Soft X-ray Absorption and Emission Studies of Rechargeable Battery Electrodes to Clarify the Redox Reactions

Daisuke Asakura[1], Takaaki Sudayama[1], Hirofumi Matsuda[1,2], Eiji Hosono[1]
[1]Research Institute for Energy Conservation, National Institute of Advanced Industrial Science and Technology (AIST)
[2]AIST-UTokyo Advanced Operando-Measurement Technology Open Innovation Laboratory
daisuke-asakura@aist.go.jp

Improving the energy density and power density of electrode materials for Li-ion batteries (LIBs) is highly important to further develop electric and hybrid-electric vehicles. For the improvements, understanding the charge-discharge mechanisms from a viewpoint of the electronic structure is indispensable. Recently, electronic-structure analyses of the electrode materials using soft X-ray (SX) spectroscopy have been of particular importance. We have been studying the redox reaction of various electrode materials by using soft X-ray absorption spectroscopy (XAS) and soft X-ray emission spectroscopy (XES). These SX spectroscopic methods are very powerful to investigate the 3*d* orbitals of transition metals (TMs) and 2*p* orbitals of ligand elements such as oxygen in TM-oxide electrode materials.

The sample preparation and charge-discharge experiments for *ex situ* measurements were performed at AIST. The XAS measurements were carried out various synchrotron facilities, and the XES measurements were performed at BL07LSU and BL27SU of SPring-8. The XAS and XES spectra were analyzed by use of the configuration-interaction full-multiplet (CIFM) calculation [1-3].

For the Mn *L*-edge XAS and XES of $LiMn_2O_4$ cathode, a huge charge-transfer (CT) effect from the O 2*p* to Mn 3*d* orbitals has been found for the Mn^{4+} state, while the Mn^{3+} state has a large CT effects. This is completely different from the case of $LiFePO_4$ cathode with a very weak CT effect from the O 2*p* to Fe 3*d* orbitals for both Fe^{2+} and Fe^{3+} states. We explained that the changes of CT effects during lithiation/delithiation could be related to the corresponding cycle performances.

In the presentation, several XAS and XES results for other cathode materials will be shown [4-6]. Moreover, our *operando* XES system for LIB developed at BL07LSU will be introduced [7].

Acknowledgements
Parts of this work were conducted under the international joint research program for innovative energy technology by METI, Japan and AIST-UTokyo Advanced Operando-Measurement Technology Open Innovation Laboratory.

References
[1] Y. Nanba *et al*., J. Phys. Chem. C **116**, 24896 (2012).
[2] Y. Nanba *et al*., Phys. Chem. Chem. Phys. **16**, 7031 (2014).
[3] D. Asakura *et al*., J. Phys. Chem. Lett. **5**, 4008 (2014).
[4] D. Asakura *et al*., ChemPhysChem **17**, 4110 (2016).
[5] D. Asakura *et al*., AIP Adv. **6**, 035105 (2016).
[6] D. Asakura *et al*., Phys. Chem. Chem. Phys. **19**, 16507 (2017).
[7] D. Asakura *et al*., Electrochem. Commun. **50**, 93 (2015).