

Breakthrough in energy density of lithium ion batteries by spectroscopic X-ray diffraction

Global paradigm shift in energy supply and usage, which partially stems from the accident of nuclear power plant, calls for emergence of next-generation battery. Among various energy storage systems, lithium-ion batteries (LIBs) are the most promising candidates not only for portable electronics but also for large-scale energy storage at present. In practice, LIBs greatly contributed to the recent commercialization of ecofriendly electric vehicles. Although many studies on their performance have been made, there is still room for improvement of LIBs in terms of energy density per volume associated with how to strike a balance between the amount of active materials and pore volume for Li+ diffusion in the composite electrode being composed of the active materials, binders and conductive agents. Such a manufacturing problem known as "packinglimitation" tends not to be spotlighted presumably because of analytical requirements totally different from those used in material synthesis.

Besides, recent progress on synchrotron optics using a compact channel-cut monochromator paved the way for the simultaneous use of Spectroscopy and Diffraction, resulting in successful understanding of electrochemical reactions for two-phase-coexistence-type-compoundelectrode in LIBs [1]. This methodological approach motivated us to work out "spectroscopic X-ray diffraction (S-XRD)" in the true sense of the word. If, instead of using white X-rays as is often the case with energydispersive XRD, continuous irradiation with highly monochromatic X-rays in wide-ranging energy region was available, the diffraction spectrum as a function of the X-ray energy would be obtained [2]. This article covers a brief description as to the principle of S-XRD and introduces operando inspection for LIBs using highenergy-density electrodes as a demonstration analysis to break the ice for future industrial applications.

S-XRD is based on the rotation of the compact

channel-cut crystal, indicating that a slight change in the height of the exited beam after the monochromator is inevitable (Fig. 1(a)). In the case of beamline **BL28XU**, the gap of the Si monochromator system is as small as 3 mm. The height change, less than 0.2 mm at the largest in our standard setup (5-30 keV), is smaller than the vertical width of the whole incoming beam. Thanks to two guadrant slits located at the downstream of the monochromator, the position, divergence and incident angle of the monochromatic X-ray on the sample are substantially unchanged with the energy change [2]. Note that the higher harmonics was eliminated by placing double Rh coated mirrors after the monochromator. Here, let us explain several important features of S-XRD. The spatial resolution, h, in the direction of the scattering vector under a symmetrical confocal condition using the incident- and receiving-slits is given in the following equation:

 $h = w/\cos(2\theta/2)$

where *w* is the window size of the slit and 2θ is the angle determined by the incident X-ray and detector directions. The profile resolution, i.e., $\Delta d/d$, can be expressed as the contribution of the angular divergence ($\Delta \theta$) including the angle of view geometrically defined by the instrument and the energy resolution of monochromating device (ΔE) as follows:

$$\left|\Delta d/d\right| = \left|\Delta E/E\right| + \left|\cot\theta\right|\Delta\theta$$

where $\Delta E/E$ is the bandwidth of the Si₁₁₁ channelcut monochromator which typically offers the energy resolution on the order of 10⁻⁴ at BL28XU.

We compare powder XRD data for $Li_1Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) film-type sample by the energy-scanning and angle-scanning XRD methods (see Fig. 1(b)). The vertical axis of the diffraction spectrum was normalized by the incident beam



Fig. 1. (a) A schematic drawing of the energy-scanning confocal XRD analysis, (b) energy-scanning XRD spectrum (top) and angle-scanning XRD pattern (bottom) for the film-type electrode containing $Li_1Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$.

intensity, the self-absorption, the detection efficiency, and the Lorentz's polarization factor. Importantly, the obtained *d*-values and peak intensities are fairly the same as those estimated from the angle-scanning XRD pattern. This result definitely demonstrates the great potential of S-XRD as a microscopic inspection of Li⁺ concentration in the electrode of LIBs during the battery operation.

When the electrode density is increased, the specific capacity decreases and finally yields a poor value. This is the packing-limitation in LIBs. To tackle this issue, we focused on the decrease in free space (pore) governed by the amount of active materials in the electrode [3]. Judging from a way of the Li+ transport in the composite electrode, the denser conformation should be disadvantageous to the Li+ supply to the deepest part and evokes terrible rate-performance. The operando analysis aiming the reaction difference between the inner and outer parts of such a densely packed electrode may pick up the cause of the packing-limitation. Figure 2 shows the variation in Li⁺ concentration of NCM at four different depths of the 18% porosity electrode at various discharge rates. Similar lithiation behavior was observed at the four divided positions of the electrode in the low-rate operation (0.1C), indicating that the electrode worked homogeneously. At higher-rate operation (0.5C), the

Li⁺ concentration differed between positions (i) and (iv). This difference suggests that the packing-limitation is essentially induced by the high-rate operation. Further high-rate operation, 1C, makes the discharge time shorter. The Li⁺ concentration for the electrode surface, position (i), at the 1C operation definitely accounts for the cell potential identical to the cut-off potential. Thus, the deterioration of the discharge capacity observed in this study can be explained by the delay of Li+ transport to the current collector side. Interestingly, the concentration differences among the positions after the discharge were relaxed in response to the potential difference exactly at the end of the discharge. These direct evidences indicate that rate-dependent packinglimitation originates from a bad accessibility of the Li+ at the deepest part in the composite electrode. This study points out the essential advantage of thinner film-type electrodes in LIBs application and offers a concept to overcome this issue via installation of some shortcut for Li+ diffusion to the composite electrode.

Lastly, we would like to emphasize again the importance of using S-XRD to understand what gives rise to the limitation of battery performances including the energy density. Further developments in the beamline optics and sources which allow us to brave a variety of scientific adventures, we believe, will boost the growth of battery industry.



Fig. 2. (a) Illustration of the confocal points written on SEM image of the cross-section in the composite electrode. (b) Li⁺ concentration of the active material (NCM) densely packed in the composite electrodes $(\sim 18\%$ porosity). The open symbols (circle, triangle, square, and diamond) correspond to positions (i), (ii), (iii) and (iv), respectively, in the cross-section of the electrode in the top. The lines correspond to the change in cell potential depending on the time. The broken lines show the end of the cell discharge, indicating the specific capacity of the cell.

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