Charge-discharge mechanism of electrode materials for Li-ion batteries as seen via soft x-ray absorption/emission spectroscopy

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To improve the performance of electrode materials for Li-ion batteries, understanding the charge-discharge properties from a view point of electronic structure, i.e., revealing redox reaction of the transition-metal (TM) in the electrode materials during Li-ion insertion/extraction is highly important. Core-level photoemission spectroscopy and x-ray absorption spectroscopy at the TM *K* edge have widely been used to study the valence change of the electrode materials during the charge/discharge process. However, these methods are not so suitable to extract the information of TM 3*d* orbitals such as crystal-field splitting and charge-transfer (CT) effect.

In order to clarify the TM 3*d* electronic structure in detail, we utilized high-energy-resolution soft x-ray emission spectroscopy (XES) which can element-selectively reveal the TM 3*d* orbital below the Fermi level. In this study, the Mn 3*d* electronic structure of $LiMn_2O_4$ was investigated. Spinel-type $LiMn_2O_4$ is a typical cathode material for Li-ion batteries [1]. The average valence of Mn is expected to be $Mn^{3.5+}$ at the initial state. At the charged state (Li-extracted Mn_2O_4), the Mn should be oxidized from $Mn^{3.5+}$ to Mn^{4+}.

$LiMn_2O_4$ powder was fabricated by a sol-gel method. The cubic crystal structure was confirmed by x-ray diffraction. The electrochemical experiments were carried out according to Ref. 2.

Soft x-ray absorption spectroscopy (XAS) and XES measurements at the Mn $L_{2,3}$ edges were performed at BL07LSU in SPring-8. The total electron-yield mode was employed for the XAS. The XES measurements were carried out using an ultra-high-resolution XES spectrometer, HORNET [3]. The energy resolution was set to $E/\Delta E = 3200$. All the XAS and XES measurements were performed at room temperature.

Figure 1 shows the Mn $L_{2,3}$-edge XAS of $LiMn_2O_4$ for the initial, fully-charged, and discharged states. According to previous XAS studies for several Mn compounds and multiplet calculations [4], the multiplet structure of the initial-state spectrum suggests that Mn^{3+} and Mn^{4+} states coexist. In the L_3 region, the peaks at 640 and 642 eV were ascribed to the Mn^{3+} state and those at 640.8 and 643 eV were attributed to the Mn^{4+} state. At the charged state, the Mn^{3+} component decreased and the Mn^{4+} character was enhanced, suggesting the oxidation of Mn by charging.

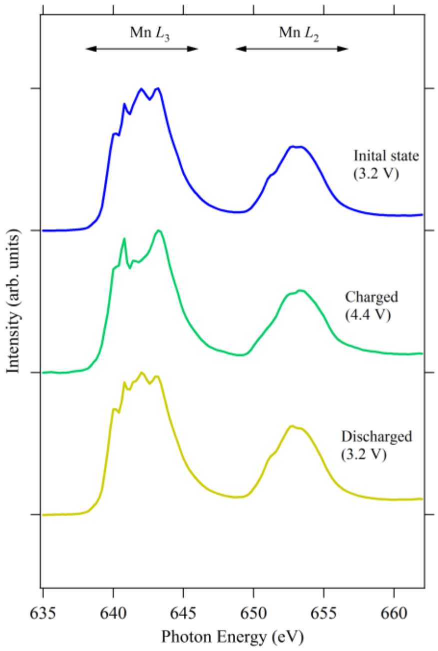

Fig. 1: Mn $L_{2,3}$-edge XAS for $LiMn_2O_4$ during charge-discharge.

