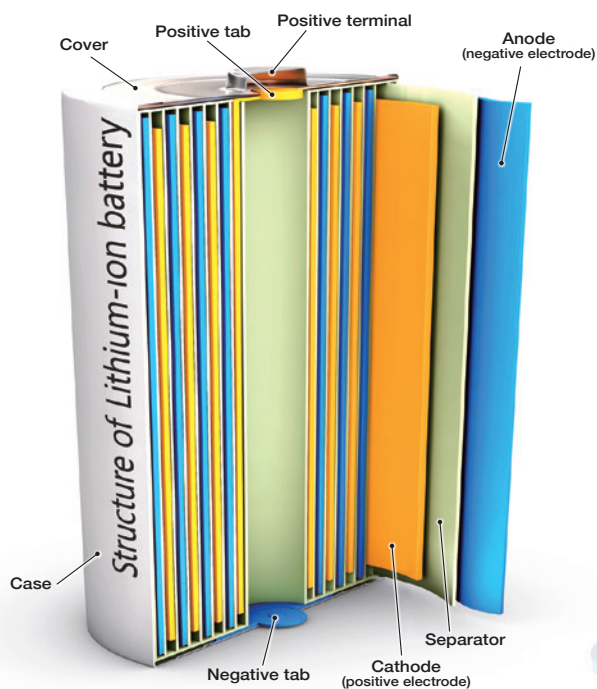


Solutions for Innovation

LIB^{Lithium Ion Battery}note



Specimen Preparation / Observation Instruments

CP / Cooling CP / FIB-SEM

Observation & Analysis Instruments and Attachments

SEM / EPMA / TEM

Surface Analysis Instruments

AES / XPS

Spectrometers / Detectors

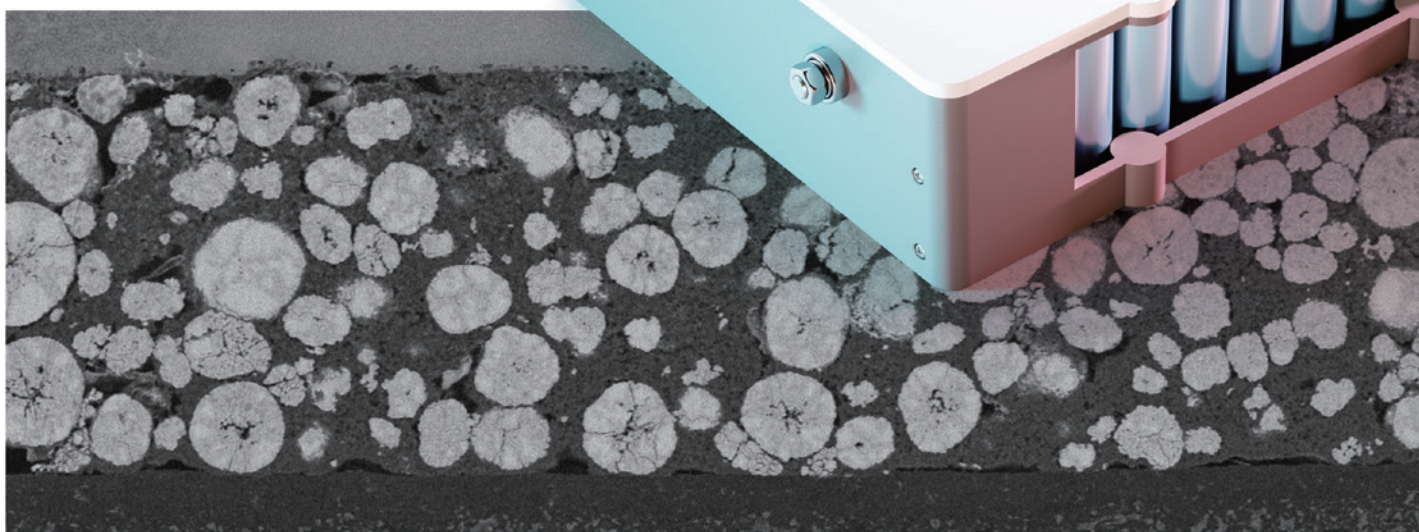
XRF / EDS

Mass Spectrometers

MS(GC-MS) / TG-MS

Nuclear Magnetic Resonance spectrometer / Electron Spin Resonance spectrometer

NMR / ESR





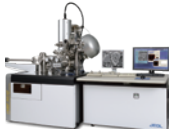





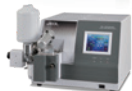



Introduction

The role of lithium ion batteries (LIBs) has been enhanced with accelerated introduction of recyclable energy, towards the carbon neutral society and the decarbonized society. In order to achieve carbon neutrality by 2050, which is to “reduce overall greenhouse gas emissions to net zero”, the technology of LIBs has become of a prime importance. Rapid technology shift to mobile phones, personal computers, and various electric vehicles (xEV) around the world, requires LIBs. In addition, LIBs are widely used as rechargeable battery cells for large energy storage systems (ESS) such as solar- and wind-power generation sources. For the research & development of safe and high-performance LIBs and quality control of these batteries, analyses and evaluations using various high-performance evaluation instruments are required. JEOL offers a wide variety of Scientific Instruments available for research & development and quality improvement of LIBs. This LIB Note has been created for your understanding of JEOL Scientific Instruments, from the viewpoint of the principles and functions of those instruments, which are described in Applications Notes of “Battery Note” and “Solid-state Battery Note” introducing the solutions provided by the instruments.

INDEX

Introduction	P 1
Features of Instruments	P 2
LIB and All-Solid-State-Battery	P 3
Analytical Methods and Tools for LIB Materials	P 4
Air-Isolated Transfer System	P 5-6
1. Specimen Preparation / Observation Instruments	
1-1. Cross Section Preparation System (CP / Cooling CP)	P 7-10
1-2. Focused Ion Beam - Scanning Electron Microscope (FIB-SEM)	P 11-14
2. Observation & Analysis Instruments and Attachments	
2-1. Scanning Electron Microscope (SEM)	P 15-20
2-2. Electron Probe Microanalyzer (EPMA)	P 21-22
2-3. Transmission Electron Microscope (TEM)	P 23-28
3. Surface Analysis Instruments	
3-1. Auger Electron Spectrometer (AES)	P 29-32
3-2. X-ray Photoelectron Spectrometer (XPS)	P 33-34
4. Spectrometers / Detectors	
4-1. X-ray Fluorescence Spectrometer (XRF)	P 35-36
4-2. Energy Dispersive X-ray Spectrometer (EDS)	P 37-42
5. Mass Spectrometers	
5-1. Mass Spectrometer: Gas Chromatograph Mass Spectrometer (MS: GC-MS)	P 43-46
5-2. Thermogravimetry-Mass Spectrometer (TG-MS)	P 47-48
6. Nuclear Magnetic Resonance spectrometer / Electron Spin Resonance spectrometer	
6-1. Nuclear Magnetic Resonance spectrometer (NMR)	P 49-52
6-2. Electron Spin Resonance spectrometer (ESR)	P 53-54
Conclusion	P 55-56

Features of Instruments

	Instruments	Features and Applications
	X-ray Fluorescence Spectrometer (XRF)	<ul style="list-style-type: none"> • Quick average composition evaluation with simple preparation • High quantitative accuracy in ppm-order • High-accuracy evaluations of composition ratio and impurities of products for positive-electrode (cathode) active materials
	X-ray Photoelectron Spectrometer (XPS)	<ul style="list-style-type: none"> • Chemical state analysis (including lithium) on top surfaces • Specimen damage is low due to X-ray irradiation, effective for analysis of solid-electrolyte materials • Minimal effect of oxidation by ultra-high vacuum • Chemical state analysis by depth profiling from surface to inside
	Auger Electron Spectrometer (AES)	<ul style="list-style-type: none"> • Chemical state analysis on top surfaces -smaller area analysis compared to XPS- • Chemical state analysis of lithium • Minimal effect of oxidation by ultra-high vacuum • Chemical state analysis by depth profiling from surface to inside
	Scanning Electron Microscope (SEM)	<ul style="list-style-type: none"> • High-resolution morphological observation • Compatibility with various attachments • Elemental analysis (Energy Dispersive X-ray Spectrometer: EDS) • Crystal orientation analysis (Electron Back Scatter Diffraction: EBSD) • Soft X-ray Emission Spectrometer (SXES) • Observation of non-conductive polymers such as separator, using low accelerating voltage
	Electron Probe Microanalyzer (EPMA)	<ul style="list-style-type: none"> • Morphological observation • Quantitative analysis of trace elements in micro areas • Soft X-ray Emission Spectrometer (SXES) • Analysis of transition metals in positive-electrode (cathode) active materials
	Transmission Electron Microscope (TEM)	<ul style="list-style-type: none"> • Structural observation in nano-areas • Atomic resolution observation • High spatial resolution elemental analysis • Crystal structure analysis by electron diffraction • Chemical structure analysis by EELS
	Nuclear Magnetic Resonance spectrometer (NMR)	<ul style="list-style-type: none"> • Structural analysis • Structural analysis and evaluation of positive & negative electrodes (cathode & anode) and solid electrolyte materials by solid-state NMR • Ion conductivity evaluation of materials by lithium diffusion coefficient evaluation
	Mass Spectrometer (MS)	<ul style="list-style-type: none"> • Mass spectrometry • Analysis of gas evolved from inside the batteries • Evaluation of thermal property in combination with TG • Operando analysis during charge-discharge cycles
	CROSS SECTION POLISHER™ Cooling CROSS SECTION POLISHER™ (CP / Cooling CP)	<ul style="list-style-type: none"> • Cross section preparation for cross sectional observation & analysis applicable to a broad range of instruments • Holders for air-isolated transfer enabling a linkage with various instruments
	Focused Ion Beam – Scanning Electron Microscope (FIB-SEM)	<ul style="list-style-type: none"> • Preparation of cross section specimens for SEM and thinned specimens for TEM • Air-isolated specimen preparation by Transfer Vessel • CP-FIB-TEM linkage holder for applications from SEM cross sectional observation & analysis to specimen preparation for TEM observation
	Energy Dispersive X-ray Spectrometer (EDS)	<ul style="list-style-type: none"> • X-ray energy spectroscopy using a semiconductor detector • Easy, fast, simultaneous multi-elements analysis in micro-areas (analyzable elements: Be to U) • Automatic elemental analysis function during observation (Live Analysis, Live MAP) • Time-shift visualization of focused data area in mapping data (Playback Analysis) • Structural analysis by phase analysis function • Installable to a wide range of analysis instruments such as TEM, SEM, FIB, and EPMA
	Electron Spin Resonance spectrometer (ESR)	<ul style="list-style-type: none"> • Accurate g-value and identification by simultaneous measurement with Mn marker • Data analysis with simple operations • Achieving electron-spin detection with higher sensitivity than nuclear-spin detection by NMR

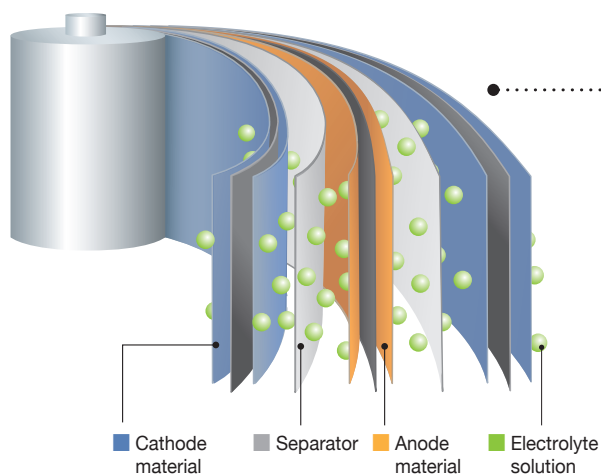
LIB and All-Solid-State-Battery

LIB and All-Solid-State-Battery

Liquid-based lithium-ion batteries that are currently used are called “LIB”. LIBs perform charging and discharging by making lithium ions move between the positive and negative electrodes (cathode and anode) in an electrolyte solution. They have separators of polymer between the positive and negative electrodes (cathode and anode) to prevent short circuits, and an electrolyte of organic solvent is used to conduct ions.

All-solid-state-batteries perform charging and discharging using lithium ions, which is the same as with LIBs. However, instead of an electrolyte solution and a separator located between the positive and negative electrodes (cathode and anode), a solid electrolyte is used. Replacing with a solid electrolyte can reduce the risks of smoking and ignition caused by the electrolyte solution, accelerating research of xEV and large ESS. In recent years, lithium-based rechargeable batteries have been used due to the spread of xEV. However, current LIBs have issues such as safety, crushing distance and charging time. Solid-state batteries have high energy density and safety, and are expected to have long service life. Their expectations as next-generation batteries are high and are being developed for practical use by automobile makers and battery manufactures.

Composition of Lithium Ion Battery (LIB)

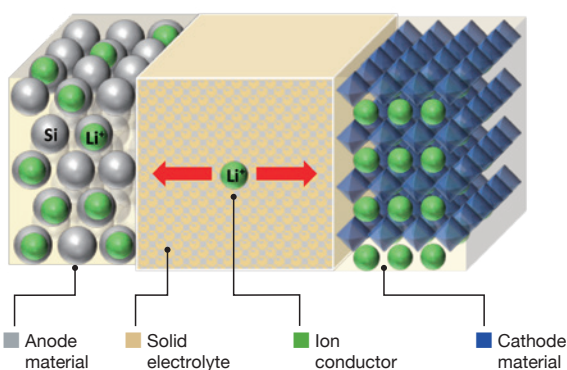


●..... The basic structure of LIBs consists of components shown in the left figure.

For the positive electrode (cathode), composite oxides containing lithium are used as the main active materials and created by kneading carbon materials as conductive assistant with polymer binders that bind them. For the negative electrode (anode), graphite carbons that can intercalate lithium are used and crated by kneading polymer binders.

Separator films for LIBs use porous polymers with narrow pores. Separator films have a shutdown function as a safety switch in case of thermal runaway by closing the pores, preventing short-circuits caused by contact between the positive and negative electrodes (cathode and anode). The electrolyte solution is created by dissolving electrolyte containing lithium by an organic solvent. Since each material uses highly reactive lithium that alters in air, it is inevitable to manufacture them in an air-isolated environment. In addition, for analysis of each material, specimen preparation, observation and analysis need to be performed in an air-isolated environment. Air-isolation instruments and those systems shown in p5 to 6 are useful.

Composition of All-solid-state-batteries



●..... The structure of All-solid-state-batteries (ASSB) is composed as shown in the left figure.

For All-solid-state-batteries (ASSB), solid electrolyte is used to conduct ions, instead of a polymer material separator and electrolyte solution between the positive and negative electrodes (cathode and anode).

Same as LIBs, the positive electrode (cathode) uses composite oxides containing lithium and conductive assistants. Additional solid electrolytes are used in ASSB. For the negative electrode (anode), other than carbons used with LIBs, silicon materials have recently been attracting attention. Since they are expected to introduce nearly 10 times more lithium than carbon materials do, researches of silicon negative electrode (anode) is progressing.

■ Analytical Methods and Tools for LIB materials

Choice of instruments for observation & analysis of LIBs

For observation and analysis of LIBs, it is necessary to choose (an) appropriate scientific instrument(s) depending on your purpose. To make such a choice, the features of the respective instruments have to be understood. It should be noted that LIBs use highly-reactive lithium and thus, air-isolated treatment is required for observation and analysis. In addition to descriptions of the features of each instrument in p2, this page introduces the detectors and instruments that enable lithium detection, and unique systems which simplify a series of procedures from specimen preparation to observation and analysis for TEM indispensable for nanostructure analysis.

Detectors and instruments enabling lithium detection

Detectors: SXES, Gather-X (EDS), EELS

Light-emission spectroscopy detectors of both the soft X-ray emission spectrometer (SXES) and Gather-X, which enable simultaneous detection of multiple elements, are used for SEM and EPMA instruments to analyze bulk specimens. SXES is advantageous for chemical-state analysis owing to its high energy resolution, but is disadvantageous for long-time elemental mapping. On the other hand, Gather-X is inferior to SXES for energy resolution, but has high detection sensitivity and thus, Gather-X enables fast detection of light elements such as lithium. However, both SXES and Gather-X are not suitable for analysis of lithium oxides because the light-emission efficiency of lithium oxides is extremely low. Thus, the Auger electron spectrometer (Auger Microprobe) and the X-ray photoelectron spectrometer (XPS) are effective for lithium in the lithium oxides. EELS (electron energy-loss spectrometer) is also used with TEM. EELS provides both high spatial resolution and high energy resolution, and enables analysis of lithium oxides.

Instruments: Auger electron spectrometer (Auger Microprobe), XPS

Both AES and XPS use an electrostatic hemispherical analyzer to detect light elements such as lithium. Both of the instruments enable chemical-state information on those elements to be obtained from Auger and photoelectron spectra. Using these instruments, lithium oxides can be detected. AES and XPS are specially utilized to analyze top surfaces of specimens. AES irradiates a specimen with an electron beam whereas XPS uses X-rays. Thus, AES with electron-irradiation, allows for analysis of a very small area, tens of nm in size. On the other hand, XPS with X-rays, enables large-area analysis of several mm in size.

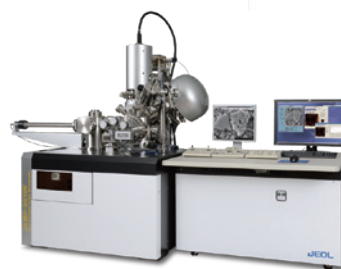
Furthermore, using reflection electron energy loss spectroscopy (REELS), AES enables acquisition of information from regions being a little deep from the surface.



Soft X-ray emission spectrometer (SXES)



Gather-X



JAMP-9510F



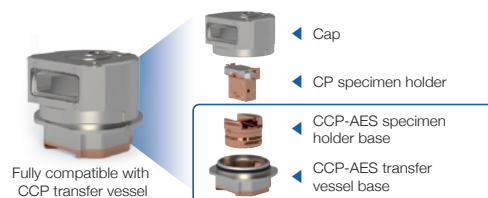
JPS-9030

Air-isolated transfer systems and related tools

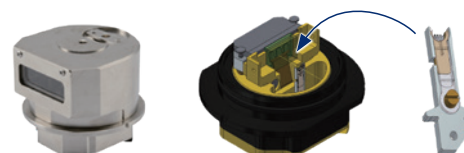
Air-isolated transfer systems are essential for observation and analysis of LIB materials. JEOL provides tools that enable direct transfer of materials, from the instruments performing cross-section preparation of the materials, into the instruments performing observation and analysis of the cross-sectioned materials.

In addition to compatible holders for SEM/EPMA/FIB, a new compatible holder for AES has become available.

Furthermore, a holder enabling linkage between CP, FIB and TEM, has been added to the lineup of the holders. Conventionally, tweezers are required to handle very small (thin) TEM specimens, but this treatment is significantly difficult in the glove box. This new holder enables a TEM specimen to be placed on a TEM holder without using tweezers. Since the TEM holder tip (shuttle retainer) is stored in the CP holder, after cross-section preparation by CP, the TEM specimen can be thinned on the shuttle retainer in a FIB system. For placing the specimen on the TEM holder, it is only needed to attach the shuttle retainer to the holder tip.



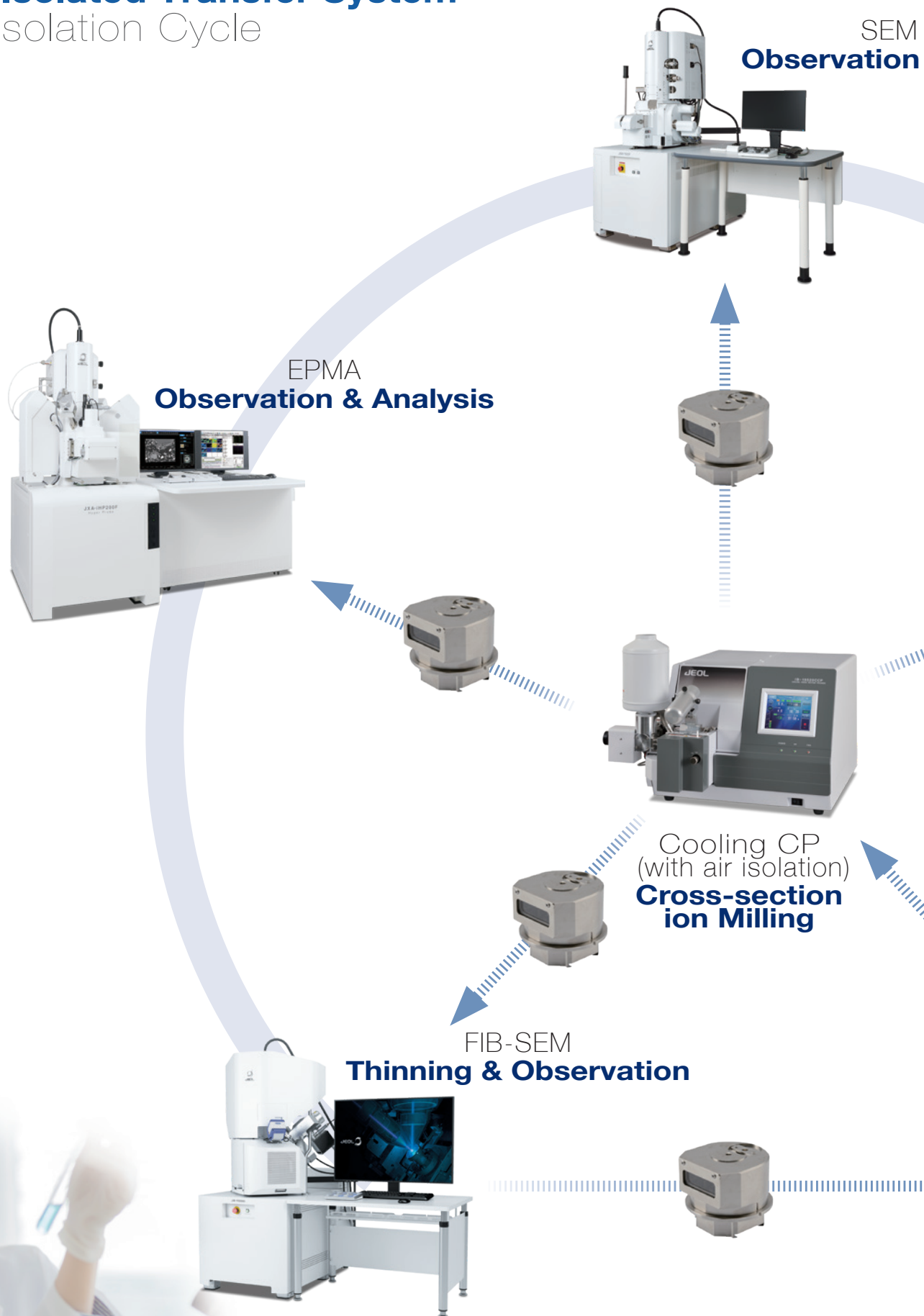
AES compatible transfer vessel holder



CP-FIB-TEM linkage holder

Air-Isolated Transfer System

Air Isolation Cycle



& Analysis



AES
Observation & Analysis



XPS
Observation & Analysis

TEM
Observation & Analysis



Glove box



1 - 1

Cross Section Preparation System

CROSS SECTION POLISHER™ (CP)

Cooling CROSS SECTION POLISHER™ (Cooling CP)

CROSS SECTION POLISHER™ (CP)

Cross section preparation is needed for observing the inside of a specimen. To perform higher-accuracy observation and analysis of the internal structure of the specimen, a uniform cross section with suppressed mechanical damage, is required. The CROSS SECTION POLISHER™ (CP) adopts a broad argon (Ar) ion beam for preparing a uniform cross section with a reduced strain caused by milling.

CP can perform milling of a variety of specimens, such as metals, polymers, composite materials, laminated materials and brittle materials. CP is used to prepare cross sectional specimens for a broad range of analysis instruments of SEM/FIB/EPMA/AES.

The Cooling CP features ion-milling with a specimen kept cooled, enabling heat-sensitive specimens to be milled while suppressing thermal damage to the specimens.

Furthermore, the CP is fitted with an air-isolated transfer system. This unique system is effective for battery materials which are likely to react with air. In air-isolated transfer, the use of CP and compatible holders for analysis instruments (SEM/FIB/EPMA/AES) makes it possible to directly transfer the specimen from CP into each instrument.

Cross section specimen preparation in an air-isolated environment – Observation & Analysis

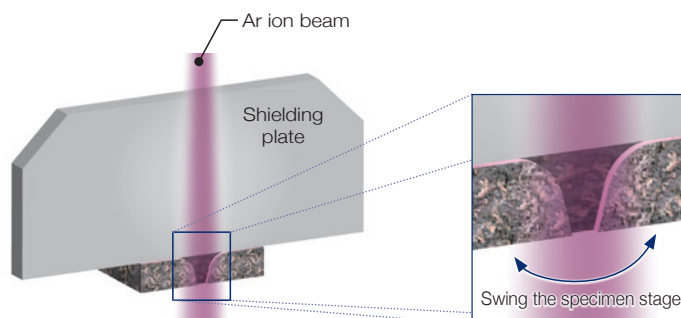


Glove box



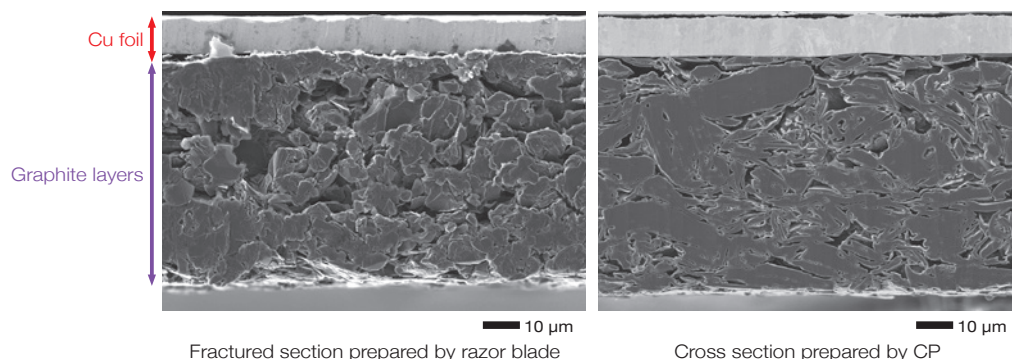
Cooling CP

Principle of ion-milling by CP



In the CP, a shielding plate is mounted on the upper portion of the specimen, and then the portion protruding from the shielding plate is irradiated with a Broad Ar ion beam. This procedure enables a uniform cross section to be prepared along the edge of the shielding plate. In order to create such a uniform section, the stage is swung to vary the direction of ion-beam irradiation during milling, reducing streak-like milling marks.

Comparison of cross section fractured by razor blade and cross section milled by CP



The cross section prepared by CP demonstrates suppression of deformation and failure in the section due to tensile-stress, enabling observation of voids in the boundary between the Cu foil and graphite layers and in the graphite layers. CP features cross section preparation of a brittle material.

(Specimen: Graphite Anode for LIB, SEM secondary electron image)
Sample courtesy: Assistant Professor Hirokazu Munataka at Tokyo Metropolitan University



For details, see SEM
(p15 to 20)



For details, see FIB-SEM
(p11 to 14)



For details, see EPMA
(p21 to 22)



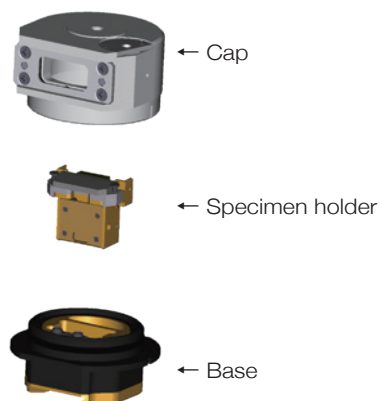
For details, see AES
(p29 to 32)

Observation & Analysis instruments

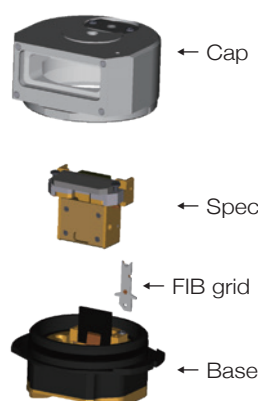
Direct transfer into various analysis devices (Transfer Vessel)

The following specimen holders can be transferred without exposure by a base and a cap.

