The latest X-ray diffraction techniques for advanced research and development in lithium-ion battery materials

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1. Introduction

The materials used in the manufacture of lithium-ion batteries include positive electrode materials, negative electrode materials, electrolytes, separators, binders (for positive and negative electrodes), and cladding materials (for battery housings). Research and development on these materials is active and ongoing.

This paper describes recent expectations for X-ray diffractometers in research and development activities that seek to improve the performance of such materials. It also introduces measurement methods that respond to those expectations.

2. Use of *in situ* cells to analyze changes in crystal structure during charging and discharging

It is recognized that controlling charging and discharging conditions extends the service life of lithium-ion batteries. This control requires more than observations of electrode structures in the fully charged/discharged state; it requires real-time measurements of the relationship between the states of charge/discharge and the electrode structures using in situ cells. The 2011 Spring issue of Rigaku Journal introduced the results of in situ X-ray diffraction measurements of changes in the crystal structure of olivine-type positive electrode LiFePO₄ (provided by Tatsuya Nakamura, Professor, Graduate School of Engineering, University of Hyogo) using lithium-battery cells⁽¹⁾. In this experiment, when the state of charge (SOC) was 0%, the material was LiFePO₄. However, as SOC increased, X-ray diffraction peaks generated by FePO₄ began to appear. At 100% SOC, X-ray diffraction patterns indicated a near-complete FePO₄ phase after a coexistence state of two phases. Professor Nakamura and Yashiro (of Rigaku Corporation) et al. recently showed that a slight peak shift occurs at 20% SOC relative to 0% SOC, and that lattice constants decrease by around 0.05%. However, virtually no change in lattice constants occurs from that state to 60% SOC. These findings were presented in the conference held by the Electrochemical Society (U.S.A.) in October 2011⁽²⁾. As this example suggests, we believe detailed analyses of changes in crystal structure during charging and discharging will become increasingly important in controlling charge/discharge states.

3. Observations of trace quantities of coexisting compounds

Research and development efforts currently target various compounds for use as positive and negative electrode materials. Since positive electrode materials are multi-element metal oxides, compounds differing slightly in composition or crystal structure may be mixed in during synthesis, or slight changes may occur in the crystal structure or composition of the material during repeated charges/discharges. In addition, trace amounts of compound may be deliberately added to improve the material performance. Conventionally, Xray diffractometry has been used for qualitative and quantitative analysis of trace amounts of coexisting compounds and for analysis of polymorphic compounds having identical chemical composition but different crystal structure. This method is widely used for both inorganic and organic materials. We expect similar demand to grow in the field of lithium-ion battery materials.

3.1. Measurements using D/teX Ultra, high-speed one-dimensional detector

The features and characteristics of the D/teX Ultra high-speed one-dimensional detector have been described in Rigaku Journal⁽³⁾. This detector offers roughly 100 times the detection sensitivity of scintillation counters. It is ideally suited to measurements of materials for lithium-ion batteries, because this detector offers high energy resolution that reduces the effects of fluorescent X-rays from Co, Fe, or other materials found in the positive electrode material of the lithium-ion battery. Figure 1 compares measuring results of CoLiO₂, removed from a coin cell battery charged and discharged 100 times, using a scintillation counter and the D/teX Ultra.

3.2. Measurements using Kα1 optics and D/teX Ultra

When a Cu target is used as an X-ray source, the following three K-series X-rays with neighboring wavelengths are included: $K\beta 1$ 1.392 Å, $K\alpha 1$ 1.541 Å, and $K\alpha 2$ 1.544 Å. With the most common X-ray diffraction measurement method, a nickel filter is used to remove peaks by $K\beta$ X-rays. However, this also reduces the intensity of the sample's other diffraction peaks.

To offset this drawback, the K α 1 optic system is used to extract only K α 1 X-rays. Top level researchers in the field of lithium-ion battery who visit the Rigaku

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Fig. 1. Comparison of results of LiCoO₂ measurements.



Fig. 2. Schematic of SmartLab with $K\alpha 1$ optics and D/teX Ultra.



Fig. 3. Results of measurement and analysis.

laboratory often show great interest in the following two newest Rigaku systems. These systems allow to measure infinitesimal impurities in positive electrode materials:

- 1. The combination of Rigaku's SmartLab Automated Multipurpose X-ray Diffractometer, the $K\alpha 1$ optics, and the D/teX Ultra,
- 2. The combination of the K α optics (K α 1 and K α 2

with intensity ratio of 2:1), monochromator, and the D/teX Ultra.

Figure 2 shows a schematic of the SmartLab combined with the K α l optics and D/teX Ultra.

To date, measurements of infinitesimal compounds have been very hard to perform without a synchrotron radiation facility like SPring-8. However, the capacity to



Fig. 4. Crystal structure obtained.

measure minute peaks against background noise in ordinary laboratory settings is expected to advance studies of the positive and negative effects of trace coexisting compounds.

4. Structure analysis of the positive electrode materials of lithium-ion battery based on powder X-ray diffraction data

In the field of lithium-ion battery materials, researchers have expressed more interest in analyzing crystal structures based on powder X-ray diffraction data. Introduced below is an example of an structure analysis of $\text{LiFe}_{0.8}\text{Mn}_{0.2}\text{PO}_4$, an FeMn olivine-type positive electrode material offering excellent thermal stability and safety (sample courtesy of Nobuya Machida, Professor of Department of Chemistry of Functional Molecules, Konan University).

A baked at 550°C sample was measured using

 Table 1.
 Crystallographic data.

LiFe0.8Mn0.2PO4		
P <i>nma</i>		
10.3463(5)		
6.0219(3)		
4.7046(2)		
4		
3.57		

 Table 2.
 Structural parameters.

Label	Occupancy	Fractional coordinates			emperature factor
		x	У	Ζ	B (Å-2)
Fe/Mn	0.8/0.2*	0.28189(5)	1/4	0.0253(8) 0.58(4)
Р	1	0.0947(1)	1/4	0.5831(2)	0.56(3)
01	1	0.0962(3)	1/4	0.2603(5	0.36(6)
O2	1	0.4558(3)	1/4	0.7922(4	0.50(6)
O3	1	0.3348(2)	0.5495(3)	0.2163(3	0.33(4)
Li	1**	0 ``	0 ``	0	1.1(2)

*The ratio of Fe to Mn was fixed (due to the nearby atomic scattering factor.)

** We attempted to obtain the precise occupancy of Li, but since the value was 1.00(1), we set the ratio to 1.

the Ultima IV Protectus general-purpose X-ray diffractometer. The results obtained are given in Fig. 3, Fig. 4, Table 1, and Table 2.

Using this method, the relationship between fine structure of various battery materials and their performance will be easily verified in ordinal laboratories.

References

- (1) The Rigaku Journal (English version), 27 (2011), No. 32–35.
- (2) T. Nakamura, S. Masuda, Y. Yamada, H. Takahara and W. Yashiro: 220th ECS Meeting and Electrochemical Energy Summit (2011), Session B6, Abstract No. 647.
- (3) The Rigaku Journal (English version), 24 (2008), No. 30–32.