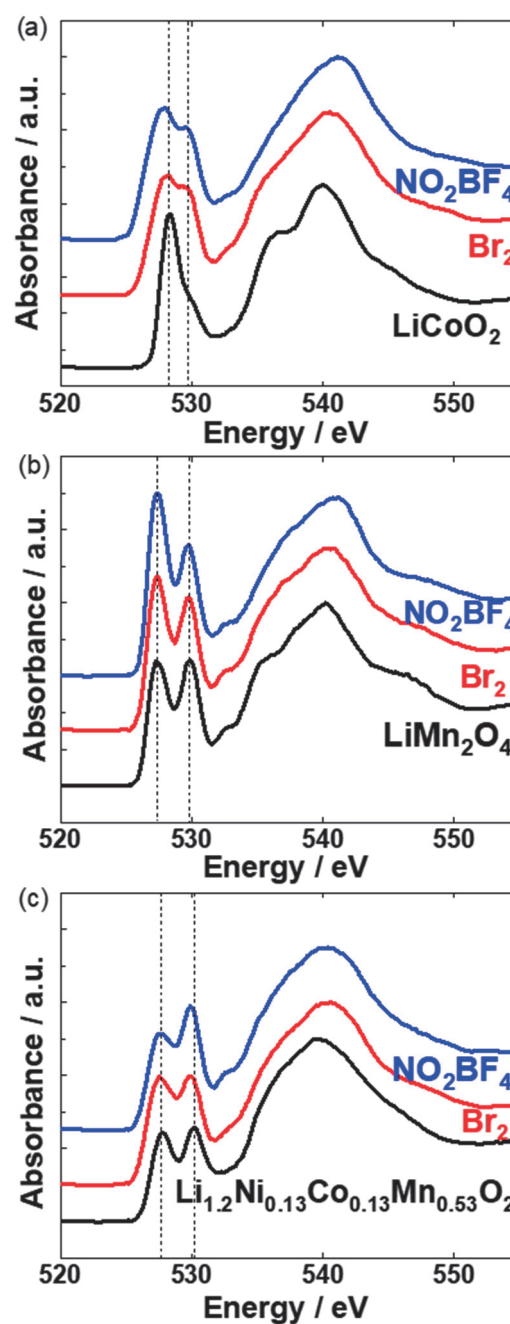


**Fig. 1** X-ray diffraction patterns of the prepared and delithiated powders for (a) $LiCoO_2$, (b) $LiMn_2O_4$, and (c) $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$.



**Fig. 2** O *K*-edge XAS of the prepared and delithiated powders for (a) $LiCoO_2$, (b) $LiMn_2O_4$, and (c) $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$.
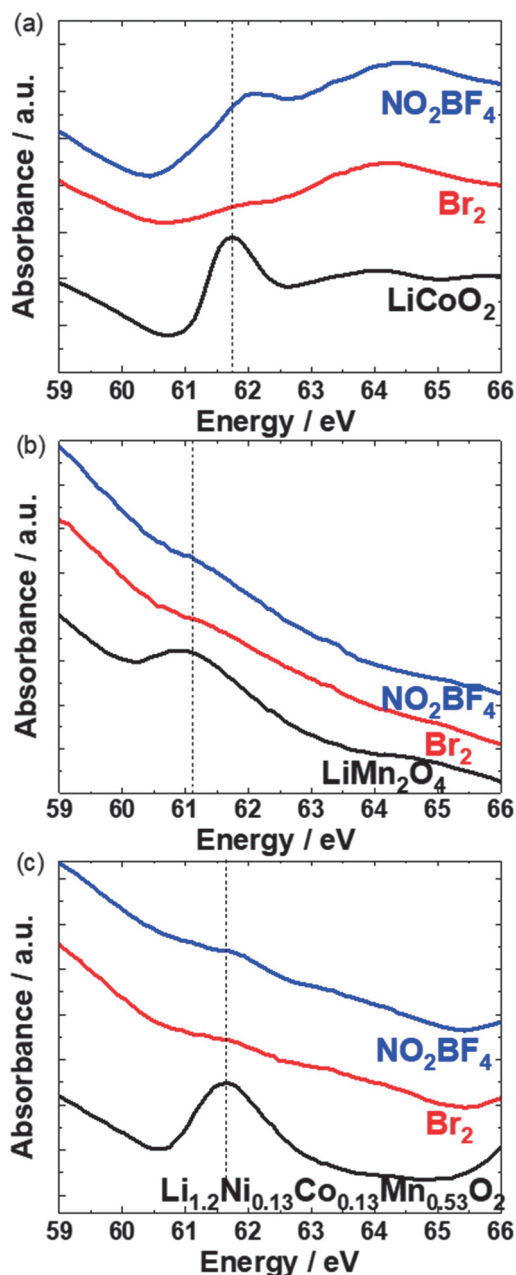
**Fig. 3** Li $K$-edge XAS of the prepared and delithiated powders for (a) $LiCoO_2$, (b) $LiMn_2O_4$, and (c) $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$.

