

Electronic state analysis of metal and oxygen in positive electrodes for lithium ion secondary battery

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Series of Li-rich layered oxide systems are attracting attention as high-capacity positive electrode materials for the next-generation lithium ion secondary batteries. We evaluated X-ray absorption spectroscopy (XAS) using soft X-ray for Li_2MnO_3 and $\text{Li}(\text{Li}_{0.16}\text{Ni}_{0.15}\text{Co}_{0.19}\text{Mn}_{0.50})\text{O}_2$ at 3d transition metal L -edge and O K -edge spectra. Both the metal cation and the O anion contributed in the charge compensation of Li-ion insertion/extraction reactions. The O anion formed a localized electron states that was independent of the metal cations [1, 2]. Generally, charge compensation for the Li-ion insertion/extraction in the conventional positive electrode materials is explained by the redox reaction of metal cation. However, in Li-rich layered oxides, the O anions contributed to the charge compensation in addition to the metal cations. Generally, oxidation of O anion would result in the evolution of O gas, which causes a material deterioration. Our study revealed that the O anion reversibly contributed in the redox reaction in the Li-rich layered oxides. However, the detail mechanism that achieved the stabilization of inherently unstable oxidized oxygen anion state is not yet thoroughly understood. The redox reaction of the oxygen anion should be considered in relation to the electronic state of the counter metal cation that forms the hybrid electron orbitals. Therefore, in this study, electronic structure analysis of metal cation and O anion was performed for layered oxide cathode materials LiVO_3 and Li_2MnO_3 .

The samples were synthesized by solid state reaction method. Li-ion was chemically extracted from the samples using NO_2BF_4 as the oxidation reagent. The Mn L - and O K -edge XAS spectra were collected at BL-11, SR Center, Ritsumeikan University. The XAS spectra were simultaneously obtained in the partial electron yield (PEY), the total electron yield (TEY) mode, and the partial fluorescence X-ray yield (PFY) mode. For the Mn L -edge PFY XAS, the inverse partial fluorescence yield (IPFY) spectra were collected.

Figure 1 shows the Mn L -edge and O K -edge XAS spectra in the TEY mode of Li_2MnO_3 . In pristine sample, the L -edge XAS peaks coincided with those of MnO_2 indicating Mn^{4+} , showed L_{III} -edge main peak at 643.1 eV, sub-peak at 640.6 eV, and L_{II} -edge peak at 653.4 eV. For delithiated samples, the main

peak intensity at the L_{III} -edge decreased and the sub-peak intensity increased. The L_{II} -edge peak shifted to lower photon energy. This suggests the reduction of Mn ions. The O K -edge XAS spectrum also varied after the Li-ion extraction. The difference O K pre-edge XAS spectra of delithiated samples from pristine sample indicated the formation of the peroxide and superoxide ionic-like states after the delithiation. Hence, the charge compensation in Li_2MnO_3 is achieved by the oxidation reaction of O anions. This result is the same with the electrochemically treated Li_2MnO_3 electrode [1]. On the other hand, both the V L -edge and O K -edge XAS spectra of delithiated LiVO_3 samples implied oxidation. Therefore, it is considered that the extraction of Li-ion in LiVO_3 is charge compensated by the electron extraction from the hybrid orbital composed of V 3d and O 2p orbitals.

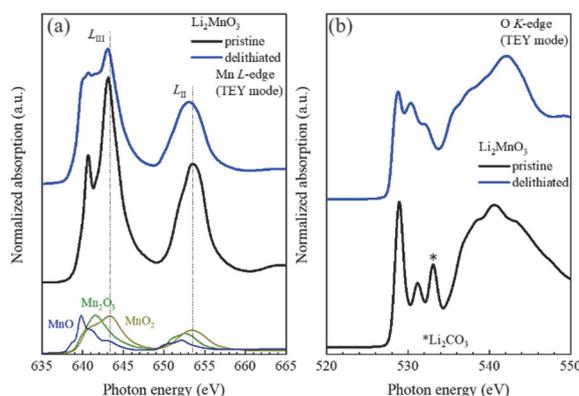


Fig. 1 (a) Mn L -edge and (b) O K -edge in TEY mode for Li_2MnO_3 .

References

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