

# An Investigation of Electronic Structure of Novel Electrode Materials for Li-ion Batteries by Soft X-ray Absorption and Emission Spectroscopy II

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To improve the performance of electrode materials for Li-ion batteries, it is essential to understand the charge-discharge properties from a view point of electronic structure (i.e., redox reaction during Li-ion insertion/extraction). In the field of electrochemistry, hard x-ray absorption spectroscopy at the transition-metal (TM) *K*-edge has become a standard tool to study the electronic structure of the electrode materials because the valence-state change can be observed as the main peak shift. Furthermore, *in situ* measurements can easily be performed due to the vacuum-free apparatus with use of hard x-rays. However, the detailed information of 3*d* orbital such as crystal-field splitting and charge-transfer energy is hardly obtained since the 1*s* → 4*p* absorption is dominant for *K* edge. On the other hand, soft x-ray absorption (XAS) can provide direct information of TM 3*d* orbital because 2*p* → 3*d* absorption is dominant. Similarly, soft x-ray emission spectroscopy (XES) is a powerful tool to observe the TM 3*d* orbital below the Fermi level. Therefore, *in situ* XAS/XES will become the most promising method to study the redox reaction of the electrode materials if electrochemical *in situ* cell to separate the vacuum and atmosphere is developed.

We started developing the electrochemical *in situ* cell with modifying the *in situ* cell for liquid and gas samples [1]. The *in situ* cell which has been used at SPring-8 separates the sample in the atmosphere from the vacuum by a Si<sub>3</sub>N<sub>4</sub> window as thin as ~100 nm. We coated pasted LiMn<sub>2</sub>O<sub>4</sub>, which is a well-known cathode material [2], onto the window.

In general, Li-ion battery for an electrochemical test consists of working electrode (cathode), counter electrode (CE), reference electrode (RE) and electrolyte; Li metal is used for CE and RE and organic electrolyte is employed. However, it is not easy to handle Li metal in terms of chemical safety. For simplicity, in this study we employed Pt-wire CE, Ag/AgCl RE, and 1 M LiNO<sub>3</sub> H<sub>2</sub>O solution without the safety problem while the voltage is lowered by ~3 V.

The *in situ* cell was successfully assembled. The aqueous electrolyte did not leak from the cell. No short circuit was confirmed. Then, we equipped the vacuum chamber with the cell. The thin Si<sub>3</sub>N<sub>4</sub> window with the pasted LiMn<sub>2</sub>O<sub>4</sub> was successfully maintained between the vacuum and electrolyte with the ambient pressure. Figure 1 shows the result of cyclic voltammetry test with the *in situ* condition. The two peaks observed for each charge/discharge process were of the redox reaction to be attributed to Mn<sup>3+</sup> ⇌ Mn<sup>4+</sup> [2]. An over potential of the

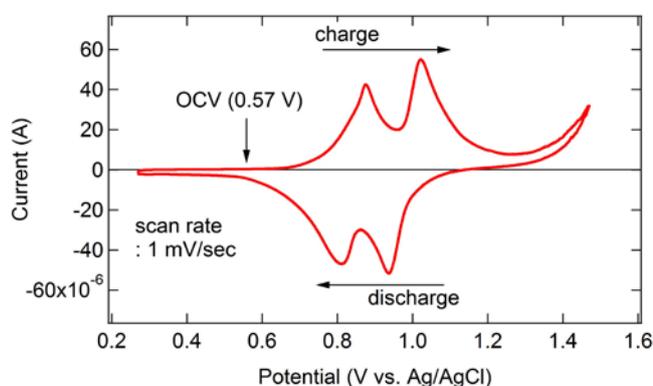


Fig. 1: Cyclic voltammogram for LiMn<sub>2</sub>O<sub>4</sub> with the *in situ* condition. The difference of the redox peaks between charge and discharge processes is of the over potential.

cell was observed, but it was small enough.

XAS and XES measurements were performed at BL07LSU in SPring-8. The total electron-yield mode was employed for the Mn  $L_{2,3}$ -edge XAS. The *in situ* XES measurements were carried out using the *in situ* cell and ultra-high-resolution XES spectrometer, HORNET. All the XAS and XES measurements were performed at room temperature.