The decrease of the lattice constant is explained by the smaller ionic radii of tetravalent of manganese ion than that of the trivalent ion [18].

The XRD patterns of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$ are provided in Figure 1(c). Most of the peaks can be indexed to the $R3/m$ space group the same as $LiCoO_2$ without the peaks around 21°. These unindexed peaks are attributed to the structure derived from the arrangement found in $Li_2MnO_3$, and shows good agreement with the previously reported XRD patterns [19]. The angle change of the diffraction peak for the lithiation tends to be the same as the result of $LiCoO_2$. The Li-excess system exhibits the crystal structure based on the layered rock salt structure in which excess lithium occupies the transition metal site [20], and the general tendency of the crystal structural change accompanying delithiation corresponds to the change of $LiCoO_2$.

From the above results, the prepared and delithiated samples show good agreement with the previously reported XRD, and no detection of impurities due to chemical delithiation is confirmed. Therefore, the preparation of thecharged electrode materials without the second phase is confirmed. The XAS analysis was performed using these samples.

O $K$-edge XAS of the prepared and delithiated $LiCoO_2$, $LiMn_2O_4$, and $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$ are shown in Figs. 2(a), (b), and (c) respectively. In the spectra of the transition metal oxides at O $K$- edge, the characteristic peaks appear around 527 to 532 eV and above 535 eV. The former peaks are due to hybridized orbital between metal-3d and O-2p states [2,4]. In the latter energy region, it is considered to be a peak due to the sp hybrid orbital (4s + 4p) and O 2p electrons of Co and Mn [2]. In the case of $LiCoO_2$ and $LiMn_2O_4$, the peak intensity on the low energy side increases with the delithiation. As the dominant change of the low energy peak, the electronic structure change for charge compensation in the delithiation occurs in the strongly hybridized transition metal 3d and O 2p orbitals. Also, in $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$, the peak intensity at 527 eV is increased in delithiation by $Br_2$, which indicates that the contribution of the transition metal 3d-oxygen 2p hybridized orbital is large. On the other hand, in the case using $NO_2BF_4$ corresponding to the high voltage charge, this peak is lowered, and the peak intensity around 532 eV is increased, which implies oxygen release from the crystal structure at the high voltage and the contribution of the new level at oxygen 2p orbital for charge compensation. The above spectral changes show good agreement with the reported behavior [7].

Li $K$-edge XAS of the prepared and delithiated $LiCoO_2$, $LiMn_2O_4$, and $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$ are shown in Figs. 3 (a), (b), and (c), respectively. In the spectra near Li $K$-edge, the peaks are generally complicated because the $M$-edges of 3d transition metals overlap. For the prepared $LiCoO_2$, $LiMn_2O_4$, and $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$, the peak at 61.7, 61.1 and 61.8 eV appear, respectively. These main peaks are weakened by the chemical delithiation, representing that these peaks are Li $K$-edge since it is assumed that the composition other than lithium does not change. In addition, since the peak position is changed for the chemical delithiation, the electronic structure of lithium is changed by the charge/discharge reaction. Furthermore, the energy level formed by lithium is broadest in $LiMn_2O_4$ and sharpened in the order of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$ and $LiCoO_2$. Li $K$-edge XAS of LiF and $Li_2CO_3$ shows sharp peaks at 62 and 67 eV,

respectively [21], and these signals are observed at the electrode after charging the lithium-ion battery. On the other hand, in the chemically delithiation, since no increase in the intensity at this position is observed, a spectrum reflecting the charge state of the active material can be obtained by the chemical delithiation method.

The analysis of Li $K$-edge XAS experimentally shows that the electronic state of the carrier ion changes depending on the host structures. The chemical delithiation method is useful to analyze the electronic state of lithium for charged/discharged active materials. The correlation between the electronic structure and ionic conductivity has not been analyzed at present, and further analysis is needed.

## 4. Conclusion

In order to analyze the electronic state of lithium, which is the carrier of the electrode active material, $LiCoO_2$, $LiMn_2O_4$, and $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.53}O_2$ were prepared, and the chemical delithiation treatment was performed, which reflects the charged state. The electrode materials subjected to the chemical delithiation show the same tendency as the changes in XRD and O $K$-edge XAS that have been previously reported. In the case of Li $K$-edge XAS, the peak identification is difficult because of overlapping with the absorption peaks at transition metal $M$-edge. Li $K$-edge absorption peak can be identified by considering the delithiated state of the electrode materials. Among the cathode materials, the changes in the peak position and the peak width at Li $K$-edge are observed, implying that the electronic structure of lithium is unique to the materials. This study demonstrates that the electronic state of the carrier ion changes depending on the host structures. The chemical delithiation method is useful to analyze the electronic state of lithium for charged/discharged active materials.

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