

Solutions for Innovation

LIBnote

Morphology Observation & Surface Analysis Instruments

XRF / XPS / EPMA / AES / SEM / TEM / CP / FIB

Chemical Analysis Instruments

GC-MS / NMR

Fabrication Systems

Roll to Roll Electron Beam Deposition Systems

RF Induction Thermal Plasma System for Nano Particle Synthesis



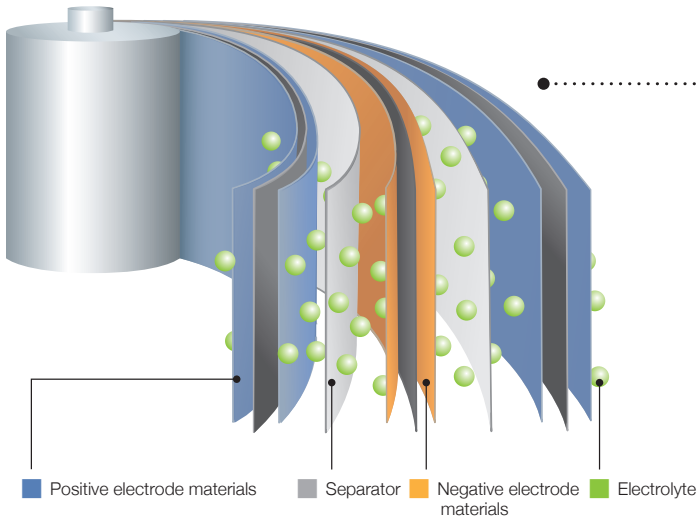
Introduction

The applications for lithium ion batteries (LIB) cover a wide range of fields, from power sources for computers and mobile devices to automobiles. In this context, demands are increasingly accelerated for higher performance (battery output, stability, etc.) and higher safety of batteries. In order to improve the performance and quality of LIB, analysis and evaluation that combine various high-performance evaluation systems are required. JEOL offers a full line-up of equipment to support the development of new LIB technologies and to improve product quality, including morphological observation instruments at the micrometer to nanometer scale, surface analysis instruments and chemical analysis systems to create high-performance coatings and powders. This LIB note offers solutions for researchers and engineers who are looking for the best equipment for their applications.

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Lithium Ion Battery Basic Structure & Fabrication Process

