MS085.O05

Electronic structure of oxide electrode materials studied by compton profiles

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Li_xCoO_2 and $Li_xMn_2O_4$ are widely used as the positive electrode materials for Li-ion rechargeable battery. These materials have octahedron structures formed by the transition metal and oxygen atoms and this structure plays a key role in electrode reaction. However, the electrode reaction of these materials is not fully understood yet. So far, it has been believed that redox reaction with lithium (de)intercalation occur through the 3d orbitals of transition metal. On the other hand, it is reported that O-2p orbital play an important role on the redox reaction [1]. In this study, we revealed the redox orbital of these materials and found a descriptor for the oxide electronic conductivity in battery materials. This descriptor is related modification of 3d orbital of transition metal [2-3].

Compton profile measurement was performed on the BL08W at the SPring-8 synchrotron facility. The incident X-ray energy was 115 keV. The scattering angle was fixed to 165 degrees. The Compton scattered X-ray intensities were measured by position sensitive two-dimensional detector. The measurement was performed room temperature. Polycrystalline of $Li_xMn_2O_4$ (x = 0.476, 1.079, 1.233) and Li_xCoO_2 (x = 0, 0.5, 0.625, 0.75, 1) samples were prepared by extracting lithium chemically. The lithium composition was confirmed by inductively coupled plasma (ICP) analysis.

Results of our Compton profile measurements for $Li_xMn_2O_4$ and Li_xCoO_2 show an increment of itinerant electrons with lithium insertion. By comparing experimental results with first-principles calculations, we deduce that this increase of itinerant electrons has oxygen 2p character. Therefore, the redox reaction occurs via oxygen 2p orbitals in both materials. On the other hand, 3d orbitals of transition metal becomes less localized at the range of Li concentration corresponding to the optimal battery performance both for the $Li_xMn_2O_4$ and Li_xCoO_2 cathodes. This 3d orbital delocalization effect is associated with electron conductivity properties. Therefore, Compton scattering spectroscopy can provide new descriptors for electrode conductivity.

This work was supported by the Japan Science and Technology Agency, MEXT KAKENSHI, and the U.S. Department of Energy (Basic Energy Science/Division of Materials Science)

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Keywords: Battery materials, Compton profile, Electronic structure