Operando X-ray Diffraction for Battery materials

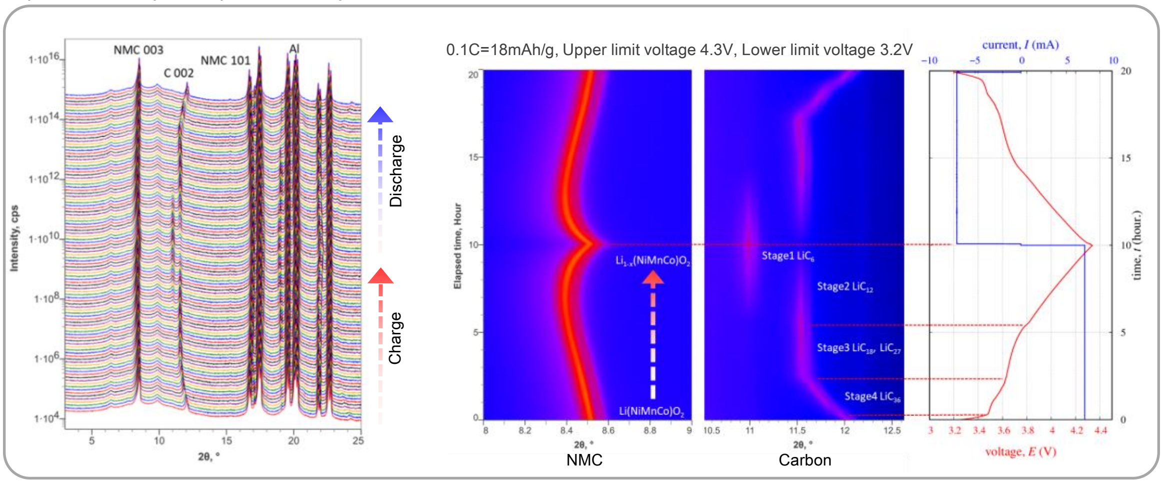
The use of lithium-ion batteries is expanding to power supplies for mobile devices such as smartphones and tablet devices, and to power supplies for vehicles such as electric vehicles and plug-in hybrid vehicles in order to comply with strict environmental regulations.
Lithium-ion secondary batteries are required to have higher performance, and research on next-generation battery materials is being actively conducted. Especially for secondary batteries aimed at electric vehicles, it is important to ensure long life and safety.
As with other battery systems, cathode and anode materials are important factors in determining the performance of lithium-ion secondary batteries. In particular, research on the degradation mechanism of batteries aiming at prolonging their life has been widely conducted.
In such research, it is important to grasp the interaction between the positive electrode, the negative electrode, and the electrolyte, and it is necessary to analyze what kind of reaction occurs during the charge / discharge process.
If you are interested in XRD analysis for characterization during charge / discharge process, Rigaku will strongly support your research as an ideal partner. Rigaku has a powerful X-ray source and optimized analysis tools for operand analysis of laminated batteries, coin cells and all solid state batteries.

XRD applications

Cathode / Anode material
- Phase ID
- Phase quant
- Lattice constant
- Structure analysis
  - Rietveld analysis
  - BVS(Bond Valence Sum)
  - PDF analysis

Separator
- Orientation
- Crystallinity
- Nano scale structure

Operando analysis of pouch battery cell



Operando measurement of pouch cell lithium battery using two-dimensional detector

For the development of lithium ion secondary batteries with high capacity, high stability and long life, it is important to evaluate the crystal structure of the positive and negative electrode materials and the stability of the crystal structure during the charge and discharge process.
SmartLab with Mo source and HyPix3000 detector can acquire up to 131 transmission X-ray diffraction images per second. By using a pouch cell attachment, it is possible to create a high-speed charge / discharge environment while keeping the sample temperature constant, and observe the rapid change in crystal structure that occurs from the surface of the lithium-ion battery to the internal region.

Fig.1 shows a measurement photograph of a combination of a pouch cell attachment and a two-dimensional detector. $LiFePO_4$ was used as the cathode material of the pouch cell, and charging and discharging were performed at a charge rate of 2C and a discharge rate of 1C, and the measurement was repeated by the transmission method for an exposure time of 10 seconds, and the time change of the X-ray diffraction profile was observed.
Fig.2 shows the two-dimensional diffraction image observed during charging. The characteristic diffraction peaks of $FePO_4$ and $LiFePO_4$ indicated by the dotted line were observed.
Fig.3 shows the profile map and voltage graph of the region shown in Fig.2, and the graph of the diffraction peak intensities of $FePO_4$ and $LiFePO_4$. A reversible crystal phase change was observed between $FePO_4$ and $LiFePO_4$ during charge and discharge.