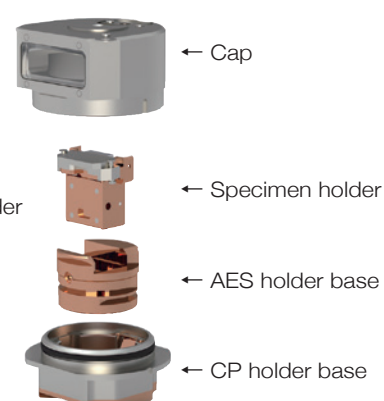
CP-SEM compatible, CP-EPMA compatible transfer vessel



CP-FIB compatible transfer vessel



CP-AES compatible transfer vessel

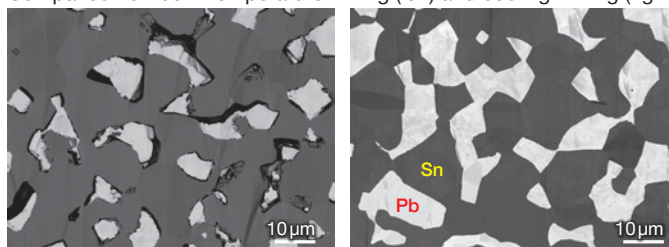


Cooling function

Effect to suppress thermal damage

Figures on the right show SEM backscattered electron images of a low melting Sn-Pd solder, acquired by room-temperature milling and by cooling milling. In room-temperature milling, voids are seen on the boundary of Sn-Pb due to thermal damage by beam irradiation. In cooling-milling, a cross section with no void is obtained by suppressing thermal damage. Thus, the cooling function enables a uniform cross section with a reduced thermal damage to be prepared.

Comparison of room-temperature milling (left) and cooling-milling (right)



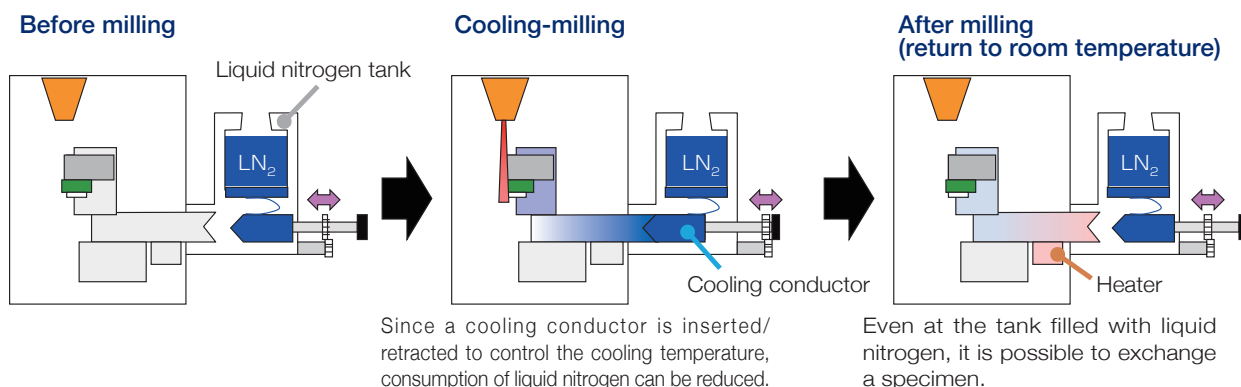
High-throughput cooling system

This cooling system automatically performs operations to return the sample to room temperature after the cooling-milling by setting the conditions.

The liquid nitrogen vacuum tank can be evacuated from the side of the instrument to maintain the cooling retention time and sample cooling temperature performance.

Temperature setting range for specimen stage cooling: $-120\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$ ($1\text{ }^{\circ}\text{C}$ step)

Retention time for specimen cooling: 8 h or more ($-120\text{ }^{\circ}\text{C}$)

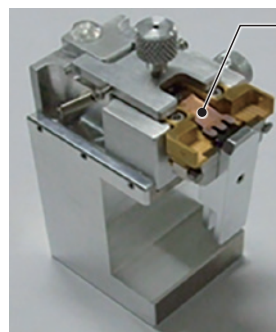


Easy operability

Easy specimen placing

Since the clipping method is used for fixing a specimen, the specimen can be easily mounted in the glove box and effective for brittle specimens.

- **Specimen-mounting tool**
The clipping portion can be kept open while mounting the specimen.
- **Protrusion amount setting tool**
A certain amount of specimen protrusion from the shielding plate can be set.



Clipped part

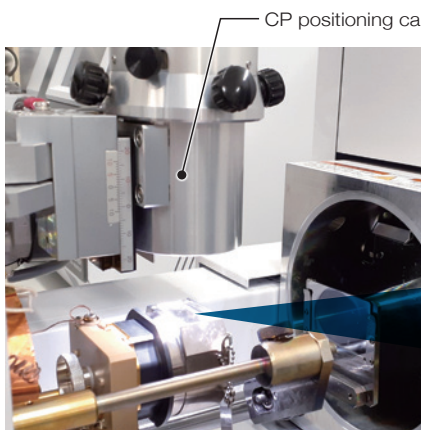


Protrusion amount setting tool
Right: For protrusion amount 50 μm
Left: For protrusion amount 100 μm

Specimen-mounting tool

Checking the ion-milling position

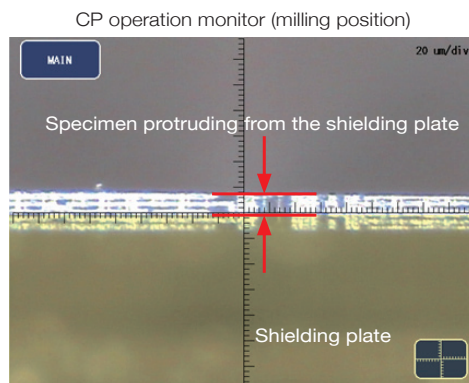
The milling position can be checked and adjusted by observation through the window of the transfer vessel.



CP positioning camera



Observation window

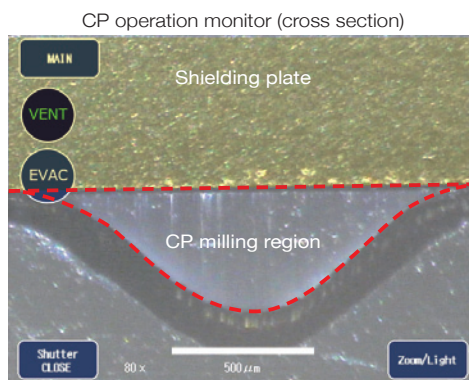


CP operation monitor (milling position)

Checking the cross section

The cross section can be checked in real time on the CP operation monitor, via the monitoring camera in CP. You can stop milling or change the milling time according to needs.

Magnification: 20x, 40x, 60x, 80x, 100x



CP operation monitor (cross section)

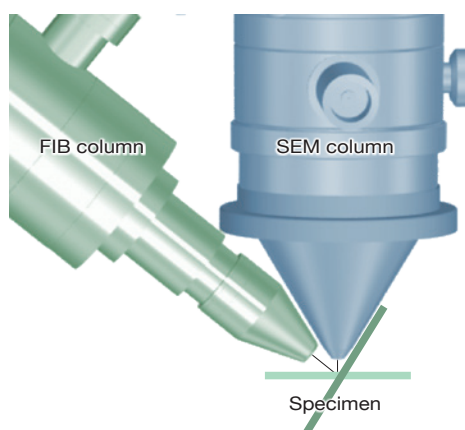
1-2 Focused Ion Beam - Scanning Electron Microscope (FIB-SEM)

The focused ion beam (FIB) system focuses an ion beam generated from an ion source and scans the beam on the specimen surface, for pinpoint-milling a micro-region and for observing the processed region.

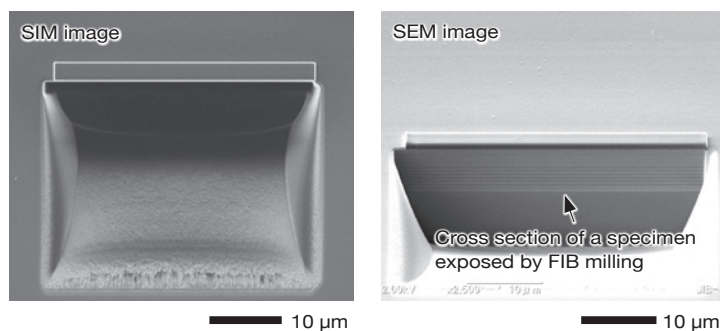
Owing to its high milling accuracy and high milling speed, the FIB system is used for a wide range of applications from specimen preparation for SEM & TEM to fine milling. The FIB system also enables 3D imaging of serially sliced cross sections. The acquired images of the stacked slices are reconstructed on a computer to generate a 3D image, leading to intuitive and stereoscopic analysis.

The FIB-SEM system is an instrument which accommodates both an SEM column and a FIB column in a specimen chamber. That is, the SEM enables you to rapidly observe and analyze a cross-section specimen prepared by FIB while the specimen is kept in the same instrument.

Schematic of columns of FIB-SEM



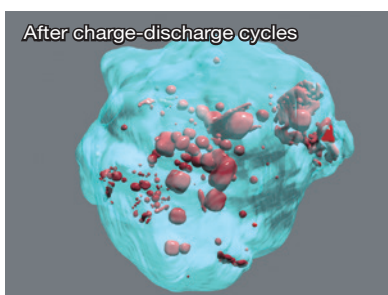
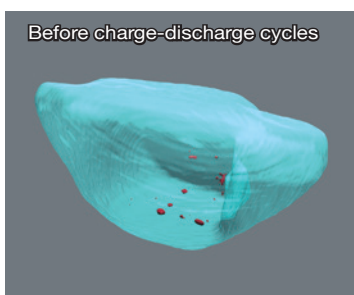
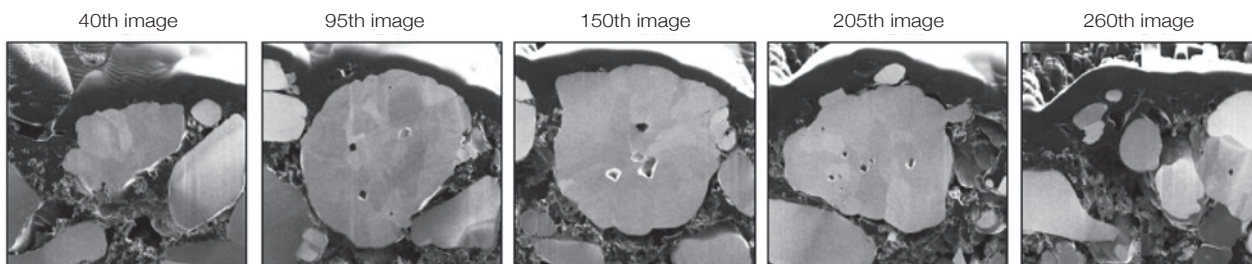
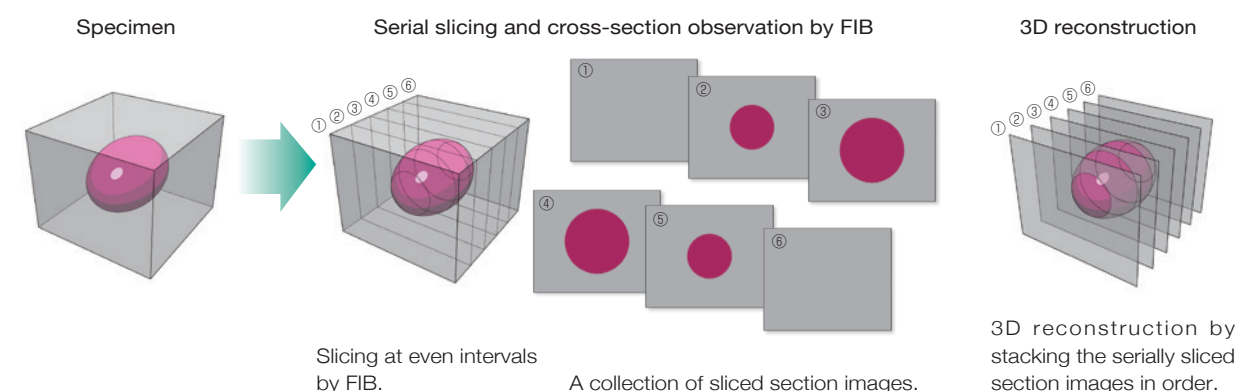
FIB (SIM) image immediately after milling and SEM image for tilted observation



Example of 3D reconstruction by FIB: Cathode active material (lithium-cobalt oxide particle)

Three-dimensional reconstruction is performed by automatically collecting 3D slice cross-sectional images by slicing them at equal intervals, and sequentially stacking these images through computer processing.

Principle of 3D observation



	Before charge-discharge cycles	After charge-discharge cycles
Particle volume (μm^3)	1321.08	2298.26
Void volume (μm^3)	0.35	26.86
Void rate (%)	0.03%	1.17%

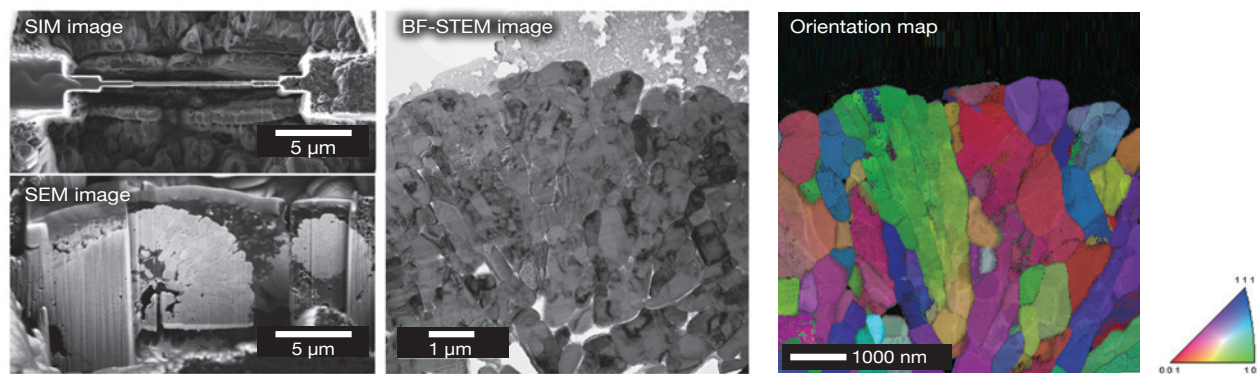
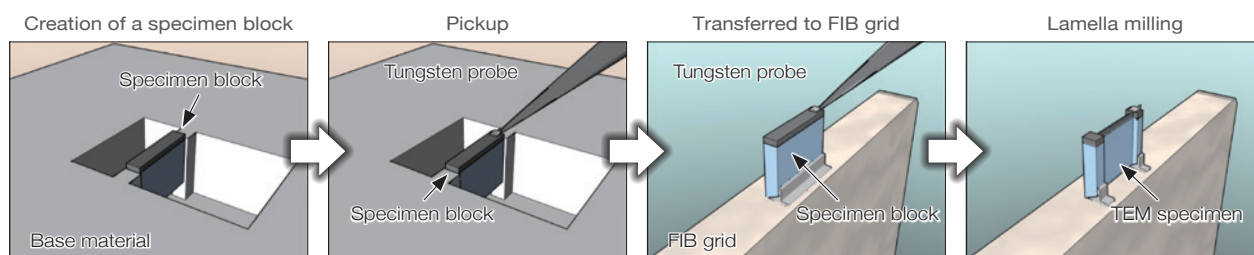
3D observation of a specimen of lithium-cobalt oxide particle was performed before and after charge-discharge cycles. The top images show part of serially sliced cross-section (SIM) images whereas 3D reconstruction results are shown at the bottom left. Voids are confirmed in these cross-section images, and furthermore, 3D distribution of the voids is revealed by 3D reconstruction. From color-coded 3D data, the volume of particle and void was respectively calculated, and the void rate was obtained from the ratio of void volume to particle volume. 3D reconstruction image enables you to statistically evaluate and analyze voids.

Example of TEM specimen preparation by FIB: Cathode active material particle (lithium-cobalt oxide particle)

The procedures of TEM specimen preparation by FIB are as follows.

First, protective coating is applied onto the position and its periphery where a milled specimen for TEM will be prepared. Then, this region (including bottom portion) is milled for creating a specimen block. The created specimen block is picked up with a tungsten probe and transferred to a half-moon shaped TEM grid (FIB grid). Finally, the transferred specimen block is milled to a thin section with a thickness allowing TEM observation (lamella milling).

TEM specimen preparation procedures



SIM: Scanning Ion Microscope SEM: Scanning Electron Microscope BF-STEM: Bright Field - Scanning Transmission Electron Microscope

Three images just above are examples of SIM/SEM/TEM images taken from a cross-sectional TEM specimen of a cathode active material (lithium-cobalt oxide particle), prepared by FIB under an air-isolated environment.

The left-edge SIM image and SEM image, show a specimen being milled by FIB for TEM observation of this specimen, so that a part of lithium-cobalt oxide particles is sliced with a thickness of less than 100 nm. After that, the prepared specimen was subjected to air-isolated transfer to a TEM. The center BF-STEM image demonstrates to clearly visualize lithium-cobalt oxide particles.

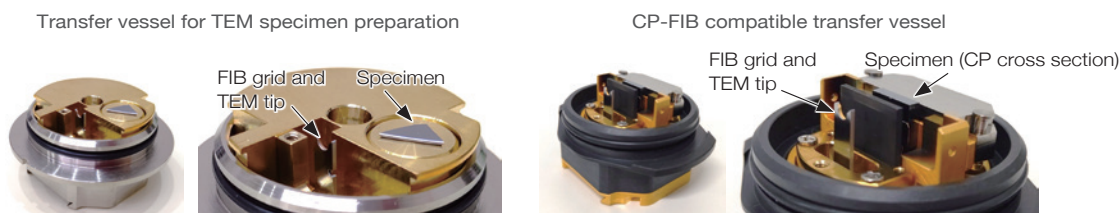
Furthermore, a crystal orientation map, acquired by precession electron diffraction (PED), is shown to the right. The orientation of crystals in the lithium-cobalt oxide particles is colored by the color keys at the lower right. The right orientation map clearly elucidates the distribution and crystal orientation of the primary particles with a diameter of several 10 nm.

TEM observation and analysis are useful for studying crystal structures ranging from a few micrometers to extremely small-regions.

Introduction of accessories effective for air-isolated TEM specimen preparation

• Transfer vessel for TEM specimen preparation by FIB

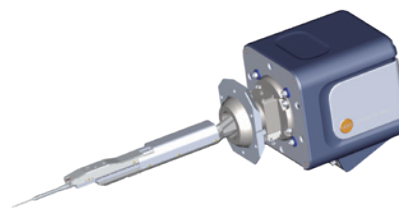
The transfer vessel is a specimen holder that has an airtight cap, enabling air-isolated transfer of a specimen. The FIB-SEM to TEM transfer vessel can be fitted with the sample and the FIB grid (on the TEM tip). The type of transfer vessel can be selected depending on the observation and processing direction of the specimen.



• OmniProbe 400

The OmniProbe 400 is a nano-manipulator which adopts a piezo drive system and has high positional accuracy at the nanometer-scale.

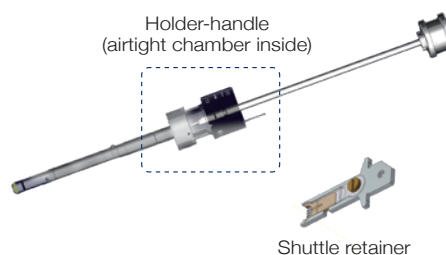
When the probe is installed in the FIB-SEM specimen chamber, the attached tungsten probe can be operated in vacuum while observing SEM and FIB images. This is effective when transferring sample blocks processed with FIB to FIB grids without exposure to air.



• Slide cover holder

The slide cover holder has a mechanism that protects a specimen from the outside air. This holder slides the head of the holder to house a specimen into the airtight chamber inside a holder-handle for protecting the specimen.

Slide cover holders are also available in a tip-on shuttle retainer type. This unique shuttle retainer serves as the tip-on holder and transfers a specimen between the FIB and TEM. For FIB milling, the shuttle retainer is attached to the transfer vessel and the specimen can be processed in the FIB system. On the other hand, for TEM observation, the shuttle retainer can be easily transferred to the slide cover holder for easy transfer to the TEM. Such a specimen transfer using the shuttle retainer greatly improves workability inside the glove box where hand-working (using tweezers) of handling a very small thin-film specimen is difficult.



2-1 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) focuses an electron beam emitted from an electron source, and scans the surface of a bulk specimen with the focused electron beam, for observing the specimen surface in a micro-area. SEM also detects various signals such as characteristic X-rays generated by electron-beam irradiation, for analyzing the specimen surface and a region being a little deep from the surface.

With a FE (field emission)-SEM capable of high-resolution observation and a wide range of analyses, diversified functions are provided including; versatile imaging using a variety of detectors, elemental analysis by EDS (energy dispersive X-ray spectroscopy), crystal orientation analysis by EBSD (electron backscattered diffraction) and chemical state analysis by SXES (soft X-ray emission spectroscopy). In this section, a Schottky FE-SEM JSM-IT800<SHL> and its analytical applications are introduced.

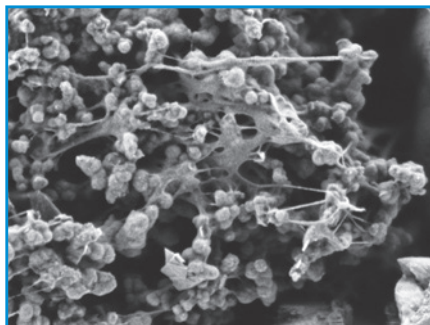


Detection system of JSM-IT800<SHL>

UHD (Upper Hybrid Detector)

A detector placed in the objective lens efficiently detects electrons generated from a specimen.

Specimen: Conductive assistant and binder on NMC
Accelerating voltage 0.3 kV Magnification x100,000



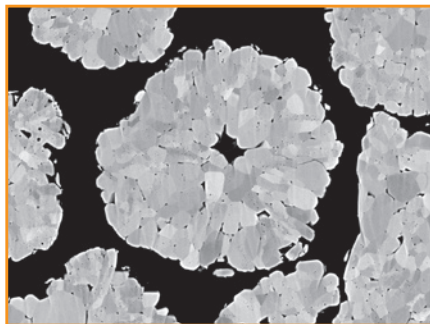
SHL (Super Hybrid Lens)

An electromagnetic/electrostatic field superposed objective lens is achieved by combining magnetic lens and electrostatic lens.

BED (Backscattered Electron Detector)

A detector suitable for acquiring compositional, topographic and channeling contrast.

Specimen: NMC particle cross section
Accelerating voltage 5 kV Magnification x7,000

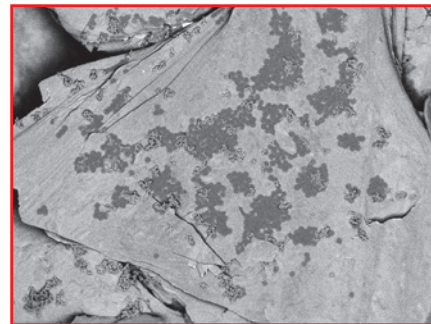


- Secondary electron
- High angle backscattered electron
- Middle and low angle backscattered electron
- Very low angle backscattered electron

UED (Upper Electron Detector)

A detector placed above the objective lens detects secondary electrons and backscattered electrons that are emitted at high angles. An energy filter placed just below the detection plane enables acquisition of surface-morphological and compositional images.

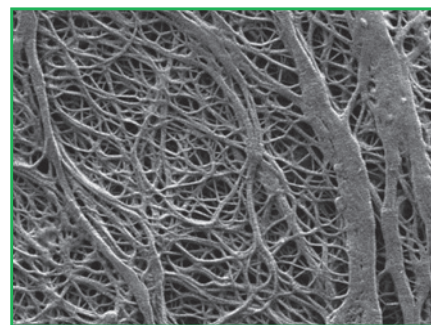
Specimen: Graphite anode
Accelerating voltage 1.1 kV Magnification x6,500
Backscattered electrons acquired



SED (Secondary Electron Detector)

A detector to acquire topographic images.

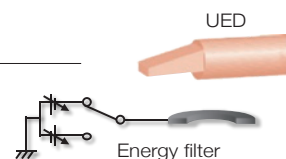
Specimen: separator
Accelerating voltage 0.8 kV Magnification x20,000
Pt coating 2 nm



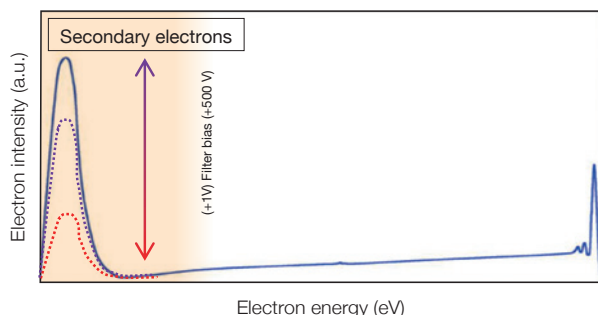
BD mode (Beam Deceleration)

Enables deceleration of the beam before it lands on the specimen by applying a bias voltage up to the specimen stage. Thus, high resolution is achieved even at low accelerating voltage.

JSM-IT800<SHL> Signal selection using UED energy filter

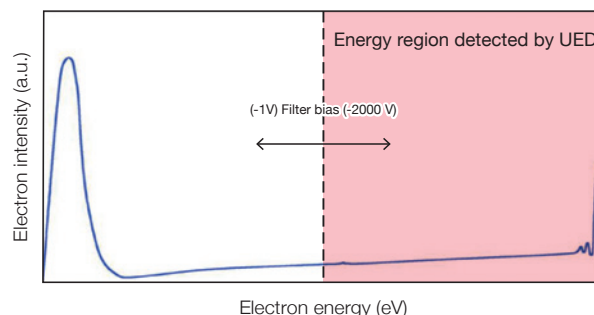


When positive voltage is applied to UED energy filter



With filter bias (+1 to +500 V), the number of detected electrons for secondary electron energy band (especially a few eV) is mainly controlled. Setting a higher voltage enables acquisition of a greater amount of secondary electrons. Under this condition, electrons which cover backscattered-electron energy region are also detected, but information on secondary electrons is dominant.

