

Changes in electronic structure of the electrochemically Li-ion deintercalated LiMn_2O_4 system investigated by soft X-ray absorption spectroscopy

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Abstract

The electronic structure of the electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ system has been investigated for various Li compositions using soft X-ray absorption spectroscopy (XAS) for oxygen K-edge and Mn $L_{\text{II,III}}$ -edge. To get reasonably good XAS spectra for the electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ system, we made a binder free LiMn_2O_4 film electrode using electrostatic spray deposition (ESD) technique. From the Mn $L_{\text{II,III}}$ -edge XAS, it is found that the peak shifts to higher energy with the Li-ion deintercalation and this is due to the increase of the average oxidation state of the Mn ion. From the oxygen K-edge XAS, the Li-ion deintercalation gives rise to a gradual increase in pre-edge peak intensity but mostly does not effect its peak shape.

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Keywords: Soft X-ray absorption spectroscopy; $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$; Lithium rechargeable batteries; XAS

1. Introduction

Extensive research on the electronic structure of the Li-ion intercalated cathode material has been carried out. The local structure of the transition metal ion of the cathode has been investigated using X-ray absorption spectroscopy (XAS) [1–4]. The XAS study for the Li-ion intercalation–deintercalation has been mainly investigated from the viewpoint of metal ion. The absorption peak features of the metal K-edge spectrum include useful structural information, such as the oxidation state of chemical species, their site symmetries, and covalent bond strength. In this case, the small pre-edge peak has been used to infer the electronic structure of the central atom since the transition is very sensitive to chemical environments in spite of the electric dipole-forbidden transition. From the peak position and intensity of the metal K-edge XANES spectra, it has been reported that the Li-ion deintercalation leads to an increase of the average oxidation state of the transition metal ion and distortion of the local structure around the metal atom. However, the XANES spectra could not give any direct information of the role of oxygen in the charge compensation process. Only the contribution of an oxygen atom could be indirectly inferred

from the peak intensity for an electronic transition of 1s electron to 4p orbital with the shakedown process.

Numerous spectroscopic studies of soft X-ray absorption have been carried out for the quantitative study of electronic structures for various manganese oxides [5–11]. Direct information about the unoccupied molecular level can be obtained from the intensive absorption peaks of Mn $L_{\text{II,III}}$ -edge XAS. These represent the intense main 2p → 3d transition, unlike the weak pre-edge peak of 1s → 3d transition in Mn K-edge XAS. The electric dipole-allowed 1s → 2p transition of oxygen K-edge X-ray absorption spectroscopy also provides direct probe of the oxygen oxidation state and the Mn–O bonding interaction as the 2p orbitals of the oxygen ligand are involved in bonding to the Mn metal ions with octahedral symmetry. The characteristic pre-edge features correspond to the electronic transition from the oxygen 1s core electron to the unoccupied molecular level by the hybridization of Mn 3d orbital with oxygen 2p orbital. Therefore, the spectroscopic application of these soft X-ray absorptions to a $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ system can be a useful technique that estimates the degree of oxygen contribution for the charge compensation in the Li-ion intercalation–deintercalation process.

Despite all the advantages of soft X-ray absorption for the investigation of the electronic structure of cathode materials for Li rechargeable batteries, its application to

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electrochemically Li-ion deintercalated cathode materials has been limited so far. This is because the composite electrode consists of the lithium transition metal oxide and some additives including an organic binder and carbon, which could reduce the quality of the data. In the present study, we have made binder free film electrode without any co-additives using electrostatic spray deposition (ESD) technique. This has made possible an improved interpretation of O K-edge spectra for a electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ system. The electronic structures of the $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ system have been investigated on the basis of Mn L_{II,III} and oxygen K-edge XAS studies thereby giving a better understanding of the electronic structure of an electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ system.

