## Tackling the safety issue of lithium ion batteries at Kyoto University & NEDO beamline

Lithium ion batteries (LIBs) have been widely used in power supply applications, e.g., mobiles, electric vehicles and renewable energy storage devices. Most LIBs use a variety of organic electrolytes because of a wide potential window despite rigorous reactivity with the atmosphere. Their safety in normal use is no longer questionable, but this is not true in cases of improper use as seen in the recent accidents in the aircraft industry. A real-time analysis of unexpected reactions occurring in the LIBs in overcharge states would contribute to the improvement of their safety, while many disassembly analyses have already provided limited information. In particular, it is still difficult to analyze active materials in commercial LIBs directly owing to thick outer cases. Therefore, in situ analyses of such commercial products seem challenging in various charge/discharge states including the overcharge region. In this article, we would like to introduce an in situ pinpoint XRD analysis system and a recently developed glove box-integrated diffractometer to deal with the safety problem latent in the commercial LIBs mentioned above.

In general, the electrochemical reaction in the LIBs can be understood by gradual or drastic changes in crystal structure associated with Li<sup>+</sup> insertion/desertion. Firstly, we developed an *in situ* XRD method with a confocal geometry to attain a spatial resolution of several tens of micrometers. A schematic drawing of the confocal method is shown in Fig. 1(a). Incident and receiving slits that collimate the incident and

diffracted X-rays form a confocal area with a lozenge shape. Its spatial resolution *h* is given as:

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

where w and  $2\theta$  are the slit width and diffraction angle, respectively. This confocal setup with a highly penetrative X-ray realized a pinpoint XRD analysis, which allowed us to understand the crystal structure of sealed materials.

The commercial LIB investigated in this study consists of a LiCoO<sub>2</sub> layer on an Al current collector as a cathode, graphites on a Cu current collector as an anode, and probably conventional organic electrolytes. These components were wholly packaged in an Al container, the wall thickness of which is about 300 μm. The LIB package connected to a mobile phone was placed on a multi-axis diffractometer installed at beamline BL28XU [1], as shown in Fig. 1(b). The observation area, i.e., confocal area, is controlled by changing the position of the mobile phone. Figures 1(c) and 1(d) show in situ XRD patterns during 2 h charge and 5 h discharge reactions, respectively. The diffraction peak corresponding to the AI container on the surface of the LIB package remains unchanged during the charge and discharge reactions. On the other hand, the electrode deeply packed in the battery exhibits a distinct diffraction peak shift at  $2\theta = 4.9$ -5.0°, which is assigned to LiCoO<sub>2</sub>-related compounds  $(Li_{1-x}CoO_2)$  during the operation of the mobile phone. This is due to a change in crystal structure associated



Fig. 1. (a) Schematic drawing of the confocal XRD analysis of the commercial LIB. (b) View of the measurement. *In situ* XRD patterns obtained on surface and electrode positions of the battery during (c) charge and (d) discharge process.



Fig. 2. Photograph of the glove box-integrated diffractometer developed through a collaboration with Rigaku-Aihara Corporation.

with the Li<sup>+</sup> insertion/desertion. Thus, our study demonstrates the great potential of confocal XRD as a time-resolved pinpoint analysis technique for commercial LIBs.

Secondly, as a fundamental study for the LiCoO<sub>2</sub> electrode in the overcharge state, a see-through cell convenient for examining a certain type of oxidation was prepared under inert atmosphere and subjected to the following analysis. The cell was preliminarily conditioned by performing charge/discharge cycles up to the second discharge process. A fast XRD analysis based on consecutive snapshots acquired from a one-dimensional pixel array detector was carried out using the glove box-integrated diffractometer (see Fig. 2) installed at BL28XU to prevent possible hazards, e.g., thermal runaway, fire and explosion, in the overcharge state. Figure 3 shows *in situ* XRD

patterns of the cell during the third charge process. At the beginning of the charge process, two diffractions for AI and three diffractions for Li1-xCoO2 in the O3 structure were observed. Through charging the cell until 5.0 V indicated by the broken line, Li<sub>1-x</sub>CoO<sub>2</sub> in the H1-3 structure appeared and finally transformed into Li<sub>1-x</sub>CoO<sub>2</sub> in the O1 structure. This structural transformation induced by the electrochemical extraction of Li<sup>+</sup> from the LiCoO<sub>2</sub> active material is fairly consistent with the earlier studies reported in the literature. Interestingly, it is found that the diffraction peak at around  $2\theta = 9.7^{\circ}$  continues to shift to a lower angle until the potential of 5.5 V (the so-called overcharge state in this material system), indicating that the Li<sub>1-x</sub>CoO<sub>2</sub> in the O1 structure is still active in the potential region. At a potential higher than 5.5 V, the peak positions of the Li<sub>1-x</sub>CoO<sub>2</sub> in the O1 structure become constant and noisy current is observed. This behavior can be explained by the inevitable decomposition of the electrolyte used at the high potential. To the best of our knowledge, this is the first in situ XRD study on LiCoO<sub>2</sub> electrodes in the extraovercharge state (more than 5.5 V).

In conclusion, we showed two *in situ* analyses. The confocal XRD analyses carried out at BL28XU successfully visualized the phase transition behavior of the LiCoO<sub>2</sub> active material depending on the electrochemical potential in the commercial LIBs. Also, a LiCoO<sub>2</sub> electrode in the extra-overcharge state was investigated in detail by means of the glove box-integrated diffractometer. Further development of synchrotron-based analyses will strongly promote the wide spread use of the LIBs.



Fig. 3. (a) In situ XRD patterns and (b) charge curve for the LIB cell used in this study. "LCO" in the figure means  $LiCoO_2$ -related compounds.

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## References

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