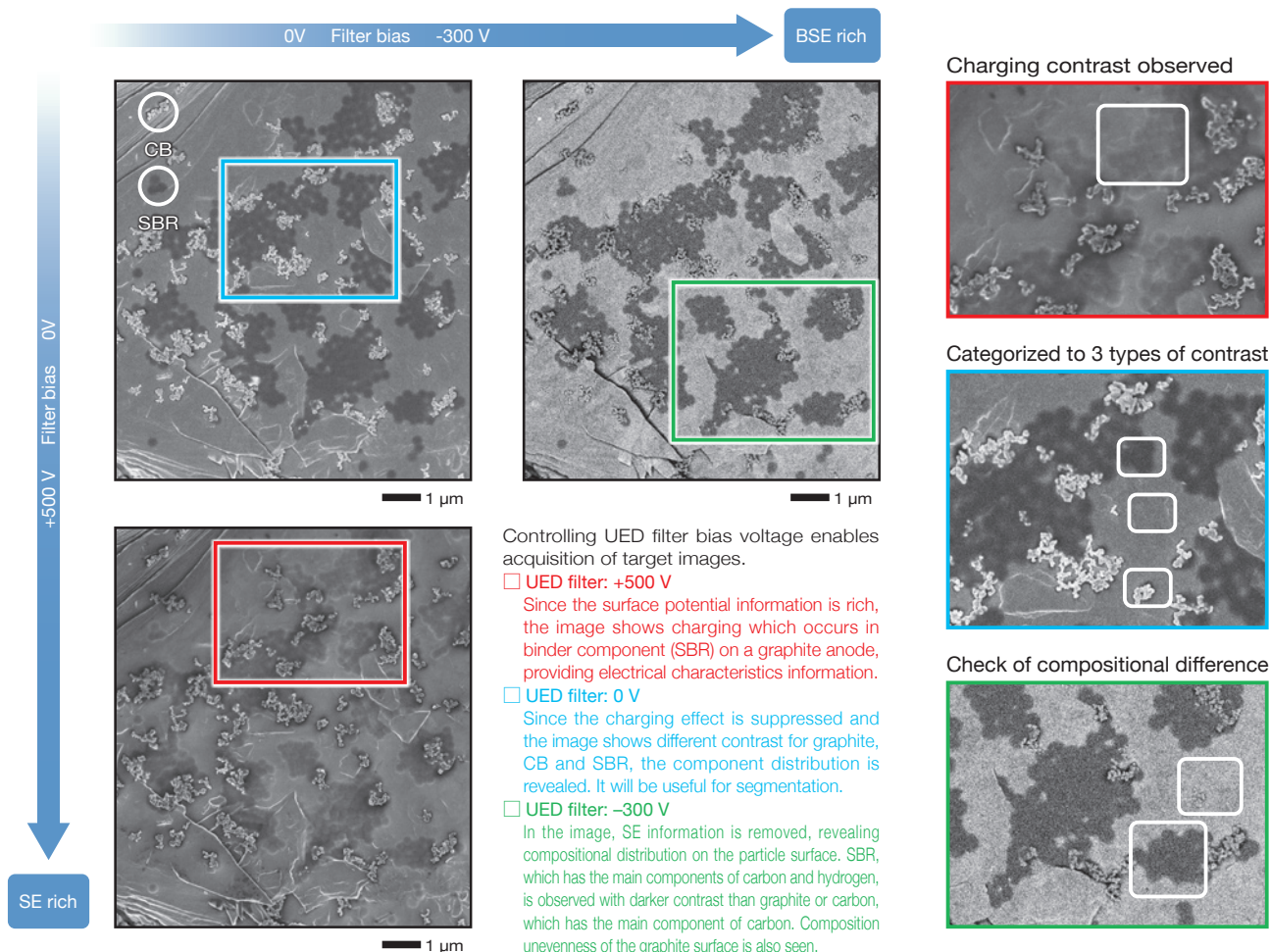
When negative voltage is applied to UED energy filter



With filter bias (-1 to -2000 V), the threshold value of the energy of electrons detected by UED, can be controlled. Electrons, which have higher energy than UED filter bias, are detected by UED. When applying a voltage of -several 100 V or more, the backscattered electron image which reflects much compositional information, can be acquired.

Applications to battery material

Specimen: LIB anode sheet Observation condition: 1.1 kV, UED, Same area observation SBR: Styrene-Butadiene rubber CB: Carbon Black



Main analytical tools installable on JSM-IT800<SHL>

EDS: Analytical method to detect characteristic X-rays generated by interactions with electron beams, for easily performing distribution measurement and qualitative & quantitative analyses of constituent elements in a specimen. Windowless EDS allows for detection of metal Li.

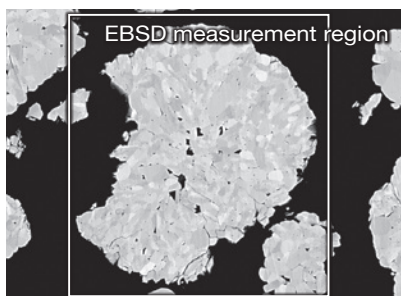
SXES: High energy resolution X-ray spectroscopy to resolve soft X-rays (characteristic X-rays with extremely low energies of 0.1 to 2 keV) by a diffraction grating, for obtaining soft X-ray spectra which reflect chemical states of constituent elements in a specimen. Thus, the method is used for chemical state analysis. With SS-94000SXES (SXES-LR), mainly the detection and chemical state analysis of metal Li can be made.

EBSD: Analytical method to measure the local orientations of a crystalline specimen from an electron backscatter diffraction (EBSD) pattern, where a bulk specimen is largely tilted (about 70°) from the horizontal plane and is probed by the electron beam to acquire an EBSD pattern. The method is used for analysis of crystal orientation and crystal grain size.

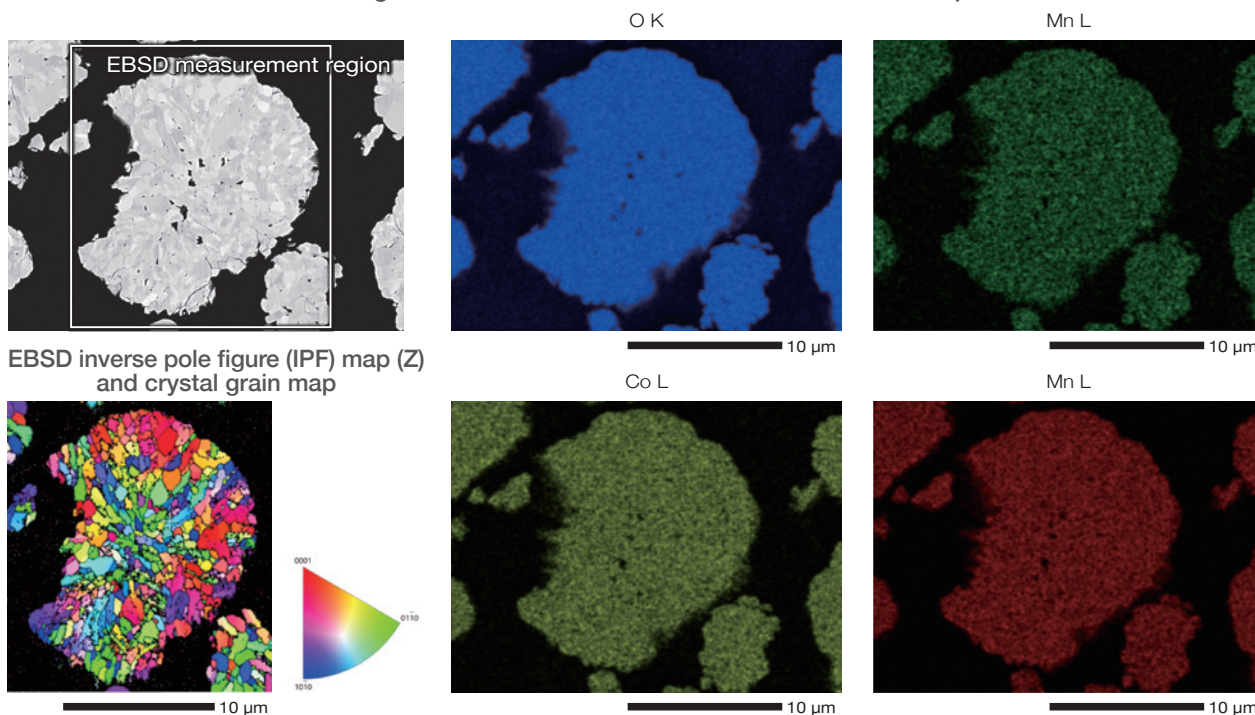
Analysis example using JSM-IT800 fitted with EDS/EBSD

EDS & EBSD analyses were performed for a cross section of a ternary (nickel, manganese, cobalt) cathode material. With EBSD measurement and EDS analysis, the quality of cathode material and the degradation of the material after cycle testing can be evaluated.

SEM backscattered electron image



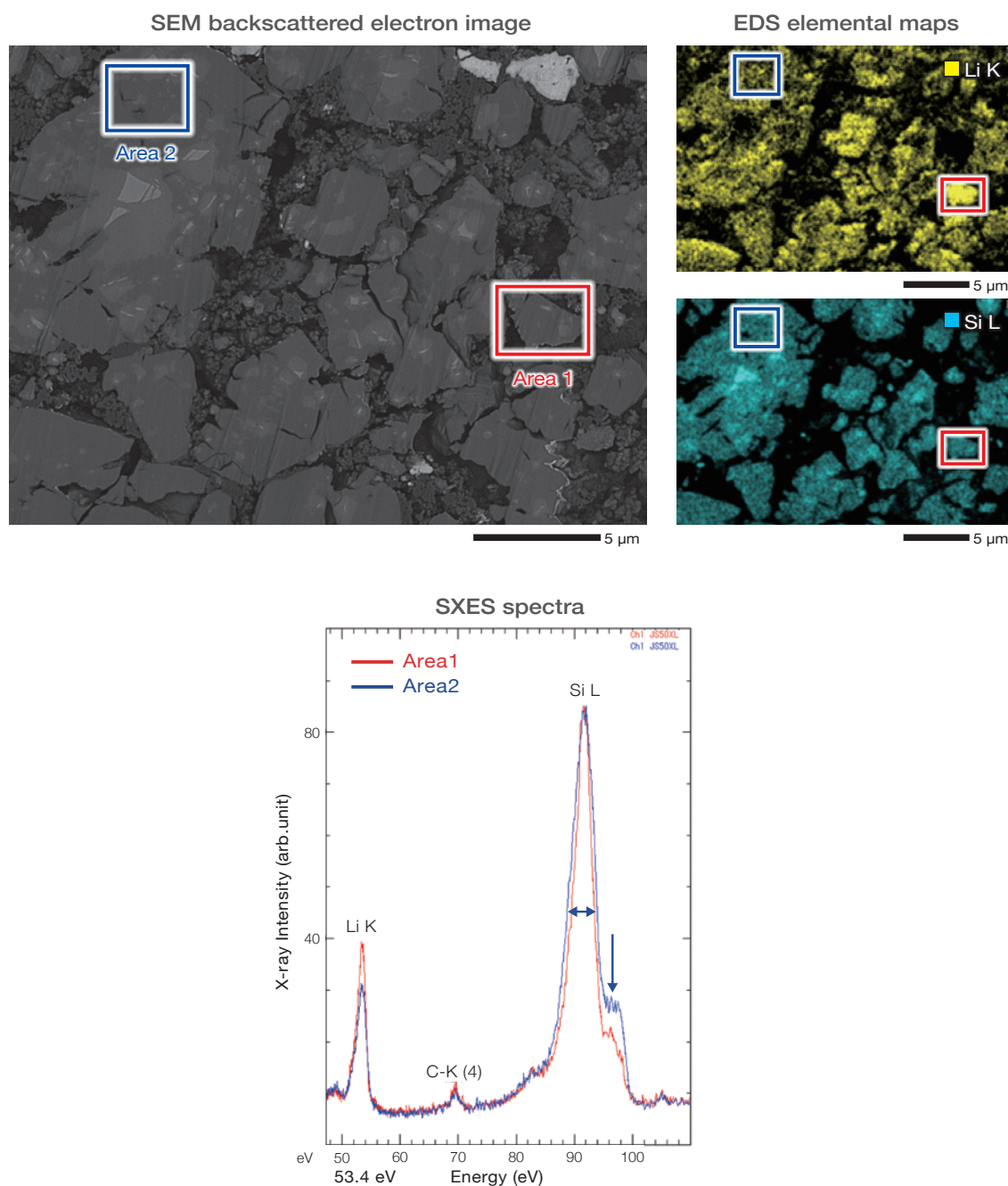
EDS elemental maps



Specimen: NMC particle cross section Observation condition: 5 kV(EDS), 15 kV(EBSD) EDS/EBSD: OXFORD Ultim Max/Symmetry

Analysis example using JSM-IT800 fitted with Windowless EDS/SXES

EDS & SXES analyses were performed for a cross section of a silicon anode material in a solid-state battery. Windowless EDS which efficiently detects low-energy characteristic X-rays, enables lithium distribution in the silicon anode layer to be roughly examined in a short time. SXES analysis was applied to particles in Area 1 and 2 where the Li intensity differs to each other. The peak position (~53.4 eV) of an Li K emission spectrum is revealed to be different from that of metal Li (~54 eV). From the difference in spectral shape of an Si L emission spectrum, it is found that in the anode, particles having a different progress of Li-Si alloying by charging, are present. Combining EDS and SXES makes it possible to easily analyze lithium distribution in the anode layer and chemical states of the anode active material.



Specimen: Cross section of an Si anode material (charging rate 80%) in a solid-state battery
Observation condition: 3 kV EDS/SXES: DrySD™ Gather-X(JEOL) /SS-94000SXES(JEOL)
Sample courtesy: Professor Atsunori Matsuda, Dept. of Electrical and Electronic Information Engineering, Toyohashi Univ. of Technology

Cooling & Air-isolation accessories

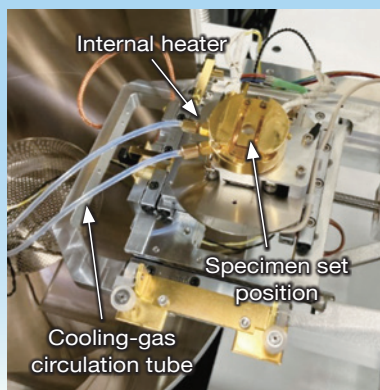
Figures below show the cooling & air-isolation accessories for SEM. Observation and analysis can be made while cooling a specimen by circulation of cooled nitrogen gas, enabling “in-situ” observation and analysis for a reduced state change of the specimen due to electron-beam irradiation and for a specimen temperature change. When a special specimen exchange rod (exchange chamber) for air isolation is configured, specimens that are likely to react with air can be analyzed.

JSM-IT800

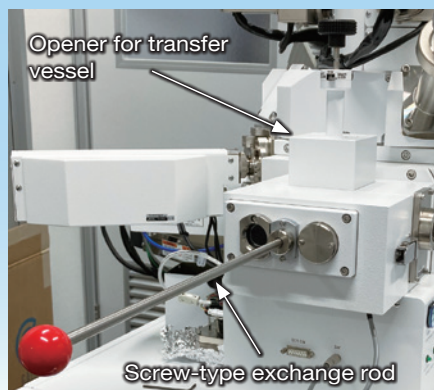
When a cooling stage unit is attached



Cooling & heating stage (Gatan C1003)



Air-isolated specimen exchange chamber for cooling stage



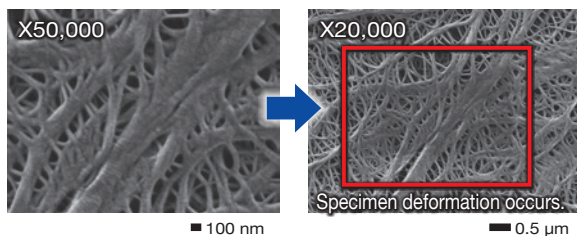
Observation example using the cooling stage

A separator used for LIB was observed using the cooling stage. Even at a low accelerating voltage of 800 V, a specimen was deformed by electron-beam irradiation during high-magnification observation at room temperature. But when the specimen was cooled at $-100\text{ }^{\circ}\text{C}$, the specimen was not deformed even during high-magnification observation. Thus, specimen cooling can reduce deformation of a specimen due to electron irradiation.

Specimen: Separator, Accelerating voltage 0.8 kV ※ Pt coating 2 nm

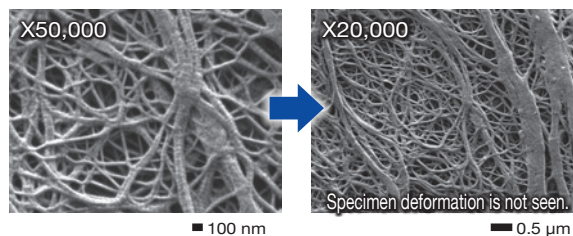
Room temperature

SEM secondary electron image



Cooling at $-100\text{ }^{\circ}\text{C}$

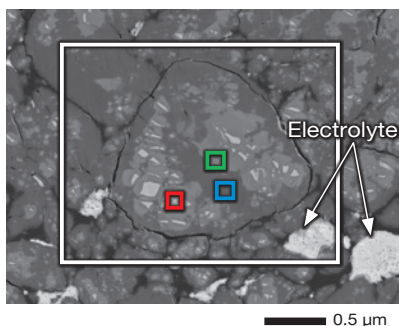
SEM secondary electron image



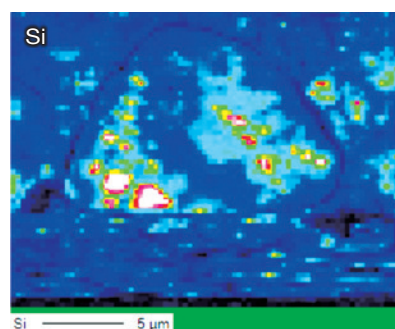
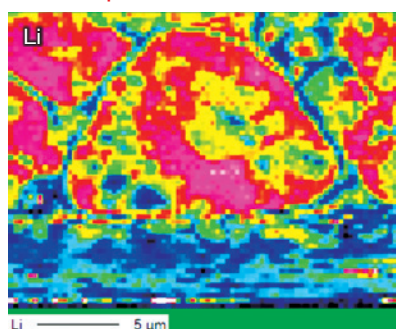
Analysis example using the cooling stage: SXES

A cross section of a silicon anode material in a solid-state battery was subjected to SXES analysis (mapping). In analysis at room temperature, it is found that specimen drift or deformation occurs because SXES analysis requires large probe current and as a result, solid electrolyte is likely to deteriorate. On the other hand in cooling analysis at $-120\text{ }^{\circ}\text{C}$, deterioration of the specimen due to electron-beam irradiation is reduced for stable analysis. As a result, it is found that elemental distribution of the solid electrolyte part can be obtained. Spectral extraction was applied to the obtained mapping result. In each area of A, B and C, the Li intensity and the chemical states of Si were found to be different, providing difference of charging states inside Si particles.

SEM backscattered electron image

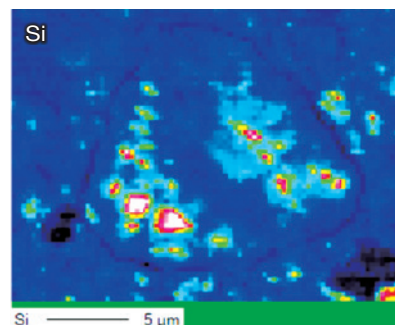
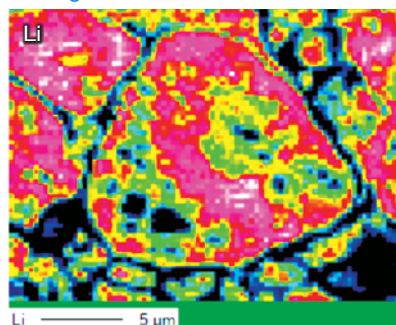


Room temperature



SXES elemental maps

Cooling at $-120\text{ }^{\circ}\text{C}$



Specimen: Cross section of an Si anode material (charging rate 50%) in a solid-state battery

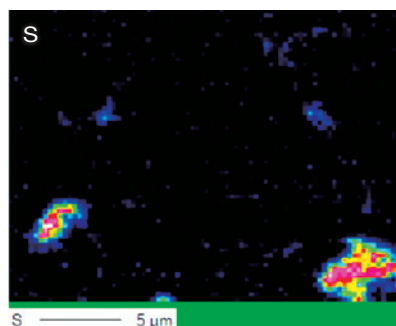
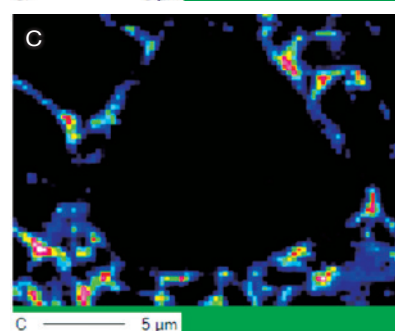
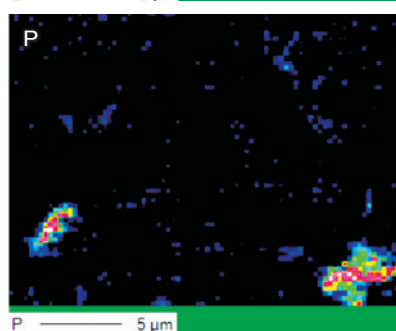
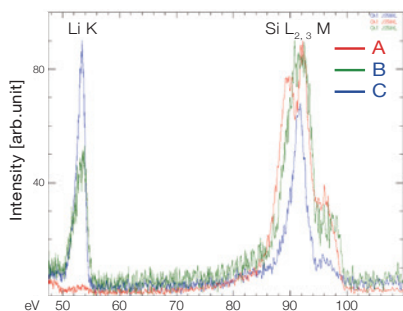
Observation condition: 5 kV, 50 nA, Cooling at $-120\text{ }^{\circ}\text{C}$

SXES: SS-94000SXES(JEOL)

Sample courtesy:

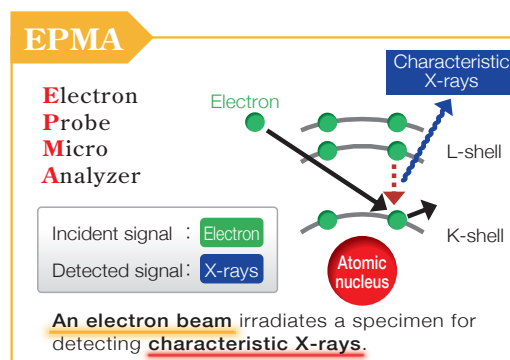
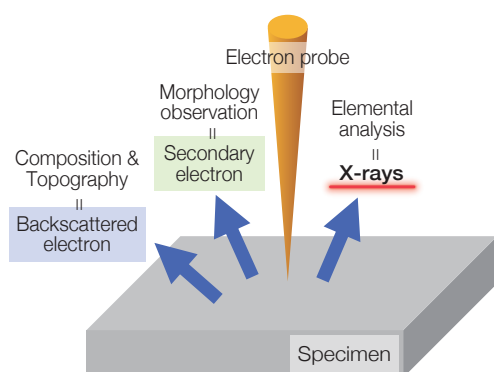
Professor Atsunori Matsuda
Dept. of Electrical and Electronic Information
Engineering, Toyohashi Univ. of Technology

Comparison of SXES spectra (cooling at $-120\text{ }^{\circ}\text{C}$)



2-2 Electron Probe Microanalyzer (EPMA)

The electron probe microanalyzer (EPMA) irradiates a specimen with an electron probe to detect characteristic X-rays generated from the specimen for elemental analysis. EPMA is equipped with multiple wavelength dispersive X-ray spectrometers (WDS) with high energy resolution, and uses a focused electron probe, allowing for elemental analysis on a small area of the order of micrometer to sub-micrometer and trace element analysis. EPMA also makes it possible to observe morphologies and compositions by secondary and backscattered electron images.

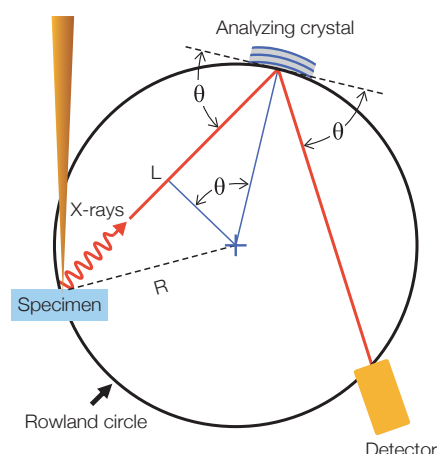


Wavelength Dispersive X-ray Spectrometer (WDS)



Features

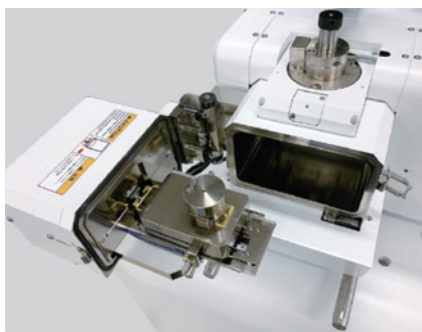
- Wavelength dispersive X-ray spectrometer (WDS)
- Analyzable elements: (Be) B to U
- Analysis region: several μm (point analysis) to several cm (line analysis, map analysis)
- Analysis depth: approx. $1 \mu\text{m}$
- Detection limit: Several tens of ppm



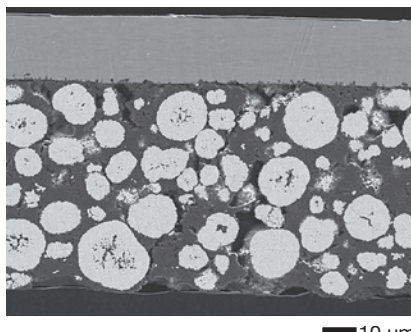
WDS is designed so that the specimen (analysis point), analyzing crystal and detector are always placed on the Rowland circle. Then, WDS detects the X-ray whose wavelength satisfies the Bragg's law.

Air-isolated analysis

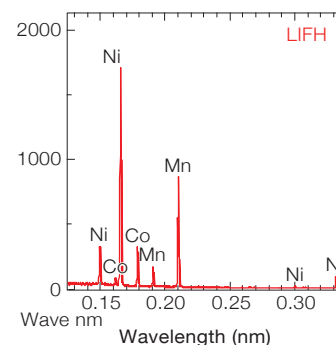
Since a battery material which is easy to degrade, rapidly transforms when exposed to air, it is needed to analyze the specimen with shielding air. To do this, the transfer vessel is used. The specimen subjected to sampling in an inert-gas environment, can be transferred to the EPMA specimen exchange chamber without exposing it to air, due to the help of the transfer vessel. When the transfer vessel is used with an air-isolation CP (CROSS SECTION POLISHER™), the air-isolated system plays a role from cross-section sample preparation to elemental analysis.



Transfer vessel attached to a dedicated holder adapter



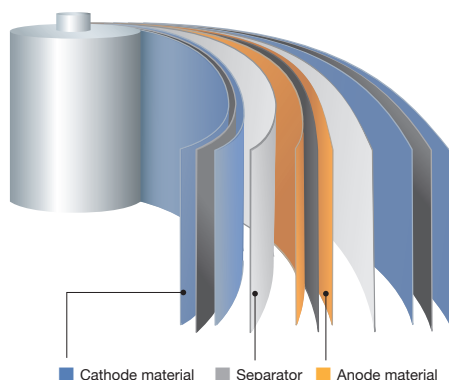
Cross section of a cathode after charge-discharge cycles, milled with an air-isolation, cooling CP



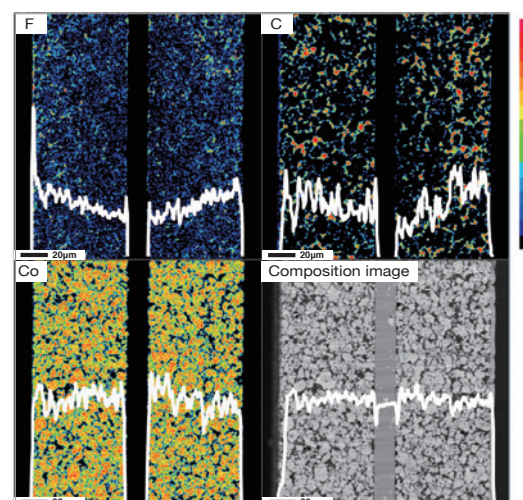
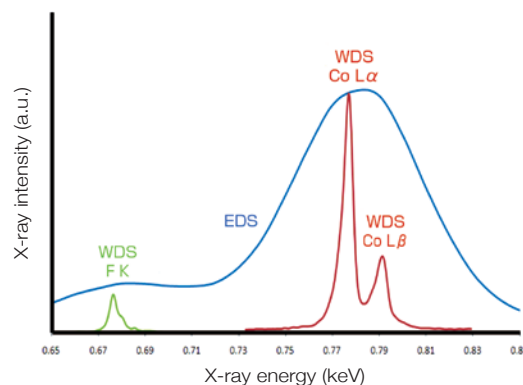
WDS spectrum acquired from a cross section of a cathode active material

Qualitative analysis and large area analysis of cathode materials

The spectra to the right are qualitative analysis results for Co (active material) and F (electrolyte) contained in a cathode material after charge-discharge cycles. The EDS results show a low energy resolution and a high background level, and the F K-line is overlapped by Co; thus the peak is difficult to detect. With WDS, there is no effect of Co $L\alpha$, β -line, allowing detection of the F K-line.