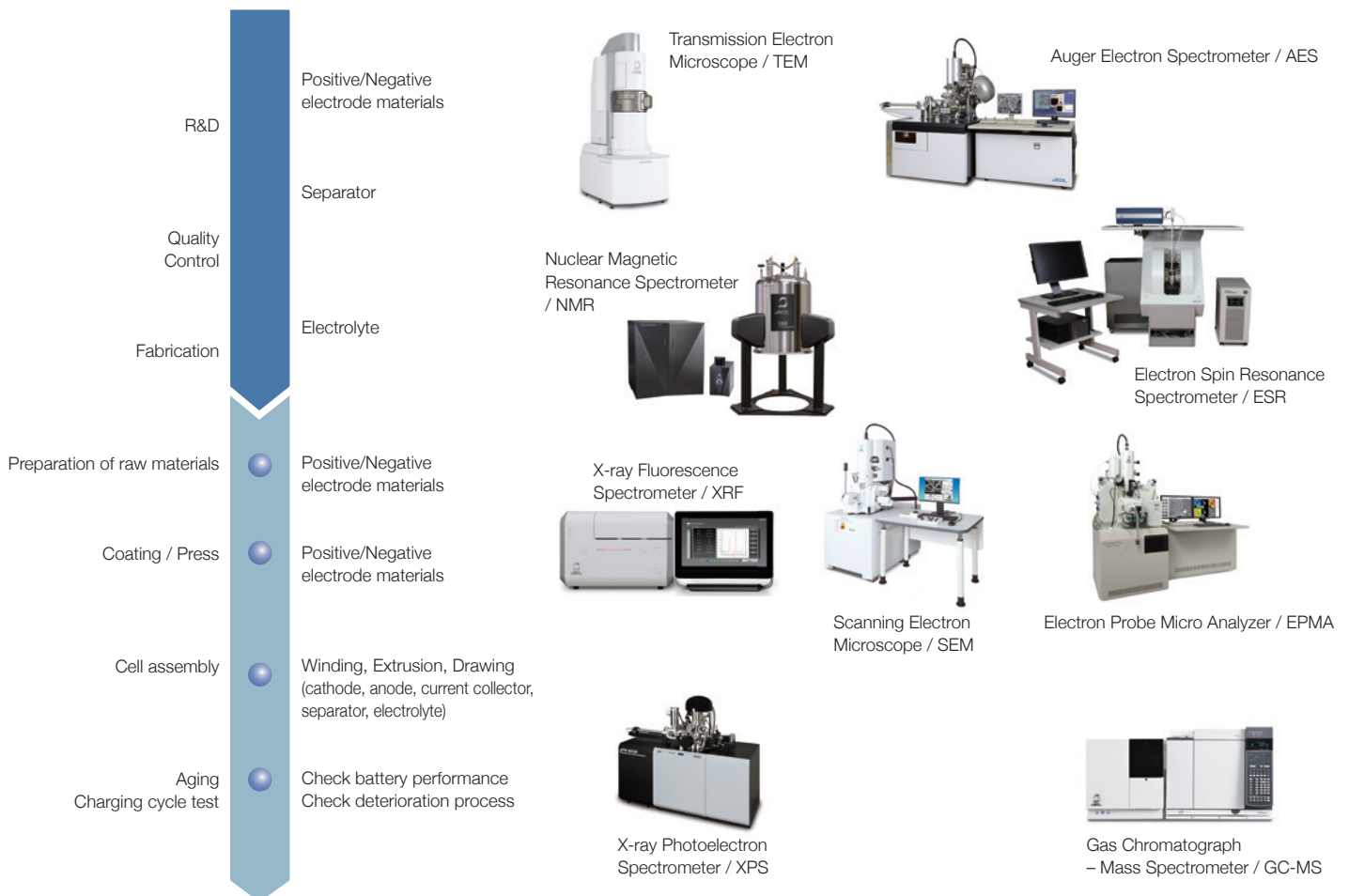


..... The basic structure of LIB consists of various components, as shown in the figure on the left.

These components have a variety of forms, such as powders, sheets and liquids. Materials constitute the components are subjected to various evaluations, including evaluations after assembly and evaluations after repeated charge/discharge cycles.

The figure below shows examples of the equipment that is suitable for materials evaluations at the R&D level, and the equipment useful for making the evaluations for each step of the fabrication process.

.....
 JEOL offers analytical instrument solutions for each process



1. Morphology Observation & Surface Analysis Instruments

1 - 1 Features to Consider for Instrument Selection

The tables below show the criteria for selecting instruments for material evaluation purposes. Table 1 lists the features of each instrument, and Table 2 shows a comparison of the specific characteristics of each instrument.

Features of instruments to support the development of LI ion batteries 1

	Instrument	Features
	 XRF : X-ray Fluorescence Spectrometer	Suitable for rapid specimen average composition analysis (just a few minutes to obtain a result, including sampling and measurement). Measurements are possible under both vacuum and atmosphere. Fluid samples as well as solid samples can be used. Can be used for screening of transition metals, such as Fe, Co, and Ni: for positive electrode materials.
	 XPS : X-ray Photoelectron Spectrometer	Li is observable . An ideal system for chemical bonding state analysis of the sample surface . Chemical state analysis of the electrode interface is possible using Depth Profile.
	 EPMA : Electron Probe Micro Analyzer	Multi-channel WDS allows micro area element analysis with a high energy resolution . Secondary electron images and backscattered electron images make it possible to observe the surface morphology.
	 AES : Auger Electron Spectrometer	Li is observable . Depth profiling and chemical bonding state analysis as well as surface analysis for micro area is possible . Secondary electron images and backscattered electron images make it possible to observe the surface morphology.
	 SEM : Scanning Electron Microscope	High resolution morphology observations of the surface, including structural analysis of materials at a nanometer-scale with low accelerating voltages. Available attachments include EDS and WDS, enabling element analysis.
	 TEM : Transmission Electron Microscope	Offers structural analysis at atomic resolution , element analysis with EDS, and chemical state analysis using EELS (a thin film specimen is required) Can directly detect Li with EELS

EDS : Energy dispersive X-ray spectrometer EELS : Electron Energy Loss spectrometer WDS : Wavelength Dispersive X-ray spectrometer
Depth profile : Function to perform analysis while etching the surface with Ar ion