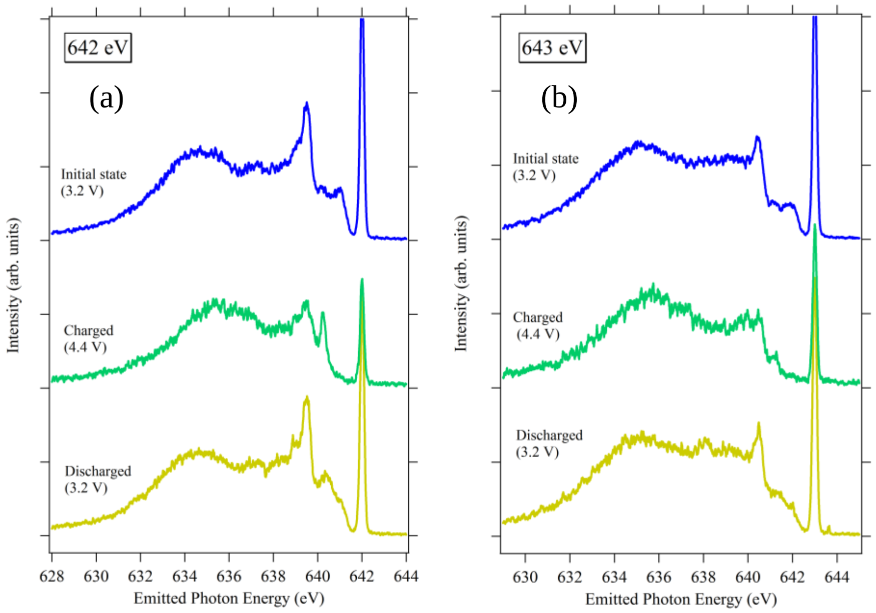

Fig. 2: Resonant XES for $LiMn_2O_4$ with E_i = (a) 642 and (b) 643 eV.

The discharged-state XAS spectrum is almost the same as the initial-state one. Thus, a reversible redox reaction of $Mn^{3.5+}$ to Mn^{4+} was confirmed.

To separately discuss the Mn^{4+} state from Mn^{3+} one, we chose excitation energies (E_i) of 642 and 643 eV for XES since the Mn^{3+} and Mn^{4+} characters should be enhanced at 642 and 643 eV, respectively. Figure 2 displays the resonant XES results with E_i = 642 and 643 eV. The *dd*-excitation peaks from 637 to 641.5 eV obviously changed during charge-discharge. Remarkably, the peak at 641 eV nearest to the elastic peak, which was observed for the initial state, disappeared by charging and emerged in the discharged-state spectrum. This result indicates that the peak at 641 eV is attributed to the Mn^{3+} state and that the electron near the Fermi level was removed by charging. The Mn^{4+} state should be dominant for the charged state. In the case of E_i = 643 eV (Fig. 2(b)), changes of the *dd*-excitation peaks between the initial and charged states were small compared to the case of E_i = 642 eV, which confirms that the Mn^{4+} character should be enhanced for the initial state with E_i = 643 eV. Furthermore, the CT excitation from 630 to 637 eV observed in the initial-state spectrum with E_i = 642 eV approached to the elastic peak by ~1.5 eV for the charged state, indicating the CT effects between the Mn^{3+} and Mn^{4+} states should be different. In addition, the discharged-state spectra did not absolutely reproduce the spectral shape of the initial state as for the region from 639.5 to 641.5 eV in the case of E_i = 642 eV and that from 640.5 to 642.5 eV for E_i = 643 eV while the other parts were reproduced. The charge-discharge process should slightly affect the crystal field with a Jahn-Teller distortion on the Mn^{3+} site. The small changes of the Mn^{3+} state which were hardly observed in XAS could be detected by use of high-energy-resolution resonant XES.

In summary, XES measurements for $LiMn_2O_4$ were performed to reveal the Mn 3*d* electronic structure during charge-discharge process. We demonstrate that the Mn^{3+} and Mn^{4+} states are successfully distinguished by using high-energy-resolution resonant XES. In future, multiplet calculations will be performed to determine the electronic-structure parameters for both the Mn^{3+} and Mn^{4+} states.

References

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