Cathode material: LiCoO_2 , LiMn_2O_4 , LiFePO_4 etc.
 Anode material: C, Si, SnO_2 etc.
 Electrolyte: LiPF_6 , LiClO_4 etc.



The right images are elemental maps of a cross section of a deteriorated LIB cathode material through repeated charging-discharging. It is shown that the signal intensities of F and C were increased, as F and C have migrated from the collector (Al) at the center.

The line profile in the elemental maps is obtained by averaging the intensity in the longitudinal direction. What should have originally been a homogeneous distribution of the elements is now shown to be biased, which is considered to give rise to deterioration of the battery performance.

A feature of EPMA is the ability to confirm very small changes in elemental distribution. The analysis region is $180\text{ }\mu\text{m} \times 180\text{ }\mu\text{m}$.

2-3 Transmission Electron Microscope (TEM)

The transmission electron microscope (TEM) illuminates a thin specimen (thickness 100 nm or less) with an electron beam to form a magnified image or an electron diffraction pattern using transmitted and scattered electrons, produced by electromagnetic lenses. Modern TEMs are equipped with scanning transmission electron microscopy (STEM) functions and spherical aberration (Cs) correctors for clear observation of atoms. Furthermore, the use of characteristic X-rays generated by interactions of the incident electrons and specimen allows for atomic-resolution elemental analysis. TEM can also acquire a secondary electron image.

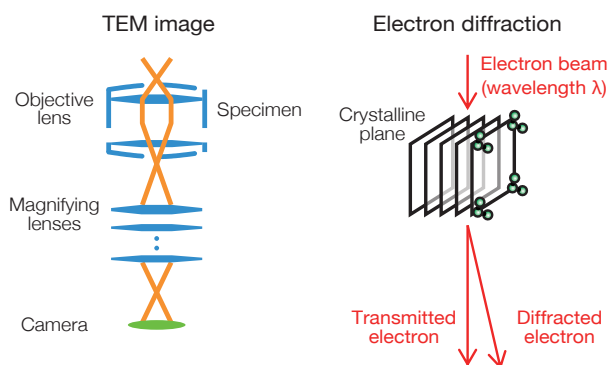
In LIB analysis, TEM enables direct observation of Li atom. Air-isolated transfer makes it possible to observe and analyze the anode & cathode and electrolytes, and to simultaneously acquire chemical states, crystalline information, bonding states, etc.



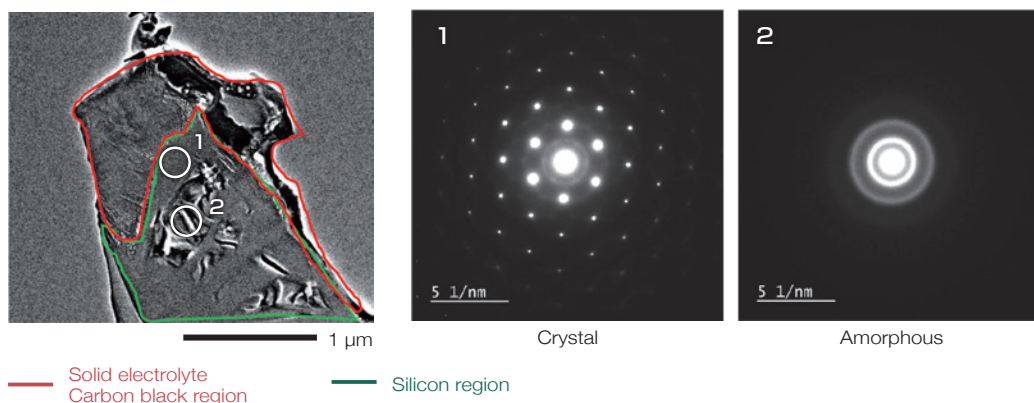
TEM image and electron diffraction

An electron beam emitted from an electron source, passes through a specimen. Then, a TEM image is formed by the objective lens and subsequent magnifying lenses. Morphological and internal-structure observation can be made at the order of a few millimeters down to the atomic-scale order. Information on specimen density, constituent atoms and crystalline states contributes to TEM image formation, and the contrast of TEM image reflects the structure difference in the specimen.

Electron diffraction utilizes diffraction phenomena, which occur when an electron beam passes through a specimen as a wave nature. TEM magnifies diffraction spots converged by the scattered electrons, on the back focal plane of the objective lens. The electron diffraction pattern enables acquisition of crystalline information on the specimen.



Observation and analysis of a silicon anode using TEM image and electron diffraction



Figures above show part of silicon particles in a silicon anode. The green frame shows a silicon particle, but different contrasts can be seen at positions (1) and (2) due to structural differences. Electron diffraction enables us to obtain crystal structure, crystal orientation and crystalline states.

In position 1, strong diffraction spots are observed; on the other hand, position 2 shows a characteristic diffraction pattern, called “halo pattern”. Thus, position 1 is highly crystalline, whereas position 2 is amorphous.

Scanning transmission electron microscopy image (STEM image)

STEM is an observation method which converges an electron probe by electromagnetic lenses and scans a thin specimen with the converged probe, so as to detect transmitted and scattered electrons from the specimen for acquisition of a Scanning TEM image. STEM images are categorized depending on detectors, to STEM-BF image and STEM-ADF image.

Features of STEM-BF image

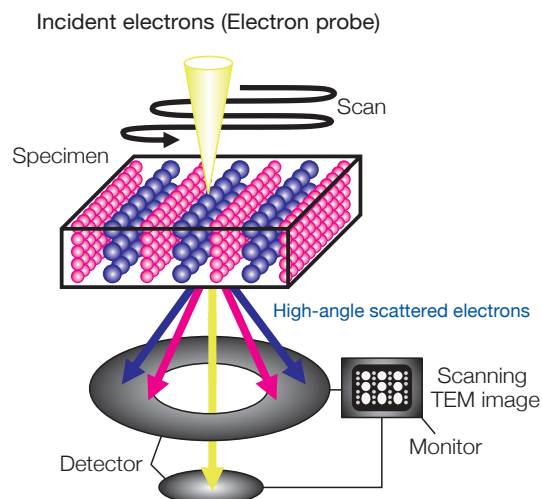
BF: Bright Field

- Scanning TEM image formed by transmitted and low-angle scattered electrons.
- Interference image similar to TEM image
- Contrast is reversed due to difference in focus and specimen thickness.

Features of STEM-ADF image

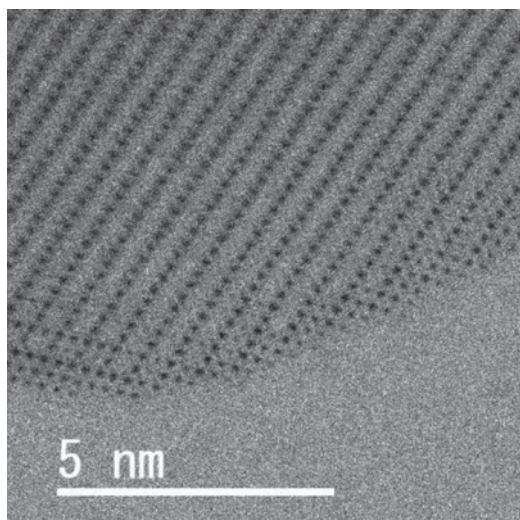
ADF: Annular Dark Field

- Scanning TEM image formed by high-angle scattered electrons.
- Compositional image (Z contrast): Image intensity is approximately proportional to the square of the atomic number.
- Non-interference image
- Contrast is not reversed irrespective of difference in focus and specimen thickness.

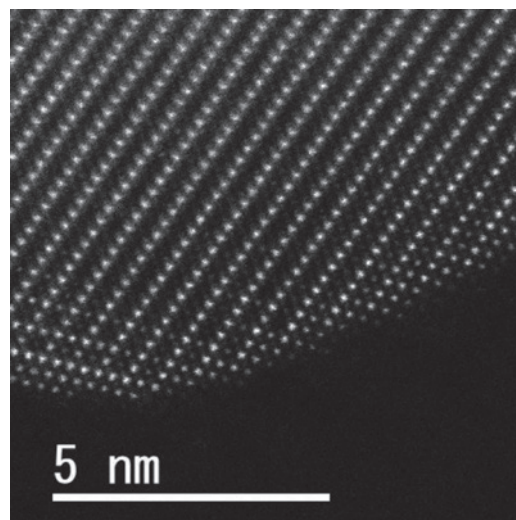


Observation example of a ternary cathode material by STEM

STEM-BF image



STEM-ADF image



STEM-ADF is a method to form a Scanning TEM image by high-angle scattered electrons. This feature does not invert brightness or darkness due to differences in focus, and the image contrast is approximately proportional to the atomic number Z . Therefore, it is effective in easily interpreting differences in the constituent elements of a sample.

In the STEM-ADF image above, the constituent atomic positions of Ni, Mn, and Co show high intensity; Li and O do not contribute to image formation because they are subject to low-angle scattering. Thus, STEM-ADF is an effective technique for studying transition metal positions.

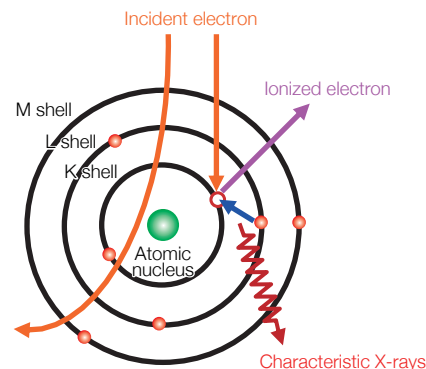
It has also been shown that in a few atomic layers near the particle surface, the number of detected atoms is increased because the above transition metals are mixed into the original Li sites.

This phenomenon of transition metal incorporation into the Li site is called "cation mixing" and causes battery degradation.

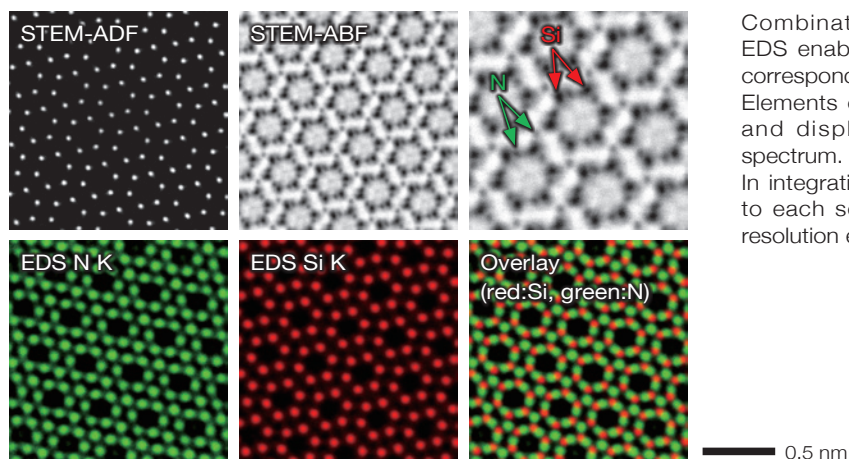
Energy dispersive X-ray spectroscopy (EDS)

When one of inner-shell electrons is excited by an incident electron, an outer-shell electron moves (transitions) to an electron vacancy, so as to relax to the ground state.

At this event, the outer-shell electron with higher energy than the inner-shell electron, emits energy (X-rays). That is, the energy of the emitted X-rays corresponds to the energy difference between the outer-shell electron and the inner-shell electron. The emitted X-rays are called "characteristic X-ray(s)" and the X-ray energy is characteristic of individual elements depending on the energy level difference. This phenomenon is utilized for qualitative and quantitative element analyses.



EDS mapping at atomic resolution using STEM

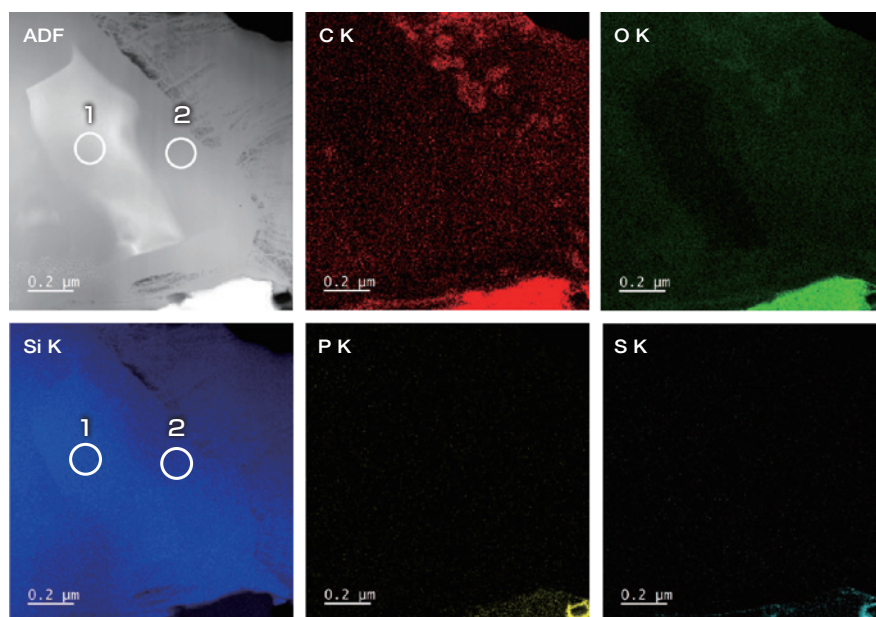


Combination of atomic resolution STEM and EDS enables us to obtain elemental information corresponding to each atomic position.

Elements of interest can be selectively visualized and displayed in overlay from the acquired spectrum.

In integration, specimen drift correction is applied to each scan, facilitating acquisition of atomic-resolution elemental maps.

Observation and analysis example of a silicon anode by STEM-ADF and EDS



The STEM-ADF image (top left) shows different contrasts at the positions 1 and 2.

EDS analysis shows that the X-ray count of silicon (Si) in position 2 is slightly lower than in position 1.

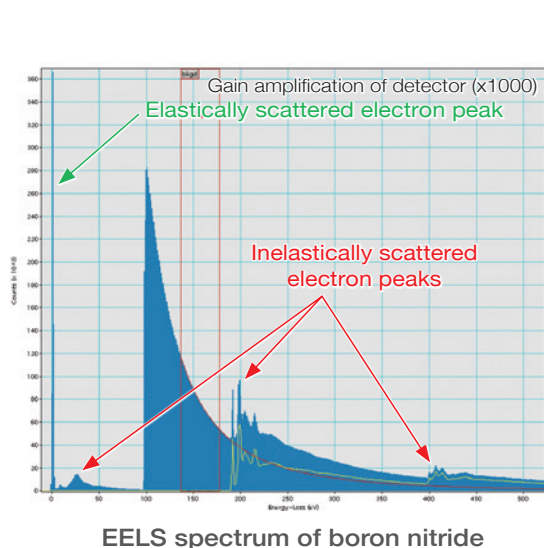
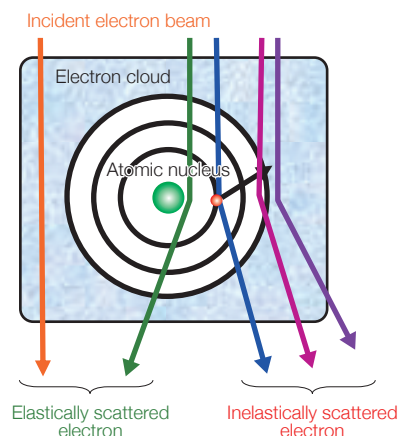
The electron diffraction results indicate that position 1 is crystalline and position 2 is amorphous. These results suggest that the density of the amorphous Si layer is decreased after charge.

Electron energy loss spectroscopy (EELS)

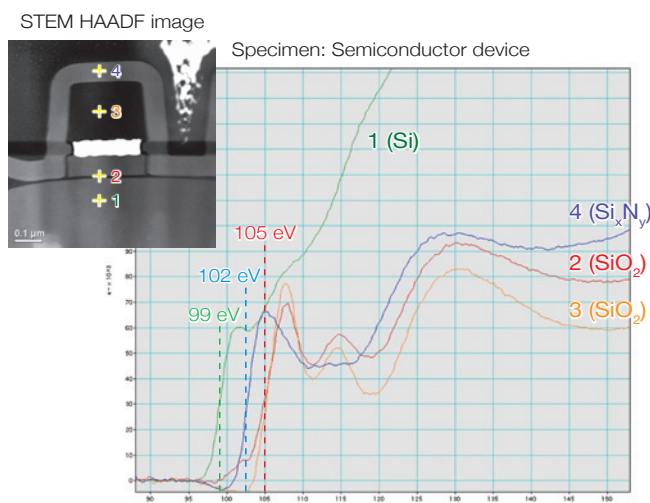
When electrons are incident into a specimen, three types of electrons pass through the specimen. “Transmitted electrons” which do not interact with the specimen, “elastically scattered electrons” which are scattered by constituent atoms without losing their energy, and “inelastically scattered electrons” which excite plasmons and inner-shell electrons while losing their energy. EELS focuses on the inelastically scattered electrons and performs analysis from spectra corresponding to the lost energy (electron energy loss spectra). Using these spectra, elemental mapping, qualitative & quantitative analyses and chemical bonding state analysis can be conducted.

Features of EELS

Similar to EDS spectra, the peaks of EELS spectra reflect the loss energy according to each element and shell orbital. The EELS spectrum provides information on the excitation of electrons into the conduction band. EELS can also capture changes in valence because the position of the peaks shifts (energy is lost) depending on the bonding state of the atoms. Specimen thickness can also be estimated irrespective of crystal and amorphous. Actually, the thickness can be measured from the zero-loss peak intensity and all of other spectral intensities in the valence-loss spectrum.

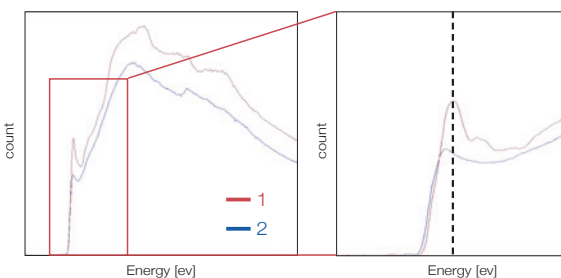
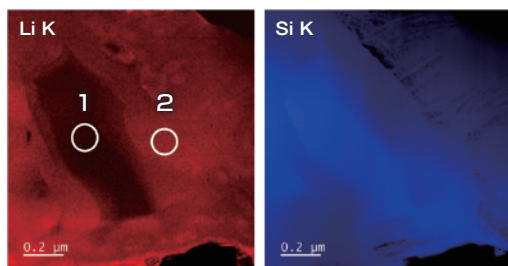


EELS spectrum of boron nitride



Spectral change depending on bonding-state difference

Analysis example of a silicon anode by STEM-EELS



Figures above show the inside of the silicon anode particle after charge, analyzed by STEM-EELS. STEM-EELS mapping shows that the Li concentration is higher at the position 2 than position 1. Analysis by electron diffraction assumed that the introduction of Li by charging would promote amorphization process of Si. EELS analysis revealed that Si $L_{2,3}$ edge peak shifted due to the introduction of Li into Si. It is considered that Li was inserted to the Si crystal by charging, causing it to change from a crystalline state to an amorphous state; the bonding state was also changed. This result complements the electron diffraction results.

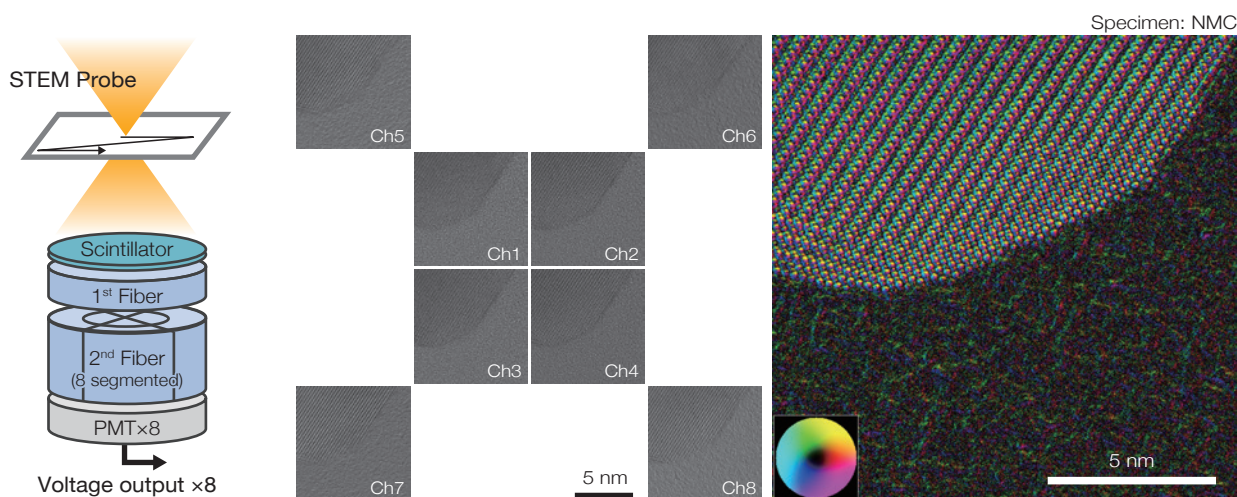
Physical property evaluation of solid electrolytes

Segmented STEM detector (Segmented Annular All Field: SAAF)

The conventional STEM detector is annular-, donut-shaped and integrates all the scattered electrons. The data conventionally acquired was limited to the details-summarized information. SAAF adopts a multiple-segmented detector to obtain angular information as well as movement quantity of electron beams. Thus, the electric and magnetic fields in the specimen can be observed. In addition, the use of a TEM equipped with a Cs corrector allows for observation of electromagnetic fields at the atomic resolution.

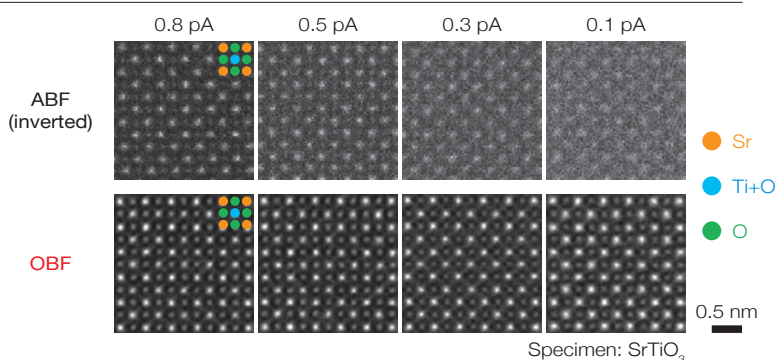
Observation example of a ternary battery material by SAAF

Eight STEM images are acquired by SAAF. Those eight images have different contrast. From these images, information on the electromagnetic fields associated with each atom, can be visualized by calculation of both angular information and movements of electron beams which depend on electromagnetic fields in a specimen.



Optimum Bright Field STEM (OBF STEM)

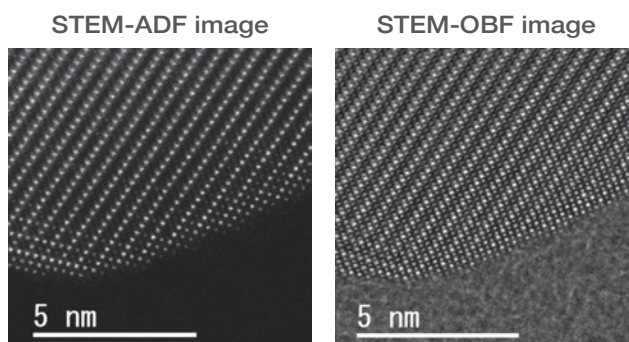
In OBF STEM, raw images acquired by a segmented STEM detector are used as the source for a phase image reconstruction, with dedicated Fourier filters to maximize the signal to noise ratio of a retrieved image. This innovative method achieves higher contrast for both heavy and light elements even under extremely-low electron dose conditions. Beam sensitive materials difficult to observe with ADF and ABF STEM methods can be easily analyzed with higher contrast at a wide range of magnifications.



Direct observation example of Li atom in a ternary cathode material by OBF STEM

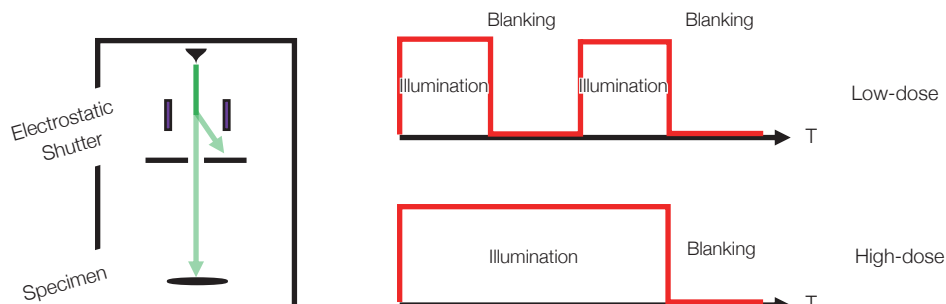
The OBF method enables us to clearly observe light elements, such as O and Li, which cannot be observed by STEM-ADF. Battery materials are likely to be damaged by electron-beam irradiation; but with OBF STEM, you can obtain a higher contrast image (see the right figure) even at a low dose of a few pA. Thus, the OBF method is suitable for observing battery materials that require the suppression of electron-beam damage.

Specimen: NMC
Probe current: 8 pA



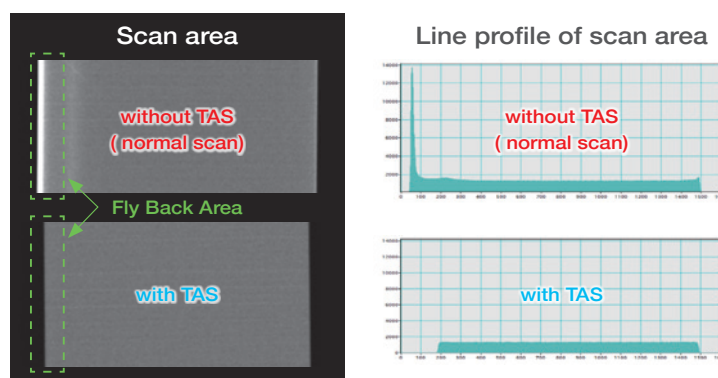
Electrostatic dose modulator (EDM)

EDM is a fast electron-beam blanking system using an electrostatic shutter. Pulsed-electron illumination is controllable with the minimum pulse width of 100 ns or less and the maximum frequency of 1 MHz. You can easily and intuitively change the microscope dose by changing only the pulse width. Pulsed illumination is also useful for reducing electron-beam damage to the specimen.



