

# Characterization in lithium ion battery

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Lithium ion battery (LIB) has been successfully applied to portable electronics for the last decade. Recently, application of LIB in the field of energy vehicles and stationary storage systems has attracted considerable attention, in order to efficiently utilize renewable energies such as solar and wind energies. As higher energy capacity and power, long-term stability, safety, and lower costs are required, further development and studies are accelerated around the globe. To attain this goal, extensive research about the materials and the configurations of the battery is being carried out. In addition, characterization techniques are strongly required because it is essential to understand the fundamental behavior of the material in the electrochemical reaction, the mechanism of cell deterioration, the interphase phenomena of the electrode and electrolyte, and many indeterminate ideas not yet well understood. The schematic illustration of a lithium ion cell is shown in Fig. 1. It is composed of a positive electrode, a negative electrode, organic liquid electrolyte with lithium-ion conductivity, and an electrically insulating polymer separator. Lithium insertion

compounds such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiFePO}_4$  are typically employed for the positive electrode. Graphite is typical for a negative electrode, and more recently Si or Sn alloy having higher energy capacities and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  with an advantage in safety are also used. The lithium ion migrates from the positive electrode material to the negative electrode material through the electrolyte and the electron flows through the external circuit from the positive electrode to the negative electrode during the charge process. An inverse reaction occurs during the discharge process. It follows that the number of lithium ions migrating between the electrodes determines the energy capacity of the cell, and the mobility and the repeatability on the migration of lithium ion affect the power and lifespan of the cell, respectively. At the interface between the electrolyte and the electrode during the charge-discharge process, passivation film called a solid electrolyte interphase (SEI) is precipitated. In the electrode, accompanied with de-intercalation/intercalation of the lithium ion, oxidation/reduction of the electrode material is taken place and the crystalline structural is converted. Additionally numerous side-reactions represented by decomposition of electrolyte and gas evolution could occur in the lithium ion cell, and all of which could affect the cell performance. Studying and controlling the phenomena therefore, are critical for the development of LIB.

At the 220th ECS fall meeting in Boston in October 2011<sup>(1)</sup>, many reports on advanced characterization were presented. In addition to conventional and basic uses of laboratory analysis tools, spatial-resolved or time-resolved functions approaches are carried out for the investigation of interfacial reaction, reaction distribution and reaction process of LIB. *In situ* analysis technique allows the analysis condition to more closely resemble the actual operating condition. Synchrotron radiation enables us to obtain higher sensitivity and resolution. *In situ* TEM observation with the atomic scale spatial resolution reveals how the electrode interface phase forms during lithium intercalation and de-intercalation<sup>(2)</sup>. The combination of time-resolved X-ray diffraction (XRD) and mass spectroscopy identifies the structural change and gas evolution during thermal decomposition of the electrode<sup>(3)</sup>. Various advanced techniques including NMR, X-ray absorption spectroscopy (XAS), X-ray tomography, neutron, FT-IR, AFM, ellipsometry, and glow discharge-optical emission spectroscopy (GD-OES) show their characterization capabilities to enhance the research and

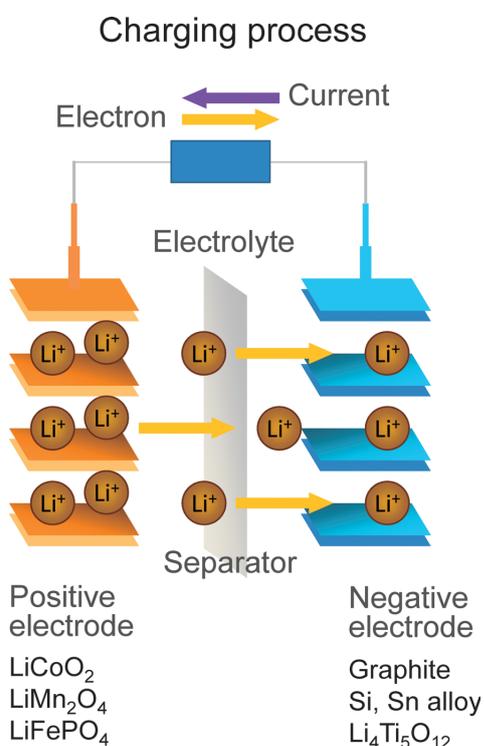


Fig. 1. Schematic illustration of lithium ion cell.

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## X-ray diffractometry

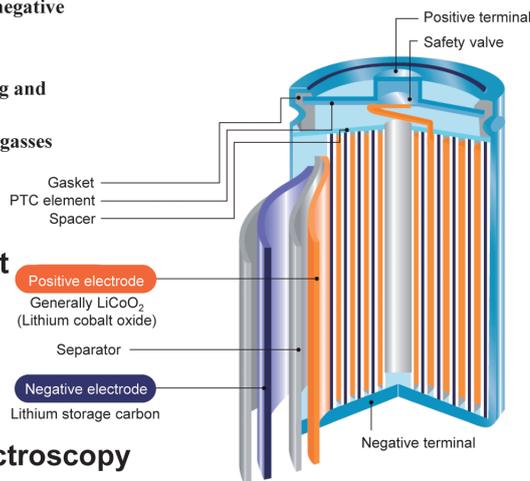
- Crystal structures of positive and negative electrode materials
- Coexisting impurities
- Structural changes during charging and discharging
- Characterization in reactive/inert gasses