First we measured the Mn  $L_{2,3}$ -edge XAS for the powdered  $\text{LiMn}_2\text{O}_4$  to determine the excitation energies used in XES. As Fig. 2 shows, the Mn  $L_3$ -edge XAS has four peaks. The multiplet structure is attributed to that  $\text{Mn}^{3+}$  high-spin and  $\text{Mn}^{4+}$  high-spin states coexist, which is consistent with previous studies [3]. To distinguish between the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  states, we chose the excitation energies of 642.8 eV (for  $\text{Mn}^{3+}$  dominant state) and 643.8 eV (for  $\text{Mn}^{4+}$  dominant state) referring the calculated spectra by multiplet calculations [4].

Next *in situ* Mn  $2p$  resonant XES (RXES) measurements were performed with the two excitation energies. The voltage was fixed to 0.57 V corresponding to the open-circuit voltage (OCV). Figure 3 shows the comparisons of the *in situ* (OCV) XES spectra with *ex situ* (powder) ones. For both excitation energies, clear differences of the  $d-d$  excitations were observed between the *in situ* and *ex situ* conditions, suggesting that both of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  states should be largely modulated by the *in situ* conditions. Most likely, adsorption of the molecules of the electrolyte would affect the pre-edge structure at -1 eV, i.e., the valence band maximum. Thus, the importance of *in situ* XES was clarified.

In summary, the electrochemical *in situ* cell with Pt-wire CE, Ag/AgCl RE and aqueous-solution electrolyte was developed. The *in situ* Mn  $3d$  electronic structure could be different from the *ex situ* one as seen in the XES results even at the OCV state. In future, we will try *in situ* XES at the charged and discharged states. Furthermore, the *in situ* cell will be improved for using Li metal CE/RE and organic electrolyte.

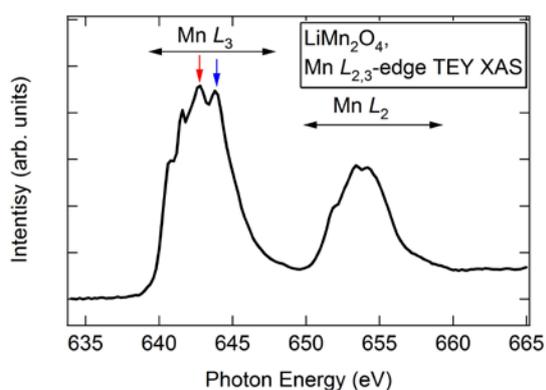


Fig. 2: Mn  $L_{2,3}$ -edge XAS for powdered  $\text{LiMn}_2\text{O}_4$ . The red and blue arrows indicate the excitation energies used in XES.

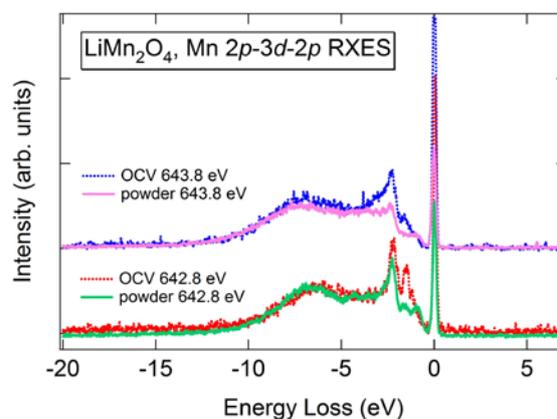


Fig. 3: *In situ* (OCV) and *ex situ* (powder) Mn  $2p$  RXES for  $\text{LiMn}_2\text{O}_4$ .

## References

- [1] T. Tokushima *et al.*, Chem. Phys. Lett. **460**, 387 (2008).
- [2] M. M. Thackeray *et al.*, Mater. Res. Bull. **18**, 461 (1983).
- [3] W.-S. Yoon *et al.*, J. Power Sources **119-121**, 706 (2003).
- [4] F. M. F. de Groot *et al.*, Phys. Rev. B **42**, 5459 (1990).