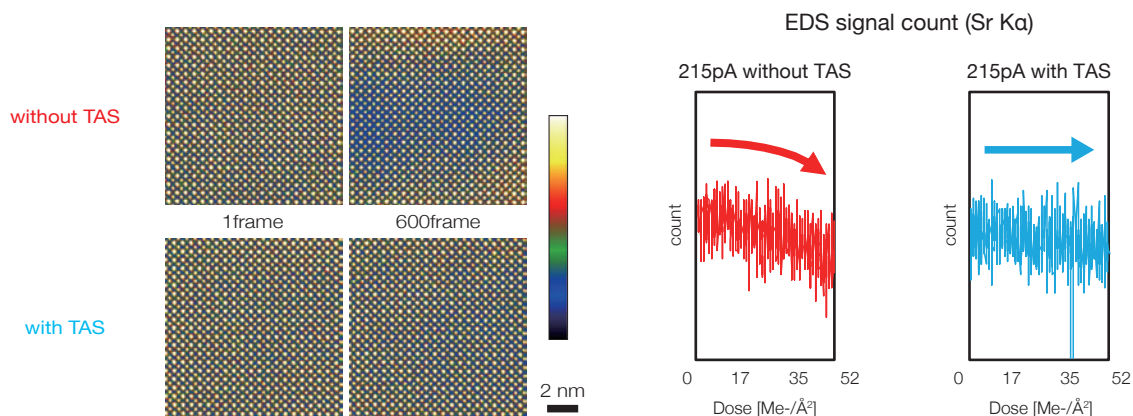
True Area Scan (TAS) system

In actual beam scanning by STEM, “Flyback Area” exists at the left end of a horizontal scan, where an electron beam is at a standby state. In this area, data is not processed as signal, but unnecessary electron radiation damage can occur, causing a break of a specimen during observation or analysis. The True Area Scan (TAS) system performs flyback blanking by EDM in synchronism with electron-beam illumination onto the Flyback Area. Thus, TAS is effective for electron-beam sensitive materials.



Example of reducing electron radiation damage by TAS

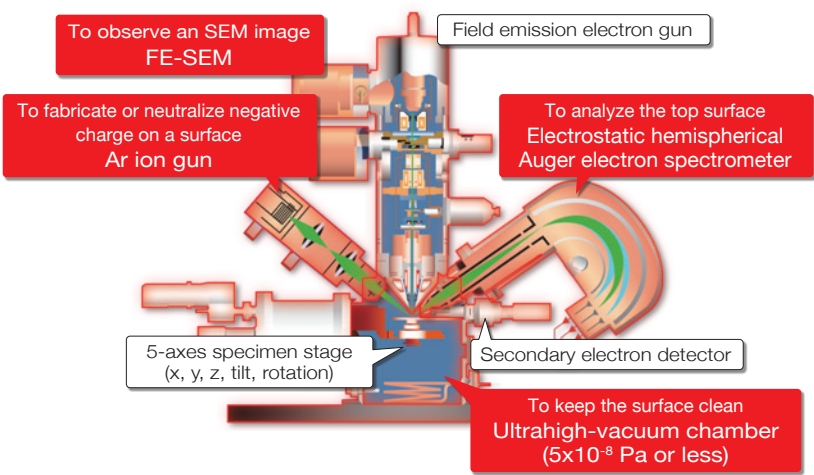
Two data with and without TAS were compared under the same conditions of sample, electron-dose, etc. Figures below show the amounts of elements detected by STEM and atomic resolution EDS mapping. STEM images show different intensities at the center of image, with and without TAS applied, thus verifying a suppressed beam damage to the sample. For EDS mapping, EDS signal counts of Sr $K\alpha$ decreased with increased dose to the sample when TAS was not applied. Since the sample which is sensitive to electron-beam illumination suffers damage, called “electron-beam drilling”, the TAS system is effective for it.



3-1 Auger Electron Spectrometer (AES)

Instrument configuration of Auger electron spectrometer

The Auger electron spectrometer (AES) is an instrument combining scanning electron microscopy (SEM) and Auger electron spectroscopy. The AES instrument features highly precise determination of positions for Auger analysis, by checking an SEM image taken with the instrument.

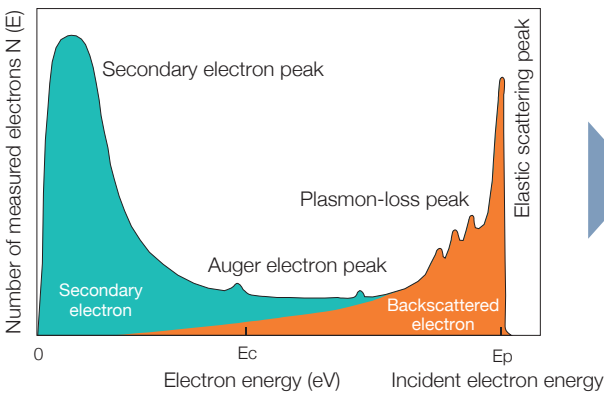


Instrument configuration	Applications
Field emission electron gun	Analysis position determination by SEM observation
Ultrahigh-vacuum chamber	Keeping the surface clean
Ar ion gun	Surface cleaning, depth profiling, charge neutralization
Electrostatic hemispherical Auger electron spectrometer	Qualitative, quantitative, and chemical bonding state analysis using Auger spectra

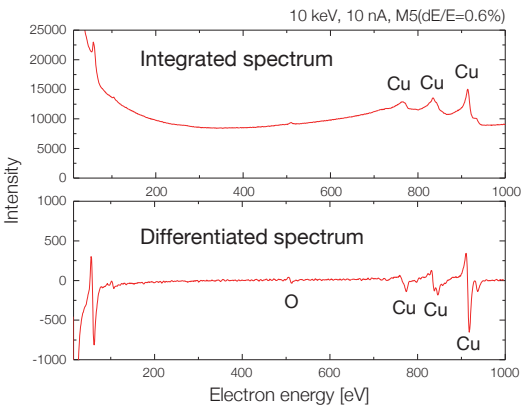
Instrument configuration and its applications of AES

Spectra acquired with Auger electron spectrometer

The Auger electron spectrometer enables acquisition of the energy distribution of electrons generated from the specimen surface due to electron-beam irradiation. In an Auger spectrum, small Auger peaks appear on a large background composed of secondary electrons and backscattered electrons. To easily remove this background, a differentiated spectrum is used for qualitative & quantitative analysis.



Schematic of Auger spectrum

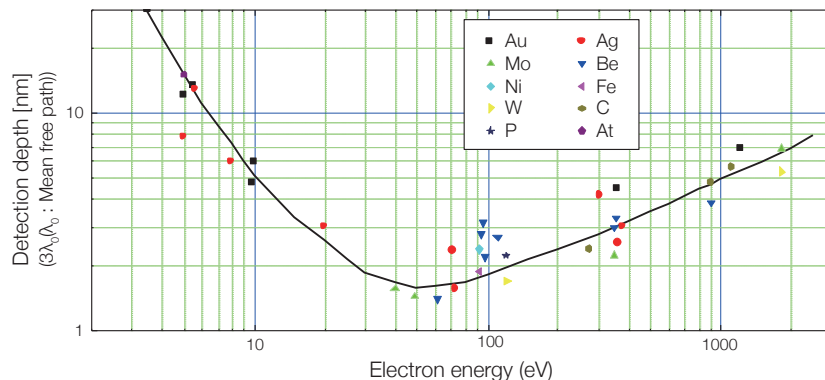


Measured spectra of Cu
(Top: Integrated, Bottom: Differentiated)

Features of Auger analysis (1) Top surface analysis: only 6 nm depth from the surface

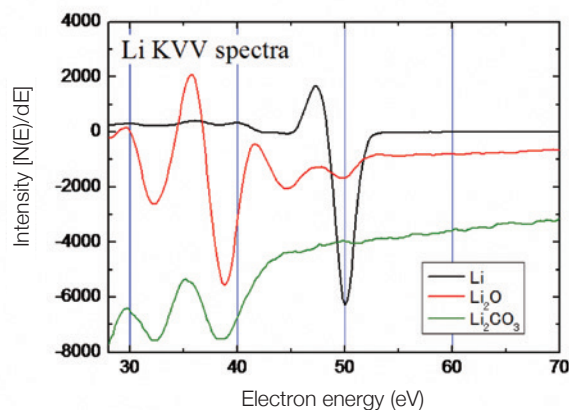
The figure below shows the relationship between electron energy and detection depth.

Auger peaks for all elements except H and He appear below about 2000 eV. Focusing on this energy region, we found that the detection depth of Auger electrons is less than 6 nm, making surface analysis by AES possible.



Features of Auger analysis (2) Detection of lithium oxide

EDS enables detection of lithium. However, detection of lithium oxide compounds is difficult. When lithium combines with oxygen to form a lithium oxide compound, the outer shell electrons become electron donating. Therefore, the transition to the inner shell is reduced, and the yield of Li-K emission is reduced. On the other hand in AES, since an electron existing in the neighboring atom is also associated with electron excitation, a peak of lithium oxide can be detected with high sensitivity.

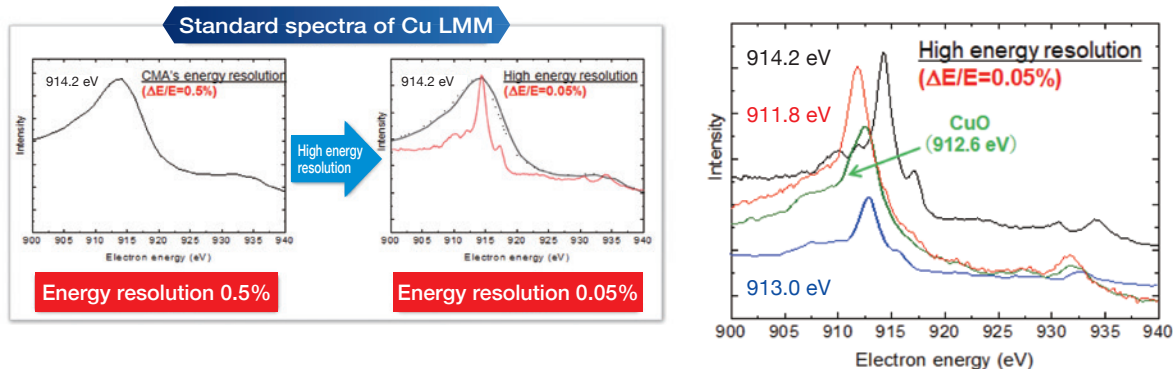


Analysis method	Detected signal	Li metal detection	Li oxide detection
AES	Li-KVV (Auger electron)	⊙	○
EDS, SXES	Li-K (characteristic X-rays)	⊙	△

Features of Auger analysis (3) Chemical bonding state analysis, and its quantitative analysis

High energy-resolution analysis mode by AES allows for acquisition of very sharp spectra, enabling investigation of the difference in peak position and peak shape depending on chemical bonding states. Multi-component materials with multiple chemical bonding states are analyzed using Peak deconvolution with the standard spectra for each compound.

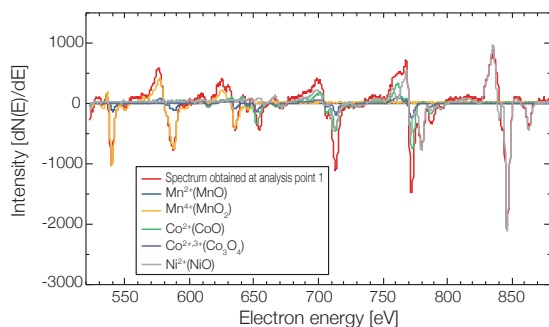
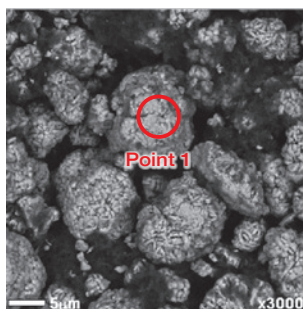
High energy-resolution measurement by Electrostatic hemispherical analyzer



Chemical state analysis by AES

Figures below show examples of chemical bonding state analysis using AES and subsequent quantitative analysis. To quantitatively measure a chemical state, the measured spectrum is decomposed into some spectra of the required chemical states by peak deconvolution, and each differential intensity is calculated after the decomposition. The result is compared with the differential peak intensity of the standard spectrum under the same acquisition conditions and converted to atomic concentration.

Active material

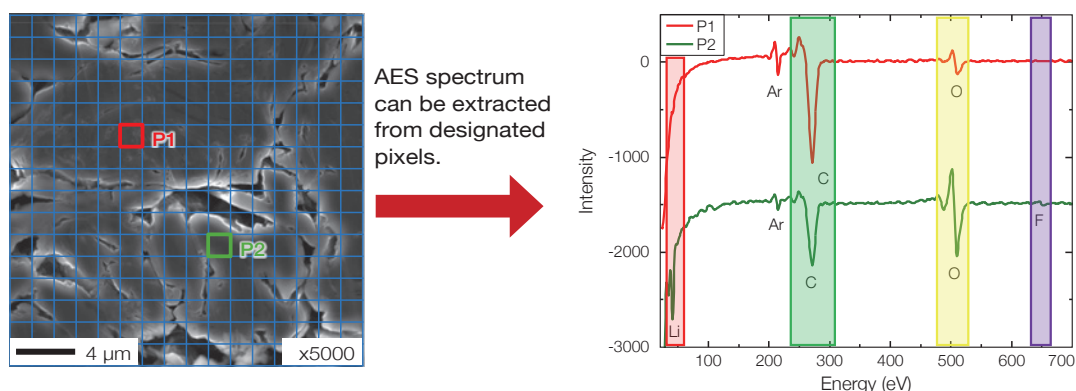


After peak deconvolution, quantitative values of the respective chemical bonding states are obtained.

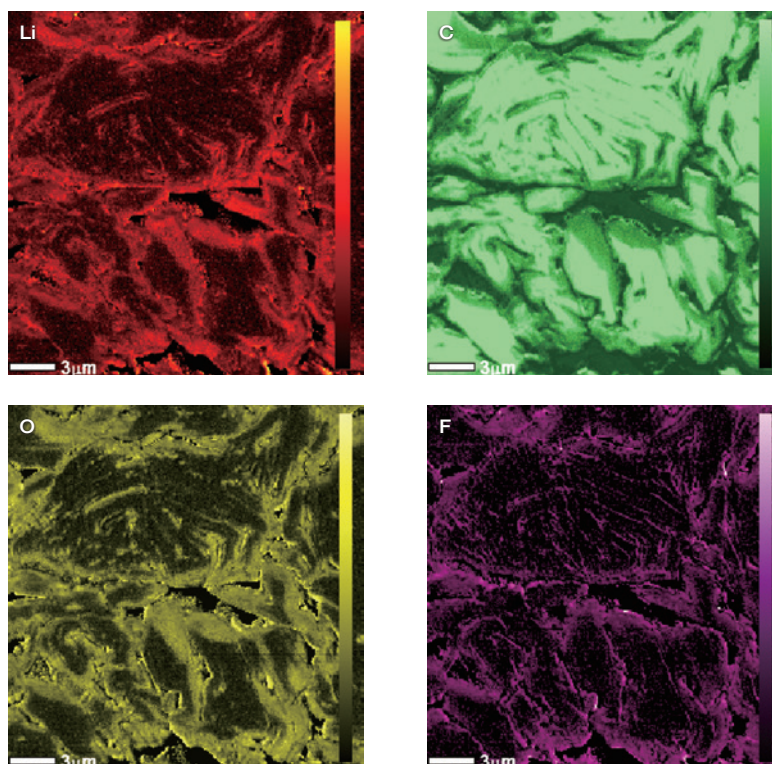
	Mn		Co		Ni	Total
	MnO	MnO ₂	CoO	Co ₃ O ₄	NiO	
Surface	28%		25%		47%	100%
	7%	21%	18%	7%	47%	100%

New function: AES Spectrum Imaging and elemental mapping of Li oxide in anode material

AES spectrum imaging, a new function, acquires hyperspectral data by storing Auger spectrum pixel by pixel. Thus, after Auger measurement, the spectra at designated pixels (in red and green frames in SEM image) are extracted. Then, selecting peaks from the extracted spectra makes it possible to obtain elemental maps. Elemental maps for Li are generally difficult to acquire because the Li peaks are often superposed onto the other peaks. However this unique feature enables easy extraction of an elemental map of the Li element.



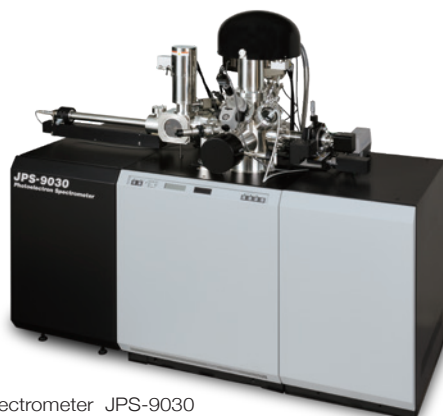
Selecting peaks from the extracted spectra enables conversion into each elemental map.



Elemental maps (10 kV, 10 nA) of cross section of a LIB anode prepared by CP

3-2 X-ray Photoelectron Spectrometer (XPS)

The X-ray photoelectron spectrometer (XPS) is the instrument that irradiates X-rays to a sample to excite and detect photoelectrons from the top surface. Thus, XPS has several features: surface-sensitive analysis, high energy resolution and analysis of any solid samples. In LIB analysis, XPS enables detection of Li (key element) and analysis of chemical bonding states. Furthermore, depth profiling enables you to analyze not only the top surface, but also the region inside the sample.



X-ray photoelectron spectrometer JPS-9030

Direct detection of Li!

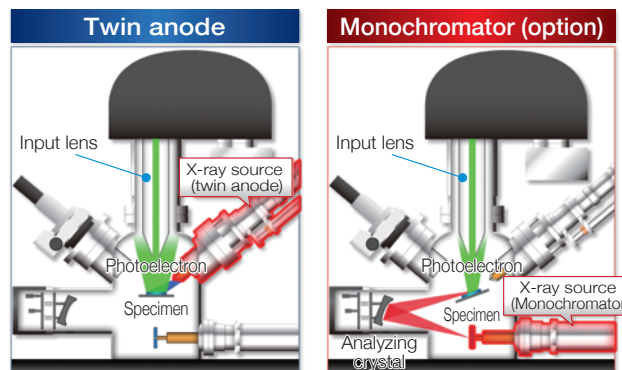
Features

- Analyzable elements: Li to U
- Surface analysis instrument (detection depth of about 6 nm)
- Chemical bonding state analysis
- Detection lower limit of about 0.1%
- Supports depth profiling

Optical system

The JPS-9030 can be equipped with a monochromator (option) or a twin anode X-ray source, enabling you to select a suitable configuration depending on analytical purpose or the specimen to be measured.

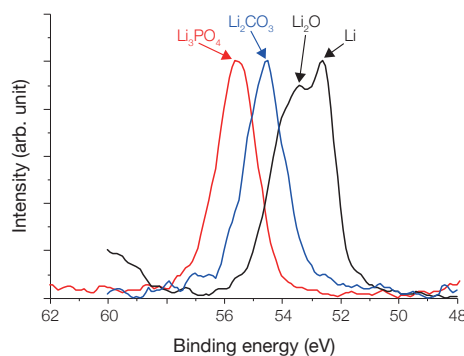
The electron optical system of the input lens for photoelectrons is designed to enable signal detection over large areas with a large focal depth, achieving highly accurate analysis with excellent reproducibility, such as for analysis of powder samples that are the raw materials of Li-ion batteries, and of electrodes after heterogeneous charge-discharge tests.



Chemical bonding state analysis

Identification of chemical bonding state by distinguishing positional difference in spectral peaks

Changes in the chemical bonding state appear as differences in the peak positions and thus, identification of the chemical bonding state of the Li can be performed by evaluating the peak positions.



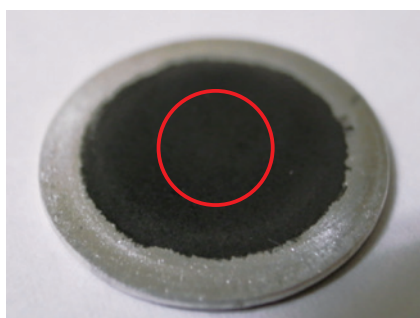
Chemical bonding state	Li1s
Li	52.6 eV
Li ₂ O	53.5 eV
Li ₂ CO ₃	54.6 eV
Li ₃ PO ₄	55.5 eV

Standard sample

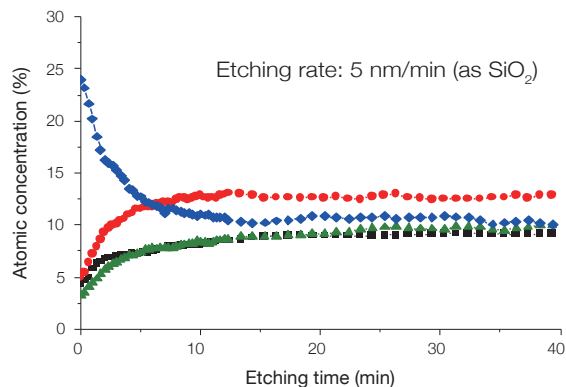
Analysis example: Depth profiling of an anode material after charge-discharge cycles

Example of depth profiling of a cathode material

The image on the left figure is a powder of the raw material for a LiB cathode material that has been molded into a tablet. Then, depth profiling was performed on the tablet and Li segregation was observed in an area on the surface (size: about 30 nm), as shown in the graph on the right figure.

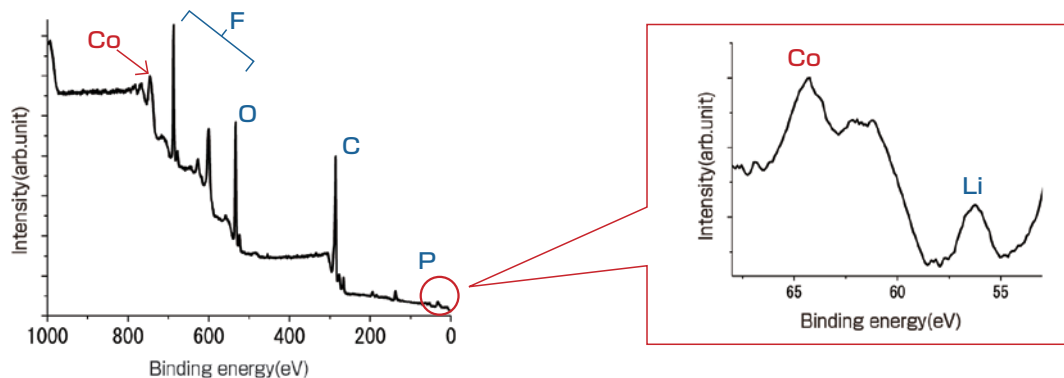


Analysis region: 1 mm diameter

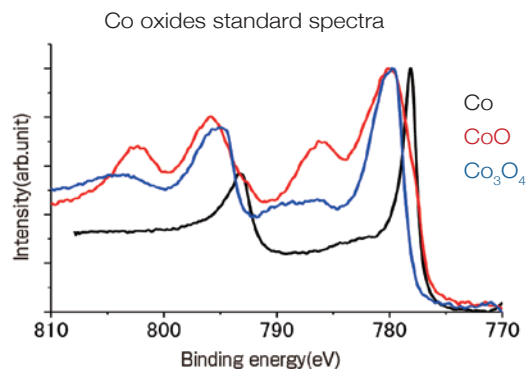
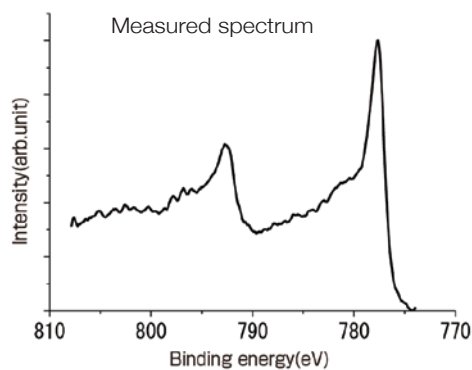


Analysis of an anode material after charge-discharge cycles

The graphs below show qualitative analysis results for an anode material. In addition to intercalated Li, Co was detected, which was originally not present in the anode.



Comparing the spectrum of Co in the anode material (below left) with the standard sample spectra of Co and Co oxides (below right) clearly shows that the Co in the anode material exists in the metallic state. It can be inferred that the Co in the cathode has been ionized, migrated to the anode, and precipitated as metallic Co.



4-1

X-ray Fluorescence Spectrometer (XRF)

The X-ray fluorescence spectrometer (XRF) is the instrument that irradiates X-rays to a sample to detect fluorescent X-rays emitted from the sample, for performing qualitative and quantitative analyses of the elements contained in the sample. XRF is used for determining steel grades, evaluating materials quality, and screening the restricted materials in RoHS regulation (Cd, Pb, Hg, Cr, Br, etc.). XRF enables rapid analysis from sample preparation to acquisition of results.

JSX-1000S "Element Eye™"



Analysis elements : C to U
 Collimator diameter : 0.9, 2.0, 9.0 mm
 Sample form : Solid, powder, liquid
 Non-destructive analysis
 Trace elements detection by primary filters
 Detection lower limit : Several ppm

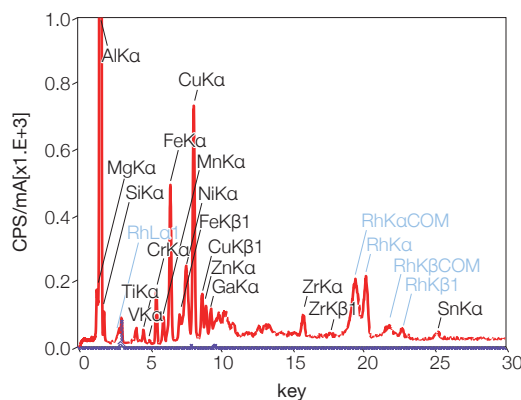
Easy and fast measurement

XRF enables anyone to perform easy and fast measurements. XRF performs elemental analysis and quantitative analysis on the order of ppm, simply by setting a solid sample on the spectrometer and measuring in several tens of seconds.

Sample setting



Spectral acquisition



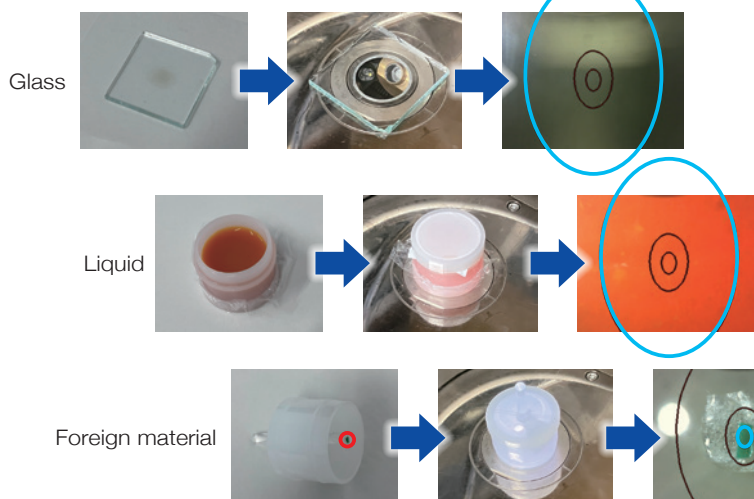
Quantitative analysis (FP method)

Chemical formula	Certified value	Quantitative value	
	mass%	mass%	3σ
Mg	0.95	1.09	0.059
Al	97.28	97.48	0.097
Si	0.67	0.42	0.034
Ti	0.053	0.058	0.004
V	0.01	0.01	0.002
Cr	0.177	0.159	0.005
Mn	0.049	0.049	0.003
Fe	0.32	0.29	0.005
Ni	0.04	0.03	0.002
Cu	0.28	0.30	0.004
Zn	0.053	0.047	0.002
Ga	0.027	0.026	0.001
Zr	0.012	0.014	0.001
Sn	0.023	0.020	0.002

Sample preparing

Sample setting

Measurement region



With XRF, a wide range of samples, ranging from conductive metals to insulative materials (high polymers, glasses, etc.), can be measured without sample pretreatment.