1C is the current value when full charge or complete discharge is completed in one hour.

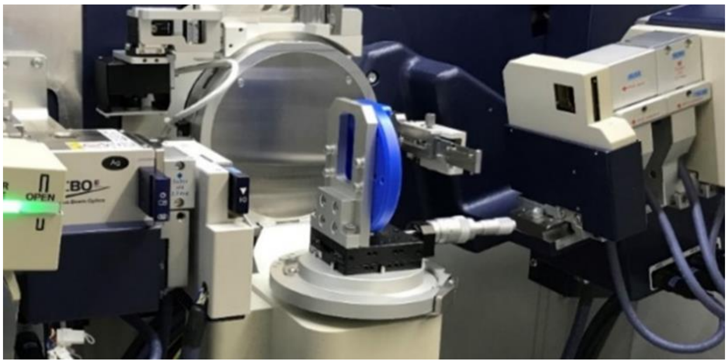


Fig.1: Static transmission measurement of pouch cell

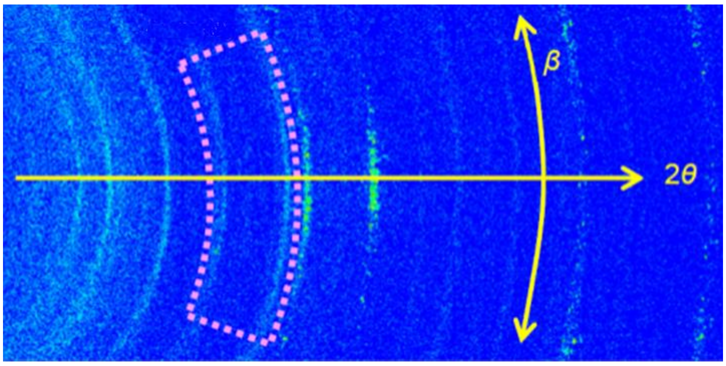
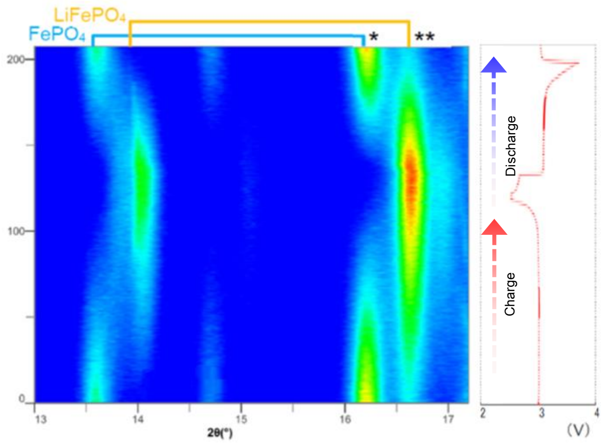
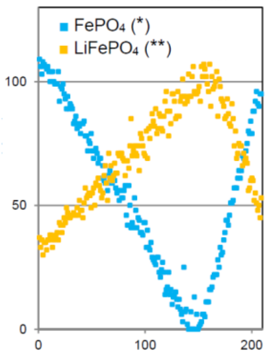


Fig.2: Two-dimensional diffraction image observed during charging





Transition of integrated intensity

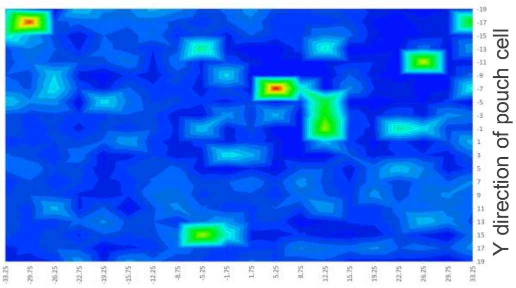
Fig.3:

Profile and voltage graph (↑)

