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Operando electronic-structure analysis for the cathode materials of Li-ion battery by soft X-ray emission spectroscopy

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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. In order to realize the improvements, understanding the charge-discharge mechanisms of the electrode materials from a viewpoint of the electronic structure is indispensable. Recently, electronic-structure analyses for the electrode materials using soft x-ray spectroscopy, which directly reveals the 3*d* orbital of transition metals, have been of particular importance.

In this study we demonstrate *operando* soft x-ray emission spectroscopy (XES) for $LiMn_2O_4$ which is a typical cathode material of LIB. We developed an *in situ* cell consisting of the $LiMn_2O_4$ thin-film cathode, a counter electrode and an electrolyte solution by modifying the *in situ* cell for the catalyst of fuel cells[1]. The *operando* XES experiments were carried out using ultrahigh-resolution XES spectrometer[2] at BL07LSU of SPring-8. The charge-discharge experiments were performed by cyclic voltammetry.

The Mn 2*p*-3*d*-2*p* resonant XES spectra revealed redox reaction of $Mn^{3+} \leftrightarrow Mn^{4+}$ due to the charge-discharge reactions[3]. Furthermore, charge-transfer effects between the Mn 3*d* and O 2*p* orbitals for each valence state were clarified by theoretical analyses using the configuration-interaction full-multiplet calculation[4]. In the presentation, *operando* XES results for other electrode materials will also be reported, and the relationship between the electronic structure and electrochemical performance will be discussed in detail.

References

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