Battery cell attachment

—In situ X-ray diffractometry for observations of structural change in electrode materials during charging and discharging—

1. Introduction

Lithium ion secondary batteries (LIBs) are widely used in compact mobile devices such as cell phones and notebook PCs. Current research and development at universities, research institutions, and companies seek to create LIBs for use in large machines, including electric vehicles. Meanwhile, competition in the development of LIBs has intensified in Asian and Western countries.

Commercializing LIBs requires improvements in capacity, stability, and longevity, which in turn entail various assessments and evaluations. Figure 1 shows aspects of LIBs that equipment manufactured and sold by Rigaku can be used to assess. Among the evaluation methods currently available, X-ray diffractometry offers a wide range of analytical capabilities that allows extensive examination of structural changes in electrode materials, such as qualitative analysis, crystallite size analysis, and Rietveld analysis.

At the 50th Battery Symposium in Japan, held in 2009, half a dozen reports were presented on *in situ* measurements of LIBs by various analytical methods. In contrast, at the 51st Battery Symposium in Japan, held in November 2010 in Nagoya, the number of reports on *in situ* measurements of LIBs numbered 18, a threefold increase. Announced at this most recent symposium were the results of experiments done at SPring-8. The

results of measurements of structural changes obtained with X-ray diffractometers while batteries are charged and discharged point to structural changes in electrode materials, even during the initial charge/discharge cycle; lithium desorption and insertion at certain points during the charge/discharge cycle; and other details, such as changes in bond distances between metal and oxygen atoms. Additionally, much work related to *in situ* evaluations is being done today in laboratory environments. The results of laboratory analyses using the battery cell attachment discussed in this paper have been reported at the 78th Meeting of the Electrochemical Society of Japan⁽¹⁾ in March 2011.

2. Measuring LIBs in the charge/discharge state

Since LIBs undergo repeated charge and discharge cycles, evaluations using an X-ray diffractometer must be done while LIBs are being charged or discharged. *Ex situ* measurements or *in situ* measurements are used to evaluate LIBs in the charge/discharge state. For ordinary *ex situ* measurements, coin cells are repeatedly charged and discharged under specific conditions. The cells are then taken apart and examined by X-ray diffraction analysis or other methods. This approach poses the following issues:



Lithium ion battery evaluation

Fig. 1. Lithium ion battery evaluation.



Fig. 2. External view of battery cell attachment.

(1) Many coin cells must be prepared for these charge/discharge tests.

Once a coin cell is taken apart, it cannot be charged or discharged. Therefore, many test cells must be prepared, resulting in the need to account for variations from cell to cell and variations among tests done by different testing personnel.

- (2) Material stability problem during disassembly. When the components of a LIB are exposed to oxygen or moisture, they may degrade or undergo reactions. This means certain awkward procedures must be done in a glove box (bag).
- (3) There is no way to determine if the disassembly affects the charge/discharge state. Disassembly may result in natural discharge.

By comparison, *in situ* measurements make it possible to analyze LIBs in their original condition without taking them apart, eliminating concerns related to the issues above.

3. Overview and features of the Rigaku-manufactured battery cell attachment

Figure 2 is an external view of the Rigaku battery cell attachment. Figure 3 shows the sample setup procedure. Figure 4 shows the battery cell attachment mounted on an X-ray diffractometer.

3.1. Main specification

• Sample dimensions:

Positive electrode diameter (standard) 15 to 16 mm (formed on aluminum foil or mesh)

Negative electrode diameter (standard) 18 to 19 mm Separator diameter 20.0 to 20.5 mm

- 2θ angle range: From 10°
- Main body material: Stainless steel
- Insulating material: Teflon
- Window material: Beryllium
- Number of poles, electrode materials: 2 poles (positive electrode: beryllium, negative electrode: stainless steel)
 Sealing material: O-ring
- Pressing and retaining the sample: After setting the



Fig. 3. Sample setup procedure.