Features of instruments to support the development of LI ion batteries 2

Instrument	Environment	Excitation source	Main detected signals	Sample form	Resolution	Element analysis function				
						Analysis depth	Detectable element range	Energy resolution	Detection concentration limit ^{*3}	
XRF	Vacuum Normal atmosphere	X-ray	Fluorescent X-ray	Bulk Fluids	1 to 12 mm Φ (analysis area)	1 mm ^{*3}	Na to U	About 150 eV (Mn K α)	Several ppm	
XPS	Vacuum	X-ray	Photoelectron	Bulk	30 μ m to a few mm (analysis area)	6 nm	Li to U	About 0.1 eV	About 0.1%	
EPMA	Vacuum	Electron beam	Secondary electron Backscattered electron Characteristic X-ray	Bulk	0.1 to 1 μ m ^{*1}	1 μ m	Be to U ^{*2}	About 10 eV	Several 10 ppm	
AES	Vacuum	Electron beam	Auger electron Secondary electron	Bulk	3 nm (Secondary electron) 8 nm (Auger electron)	6 nm	Li to U	About 0.1 eV	About 0.1%	
SEM	Vacuum	Electron beam	Secondary electron Backscattered electron Characteristic X-ray	Bulk	1.2 nm or better ^{*1}	1 μ m	WDS	B to U	About 130 eV	About 0.1%
							EDS	B to U	About 10 eV	Several 10 ppm
TEM	Vacuum	Electron beam	Transmission electron Characteristic X-ray	Thin film	0.1 nm or better ^{*1}	100 nm (sample thickness)	WDS	B to U	About 130 eV	About 0.1%
							EDS	H to U	1.0 eV(Schottky) ^{*4} 0.50 eV(Cold-FEG) ^{*4}	About 0.1%

*1 Depend on the system *2 When the optional analyzing crystal for Be is installed *3 Differs depending on the specimen and conditions *4 : Varies according to the conditions of use
For details, refer to the catalogs and data sheets for each instrument

1-2 X-ray Fluorescence Spectrometer (XRF)

The X-ray fluorescence spectrometer (XRF) is an instrument for qualitative and quantitative analyses of elements in a sample by irradiating X-rays onto the sample and detecting fluorescent X-rays emitted from it. XRF is used for determining steel grades, evaluating the quality of materials, and screening regulated elements like RoHS (Cd, Pb, Hg, Cr and Br). This instrument enables rapid analysis from sample preparation to acquisition of results.



JSX-1000S "Element Eye"™

Excellent for analysis of trace metal elements!

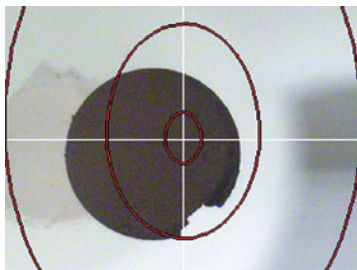
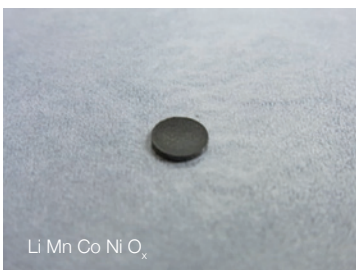
Features

- Analysis elements: Na to U
- Analysis region: 1 to 12 mm ϕ
- Sample form: solid, powder, liquid
- Non-destructive analysis
- Detection lower limit: Several ppm

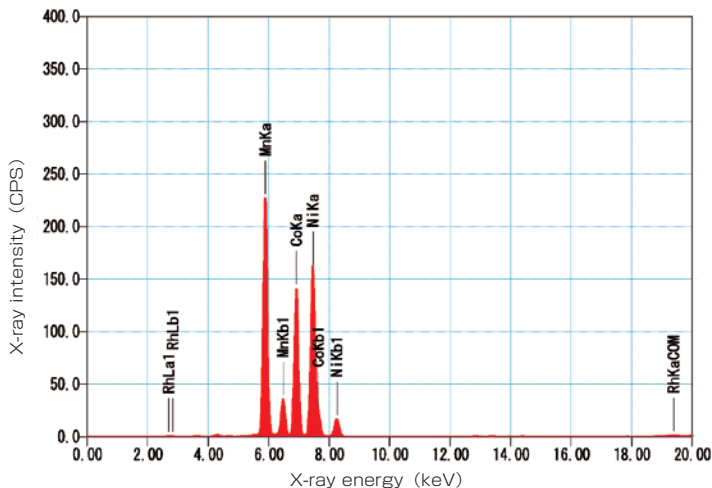
Analysis example

Positive electrode material analysis (tablet of a powder sample)

Tablets are formed of a powder material that is used for lithium ion batteries, and 30 second measurements are made, providing results that allow quantitative analysis of the element composition. The results shown here indicate that the sample is composed of the expected mixture of Mn : Co : Ni in a 1 : 1 : 1 ratio.