## Small-angle X-ray scattering measurement

- Nano-size particles and pores of positive/negative electrode materials
- Evaluation of support materials

## X-ray fluorescence spectroscopy

- Composition analysis of positive electrode
- Control of metallic impurities in electrode
- Evaluation of coating layer thickness



## Evolved gas analysis (mass spectroscopy)

- Evaluation of passivation film on electrodes
- Adsorbed materials on surfaces
- Characterization of electrode materials in a reactive gas atmosphere

## X-ray radiography X-ray CT

- Internal structures and defects
- Bonding states of terminals and devices
- Failure of electrode sheet winding

Fig. 2. Structure of cylindrical lithium-ion battery and examples of measuring methods available using Rigaku instruments.

development of LIB. The 52nd battery symposium was held in Tokyo in October 2011<sup>(4)</sup>. There were approximately 600 oral presentations and more than 2800 participants from Japan, China, Korea, and others. The sessions were conducted on an all-solid-state LIB which was expected to solve the safety problem of the flammable organic solvent and on a Li-O<sub>2</sub> battery which was expected to supplant the LIB due to the benefit of its energy density being much higher. There also came to increase reports on polymer binders and current collectors, which had received little attention, although they are important components supporting LIB engineering. The RISING project supported by NEDO (New Energy and Industrial Technology Development Organization) in Japan has focused on the development of advanced characterization techniques to comprehensively illustrate the reaction mechanism of LIB. Several studies with advanced XAS techniques were also shown during the conference. Reaction distribution and its relaxation process in the positive electrodes were studied using micro- and depth-resolved XAS techniques having the microscopically capability<sup>[5]</sup>. The results show that lithium ionic diffusion is fast in LiCoO<sub>2</sub> electrode but is not in LFePO<sub>4</sub>, and the ionic migration is affected by the slope in voltage profile of the charge-discharge reactions. The interface reaction between electrode and organic electrolyte is monitored by using total reflection—XAS with surface sensitivity<sup>(6)</sup>. It reveals only the top surface of LiCoO<sub>2</sub> electrode is reduced without any electronic load and it may be suppressed with ZnO<sub>2</sub> coating.

Among such various characterization techniques for LIB, X-ray is one of the most powerful probes. Figure 2 summarizes the laboratory analysis tools which are available from Rigaku. The structural analysis by XRD and the structural refinement with Rietveld method are

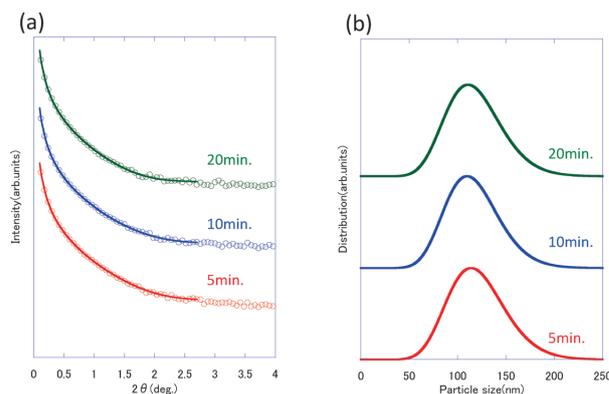
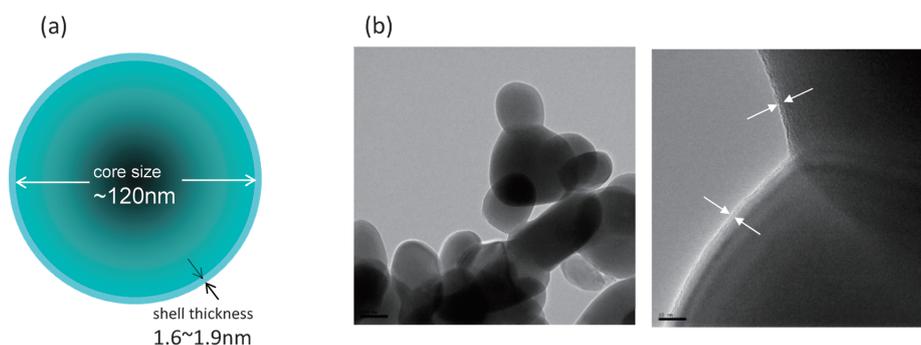
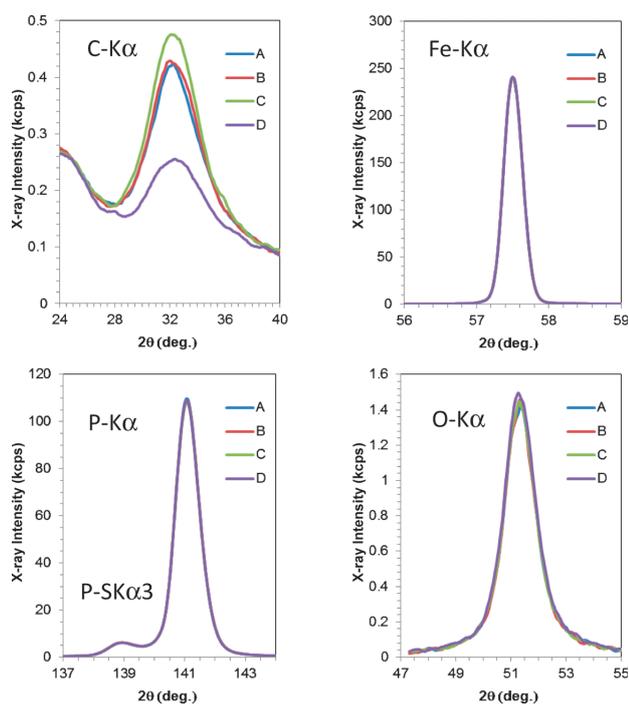