2. Experimental

LiMn_2O_4 film was prepared by the ESD method. The ESD method has been described in the literature [12,13]. Stoichiometric amounts of lithium nitrate and manganese nitrate with the cationic ratio of Li:Mn = 1:1 were dissolved in absolute ethanol and mixed to obtain a homogeneous precursor solution. A high voltage between the nozzle and Pt foil substrate atomizes the precursor solution at the orifice of the nozzle, generating a fine aerosol spray. The temperature of the substrate was kept at 300 °C during the deposition. The precursor solution was pumped at 2 ml/h rate for 1 h through a nozzle placed above the substrate. The LiMn_2O_4 precursor was deposited on the Pt substrate and annealed at 800 °C in air for 30 min. X-ray diffraction showed the LiMn_2O_4 film was single phase.

The Li-ion electrochemical deintercalation–reintercalation process was performed as follows: a three-electrode electrochemical cell was used for electrochemical measurements in which lithium foil was used for both the reference and the counter electrodes. The electrolyte used was 1 M LiClO_4 in propylene carbonate (PC) solution. All the electrochemical experiments were carried out at room temperature in a glove box filled with purified argon gas. For XAS experiments, the cells were first charged to a desired value of deintercalated Li-ion content (x -value) at a $C/5$ rate and then relaxed for a day. The electrochemical cells were disassembled in an argon-filled glove box, and the LiMn_2O_4 electrodes were taken out from the cell. These electrodes were then washed with tetrahydrofuran and dried thoroughly in a vacuum.

The soft XAS measurements of the LiMn_2O_4 were performed on U7 beamline in the storage ring of 2.5 GeV with the ring current of 120–160 mA at Pohang light source (PLS) which is the third generation synchrotron radiation source [14]. The U7 beamline, which consists of a 4.3 m long, 7 cm-period undulator and the variable-included angle plane-grating monochromator, provides the highly brilliant and monochromatic linear-polarized soft X-ray for the high

resolution spectroscopy [15]. The O K-edge and Mn L_{II,III}-edge XAS data were taken in a total electron yield mode, recording the sample current. The experimental spectra were normalized by reference signal from Au mesh with 90% transmission. The energy calibrations for O K-edge and Mn L_{II,III}-edge were made using the L-edges data of pure V and Mn metal foils, respectively. According to the measured photon absorption spectra specified as the inner shell electron excitation for the Ar, N₂ and Ne gases, the energy resolving power ($E/\Delta E$) in entire measurement range was greater than 3000. The base pressure of the experiment chamber was in 10^{-8} mbar range.

3. Results and discussion

The LiMn_2O_4 film was successfully deposited on Pt foil by electrostatic spray deposition technique. Fig. 1 shows the cyclic voltammograms obtained from the LiMn_2O_4 film during 10 cycles. The cyclic voltammogram was performed at a rate of 0.1 mV/s. Typical cyclic voltammogram of LiMn_2O_4 were observed, and were characterized by two sets of well-defined current peaks [16–18]. Subsequent cyclic voltammogram of LiMn_2O_4 shows that the LiMn_2O_4 film deposited by ESD method exhibits very stable electrochemical cycling characteristics.

The electronic structures of the Mn ions in the LiMn_2O_4 system can be investigated qualitatively by soft X-ray absorption spectroscopic study. The absorption peaks are relatively intense due to the electric dipole-allowed $2p \rightarrow 3d$ transition and are very sensitive to the oxidation state, spin state and bond covalency. Fig. 2 shows the Mn L_{II,III}-edge X-ray absorption spectra of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ system with respect to the x -value. There are two main peaks of L_{III}

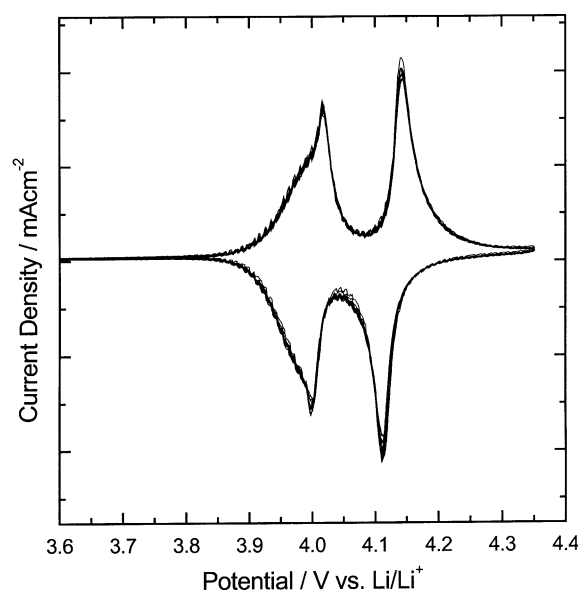


Fig. 1. Cyclic voltammograms obtained from the LiMn_2O_4 film at a scan rate of 0.1 mV/s during 10 cycles.