[Measurement conditions]
 Tube voltage : 50 kV
 Collimator : 1.0 mm ϕ
 Atmosphere : Air
 Measurement time : 30 s

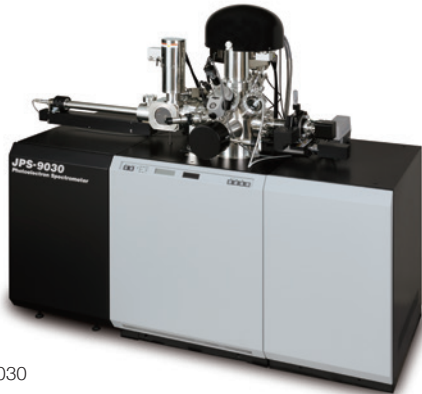


Component	Mass %	Atomic %
Mn	16.1	7.3
Co	16.9	7.1
Ni	16.4	7.0
Balance	50.6	78.6

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

1-3 X-ray Photoelectron Spectrometer (XPS)

Since direct observation of the photoelectrons excited by the X-ray is performed, XPS has various advantages, including surface-sensitive analysis, high energy-resolution analysis and analysis of any solids. As a result, for LIB analyses, it is possible to detect Li, a key component, and to analyze the chemical bonding state. Furthermore, depth profiling enables analysis of not only the surface, but also the regions inside the sample.



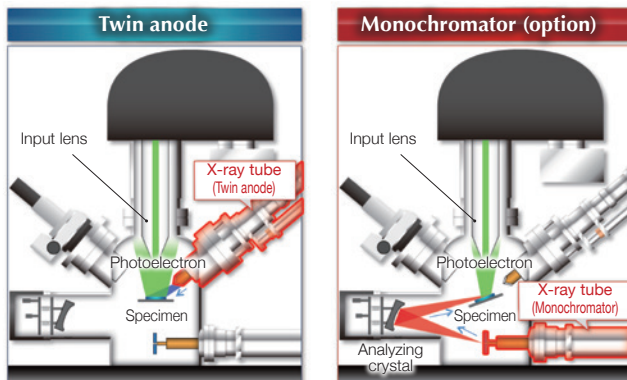
JPS-9030

Direct detection of Li !

Features

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

Optical System



• The JPS-9030 can be equipped with Monochromator (option) or Twin anode X-ray tube, enabling you to select a suitable configuration depending on analytical purpose or the specimen to be measured. Since the electron optics system of the input lens for collecting photoelectrons is designed to allow signal detection over large areas with a large focal depth, highly accurate analysis is possible with excellent reproducibility, such as for analysis of powder specimens that are the raw materials of Li-ion batteries, and of electrodes after heterogeneous charge/discharge tests.

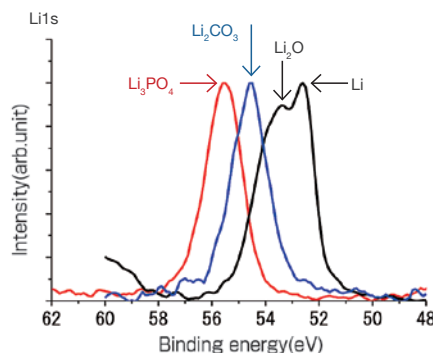
Chemical bonding state analysis

- Identification of chemical bonding state by distinguishing position differences in spectral peaks

Changes in the chemical bonding state appear as differences in the peak positions, so it is possible to identify the chemical bonding state of the Li by detecting the peak positions.



