# Oxygen K-edge XAS study of Li-rich layered cathode material Li<sub>1.2</sub>Al<sub>0.4</sub>Mn<sub>0.4</sub>O<sub>2</sub> for Li-ion battery

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#### Introduction

Li-ion batteries are widely used for small electronic devices such as mobile phones. They are typically composed of layered transition metal oxide LiMO<sub>2</sub> (M=Ni,Co,Mn) as a cathode, and graphite as an anode with a proper electrolyte, such as LiPF<sub>6</sub>. LiCoO<sub>2</sub> is first commercialized thanks to the easiness of preparation and high cyclability [1]. But it has drawbacks of high cost and limited capacity ( $\sim$ 160mAh/g). In recent years, alternative cathode materials with larger capacity have been proposed and investigated for the power sources in the future electronic vehicles (EVs). One of the candidates is Li<sub>2</sub>MnO<sub>3</sub> based Lirich layered cathode materials (LLLs), which have a large capacity (250mAh/g $\sim$ ) and high cyclability [2,3]. In the previous works, we have performed M (=Ni,Co,Mn)-Kedge XAS study of the LLLs to explain the large capacity [4,5].

In the typical cathode material LiCoO<sub>2</sub>, the charge compensation is explained by the redox reaction of the transition metal, Co. In contrast, for LLLs, the charge compensation during first voltage plateau ( $\sim 4.5$ V) is explained by the redox reaction of transition metals, too. But the oxygen release occurs during the second voltage plateau (4.5V $\sim$ ) instead of the redox reaction of the transition metal. Although the redox reaction of oxygen was suggested by the previous works, the details of oxygen redox process have not been elucidated yet.

X-ray Absorption Spectroscopy (XAS) is a very powerful tool to elucidate the electronic and atomic structures around the selected atom. In order to clarify the role of oxygen, it is promising to study O K-edge XAS of Li<sub>1.2</sub>Al<sub>0.4</sub>Mn<sub>0.4</sub>O<sub>2</sub>, where aluminum might be inert to the electrochemical reaction.

#### Experimental

The powder of  $Li_{1.2}A_{10.4}Mn_{0.4}O_2$  was prepared by a solid state reaction from Li carbonates and aluminum-manganese oxides. For the electrochemical evaluation, an aluminum laminated cell was used. It consists of cathode electrode (active material: carbon: PVDF = 8:1:1), a Li metal anode and Li metal reference electrode, and a porous polypropylene film used as a separator. The electrolyte was 1M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate (1:2 ratio by volume). XAS measurement was carried out for Pristine, first charged(1c), first discharged(1d), second charged(2c), and second discharged(2d) by three detection mode, PEY(surface sensitive), TEY, PFY(bulk sensitive) at BL-11.

## **Results and Discussion**

Fig.1 shows the charging and discharging profiles of the Li<sub>1.2</sub>Al<sub>0.4</sub>Mn<sub>0.4</sub>O<sub>2</sub> electrode. During the first charge, a large irreversible capacity was observed with two plateaus at 4.5 V and 4.6 V. However, the first discharge capacity was as small as 70 mAh/g and the second charge was around 100 mAh/g.

Fig. 2 shows Mn L-edge XAS of Mn( II )CO<sub>3</sub>, Mn( III )<sub>2</sub>O<sub>3</sub>, Mn( IV )O<sub>2</sub> as reference compounds in addition to  $Li_{1.2}Al_{0.4}Mn_{0.4}O_2$ . The valence state of Mn in the cathode can be evaluated by comparing the XAS spectrum with those of the reference



Fig.1 Charging and discharging profiles of the  $Li_{1.2}Al_{0.4}Mn_{0.4}O_2$  electrode. Each number marked in the figure is the point where the XAS measurement was performed.

compounds. The valence state of the pristine sample was found to be 4+. After the first charge (1c), it remained 4+. Therefore, the first charging process is not the oxidation reaction of Mn. The PEY and TEY spectra changed drastically upon the first discharge, giving new peaks at 640.1eV and 641.7eV, which are associated with  $Mn^{2+}$  and  $Mn^{3+}$ , respectively. Namely, Mn was reduced to +3 and/or +2 upon the first discharge in the surface region of the active electrode. Moreover, Mn was oxidized upon the second charge and reduced upon the second discharge reversibly in the surface region. On the other hand, the PFY spectrum did not change upon charge and discharge, indicating that the Mn valence number of the active electrode did not change upon charge and discharge in the bulk region.

Fig.3 shows O K-edge XAS of the  $Li_{1.2}Al_{0.4}Mn_{0.4}O_2$  electrode. In the spectra, pre-edge peaks observed at 529eV and 531.2eV are assigned to the transitions from 1s to the hybridized states of Mn 3d and O 2p orbitals. It is clear that there exist resemblances between those for the charged states, 1c and 2c, and the discharged states, 1d and 2d.



Fig.2 Mn L-edge XAS spectra for the processed  $Li_{1,2}Al_{0,4}Mn_{0,4}O_2$  cathode material and reference compounds.



Fig.3 O K-edge XAS spectra of the processed  $Li_{1,2}Al_{0,4}Mn_{0,4}O_2$  cathode material. The peak observed at 533eV is assigned to  $\pi^*(C=O)$  of  $Li_2CO_3$ .

The spectral features seem to be reproducible with the charge/discharge cycles. To make the change clear in the spectral features with cycles, the difference spectra are shown in Fig.4. After the first charge (1c-pristine), new peaks appeared at 528eV and 530.2eV in all the detection modes. They can be assigned to the transition from 1s to a  $\pi$  \* orbital of superoxide anion and a  $\sigma$  \* orbital of peroxide anion, respectively[5]. They disappeared upon discharge and reappeared upon charge only in the PFY mode (in the bulk region). Consequently, it is concluded that the oxygen in Li<sub>1.2</sub>Al<sub>0.4</sub>Mn<sub>0.4</sub>O<sub>2</sub> cathode material contributes to the charge/discharge processes by performing reversible redox reaction at the oxygen anions. In contrast, a decrease/increase of the peak intensity at 529eV was observed in the PEY and TEY modes upon discharge/second charge, respectively. It could be due to the redox reaction of Mn as the results of Mn L-edge XAS suggested because the valence state of Mn is associated with the number of O2p holes. The difference between the surface and the bulk region could be due to the irreversible oxygen release on the first charge at the surface region.



Fig.4 Difference spectra at O K-edge XAS. For example, the spectrum [1d - 1c] is the subtraction from the spectrum of 1d to that of 1c.

## References

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