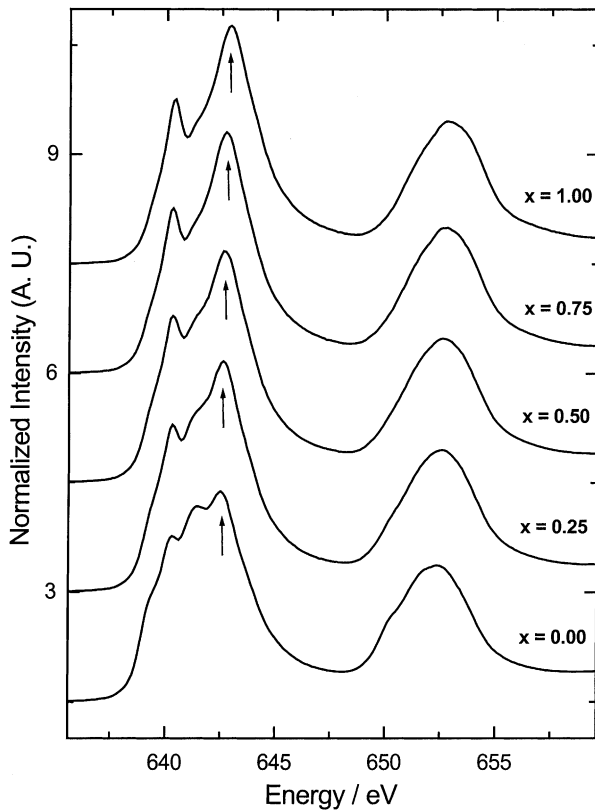


Fig. 2. Normalized Mn $L_{II,III}$ -edge X-ray absorption spectra of $Li_{1-x}Mn_2O_4$ system with respect to the x -value.

and L_{II} edges which are due to electronic transitions of Mn $2p_{3/2}$ and $2p_{1/2}$ core electrons, split by the spin-orbit interaction of the Mn $2p$ core level, to an unoccupied $3d$ level highly hybridized with the oxygen $2p$ orbital, respectively.

The Mn $L_{II,III}$ -edge XAS of $LiMn_2O_4$ film is very similar to that of the bulk $LiMn_2O_4$ compound reported earlier [11]. This shows that the $LiMn_2O_4$ film has been successfully prepared on the Pt substrate with the ESD method. The Mn $L_{II,III}$ -edge of $LiMn_2O_4$ has main peaks at ~ 642 and 652 eV, respectively. These are due to the Mn $2p$ - $3d$ electrostatic interaction and the crystal field effect of octahedral symmetry. As shown in Fig. 2, as Li-ion is de-intercalated, the Mn $2p$ spectra change shape and shift towards higher energies. In particular, the maximum of the Mn L_{III} -edge, marked by vertical arrows moves from 642.5 eV at $x = 0.0$ to 642.9 eV at $x = 1.0$. The peak shift toward the higher energy region shows directly the increase of the average oxidation state of an Mn ion with electrochemical deintercalation. It is reasonable that the higher absorption energy is necessary for the Mn ion with the higher oxidation state in order to excite the $2p$ core electron which is strongly bound to the less screened nucleus.