Metallic lithium



Chemical bonding state	Li 1s
Li	52.6 eV
Li ₂ O	53.5 eV
Li ₂ CO ₃	54.6 eV
Li ₃ PO ₄	55.5 eV

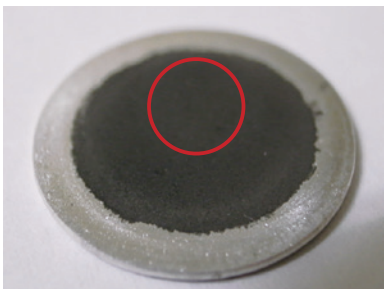
Standard specimens

Analysis example

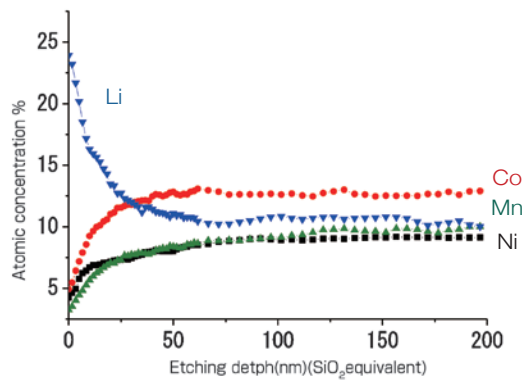
Depth profile analysis of negative electrode material after charge/discharge

• Example of depth profile analysis of positive electrode material

The image on the left is a powder of the raw material for a lithium-ion battery positive electrode that has been formed into a tablet. When depth profiling is performed, it is observed that the Li is segregated in an area size of about 30 nm on the surface, as shown in the graph on the right.

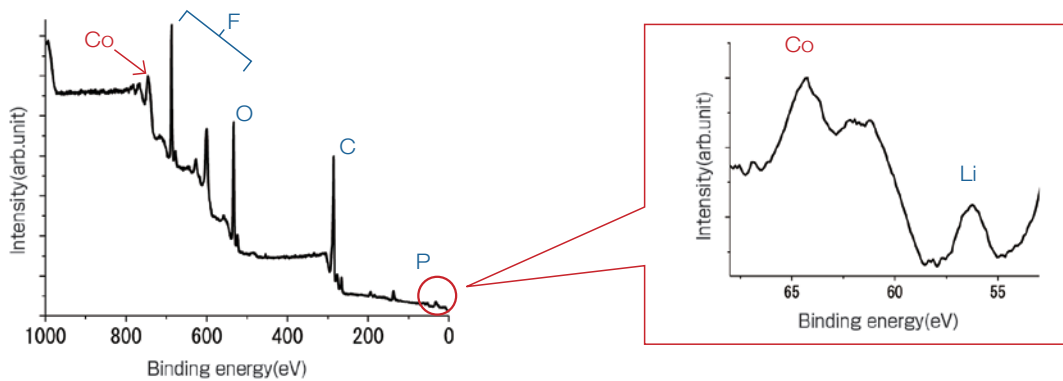


Analysis region : 1 mm ϕ

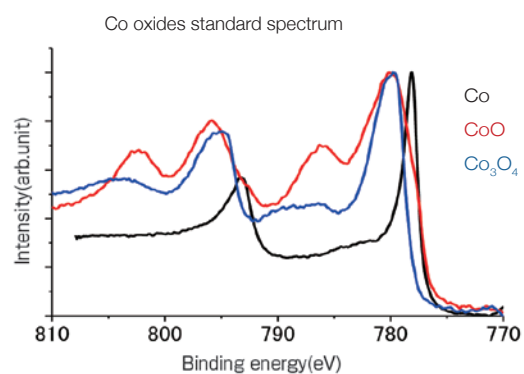
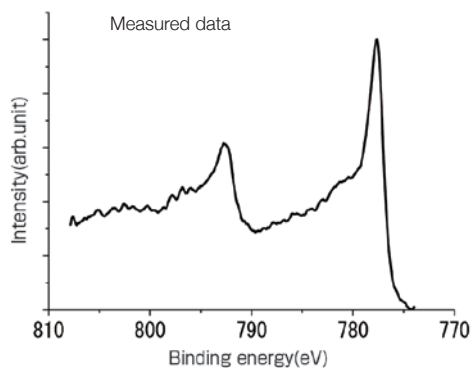


• Analysis of negative electrode material after charging/discharge cycle

The graph below shows the qualitative analysis results for the negative electrode material. Li is detected. There is also Co detected, which was not present in the negative electrode originally.



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



1-4 Electron Probe Micro Analyzer (EPMA)

EPMA that uses an electron beam as the excitation source is equipped with up to 5 channels of WDS, and is capable of elemental analysis of micro areas with a high energy resolution. In addition, the SEM functionality is excellent, making it possible to perform both analysis combined with surface morphology observations using secondary electron images and backscattered electron images.