Fig. 3. (a) SAXS measurement profiles (open circles) and calculated profiles (solid lines) for LiFePO<sub>4</sub>/C composites with various carbon coating times. (b) Particle size distribution profiles calculated from the SAXS profiles.

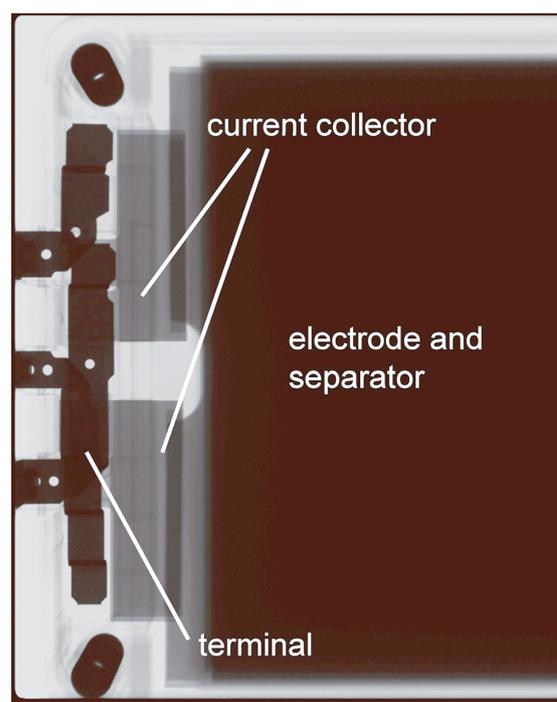
utilized to characterize the electrode materials. The sample holder attachments enable us to obtain *in-situ* XRD analysis during the charge/discharge process and during the interaction with reactive gas. The next article introduces the application of XRD for LIB research and development in detail. SAXS (small angle X-ray scattering) is useful for the evaluation of the particle size and its distribution of nano-particles. LiFePO<sub>4</sub> is usually coated with carbon to improve its electronic conductivity<sup>(7)</sup>. Figure 3 shows small angle scattering patterns obtained by X-ray diffractometer, SmartLab and the core/shell model calculation analysis are applied to LiFePO<sub>4</sub>/C composite. The calculation result of 1.6 to 1.9 nm in thickness of the carbon coat layer is in good agreement with TEM observation as shown in Fig. 4<sup>(8)</sup>. X-ray fluorescence (XRF) spectrometry is useful for qualitative and quantitative analysis of the electrode



**Fig. 4.** (a) The particle model obtained by the SAXS calculation results for LiFePO<sub>4</sub>/C. (b) The high resolution TEM image indicates 100 to 200 nm for the primary particle size of LiFePO<sub>4</sub> and 1 to 2 nm for the carbon thickness.



**Fig. 5.** XRF spectra for LiFePO<sub>4</sub>/C samples synthesized with various conditions. The carbon contents were determined to 2.3, 2.4, 2.7, and 1.0 wt% for samples A, B, C, and D, respectively by using a fundamental parameter (FP) method. This result is in agreement with the electrochemical characteristics.



**Fig. 6.** X-ray radiography image of a commercially available battery pack for an electric vehicle.

materials. It is well established in the LIB industry for quality control of the components and detection of contamination of electrodes. It is also applied to evaluate the thickness of the coating layer on the electrode film, for example thickness of Al<sub>2</sub>O<sub>3</sub> layer coated on electrode film. Figure 5 shows XRF spectra with wavelength dispersive (WD) XRF spectrometer, ZSX PrimusII for LiFePO<sub>4</sub>/C composite materials, which were synthesized with high frequency induction heating method<sup>(9)</sup>. The C peak intensity varies with the sintering condition and its amount corresponds well with the discharge capacity and the rate characteristics. X-ray radiography (2D) and X-ray computed tomography (CT) reveal the inner structures of cylindrical battery and packaged battery. The stacking structure of electrodes, space inside, and defects can be observed without interference. Figure 6

shows a typical example of X-ray radiography image by a Rigaku digital X-ray radiography system for a commercially available battery pack for an energy vehicle. These characterization capabilities available with X-ray analysis tools strongly support the research and development in the LIB field as well as other advanced industrial fields.

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