Fig. 3 shows the O K-edge XAS of the electrochemically Li-ion deintercalated $Li_{1-x}Mn_2O_4$ system. The spectrum of pristine $Li_{1-x}Mn_2O_4$ shows intense absorption peaks (A and B peaks) at ~ 530 and 532 eV and broad higher energy peaks (C and D peaks) above 535 eV. The first

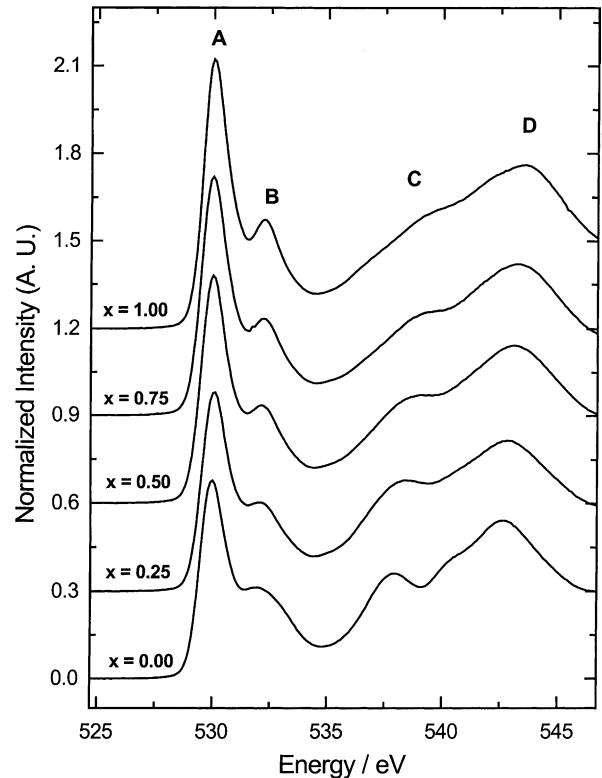


Fig. 3. Normalized O K-edge X-ray absorption spectra of $Li_{1-x}Mn_2O_4$ system with respect to the x -value.

intense peaks (A and B peaks) correspond to the transition of oxygen $1s$ electron to the hybridized state of Mn $3d$ and oxygen $2p$ orbitals, whereas the broad higher energy peaks correspond to the transitions to hybridized states of oxygen $2p$ and Mn $4sp$ orbitals. The A and B peaks correspond to the transition to an unoccupied molecular level which has Mn $3d$ -oxygen $2p$ character, since the oxygen $2p$ orbital is highly hybridized with $3d$ orbital of Mn ion with high spin electronic configuration under octahedral (O_h) symmetry. Although the oxygen $1s \rightarrow$ Mn $3d$ transition is forbidden by the electric-dipole approximation, the appearance of the absorption peak is caused by the hybridization of Mn $3d$ and oxygen $2p$ orbitals. In this case, the first structure at 531 eV is assigned to an accidental superposition of majority (spin-up) e_g and minority (spin-down) t_{2g} bands. On the other hand, the second structure at 533 eV is attributed to a band of minority e_g character. As the degree of electrochemical deintercalation increases (the x -value increases), the A peak intensity increases gradually and the peak B also evolves as a clear peak. Compared to our earlier O K-edge absorption study of the $Li_{1-x}CoO_2$ system [19], it is clear that changes in O K-edge XAS of $Li_{1-x}Mn_2O_4$ system during the charge process are relatively small. It is notable that this behavior is dramatically different from that of the electrochemically Li-ion deintercalated $Li_{1-x}CoO_2$ system where the oxygen site makes a large contribution to the charge compensation for the Li-ion deintercalation process.

4. Conclusions

The $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ film has been successfully deposited on Pt foil by electrostatic spray deposition technique. The electronic structure for the electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ film has been investigated with soft XAS at O K-edge and Mn L_{II,III}-edge. The results of Mn L-edge XAS spectra during charge show an increase of the average oxidation state of Mn ion with the electrochemical deintercalation. The spectral changes of the O K-edge XAS for $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ during charge are relatively smaller than those of the O K-edge XAS for the electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{CoO}_2$ system where the charge compensation for the electron exchange in the Li-ion deintercalation process can be largely achieved in the oxygen site.

Acknowledgements

This work was supported by the Brain Korea 21. The authors are grateful to authorities at the PLS for X-ray absorption spectroscopic measurements. This work was also supported in part by the Ministry of Information & Communication of Korea (“Support Project of University Information Technology Research Center” supervised by KIPA).

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