Fig. 4. Example: Mounting the battery cell attachment on an X-ray diffractometer.

spacer and wave washer into position, use a quick clamp to hold the sample in place.

- Rated voltage and current: 32 VDC, 3 A max.
- Terminal: Equipped with two-pole terminal for charge/ discharge

A sample is set up in the battery cell attachment inside a glove box as shown in Fig. 3. With the beryllium window facing down, the positive electrode material, separator, and negative electrode are set in place, in that sequence. Electrolyte is added, if needed.



Fig. 5. Example of measurement of lithium cobalt oxide sample.



Fig. 6. X-ray diffraction profiles of LiFePO₄ during charge process.

The spacer and wave washer are placed on top, and the metal retainer and other parts are mounted. A quick clamp is used to hold the assembly. Figure 2 shows a sample held by a quick clamp. The battery cell attachment with a sample mounted as described above is set on the attachment mounting base of the X-ray diffractometer (Fig. 4).

3.2. Main applications and features of battery cell attachment

The battery cell attachment discussed here allows Xray diffraction measurement of the battery mounted in the battery cell attachment. It does not require removal of the sample. This makes it suitable for measuring structural changes in electrode materials while varying the charge/discharge conditions in fine steps during the initial charge/discharge cycle, or during the first several cycles, rather than for observations of structural change in the electrode materials of a coin battery over the course of several dozen or more charge/discharge cycles.

Rigaku developed the battery cell attachment after consulting LIB researchers with extensive experience in the area. For example, the battery cell attachment is configured so that a battery can be mounted in the attachment easily and securely in a glove box, without screws. It allows measurement from $2\theta=10^{\circ}$, and is capable of detecting positive electrode degradation signals in a low angle range. The battery cell attachment can be mounted on several Rigaku X-ray diffractometers, including SmartLab, TTRAX III, Ultima IV, and D/MAX. (To determine if your equipment is compatible with the battery cell attachment, contact your Rigaku sales or service representative).

Figure 5 shows an example of results from measuring a lithium cobalt oxide sample at a scan speed of 50°/min using a high-speed one-dimensional detector (measuring equipment: TTRAX III, X-ray source: 50 kV, 300 mA).

4. Example of *in situ* measurement using the battery cell attachment

The advantages offered by olivine-type $LiFePO_4$ include low environmental impact and excellent thermal stability, prompting study for use as a positive electrode material for batteries for automobiles and large machinery. We evaluated the crystal structure of $LiFePO_4$ during a charge process using the battery cell attachment (samples courtesy of Professor Tatsuya Nakamura, Graduate School of Engineering, University of Hyogo).

We set $LiFePO_4$ in the battery cell attachment and performed X-ray diffraction measurements at states of charge (SOC) of 0, 40, 60, 80, and 100%. Figure 6 shows the X-ray diffraction profile and qualitative analysis results at each SOC. Only single-phase LiFePO₄ was observed at the 0% SOC, but as the SOC increased, diffracted X-rays deriving from FePO₄ began to appear. At the 100% SOC, diffracted X-rays showed a nearcomplete FePO₄ phase transition, indicating a two-phase reaction between LiFePO₄ and FePO₄ in the LiFePO₄ in the charged state.

5. Summary

At the 51st Battery Symposium in Japan held last fall, researchers involved in state of the art work stressed that clarifying the positive electrode degradation mechanism would require detailed examination of structural changes in the positive electrode from various perspectives during the initial charge and discharge cycle. Continuing progress in the research, development, and industrialization of lithium ion secondary batteries offering high performance, longevity, cost-effectiveness, and safety are strongly needed to mitigate everincreasing serious environmental problems. It is our hope that the battery cell attachment introduced in this paper will contribute to these efforts.

Reference

(1) Tatsuya Nakamura, Shin-ichi Masuda, Yuya Shima, Akari Takahara and Hisashi Yashiro: Proceedings of the Academic Lecture Session of the 78th Meeting of The Electrochemical Society of Japan, (2011), 2L04.