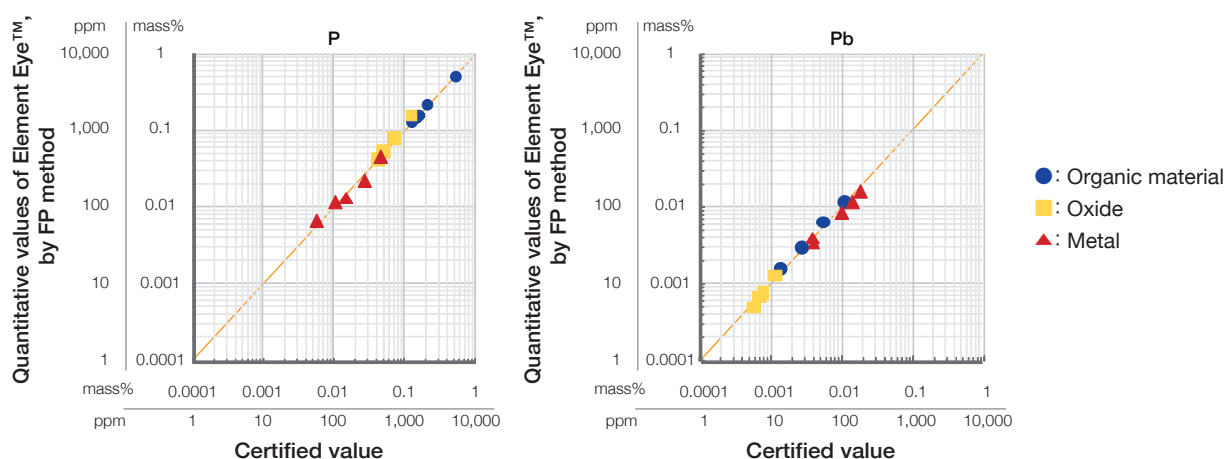
XRF enables measurement of various states of samples including bulk, powder and liquid. Furthermore, XRF is effective for micro samples such as foreign materials, because you can check the analysis position using a color camera for observing the analysis region.

Quantitative analysis using the FP method

XRF enables quantitative analysis using the FP (Fundamental Parameter) method. In quantitative analysis with the FP method, calibration curves are not required and therefore, you can perform rapid screening analysis, for example for the restricted materials in RoHS regulation.

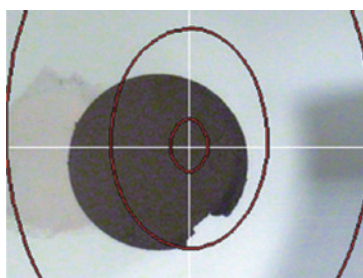
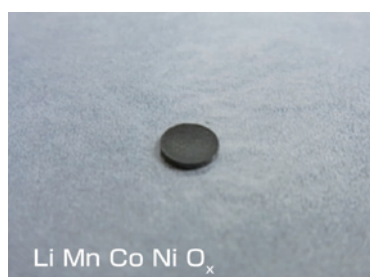
Figures below show the correlation between certified values and quantitative values obtained by quantitative analysis with the FP method for various materials for certification. The JSX-1000S, with high quantification accuracy by the FP method, enables screening analysis for any samples.

Accuracy of quantitative analysis by the FP method

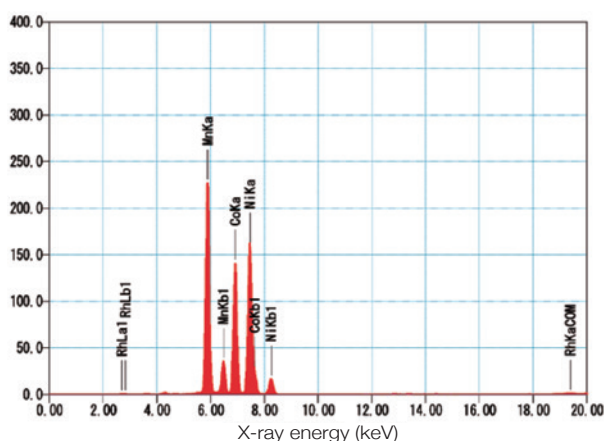


Analysis example of a cathode material (molded powder sample)

NMC is a cathode active material powder for LIBs with an element ratio of Mn: Co: Ni = 1: 1: 1. As shown below, the results of XRF analysis show that a molded tablet can be quantitatively evaluated in measurement of only 30 seconds.



Measurement conditions
Tube voltage: 50 kV
Collimator diameter: 0.9 mm
Atmosphere: Air
Measurement time: 30 s



Elements	Mass %	Atomic%
Mn	16.1	7.3
Co	16.9	7.1
Ni	16.4	7.0
Others	50.6*	78.6*

Quantitative analysis result Mn: Co: Ni ≈ 1 : 1 : 1

4-2 Energy Dispersive X-ray Spectrometer (EDS)

Energy dispersive X-ray spectroscopy is an analytical method which analyzes kinds and concentrations of constituent elements of a specimen using characteristic X-rays generated from the specimen by electron-beam irradiation onto it. Detectors for the energy dispersive X-ray spectrometer are available in various types. An EDS detector is installed into a wide range of instruments including TEM, SEM, FIB-SEM and EPMA.

Elemental analysis using EDS

EDS integration & Live function

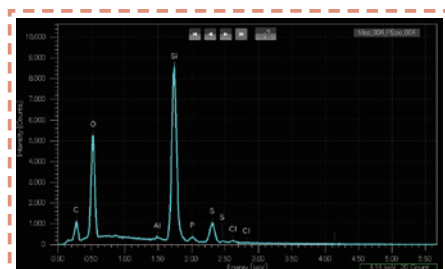
Stress-free & High throughput

Integration of an electron microscope and EDS software of JEOL, makes it possible to provide seamless operations and data acquisition from observation to analysis. The EDS Live function, which allows for simultaneous SEM imaging and elemental analysis, enables you to rapidly and efficiently find target elements or foreign materials.

Spectral analysis **Standard**

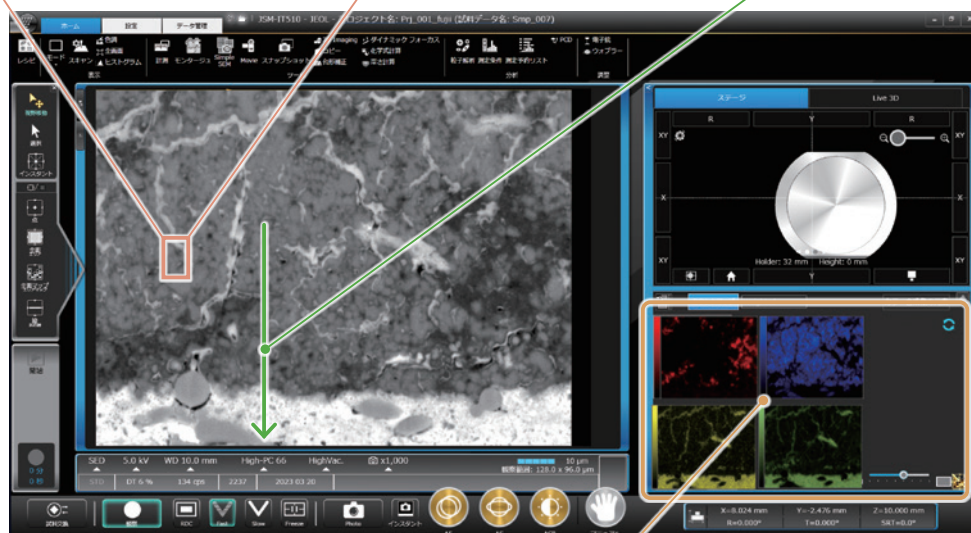
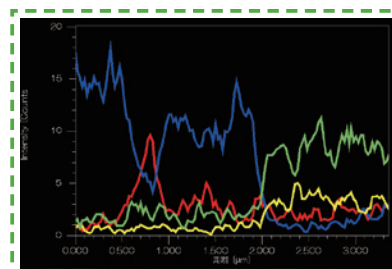
Live function available

The characteristic X-ray energy and intensity in a spectrum are analyzed, for examining kinds (qualitative analysis) and concentrations (quantitative analysis) of the elements contained in the entire observation area or in the specified area.



Line analysis **Standard**

The characteristic X-ray intensity of the elements along a specified line (one-dimensional distribution) is plotted. Useful for analyzing distribution changes of elements at a boundary of structures.



Accelerating voltage 5 kV, WD10 mm

Map analysis **Standard**

Live function available

The elements in the specified area are two-dimensionally displayed. The use of the net count map function (standard) makes it possible to separate and display spectral peaks close to each other.

Specimen: Solid-state battery

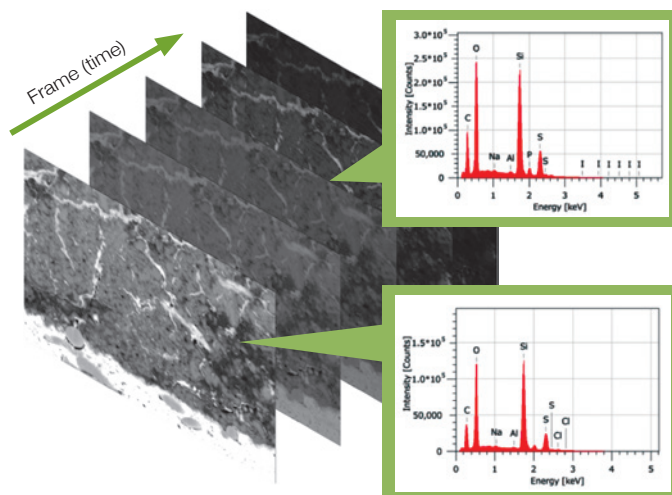
Sample courtesy: Professor Atsunori Matsuda, Dept. of Electrical and Electronic Information Engineering, Toyohashi Univ. of Technology

Applied analysis functions

Playback Analysis function

Standard

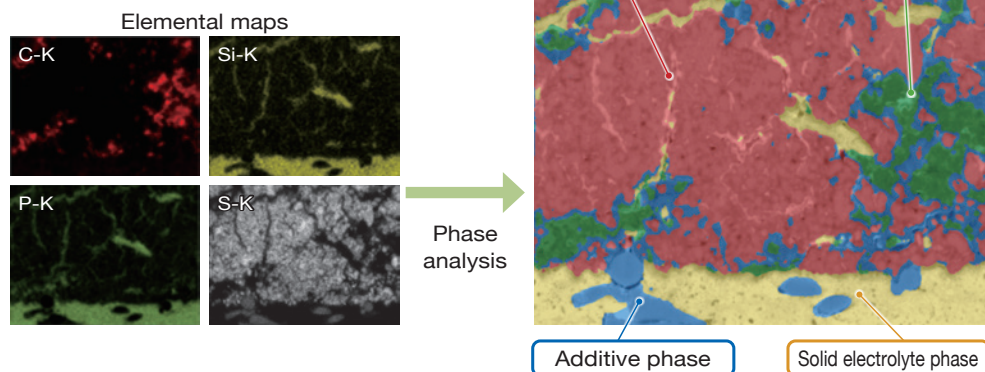
Map analysis by JEOL EDS can replay the acquired data after measurement, making it possible to observe time-series changes in a specimen. Thus, this function can help dynamic analysis of state changes of the specimen during heating or chemical reaction. Precipitation of Li can also be observed for each time series.



Phase analysis

Option

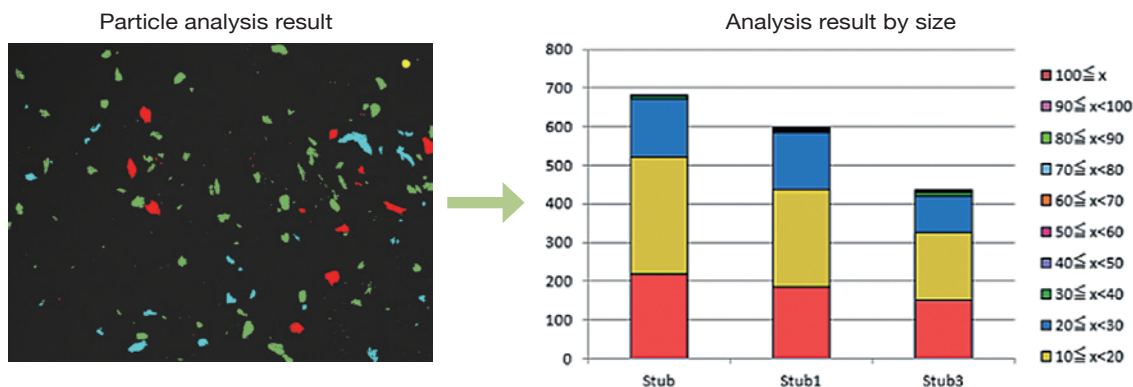
EDS phase map, applied to a designated area, displays a distribution of compounds and a combination of multiple elements (characteristic compositions) in different colors. This phase map is useful for distinguishing inclusions or boundaries in a battery material.




Particle analysis

Option

Foreign materials are differentiated from intensity differences in the SEM image for identifying the composition. Statistical processing for the number or shape of the particles makes the particle analysis useful for quality control and environmental inspection.



Features of EDS detectors

For SEM/FIB/EPMA	For FE-SEM	For TEM
DrySD™ 30, 60 or 100 detector	DrySD™ Gather-X	DrySD™ 100 detector
		
Standard type	Windowless type	Windowless type

- **Micro-area analysis**

Micro-area elemental analysis can be made; the order of μm down to nm with SEM, whereas down to the pm order with TEM.

- **Multi-elements simultaneous analysis**

All the generated X-rays can be measured simultaneously, and elements Be to U are generally detected. Windowless type detector enables detection from lithium (Li).

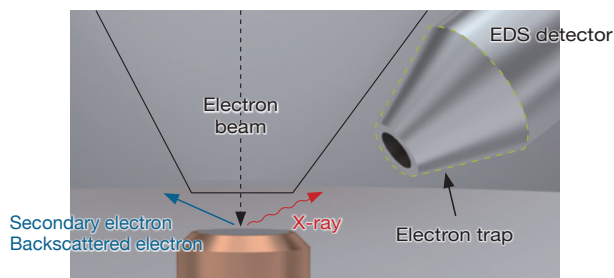
- **Fast analysis**

Compared to wavelength dispersive X-ray spectroscopy (WDS), EDS offers fast analysis, enabling acquisition of sufficient signals in a few minutes.

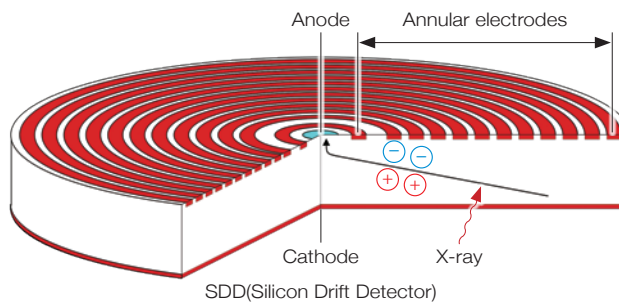
Principle of EDS detector

SDD (silicon drift detector) is adopted as an X-ray sensor for EDS. Compared to the conventional Si(Li) sensor, SDD provides faster and higher signal-to-noise ratio X-ray detection, allowing for elemental analysis with higher count rate and higher energy resolution.

X-ray detection by SDD

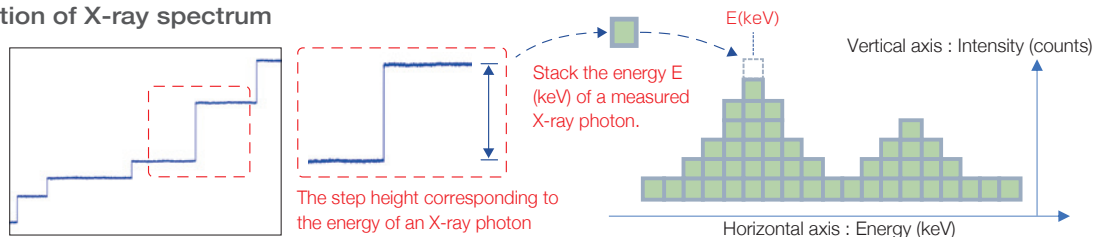


SDD detects X-rays generated from a specimen by electron-beam irradiation. The electron trap system prevents signals other than the X-rays generated from a specimen to enter SDD, e.g. secondary and backscattered electrons.



When the X-rays enter SDD, electron-hole pairs, whose numbers are proportional to the X-ray energy, are generated. The annular electrodes on SDD produce a mortar-shaped electric field, and the electric field transports the generated electrons towards the anode for converting the collected electrons into the electric signal.

Formation of X-ray spectrum



SDD outputs step-like signals as shown in Figure above. The height of each step of the signals corresponds to the energy of an X-ray photon.

Form a spectrum by accumulating the measured X-ray energy. The element is identified from the spectral peak energy (horizontal axis) whereas the concentration is obtained from the peak intensity (vertical axis).

This page introduces a JEOL Windowless EDS detector “Gather-X”, used for JEOL FE-SEMs. The features of the Gather-X and its application examples for battery materials are described.

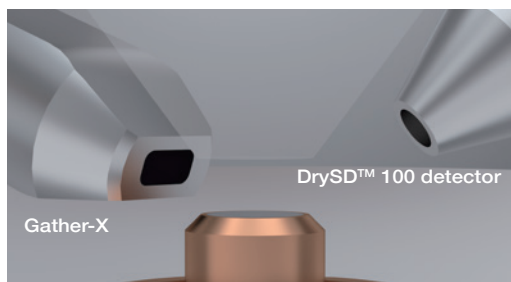


Gather-X

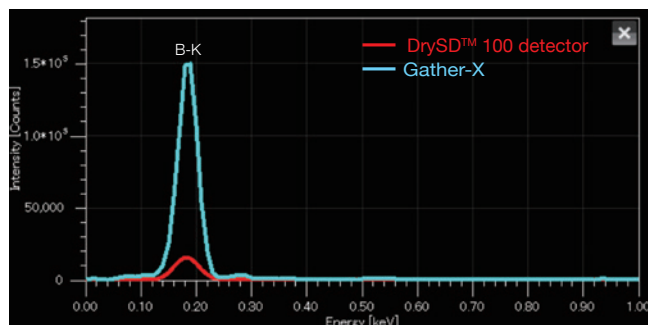
Features of Gather-X

The Gather-X, a Windowless EDS detector, has the following three features.

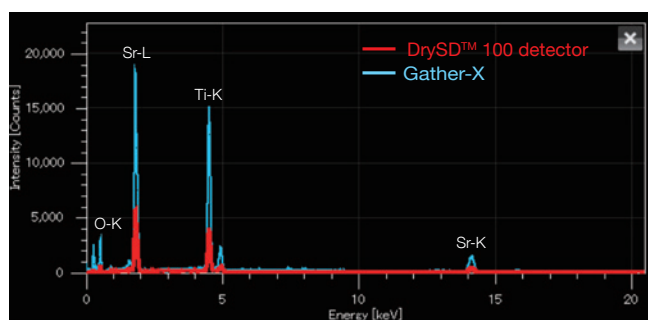
High sensitivity analysis for all energy regions



A racetrack-shaped X-ray sensor makes the detector closer to the specimen, achieving a large solid angle. Windowless EDS has high detection efficiency for light elements, and the detector is fitted with the electron trap system which allows for elemental analysis at a high accelerating voltage of 30 kV; therefore, very light elements of Li to U can be detected.

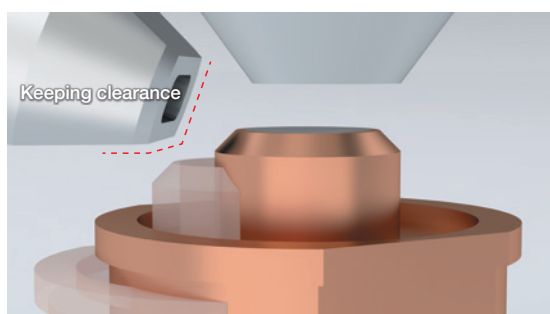


Comparison between Gather-X and DrySD™ 100 for boron
Accelerating voltage: 7 kV / Probe current: 100 pA / Live Time: 100 sec.



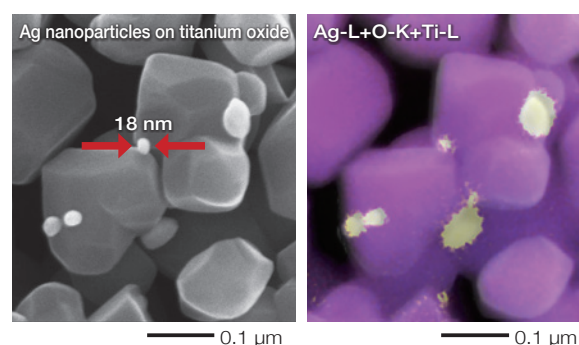
Comparison between Gather-X and DrySD™ 100 for strontium titanate
Accelerating voltage: 30 kV / Probe current: 30 pA / Live time: 100 sec.

High operability with safety system



“SEM Center”, which integrates control software for SEM and EDS, enables seamless observation to analysis. The safety system linked with the SEM instrument, provides safe operations.

High spatial resolution map



JSM-IT800<SHL> /Accelerating voltage: 5 kV / (Specimen bias -5 kV), WD 4 mm
Cream: Ag-L Purple: O-K+Ti-L

Combination of shorter WD than the standard WD, BD mode with a bias voltage to the specimen stage and low accelerating voltage, enables high spatial-resolution EDS maps to be acquired.

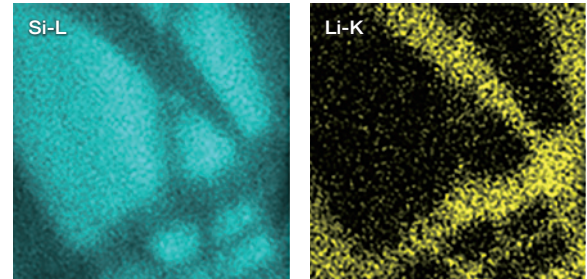
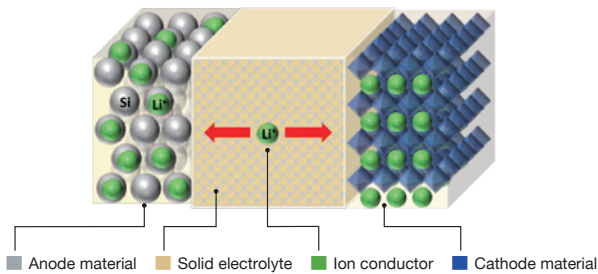
Difference between Standard type and Windowless type

In the standard EDS, the X-ray sensor is vacuum-sealed in a capsule which has a window for X-ray transmission, thus protecting the detector from contaminations during cooling of the X-ray sensor. This is advantageous for the detector to be used in low-vacuum mode and for suppressing an adverse effect from light and heat to change the spectrum (peak width, noise peak, etc.). However, X-rays of energies less than 1 keV are partially absorbed through the window, degrading the detection efficiency. But in the Windowless EDS, there is no decrease in detection efficiency; therefore this detector is advantageous for analysis of light elements such as Li essential for battery material. The X-ray sensor is protected by restricting the vacuum level of an SEM instrument during cooling of the X-ray sensor (linkage with SEM).

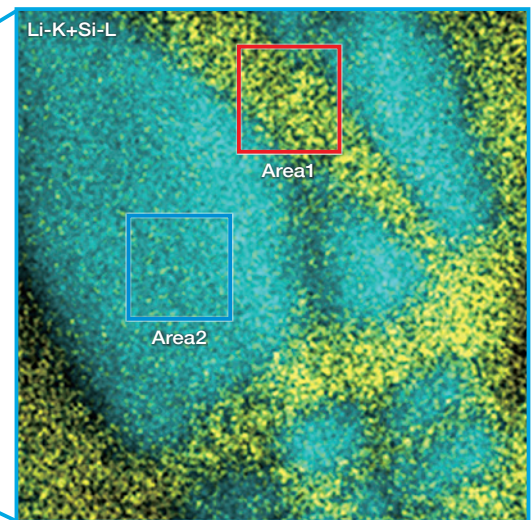
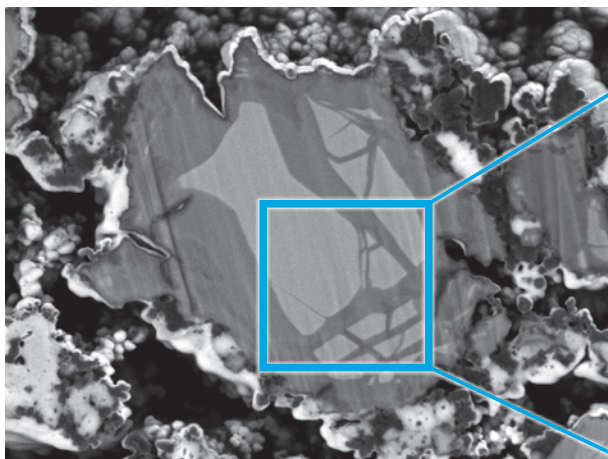
Application examples of Gather-X to battery material (solid-state LIB)

Figures show observation and analysis examples of an anode material for solid-state LIB with JSM-IT800<SHL> & Gather-X. The material was subjected to air-isolation-transferred cross section milling by CROSS SECTION POLISHER™. This Windowless EDS makes it possible to detect and differentiate low energy X-rays of lithium (Li-K: 54 eV) and silicon (Si-L: 90 eV), whose energies are close to each other.

The solid-state LIB is a next-generation battery that uses solid electrolyte between the cathode (positive electrode) and anode (negative electrode).



Specimen: Anode material for solid-state LIB



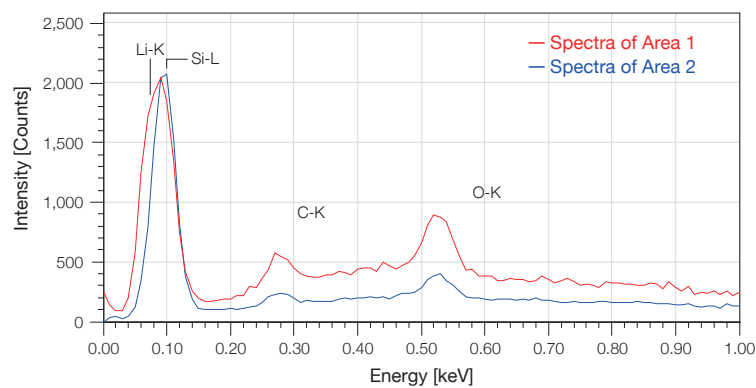
JSM-IT800<SHL> 0.5 μm

Accelerating voltage 3 kV, WD 7 mm, Probe current 0.6 nA

Acquisition time: 15 min

Sample courtesy: Professor Atsunori Matsuda

Dept. of Electrical and Electronic Information
Engineering, Toyohashi Univ. of Technology

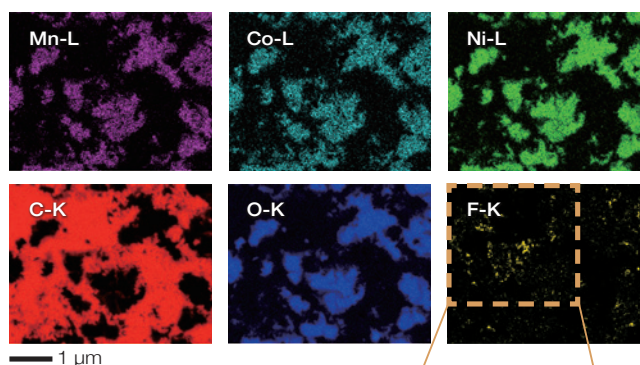
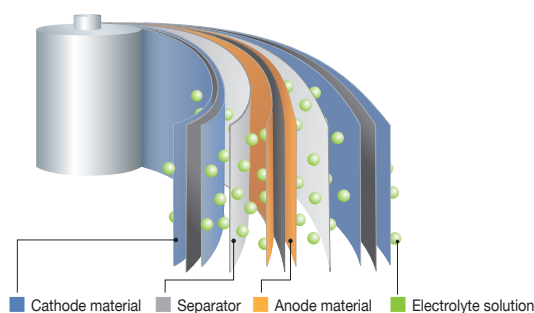


Since two X-ray spectral peaks are separated (energies close to each other), EDS maps reveal the distribution of Li and Si on the Si anode.