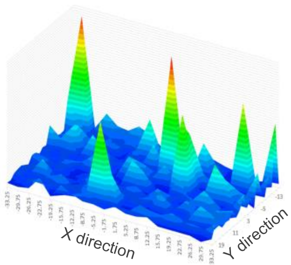
(←) Intensity change of $FePO_4$ and $LiFePO_4$ diffraction peaks

Mapping stage for pouch cell transmission measurement

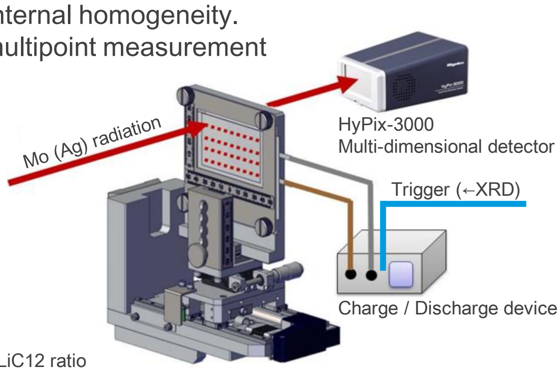
Pouch cell mapping by transmission X-ray diffraction allows analysis of internal homogeneity.
The high-brightness X-ray beam collimated to about Φ1㎜ can perform multipoint measurement in a reasonable measurement time.



X direction of pouch cell



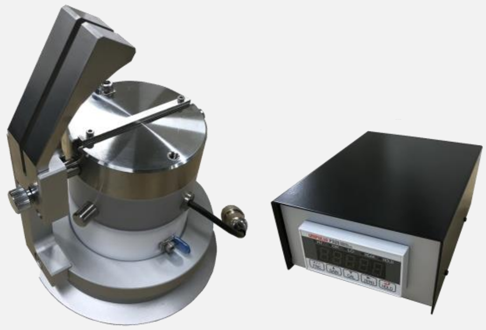
Pouch cell mapping evaluation of LiC6 / LiC12 ratio
Red: Locally high LiC6 ratio.
Blue: LiC6 / LiC12 ratio is constant



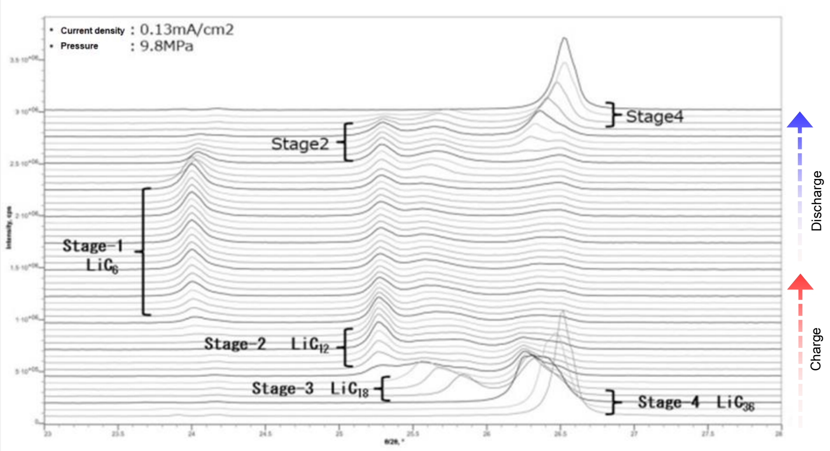
Pouch cell mapping stage
(Measureable area : 80mm x 50mm)

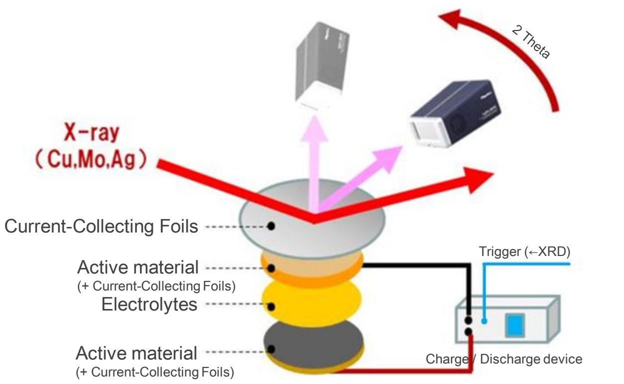
XRD measurement using operand cell for all solid state battery

Lithium-ion batteries are the most high-performance secondary batteries, and their use in vehicles is increasing. Energy density, power density, high / low temperature characteristics, safety, and lifespan need to be greatly improved for further social diffusion. Lithium-ion all-solid-state batteries are promising candidates with high potential for solving these problems, but there are some problems to be solved, such as reducing the reaction resistance of the positive electrode and improving the scientific stability of the solid electrolyte.
In the evaluation of a lithium ion all-solid battery, an electrochemical measurement is performed while a powder sample is filled in a cell and the cell is pressurized, but the electrochemical measurement result occurring inside the battery cannot be directly observed. By using the constrained all-solid-state battery cell developed by Rigaku, it is possible to track the crystal structure of the positive electrode material and quantitatively evaluate the movement of lithium ions.



