Operando photoelectron spectromicroscopy of charge/discharge process in cathode materials of all-solid-state Li-ion battery

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In a sustainable modern society, Li-ion-batteries (LIBs) play a more important role as an energy storage of electric vehicles. Understanding the operation mechanism of LIBs is essential to improve their properties, such as energy density, long cycle life, safety operation, and thermal stability. For this purpose, many *operando* studies have been reported on the electronic properties of the constituent elements using, e.g. hard X-ray absorption spectroscopy, while the character of the most functional 3d electrons in LIBs have not yet been fully understood. Recently Asakura *et al.* have successfully introduced *operando* soft X-ray absorption / emission spectroscopy as a novel technique to unravel the functional metal 3d states during lithiation/delithiation process in LIB cathode materials [1].

However, most of the *operando* synchrotron X-ray spectroscopy techniques provide average information of electrodes within several-ten or several-hundred μm of the X-ray beam size which is usually larger than the particle size of active materials in electrodes. To further understand the charge/discharge mechanisms, a spectromicroscopy with a high spatial resolution is of particular importance because that method can detect changes of various electronic structures of transition metals and oxygen, which correlate closely with the lithiation/delithiation, in the one particle.

Here we propose the use of *operando* photoelectron spectromicroscopy to add spatially resolved information with less than 100 nm resolution to the electronic structure of a few μm single-crystal LIB cathode material [2]. We developed an all-solid-state LIB cell that can operate under ultra-high vacuum condition and obtained *operando* photoelectron spectra of $LiCoO_2$ cathode at charge/discharge states using the 3DnanoESCA station at BL07LSU of SPring-8 [3].

In the presentation, we will show photoelectron images for one single-crystalline $LiCoO_2$ particle, and pin-point core-level spectra for selected points in the particle.

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