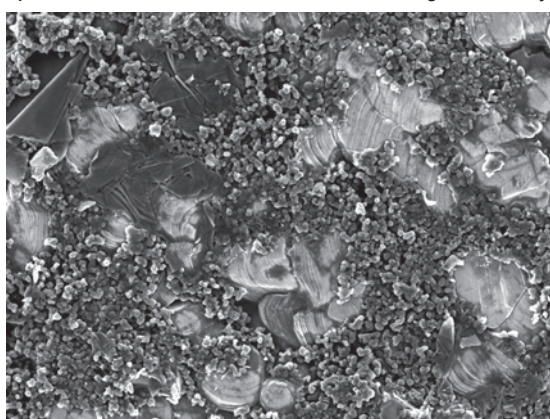
Application example of Gather-X to battery material (LIB)

Figures show observation and analysis examples of a cathode material for LIB with JSM-IT800<SHL> & Gather-X. For analyzing the constituent elements which are distributed on the surface and are sensitive to electron-beam damage, a low accelerating voltage (1.5 kV) was applied to the analysis. Analysis results visualized the distribution of active materials of manganese, cobalt, nickel and oxygen, an electron conductive assistant of carbon, and a binder of fluorine.

Composition of Lithium Ion Battery (LIB)

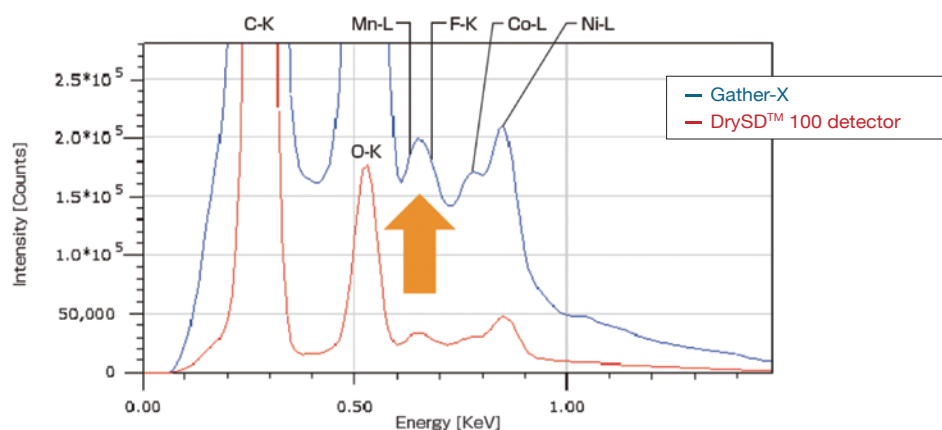
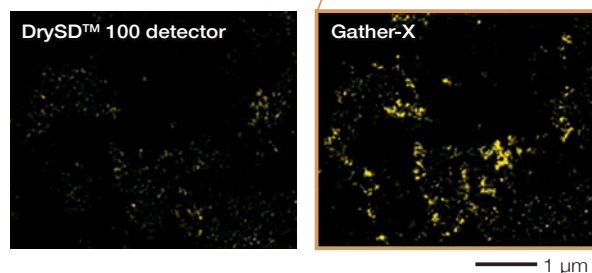


Specimen: Anode material for a lithium-ion rechargeable battery



JSM-IT800<SHL>
Accelerating voltage 1.5 kV (Specimen bias -5 kV), WD 7 mm,
Probe current 4.8 nA, Acquisition time: 13 min
Sample courtesy: Professor Atsunori Matsuda

Dept. of Electrical and Electronic Information Engineering, Toyohashi Univ. of Technology



Comparing to X-ray counts obtained by the DrySD™ 100 detector, the Gather-X provides higher counts. Thus with the Gather-X, peak separation accuracy is improved, enabling acquisition of clearer and more accurate distribution of fluorine.

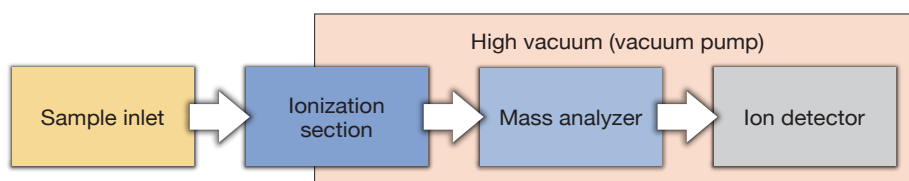
5-1

Mass Spectrometer: Gas Chromatograph Mass Spectrometer (MS: GC-MS)

Principle of the mass spectrometer

The mass spectrometer (MS) is an instrument to precisely measure the molecular mass of each chemical compound contained in a substance, and to identify each compound and its quantity.

The basic principle of MS is explained by the nature of ions. The ions (charged atoms and molecules) are separated by the mass-to-charge (m/z) ratio with the mass analyzer; then the quantity of ions having each m/z is measured with the detector for identifying each compound (qualitative analysis) and its quantity (quantitative analysis).

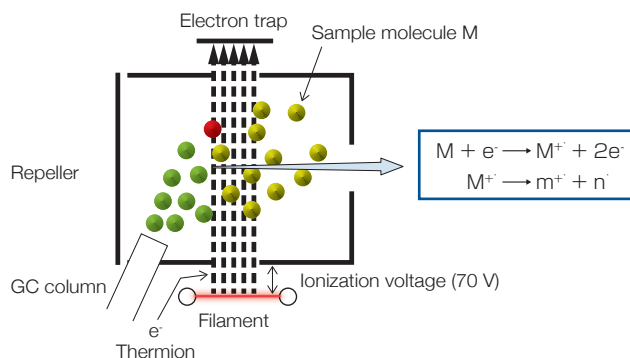


Ionization

Electron Ionization (EI)

Ions are generated by accelerating thermo electrons emitted from the filament, and irradiating them on the vaporized sample molecules.

Thermally labile or nonvolatile compounds are not suitable for ionization because sample molecules must be vaporized.



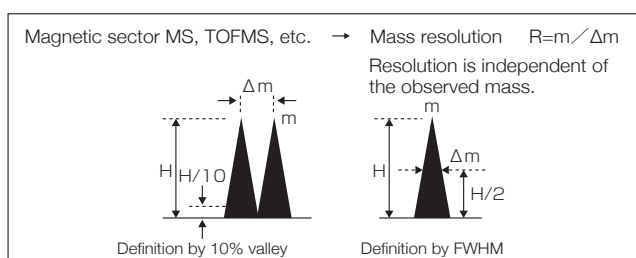
Mass analyzer

Major mass spectrometers and their mass separation methods

- | | | | |
|-------------------------------------|---|---|--|
| • Double-focusing mass spectrometer | Mass (m) \propto Magnetic field intensity (B^2) | • Time-of-flight mass spectrometer | Mass (m) \propto Flight time (t^2) |
| | Mass (m) \propto Electric field voltage (E) | • FT-ICR | Mass (m) \propto Frequency (f) |
| • Quadrupole mass spectrometer | Mass (m) \propto High frequency voltage (V) | (Fourier-transform ion cyclotron resonance mass spectrometry) | |
| • Ion trap mass spectrometer | Mass (m) \propto High frequency voltage (V) | | |

Definition of mass resolution

Performance (capability) of the instrument to separate ion peaks with different masses to each other



QMS \rightarrow Mass resolution $R=kM$ (k : separation degree, M : mass)
Resolution changes depending on the observed mass.

Example: $k = 1.5$
Resolution is 1500 at mass 1000.
Resolution is 450 at mass 300.

Direct gas analysis MS

This method is to introduce gas components by aspirating them by a vacuum of MS through a deactivated fused-silica capillary tube, and to analyze the target compounds. Instead of separating the target compounds by GC, the method introduces all of the target compounds into the MS at once. In the battery analysis field, this method is used for real-time analysis of gas evolved inside batteries, such as “in-situ” evolved gas analysis at charge-discharge cycles.

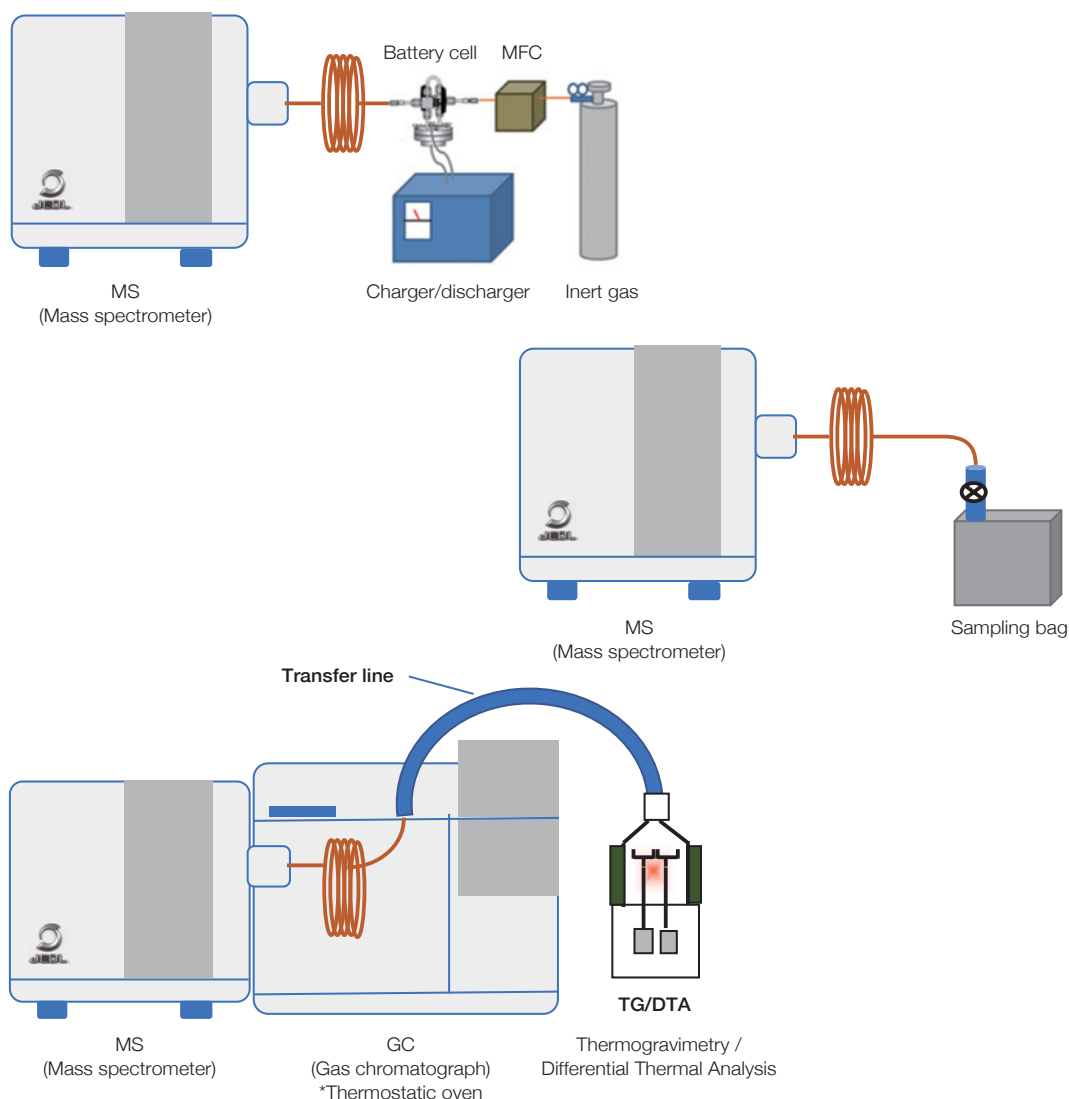
In addition, TG (thermogravimetry)-MS which does not use chromatograph, is included in this direct gas analysis method. (TG-MS is explained later)

Information obtained by Direct gas analysis MS

Real-time (operand) analysis of components stored in a container and of trace amounts of substances (including compounds transferred by a sampling bag), is used to acquire the evolved components in real time. Thus, there is no separation of each component, instead all of the components are introduced simultaneously. The horizontal axis shows time (elapsed time), enabling you to examine gas-evolving conditions and to confirm evolving phenomena.

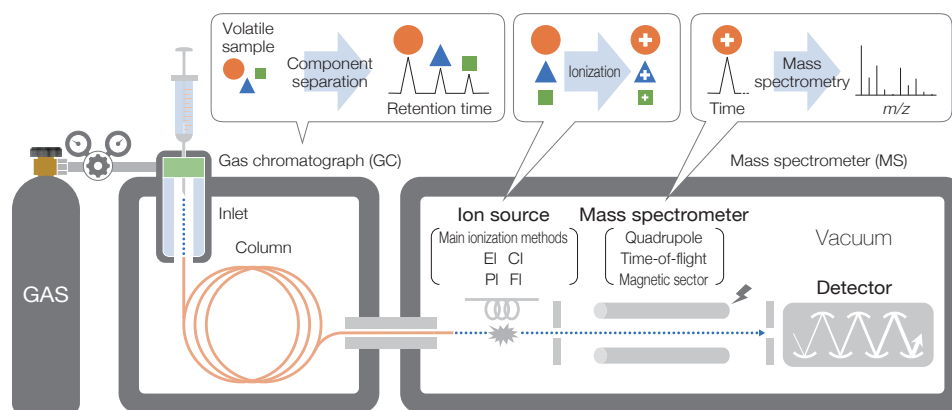
Since all of the components are introduced into MS simultaneously, analysis can be performed in the mixed-components state, making it difficult to interpret the data.

When TG is connected with MS, the horizontal axis can be converted to the temperature. This means that thermogravimetry combined with a MS enables measurement of evolved gas components, in addition to measurements of chemical and physical changes associated with vaporization, decomposition, oxidization, reduction, adsorption, etc.



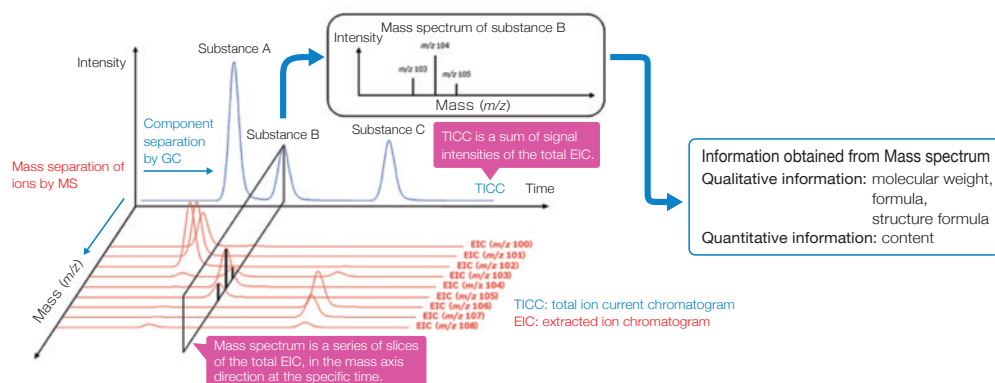
What is GC-MS?

The gas chromatograph-mass spectrometer (GC-MS) is an analytical instrument that combines GC and MS. GC separates the vaporized components in a mixture sample by means of gas-liquid partition chromatography whereas MS ionizes the components eluted from GC, then separates and detects them depending on the mass of ion, for performing qualitative and quantitative analysis of trace components in a sample. In LIB analysis, a combined use with a thermal analyzer enables evolved gas analysis of LIB materials (anode, cathode and electrolyte) as well as analysis of trace impurities in electrolytes.



Information acquired by GC-MS

A chromatogram is obtained by separating the components in a mixture sample with GC. The chromatogram in which the total ion current value is plotted with respect to the retention time, is called the total ion current chromatogram (TICC). A mass spectrum is obtained by ionizing GC-separated components and by measuring the mass (m/z) with MS. The mass spectrum provides qualitative information, including molecular weight of target component and structural information. The quantity of ions provides quantitative information, such as content of target component.



Models and features of GC-MS

JMS-T2000GC AccTOF™ GC-Alpha

High performance gas chromatograph – Time-of-Flight mass spectrometer

- Suitable for qualitative analysis
- Reproducible accurate mass measurement due to high-resolution mass spectrometry
- Unknown compounds analysis with a combination of soft ionization and AI structural analysis



JMS-Q1600GC UltraQuad™ SQ-Zeta

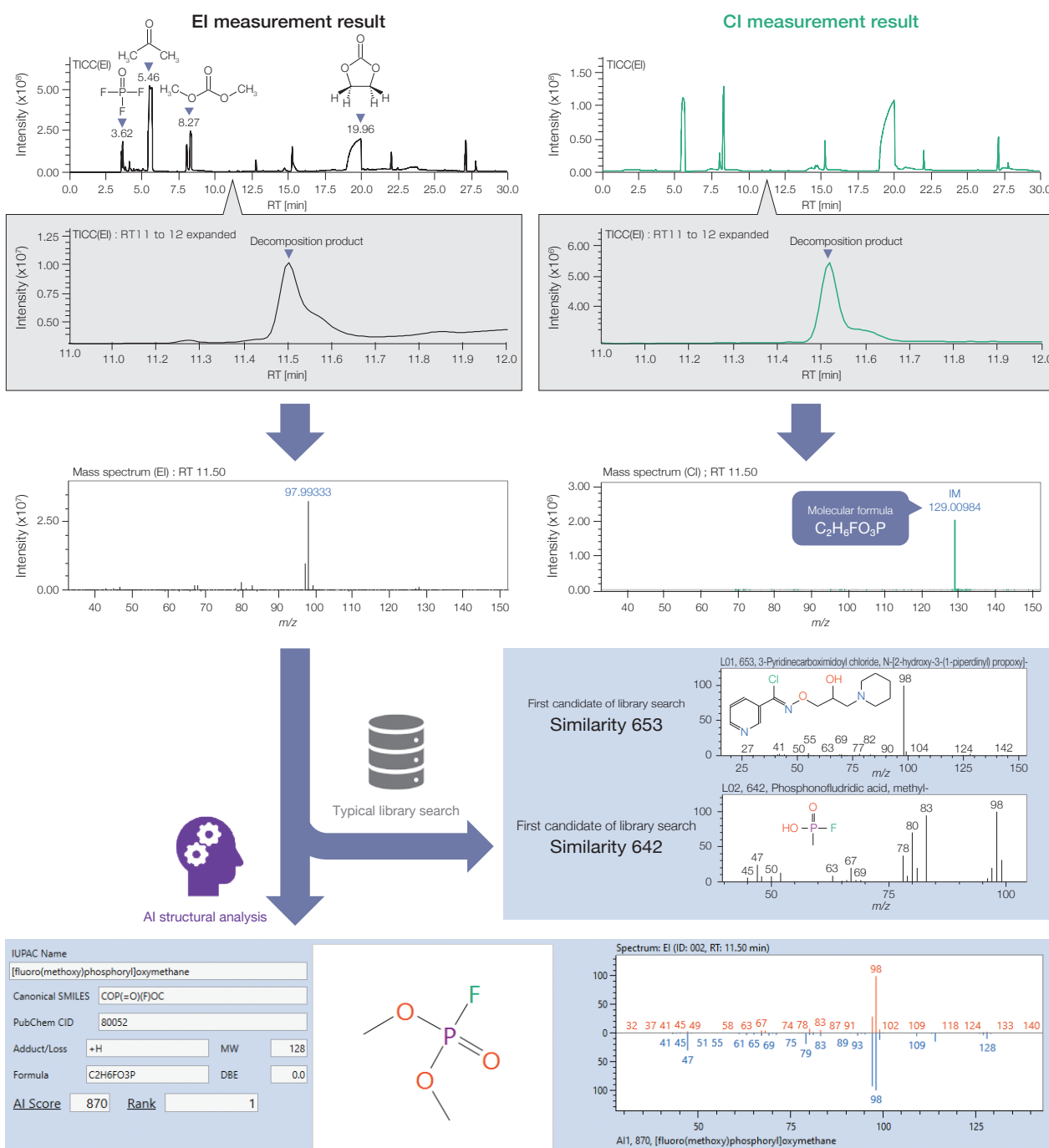
Gas chromatograph – Quadrupole mass spectrometer

- Suitable for quantitative analysis
- Single Ion Monitoring (SIM) mode allows for high sensitivity analysis
- Applicable to long-time measurements exceeding 24 hours



Degradation analysis of electrolyte using AI (artificial intelligence) structural analysis

The following examples show measurement results using the JMS-T2000GC AccuTOF™ GC-Alpha to measure the acetone extract of electrolytic solution from a LIB after charge-discharge cycles. Measurements were conducted by EI (hard ionization method) and CI (soft ionization method). While acetone (extraction solvent) and the original components of electrolytic solution are detected as the major components, trace amounts of decomposition products of electrolytes are also detected. For some decomposition products (retention time 11.50 min on TICC), AI structural analysis using the unknown compounds structural analysis software “msFineAnalysis AI”, is demonstrated. From the CI measurement result, the elemental composition of the component was determined to be $C_2H_6FO_3P$. For the structural analysis, the typical library search using the conventional database showed only a low similarity result. But AI structural analysis by “msFineAnalysis AI” showed that [fluoro(methoxy)phosphoryl] oxymethane was estimated to be candidates with the AI similarity score of greater than 800.



5-2 Thermogravimetry-Mass Spectrometer: TG-MS (Evolved Gas Analysis)

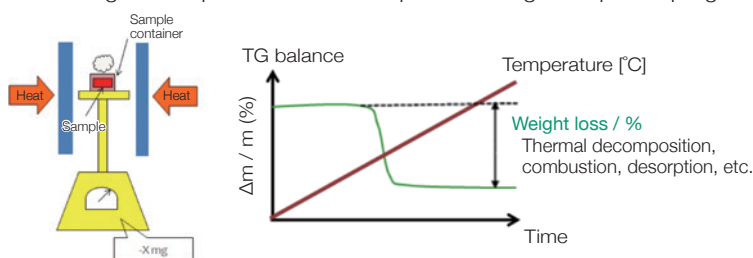
TG-MS is an instrument that integrates TG (thermogravimetry) and MS (mass spectrometer).

In TG, the sample temperature is changed, and a change of the mass of the sample and the endothermic/exothermic process are recorded. Simultaneously, gas components desorbed or created from the sample are introduced into MS for identifying the gas components.

About TG (Thermogravimetry)

TG (thermogravimetry)

TG is a method for measuring the sample mass as a function of the temperature or time while heating the sample or maintaining the temperature of the sample according to a specific program.



Information that can be obtained: **How much** sample mass (weight) is reduced **at a certain temperature time**

- ☑ **Confirmation of sample decomposition temperature, combustion temperature, and desorption temperature**
- ☑ **Evaluation of materials' thermal stability (decomposition temperature at 1% and 5%)**
- ☑ **Which component is lost**

About MS

MS (mass spectrometer)

MS is an instrument that ionizes chemical substances composed of atoms and molecules, and separates and measures the generated ions by their masses.

About TG-MS

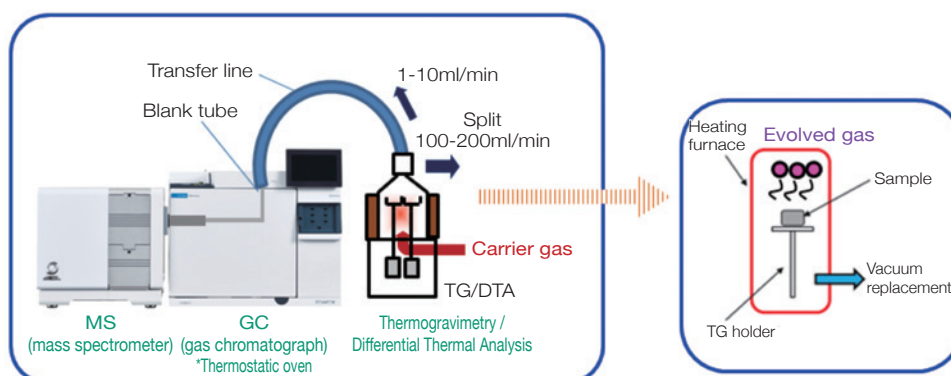
TG-MS is an instrument that integrates TG (thermogravimetry) and MS (mass spectrometer).

A sample is introduced into TG, then the inside of the furnace is heated to change the sample temperature. Using this process, TG-MS conducts simultaneous analysis of the loss of mass (weight) and endothermic & exothermic reactions, and performs real-time analysis of gas components desorbed or generated from the sample. In data analysis by TG-MS, a thermogram with time on the horizontal axis and ion intensity on the vertical axis are obtained to analyze gas components in time series. Furthermore, when plotting the temperature in the horizontal axis, the evolution temperature of the arbitrary mass can be obtained.

Merits: Simultaneous confirmation of endothermic and exothermic information, gravimetry information and evolved gas behaviors.

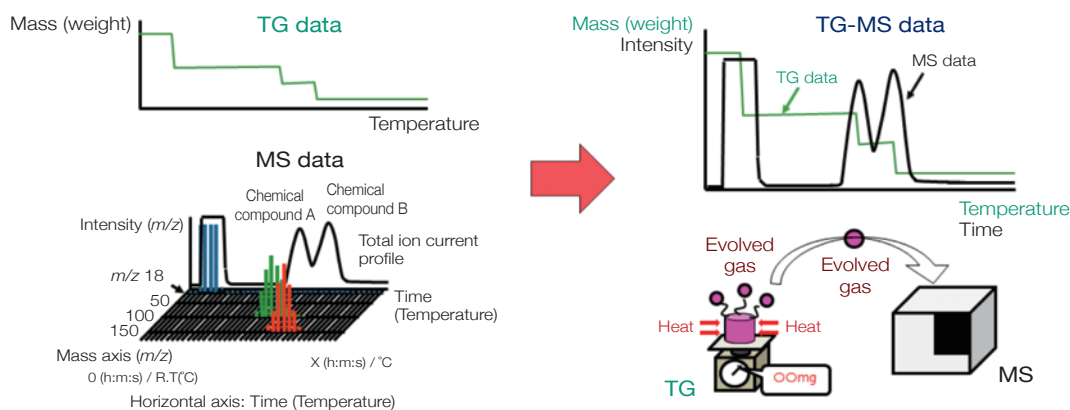
Demerits: Qualitative analysis is very difficult when multi-components gasses are simultaneously evolved.

Evolved gas analysis (EGA): analyzing the gas evolved from a heated sample (desorption, etc.)



