

Electronic State Analysis of Oxygen Anion of 3d Transition Metal Layered Oxide Materials

Masatsugu Oishi^a, Ryoshi Imura^a, Keisuke Yamanaka^b, Iwao Watanabe^b,
Yoshiharu Uchimoto^c, and Toshiaki Ohta^b

^a *Tokushima University, 2-1 Minami Josanjima-cho, Tokushima, 770-8506, Japan*

^b *Ritsumeikan University, 1-1-1 Noji Higashi, Kusatsu, Shiga, 525-8577, Japan*

^c *Kyoto University, Nihonmatsu-cho, Yoshida, Sakyo-ku, Kyoto, 606-8501, Japan*

E-mail: ooishi.masatsugu@tokushima-u.ac.jp

Next generation high-energy-density lithium ion battery (LIB) requires positive-electrode materials with high voltage and high capacity. Generally, the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) of 3d transition metal oxides is determined by the metal 3d and O 2p orbitals. The HOMO is mainly controlled by the metal 3d orbitals, and the O 2p orbitals are generally spreads below the metal 3d orbitals. Hence, the charge compensation during the Li ion insertion/extraction processes is conventionally explained by the redox reaction of metal cations. However, when the electrode is further oxidized at the higher voltage, the percentage of O 2p character increases and holes are formed in O 2p orbitals.^[1] We have reported the participation of O 2p orbitals in Li-rich layered oxide, Li₂MnO₃.^[2] However, we well know that oxidation of oxygen anions causes the destabilization of the crystal lattice, which makes reversible utilization of the oxygen redox reaction difficult.

Toward the developments of high-energy-density LIB, we must focus on tailoring of the electronic structure at the Fermi level to stably and reversibly utilize the redox couple of oxygen anions.

In the present study, we used X-ray spectroscopy (XPS) and O K- and Mn L-edge X-ray absorption spectroscopy (XAS) to study the redox reactions that occur in Li-rich and conventional 3d transition metal oxides, Li₂TiO₃, Li₂MnO₃, LiCoO₂, and LiNiO₂. In Li₂TiO₃, valence change was not confirmed from Ti L-edge XAS spectra for the Li⁺-extracted samples, but the spectra insisted that the Ti local structure changed. On the other hand, the O K pre-edge XAS spectra, reflecting the hybridized states of O 2p and Ti 3d orbitals, suggested the oxidation of O ion and also the local structure change. In Li⁺-extracted Li₂MnO₃ samples, the Mn ion was reduced, while the O ion was oxidized. Hence, the O 2p orbitals, which hybridize with Mn 3d orbitals only weakly, contributed to the oxidation process. In Li⁺-extracted LiCoO₂ and LiNiO₂ samples, both of the Co ion and O ion, and both Ni ion and O ion, respectively, were oxidized indicating the electron extraction from highly hybridized orbitals. In addition, we semi-quantitatively evaluated the amounts of O desorption from the changes of O K-edge absorption jump to that of the metal L-edge. Li₂TiO₃ showed the largest release of oxygen from the crystal lattice. The degree of the hybridization should influence the stability of O ions during the oxidation process. Details of the electronic structure at the Fermi level will be shown at the conference with the results of XPS and density functional theory calculations.

References:

[1] J. B. Goodenough and Y. Kim, *Chem. Mater.* 22 (2010) 587-603.

[2] M. Oishi, K. Yamanaka, I. Watanabe, K. Shimoda, T. Matsunaga, H. Arai, Y. Ukyo, Y. Uchimoto, Z. Ogumi and T. Ohta, *J. Mater. Chem. A* 4 (2016) 9293-9302.