Operand cell and pressure gauge
for all solid state battery

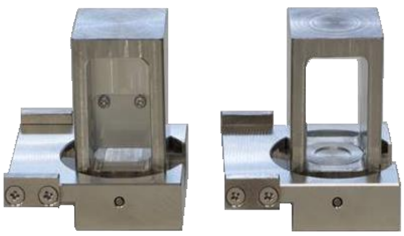




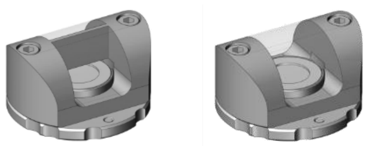
Air tight sample holder for battery materials.

Sulfide-based solid electrolytes are expected as materials for all-solid-state batteries.
$Li_7P_3S_{11}$, known as a sulfide-based solid electrolyte, is an unstable substance that readily hydrolyzes with atmospheric water vapor.

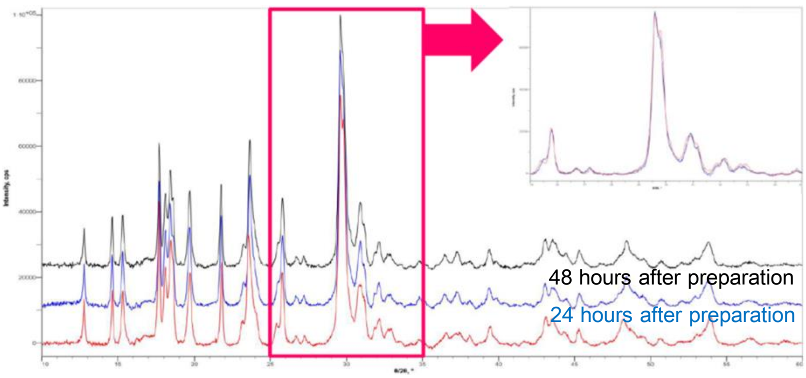
After preparing the sample in the Air tight holder in the glove box filled with Argon gas, it was taken out and subjected to XRD measurement.
Measurements were taken immediately, 24 hours and 48 hours after sample loading.
The XRD profile after 48 hours did not change from the profile immediately after the preparation.



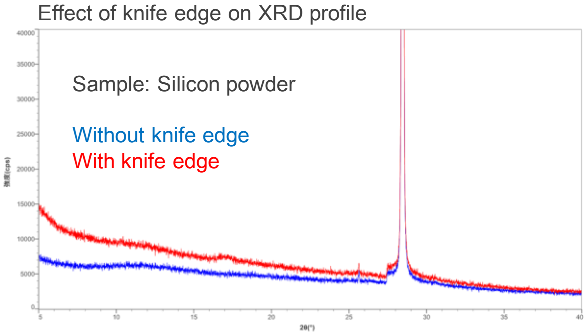
Air tight sample holder



Air tight sample holder for sample changer



Effect of knife edge on XRD profile



Transmission X-ray diffraction of all-solid-state lithium-ion battery utilizing Ag source

All-solid-state lithium-ion batteries that use solid electrolytes are superior to existing lithium-ion batteries that use liquid electrolytes in terms of safety, higher capacity, and smaller size.
Battery performance is closely related to the change in the crystal structure of the cathode material during the charge and discharge process, and operand measurements using short-wavelength X-rays with high transparency are being actively conducted. Ag tubes as well as Mo tubes can be used for short-wavelength X-rays. By combining an Ag tube and a condensing mirror, it is possible to perform operand measurement by transmission X-ray diffraction even in an all-solid-state battery that has a large absorption by the sample itself.