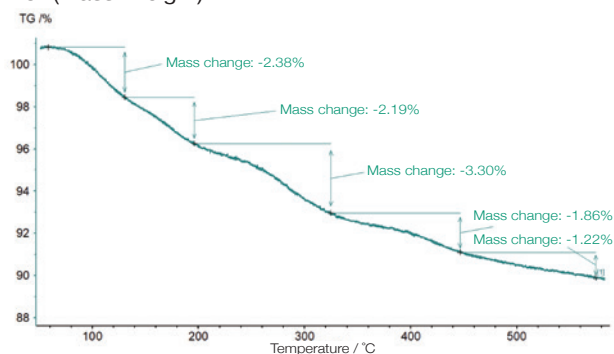
Data analysis by MS

Thermogravimetry – Mass spectrometry

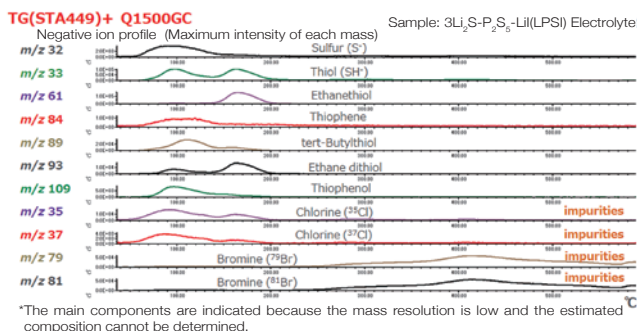


Measurement examples (sulfide-based solid electrolytes)

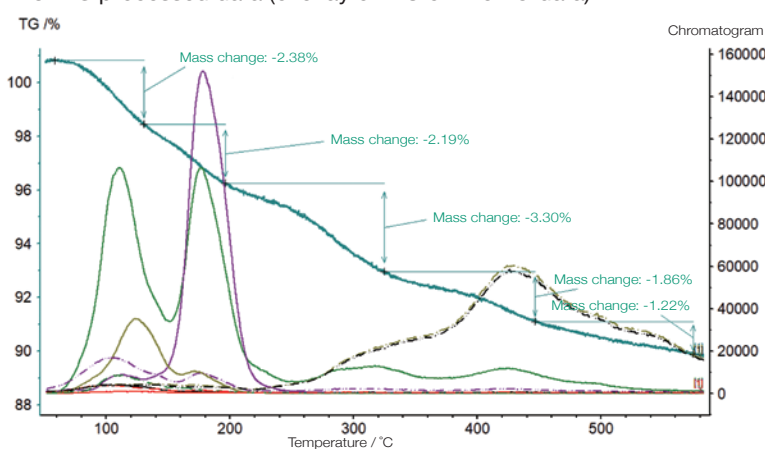
TG (mass: weight)



MS (Extracted ion chromatogram: EIC)



TG-MS processed data (overlay of EIC on the TG data)



Instrument

TG: NETZSCH
Simultaneous TGA-DSC Analyzer
STA 449 F1 Jupiter

MS: JEOL
Mass Spectrometer
JMS-Q1600GC

Sample

Sulfide-based solid electrolytes
3Li₂S-P₂S₅-LiI (LPSI) electrolyte
Liquid phase synthesis additive solvent
EP:C₅H₁₀O₂

Sample courtesy: Professor Atsunori Matsuda
Dept. of Electrical and Electronic Information Engineering, Toyohashi Univ. of Technology

6-1

Nuclear Magnetic Resonance spectrometer (NMR)

NMR is a technique that focuses on specific atoms (elements) having nuclear spins in a material, and analyzes molecular structures and states of the peripheral regions for relevant atomic nuclei. For NMR measurements, a sample is inserted into strong magnetic fields so as to give rise to energy polarization of nuclear spins; then the sample is irradiated with a radio wave for observing NMR phenomena. NMR makes it possible to acquire spectra reflecting the electronic environment and mobility of the observed nuclei, allowing for analysis of chemical state, solid structure and dynamics.

For LIB analysis, NMR is one of a few variable methods to directly observe and measure the Li nuclei, enabling acquisition of a variety of information including the quantity, chemical state and dynamics of Li in a sample, regardless of Li location, and irrespective of cathode, anode or electrolyte.



JNM-ECZL series

Instrument configuration of NMR

- **Superconducting magnet** A strong magnet to polarize nuclear spins in a sample. In general, as larger the magnetic field, the sensitivity and resolution are improved.
- **Spectrometer** The core unit of the NMR instrument which transmits radio waves and obtains NMR spectra.
- **Probe** This unit is inserted into the magnet to detect NMR phenomena of a sample. Various types of probes are used depending on the sample shape and the purpose of measurement. The probes are roughly classified into the solution NMR probe used for measuring a solution sample to analyze its chemical structure, and the solid-state NMR probe used for measuring a solid sample to analyze its solid structure.

Features of NMR and NMR applications for LIB material

- Allows for direct observation of Li (local structure and dynamics).
- Possible to observe irrespective of structures (crystal, amorphous, or solution).
- Quantitative analysis.
- Possible to observe nuclei other than Li (for LIB); e.g. ^1H , ^{19}F , ^{31}P , ^{11}B , ^{23}Na , ^{29}Si .
- Various applications for cathode, anode, electrolyte and component.

Cathode	Anode	Electrolyte
<ul style="list-style-type: none"> • Structure and degradation analysis with observation of Li (Solid-state NMR, High-speed MAS probe) <p>Complementary analysis with XRD and TEM</p>	<ul style="list-style-type: none"> • Structure analysis with observation of Li • Detection of metal Li • Structure analysis with observation of Si (solid-state NMR, in-situ measurement) 	<ul style="list-style-type: none"> • Chemical structure and degradation analysis of liquid electrolytes (solution NMR; e.g. ^7Li, ^{31}P, ^{11}B, ^{19}F) • Structural analysis of solid electrolytes, degradation analysis and amorphous analysis are also possible (solid-state NMR; e.g. ^7Li, ^{31}P, ^{11}B, ^{19}F) • Ion dynamics analysis (Diffusion NMR, Solid-state NMR relaxation & exchange measurement)

Probes mainly used for LIB analysis

• GR probe

The GR probe is a specialized NMR probe for diffusion applications that require large magnetic field gradients. Suitable for ion dynamics analysis for solid electrolytes. Using 50 A magnetic field gradient power supply, a magnetic field gradient of 2000 G/cm can be generated, allowing measurement of diffusion coefficients as small as $10^{-14} \text{ m}^2/\text{s}$.

• 3.2 mm AUTOMAS probe

The AUTOMAS probe is the most-widely-used, solid-state NMR probe with a sample-tube outer diameter of 3.2 mm. Using the Auto Sample Changer and Auto Tune Unit compatible with solution NMR via ROTORCARRIER™, the probe allows for fully-automated solid-state NMR measurements including sample load/eject, tuning, magic angle spinning (MAS) control, and temperature control. The AUTOMAS probe is effective for structural analysis and ion dynamics measurement of a variety of solid-state battery materials, including cathode, anode and electrolyte.



Diffusion probe



50 A magnetic field gradient power supply



AUTOMAS probe



ROTORCARRIER™

Physical property evaluation of solid electrolytes

Lithium ion dynamics analysis of solid electrolytes by diffusion measurement

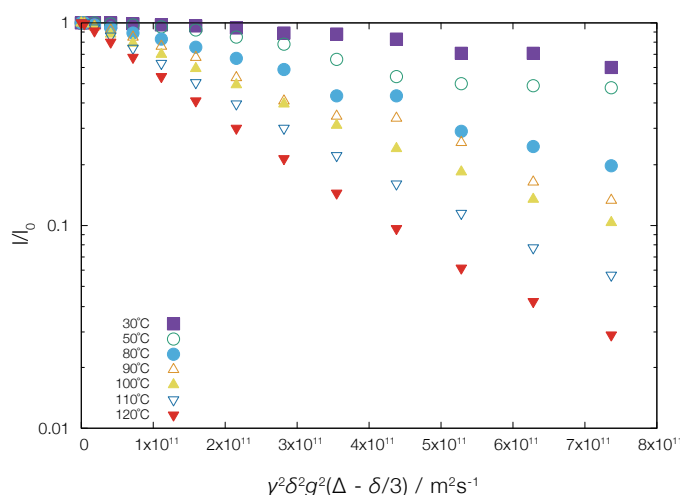
NMR diffusion experiments can measure the self-diffusion coefficients of ions in a solid electrolyte. Self-diffusion coefficients are a measure of translational motion (self-diffusion) of molecules and ions when the chemical potential gradient equals to zero. Position of molecules and ions are coded by magnetic field gradient pulses, and the diffusion of molecules and ions over time is observed as an attenuation in signal intensity.

As the magnetic field gradient intensity g is increased, the signal intensity I decreases. The self-diffusion coefficient D is obtained by fitting this with the Stejskal-Tanner equation.

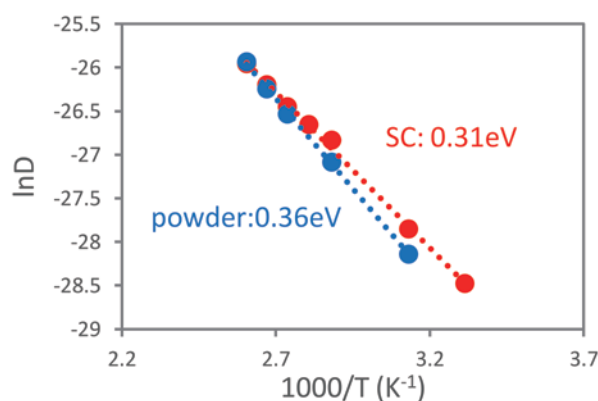
$$I(g, \delta, \Delta) = I_0 \exp(-D(\gamma g \delta)^2 (\Delta - \delta/3))$$

D : Diffusion coefficient, γ : Gyromagnetic ratio, g : Magnetic field gradient strength
 δ : Magnetic field gradient pulse irradiation time, Δ : Diffusion time

The temperature dependent diffusion plot for the oxide solid electrolyte LLTZO (figure just below) provides the diffusion coefficient at each temperature. The activation energy of diffusion motions can be obtained with an Arrhenius plot (bottom figure). Comparison of single crystal (SC) and powder samples (Powder) demonstrates that SC has a larger diffusion coefficient and smaller activation energy.



Temperature dependence of ^7Li diffusion



Activation energy of diffusion motion of Li ions
(Arrhenius plot of the diffusion coefficients)

Spectrometer:
JNM-ECZL500G
Probe:
GR probe
Measurement method:
 ^7Li Stimulated Echo LED
Sample:
LLTZO (single crystal, powder)
Sample courtesy:
Dr. Naoaki Kuwata (NIMS)
Dr. Junji Akimoto (AIST)

Chemical structure analysis of sulfide-based solid electrolytes by ^{31}P solid-state NMR

^{31}P solid-state NMR is a powerful measurement method that can quantitatively calculate the crystallinity and the content ratio of secondary phases. Here an analysis example is introduced, in which structural changes of the sulfide-based solid electrolyte LPS depending on the difference of preparation methods, were analyzed by ^{31}P solid-state NMR.

Lithium Thiophosphate samples, which have the following four kinds of structures, were created.

70LPS-g : Mixture of Li_2S and P_2S_5 was obtained with the mix ratio of 7 to 3 by the ball-mill method. Glassy state.

70LPS-gc : 70LPS-g was annealed at high temperature and crystallized.

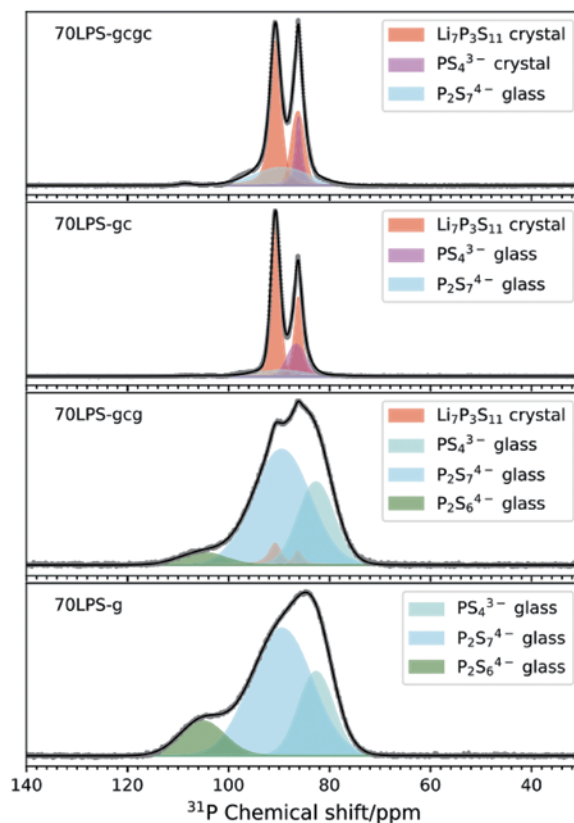
70LPS-gcg : 70LPS-gc was vitrified (glass state) again by the ball-mill method.

70LPS-gcgc : 70LPS-gcg was annealed again at high temperature and crystallized.

^{31}P solid-state NMR spectra of the four samples are shown below. Large differences of line width in the spectra are seen between crystalline samples and glass samples. Since a crystal has uniform bond length and angle, the line width is narrow for exhibiting a linear Lorentz-type spectral shape. But for a glassy state, the bond lengths and angles are distributed, resulting in thicker line widths and Gaussian-type spectral shape.

The spectrum of 70LPS-g can be separated into three types of Gaussian components, and it is found that the three units are constituted from the chemical shift range; PS_4^{3-} , $\text{P}_2\text{S}_7^{4-}$, and $\text{P}_2\text{S}_6^{4-}$. On the other hand, in the spectrum of 70LPS-gcg, which was crystallized once and vitrified again, crystal components of $\text{Li}_7\text{P}_3\text{S}_{11}$ which have a narrow line width, slightly appear and the area ratio of the three units is found to change. Thus, solid-state NMR elucidates the difference of chemical structure even in the same glassy state.

Furthermore, in comparison of 70LPS-gc and 70LPS-gcgc, 70LPS-gcgc clearly has larger PS_4^{3-} component and exhibits a Lorentzian spectral shape with a narrow line width. This result confirms that not only the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal, but also the PS_4^{3-} single unit crystal is formed. The ionic conductivity of 70LPS-gcgc is 1.7 times higher than that of 70LPS-gc, suggesting that the newly-emerged PS_4^{3-} unit forms a new ion conduction path.



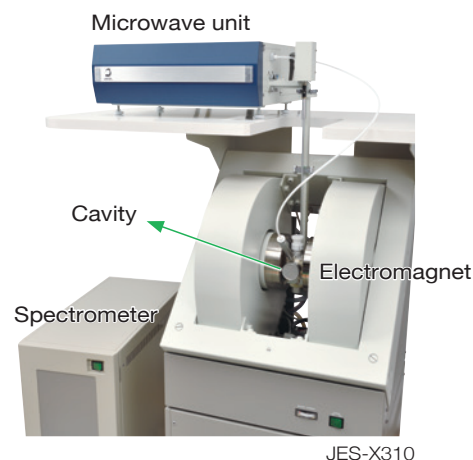
Spectrometer: JNM-ECZL500G
Probe: AUTOMAS Probe

Reference: K. Uchida, T. Ohkubo, F. Utsuno, K. Yazawa, ACS Appl. Mater. Interfaces. 2021, 13(31), 37071-37081

6-2

Electron Spin Resonance spectrometer (ESR)

Electron Spin Resonance (ESR) is a technique that allows us to observe materials with electron spin and provides valuable insights into the structure and dynamics around the spins. The principle is similar to NMR, wherein a sample is introduced into a static magnetic field to induce energy polarization of electron spins in the sample, and microwaves are applied to observe the ESR phenomenon. Electron spin is a property of only unpaired electrons and can be measured with much higher sensitivity than NMR. In ESR, microwaves of a fixed frequency are irradiated at the sample and measured while sweeping the magnetic field. Spectra obtained by ESR reflect the environment and kinetic properties of materials with unpaired electrons. In the analysis of LIB, it is one of the few methods that can directly observe Li in its metallic Li state, providing information on the amount and state of metallic Li in the material. Furthermore, ESR facilitates the evaluation of other materials with unpaired electrons.



JES-X310

Instrument configuration of ESR

- **Cavity** This is the part where the sample in the dedicated sample tube is set. Sample tubes and attachments are selected and used according to the properties of the sample and the purpose of evaluation.
- **Electromagnet** A magnetic field is applied to the sample to excite the electron spins contained in the sample.
- **Microwave unit** The excited electron spins are irradiated by microwaves.
- **Spectrometer** The acquired microwave absorption spectrum is converted to a differential waveform.

Microwave absorption occurs in a magnetic field where the target electron spin characteristics satisfy the equation on the right.

$$h \nu = g \mu_B H_0$$

h : Planck constant
 ν : resonance frequency
 μ_B : Bohr magneton
 H_0 : resonance field
 g : g-value of unpaired electron

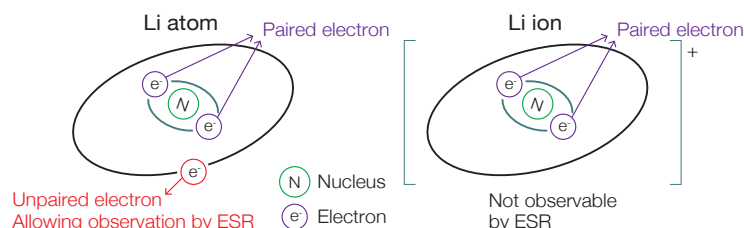
Features of ESR and ESR applications to LIB materials

- Simple preparation of measurement by inserting the sample into a quartz cell (inner diameter 4 mm) and setting it in the cavity (right figure).
- Allowing observation regardless of phase (solid, liquid or gas).
- Quantitative measurement.
- Allowing direct observation of metallic Li.
- Allowing observation of LIB materials other than Li (graphite, electrolyte, metallic compounds, etc.)

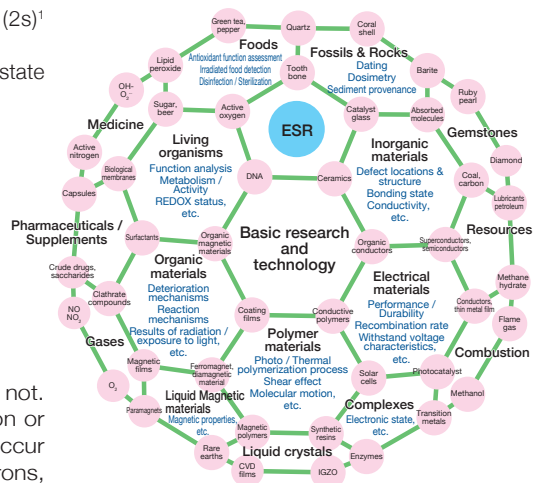
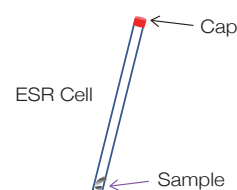
The electron spins to be observed by ESR may exist in various samples, as shown in the figure on the right, and are subjected to ESR observation.

As shown in the figure below, metallic lithium has an unpaired electron in the (2s)¹ electronic state, and this electron spin can be measured by ESR.

On the other hand, the lithium ion cannot be measured because it is (1s)² electric state and has no unpaired electron.



The ionic valence of a metal determines whether it has unpaired electrons or not. Organic materials become radicals having unpaired electrons by UV irradiation or radiation or radical reactions. In solid samples such as silicon, defects that occur during the manufacturing process or due to degradation have unpaired electrons, and these defects are the target of measurement.



Evaluation of battery materials

Mn marker for accurate g-value measurement

In solid samples, the resonance frequency varies depending on the size and shape of the sample. Thus, the resonance magnetic field changes accordingly, and it is important to identify the signal by g-values (see the equation in p 53). In particular, Li and other light elements are close in g-value and therefore, it is needed for accurate measurement and analysis. JEOL's ESR instruments incorporate Mn marker as the standard configuration, enabling accurate determination of g-values, as shown in the figure below.

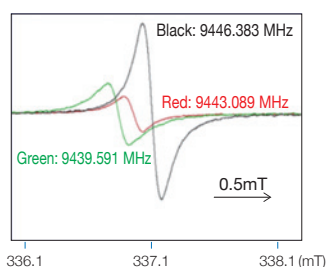


Fig.1 ESR spectra of different shape samples

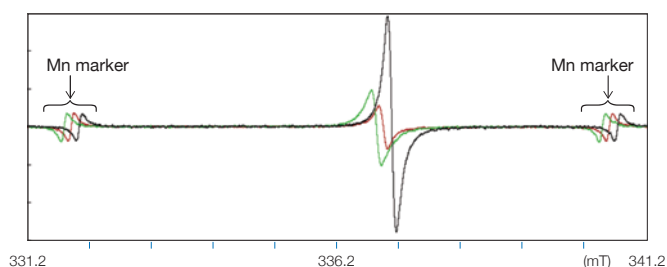


Fig.2 Spectra with Mn markers

The spectra obtained by measuring three carbon materials with different shapes are shown in Fig. 1. The numbers in Fig. 1 indicate the resonance frequency for each measurement. In such a simple comparison, they are judged to be different radicals. However, when measured simultaneously with the Mn marker, the magnetic field is found to be shifted (Fig. 2). As shown in Fig. 3, aligning the marker positions revealed the following result. That is, it was found that the signals were all obtained at a common magnetic field and $g = 2.0024$ was given, together with their linewidths equal to each other. As a result, they were shown to be identical carbon radicals.

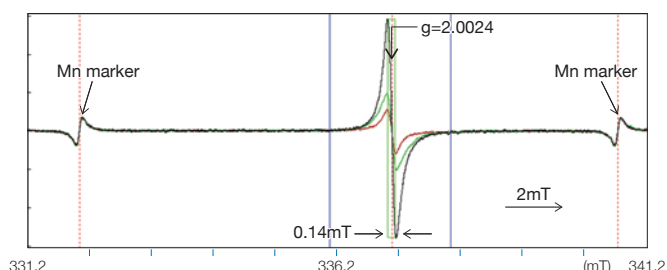
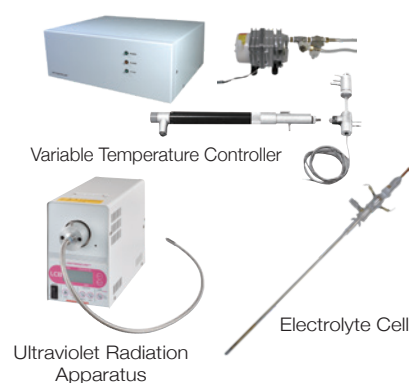


Fig.3 Spectra corrected by Mn marker

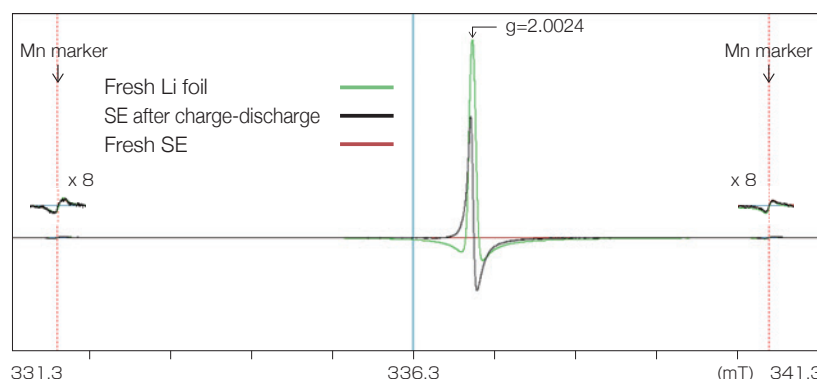
Main accessories used for ESR measurement

- **Variable Temperature Controller (ES-13060DVT5)**
This unit is used to vary and hold the sample temperature, using liquid nitrogen and air. Measurement at low temperature improves sensitivity.
- **Ultraviolet Radiation Apparatus (ES-13080UV2A)**
This unit allows for ESR measurement while irradiating a sample with ultraviolet. Light is introduced efficiently through the irradiation window in the front of the cavity.
- **Electrolyte Cell (ES-EL30)**
It is a special cell that can measure electrolysis of electrolytes in-situ. Since an exhaust port is configured, deoxidation treatment of samples can be made.



ESR applications to LIB materials -Measurements of solid-state battery materials (solid electrolytes)

Fresh Li foil and solid electrolyte (SE), raw materials of batteries, and SE after charge-discharge cycle are measured by ESR. Then, the obtained ESR spectra were compared (figure below). In the fresh SE, very little signal was observed. In contrast, the SE after charge-discharge provided a sharp Dysonian-type spectrum with a $g = 2.0024$ (calculated by signal maximum value) which was similar shape as the signal obtained from the fresh Li foil. Thus, it was suggested that Li could be precipitate in the SE after charge-discharge.



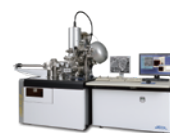
Sample courtesy:
Professor Atsunori
Matsuda
Dept. of Electrical and
Electronic Information
Engineering,
Toyohashi Univ. of
Technology



Transmission Electron
Microscope



Scanning Electron
Microscope



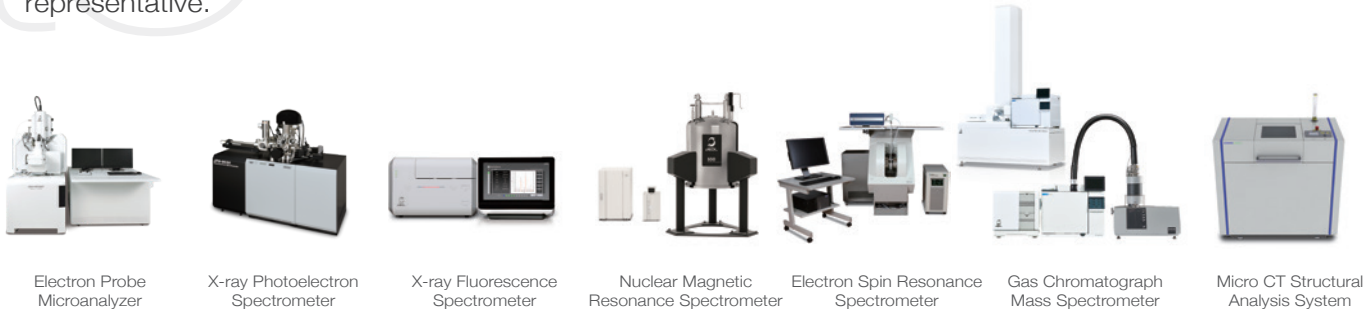
Auger Electron
Spectrometer

Materials	Analysis items	TEM	SEM	AES
Positive electrode (cathode) material	Morphological observation	○	○	○
	Elemental composition analysis	○	○	○
	Elemental distribution analysis	○	○	○
	Crystalline structure analysis	○	○ EBSD	
	Active material valence identification	○	○ SXES	○
	Coating film observation	○	○	○
	Coating film analysis	○	○ EDS	○
	CEI analysis	○		○
	Collector passive film analysis	○		○
	Chemical bonding state analysis	○	○ SXES	○
	Binder qualitative analysis	○		
	Impurity evaluation	○	○ Auto software	○
	Lithium detection	○ EELS		○
Negative electrode (anode) material	Morphological observation	○	○	○
	Elemental composition analysis	○	○	○
	Elemental distribution analysis	○	○	○
	Crystalline structure analysis	○	○	
	Chemical bonding state analysis	○	○ SXES	○
	SEI evaluation	○		○
	Lithium atom detection	○ EELS	○ EDS	○
Separator	Morphological observation	○	○	○
	Elemental composition analysis	○	○	○
	Chemical structure analysis			
	Degradation evaluation			
Electrolyte	Component / Impurity analysis			
	Degradation evaluation			
	Diffusion coefficient evaluation			
Solid electrolyte	Morphological observation	△	○	○
	Elemental distribution analysis		○	○
	Elemental composition analysis			
	Degradation evaluation			
	Evolved gas analysis			
	Li diffusion coefficient (conductivity evaluation)			
	Conductivity evaluation			
Operando	Morphological observation/Elemental analysis during charge-discharge		○	
	Evolved gas analysis during charge-discharge			

JEOL Instruments Used for Lithium Ion Battery Analysis Tasks

This LIB Note has introduced the features and application examples of the main instruments in the JEOL product lineup for the LIB analyses and evaluations. The table below lists the instruments applied to each of various tasks.

For more application case studies, please refer to “Battery Note” and “Solid-state Battery Note”. For detailed information on the instruments you have an interest, see the catalogues, specifications documents and the other technical materials. If you have any questions, please feel free to contact a JEOL representative.



EPMA	XPS	XRF	NMR	ESR	MS	XCT
○						○
○	○	○			△ TG-MS	
○	○					
○ SXES	○			○		
○						
	○				△ TG-MS	
	○					
○ SXES	○		○		△ TG-MS	
			○			
○	○	○			△ TG-MS	
	○		○	○ (Metal)		
○						○
○	○				△ TG-MS	
○	○					
○ SXES	○		○		△ TG-MS	
	○					
○ SXES	○		○	○ (Metal)		
○						○
○	○				○	
			○		○	
			○	○	△	
		○	○		○	
			○		○	
○						○
○	○					
	○				△ TG-MS	
	○		○	Li precipitate	○	
					○	
			○			
				○		
					○	

* Specifications and appearance of the instruments are subject to change without notice.

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