In situ x-ray absorption spectroscopy and first-principles calculations on structural changes of Li_2MnO_3 during charge and discharge processes

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Li-rich-layered solid-solution-system that are denoted as Li_2MnO_3–$Li[Ni_xCo_yMn_z]O_2$ have attracted much attention as promising positive electrodes in lithium rechargeable batteries, since they exhibit high capacities and good-cycle performance.[1] The end material, Li_2MnO_3 it-self also shows charging capacity value of 300mA / h, and the discharge capacity of 240mgA / h. Due to this large irreversible capacity and poor cyclability, this material is not suitable for active materials, but, to analyze the reaction mechanism or detailed behavior of charge-discharge cycles of such Li_2MnO_3–$Li[Ni_xCo_yMn_z]O_2$, the detailed structure and electronic structural information on Li_2MnO_3 system should be useful. Here, we report the results of such structure and electronic structure analysis during charge-discharge cycles to obtain new insights into origin of the irreversible capacity and poor cyclability.

X-ray absorption spectroscopy (XAS) has been widely used to analyze behaviors of positive materials, since it can probe the valence state and the local distortion around absorbing atoms that is related with battery performance.[2] Generally, the valence state is estimated by absorption “edge” or inflection point of XANES spectra, and a local structure is determined from EXAFS via bond lengths and coordination numbers. Both valence states and local structures, however, could often simultaneously change during charge-discharge processes, and thus, interpretation of XANES spectra would not be simple. Besides, since EXAFS analysis cannot provide information on bond angles, the obtained structural information is insufficient and rather limited.

To overcome such drawbacks, we combined experimental in situ XAS and first-principles XANES simulation. Since XANES reflects changes in empty orbitals, it should be sensitive to local distortions around absorbing atoms, in addition to the valence state. Furthermore, electronic structure calculations allow us to determine the valence state more accurately.

In situ XAS measurements were carried out at Mn K-edges in a transmission mode on a BL16B2 beamline at SPring-8 by using a laminate-type cell that consists of Li_2MnO_3 positive electrode and a Li metal negative electrode. Structure optimizations for electronic structure calculation were done with VASP[3], and then, XANES spectra were simulated by WIEN2k using the optimized structure.[4]

Figure 1(a) shows the results of in situ XAS measurements for Mn in Li_2MnO_3. The absorption edge remained almost the same position, and the shape of the radial structure function does not change significantly. The peak-top position of XANES, however, changed on charging suggesting the local structure and/or the electronic structure of Mn is modified. For such case, the combination with the first-principles XANES simulation is much useful. Figure 1(b) shows the result of Mn K-edge XANES simulation for Li_2MnO_3 (which is in good agreement with the experiment). During charging, the valence of Mn is not changed from the calculation. Figure 2 shows 4p-PDOS of $Li_{2-x}MnO_3$(x=0.0,0.5,1.0) obtained by projecting to each a-, b-, and c- direction. This indicates that charge state of Mn changed by the de-intercalation of Li, 4*p* orbitals change in each direction. More detailed results in which we correlated such electronic structural changes to local structural change around Mn will be presented at the Meeting.

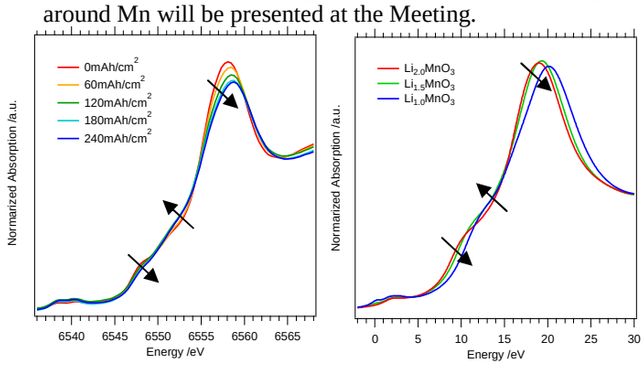

Fig. 1: (a) XANES spectra for Mn , (b) Simulated XANES spectra for Mn-K edge for $Li_{2-x}MnO_3$(x=0.0,0.5,1.0).

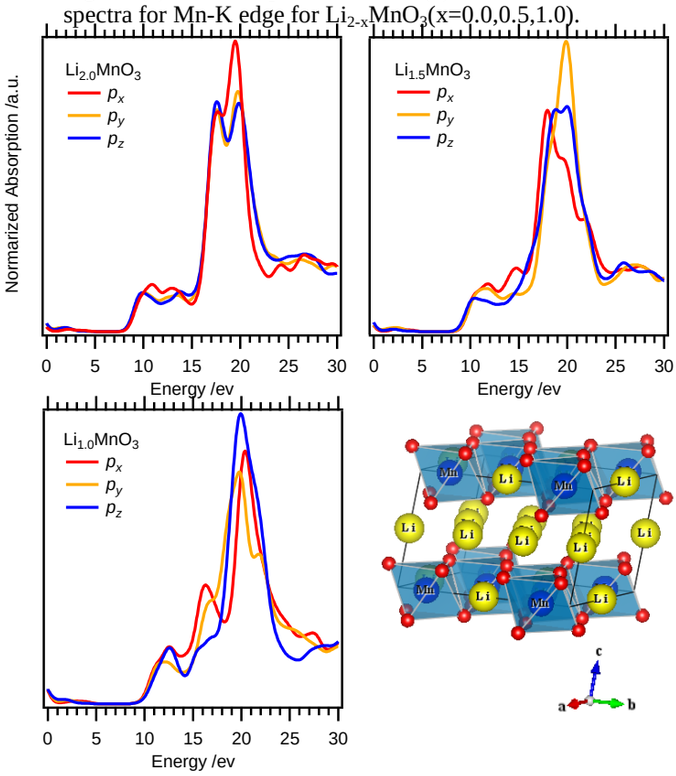

Fig. 2: Simulated 4*p* PDOS of Mn for (a) $Li_{2.0}MnO_3$, $Li_{1.5}MnO_3$ and (c) $Li_{1.0}MnO_3$ obtained by projecting the a, b, and c each direction. (d)Crystal structure of Li_2MnO_3 (C2/m)[5]

Acknowledgement: Synchrotron radiation XAS measurements were performed with an approval of Japan Synchrotron Radiation Research Institute (Proposal No. 2012B5392) .

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