Fig.1 shows the structure of a pouch cell type all-solid-state battery, and Fig.2 shows the X-ray diffraction profile measured by SmartLab equipped with an Ag source and focusing X-ray mirror. Diffraction peaks from the positive electrode material NMC (Li (Ni, Mn, Co)O_2)), which is thinner than other components, were clearly observed. Fig.3 shows (a) a multiple display of the diffraction peaks of the cathode material, (b) a profile map, and (c) a voltage / power graph at a charge / discharge rate of 0.05C = 0.05mA/g. NMC003 diffraction peak angle changed with charge and discharge.

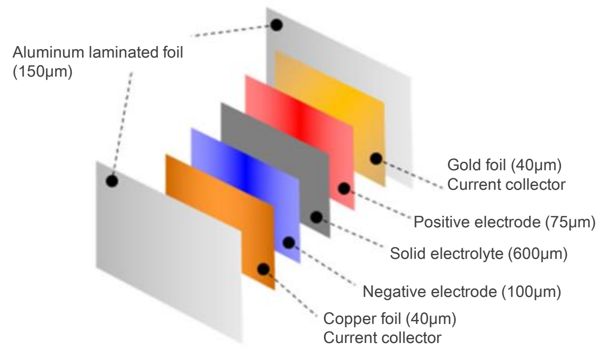


Fig.1 Structure of all solid state battery

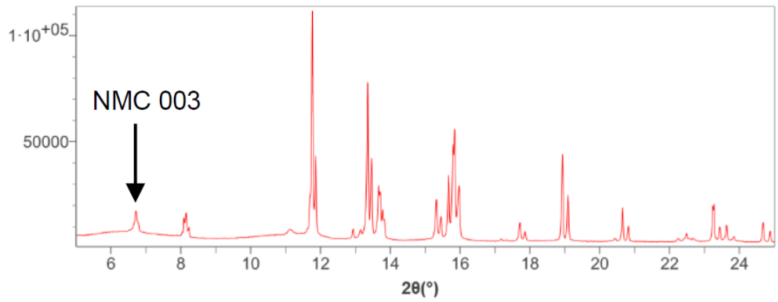
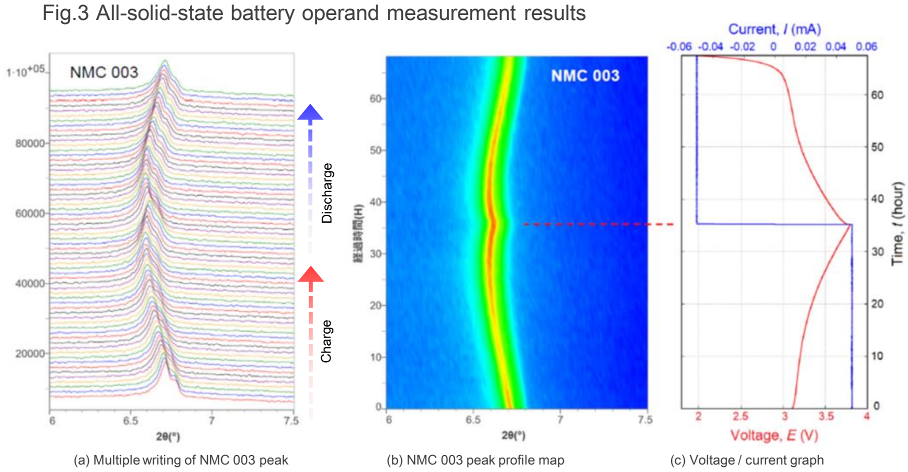


Fig.2 X-ray diffraction profile of all solid state battery

Fig.3 All-solid-state battery operand measurement results



Rigaku Corporation
3-9-12, Matsubara-cho, Akishima-shi,
Tokyo 196-8666, JAPAN
email: info-gsm@rigaku.co.jp
Tel: +81 3-3479-0618

Rigaku Americas Corporation
9009 New Trails Drive
The Woodlands
Texas USA 77381-5209
email: info@rigaku.com
Tel: +1-281-362-2300

Rigaku Europe SE
Hugenottenallee 167
63263 Neu-Isenburg, Germany
email: rese@rigaku.com
Tel: +49 6102 77999 51

Rigaku Beijing Corporation
2601A, Tengda Plaza,
No. 168, Xizhimenwai Ave.
Haidian District, Beijing, 100044, P.R. China
email: info@rigaku.com.cn
Tel: +[86] 010-88575768