Soft X-ray Spectroscopy Studies for Electrode Materials to Clarify the Electronic-Structure Change and Charge-Transfer Effects in the Lithiation and Delithiation Processes

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Improving the energy 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 of battery performance, understanding the lithiation and delithiation mechanisms from a viewpoint of the electronic structure is indispensable. Recently, electronic-structure analyses of the electrode materials using soft X-ray spectroscopy have been of particular importance. While many soft X-ray absorption spectroscopy (XAS) studies of the electrode materials have been reported, we have focused on the development of *operando* soft X-ray emission spectroscopy (XES) techniques and have revealed the relationships between the performances for several electrode materials and their electronic-structure changes during lithiation/delithiation [1,2].

Here, we demonstrated *operando* Mn L_3-edge XES for $LiMn_2O_4$. The *operando* cell consists of the $LiMn_2O_4$ thin film, a counter electrode and an electrolyte solution [3]. The *operando* XES experiments were carried out at BL07LSU of SPring-8 [4]. The XES spectra were analyzed by theoretical analyses based on the configuration-interaction full-multiplet calculation [2,5]. A large charge-transfer (CT) effect from the O 2*p* to Mn 3*d* orbitals has been found for the Mn^{4+} state. In parallel, the electronic structures and CT effects for several cathode materials have been studied by means of XAS and XES [6,7]. We explained that the changes of CT effects during lithiation/delithiation could be related to the corresponding cycle performances.

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