

An *operando* soft x-ray emission study of LiMn_2O_4 with an aqueous electrolyte solution

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Improvement of the energy density and power density of electrode materials for Li-ion batteries (LIBs) are highly important to further develop electric and hybrid-electric vehicles. In order to improve the performances, understanding the charge-discharge mechanisms of the electrode materials from a viewpoint of the electronic structure is indispensable. Soft x-ray spectroscopy, which directly reveals the $3d$ orbital of transition metals, has recently attracted much attention for the electronic-structure analyses of the electrode materials.

In this study we demonstrate *operando* soft x-ray emission spectroscopy (XES) for LiMn_2O_4 with an aqueous electrolyte solution. LiMn_2O_4 is a typical cathode material for LIB¹ and works as a cathode even for an aqueous electrolyte solution² as well as organic electrolyte solutions used for general LIB. The high-rate charge-discharge property for LiMn_2O_4 with an aqueous electrolyte solution is promising for large-scale energy storage, while a high voltage cannot be obtained for the aqueous LIBs because of the narrow voltage window for H_2O .

We developed an *in situ* cell consisting of the LiMn_2O_4 cathode, a Pt-wire counter electrode, Ag/AgCl reference electrode, and a 1 M $\text{LiNO}_3/\text{H}_2\text{O}$ electrolyte solution by modifying the *in situ* cell for fuel cell catalysts³. The *operando* XES experiments were carried out using ultrahigh-resolution XES spectrometer⁴ at BL07LSU of SPring-8. We selected 642 eV as the excitation energy in which the Mn^{3+} character should be enhanced for the Mn L_3 -edge absorption spectrum. The charge-discharge experiments were performed by cyclic voltammetry. The *operando* XES measurements were performed for the second charge-discharge cycle.

The Mn $2p$ - $3d$ - $2p$ resonant XES spectra revealed a clear difference between the pristine LiMn_2O_4 powder and open-circuit-voltage (OCV) state (i.e. before the second cycle) (Fig. 1). For the powder sample, the charge-transfer (CT) excitation below 637 eV is large and dd -excitation peaks appear from 637 to 641 eV. The configuration-interaction full-multiplet (CIFM) calculation^{5,6} (not shown) suggests

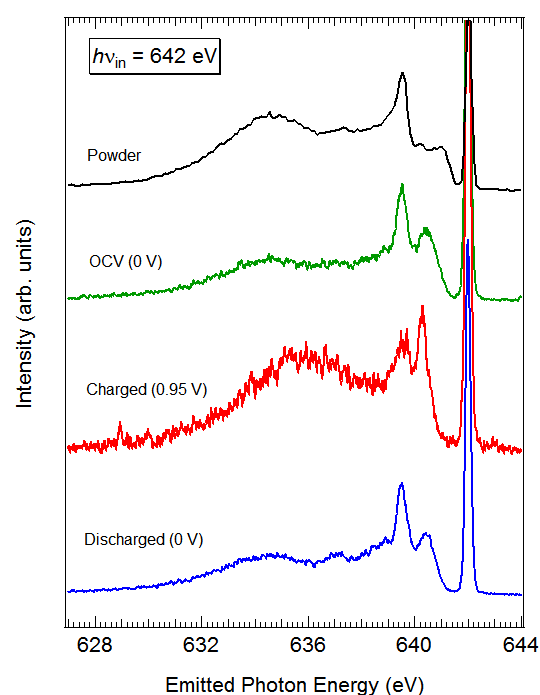


Fig. 1: *Operando* Mn $2p$ - $3d$ - $2p$ XES spectra for LiMn_2O_4 .

that the Mn^{3+} and Mn^{4+} states coexist. In contrast, for the OCV state, the CT excitation becomes small and the *dd*-excitation peaks are modified. Thus, the first cycle affects the Mn 3*d* electronic structure and reduces the CT effect between the Mn 3*d* and O 2*p* orbitals. The change of *dd*-excitation peaks imply a modification of the crystal field particularly for the Mn^{3+} site related to Jahn-Teller effect.

In going to the charged state, the profile is substantially changed, indicating the redox reaction of $\text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+}$ at the Mn^{3+} site due to the charge-discharge reactions (Li-ion extraction/insertion). The spectrum for the charged state has a large CT excitation relative to the *dd*-excitation peaks. The Mn^{4+} state should have a large CT effect. For the discharged state, the profile almost returned to that for the OCV state. A reversible redox reaction is confirmed.

In summary, *operando* XES measurements for LiMn_2O_4 with an aqueous electrolyte solution were performed to reveal the Mn 3*d* electronic-structure change during the charge-discharge process. The first cycle should modify the Mn 3*d* electronic structure especially for the crystal field. A large CT effect was found for the Mn^{4+} state. In future, the electronic-structure parameters for the Mn^{3+} and Mn^{4+} states will be determined accurately by using the CIFM calculation. The relationship between the electronic structure and electrochemical properties will also be discussed.

References

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