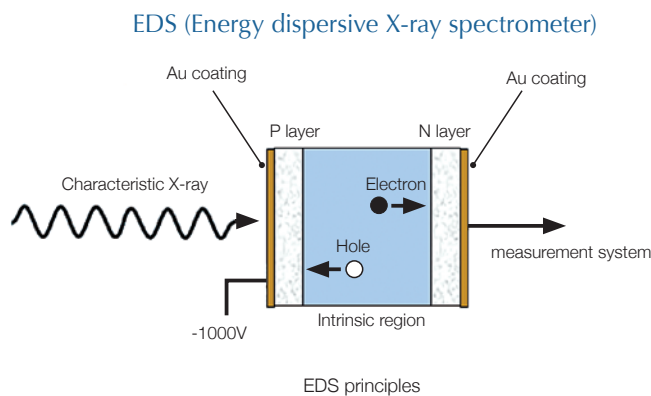
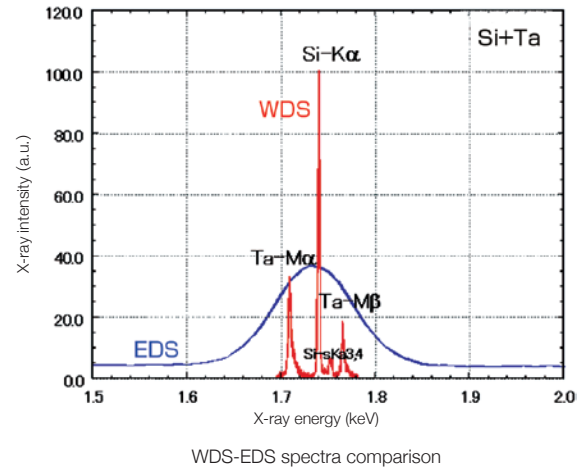
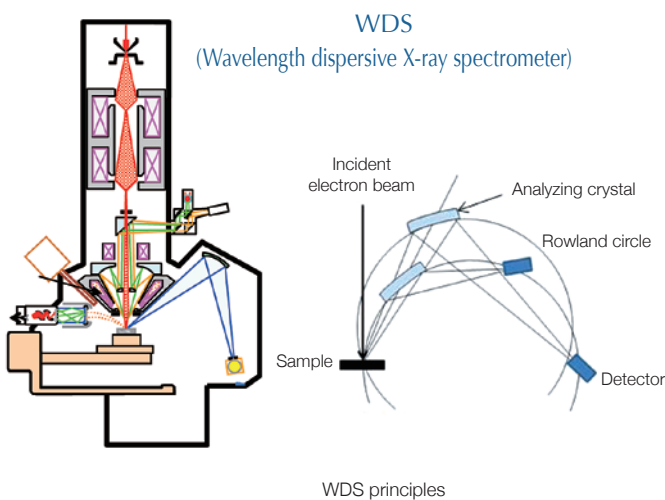


JXA-8530FPlus

Features

- Wavelength dispersive spectrometer (WDS), Max. 5 ch
- Analysis elements: (Be) B to U
- Analysis region: several μm to several cm
- Analysis depth: up to about $1\ \mu\text{m}$
- Detection lower limit: several 10 ppm
- Analysis with a large current of $2\ \mu\text{A}$ or more

Comparison of WDS and EDS



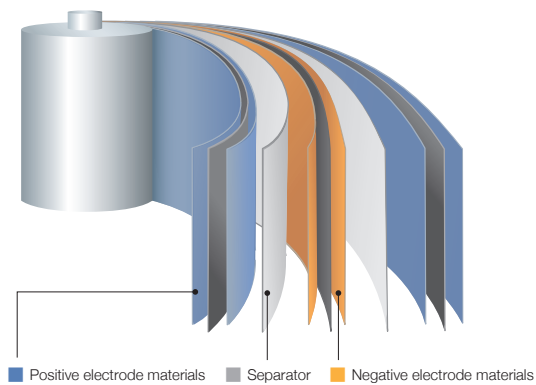
The detection principles and structures for WDS and EDS differ significantly. In comparison to EDS (lower left), which simultaneously detects all the characteristic X-rays that are generated, WDS only detects the characteristic X-ray of the target detection element.

The figure on the above right shows a comparison of the EDS and WDS analyses of Si oxides and Ta oxides in multi-layer films. The Si and Ta peaks are overlapped in the EDS spectrum, but are separated in the WDS spectrum, demonstrating the high energy resolution attainable with WDS.

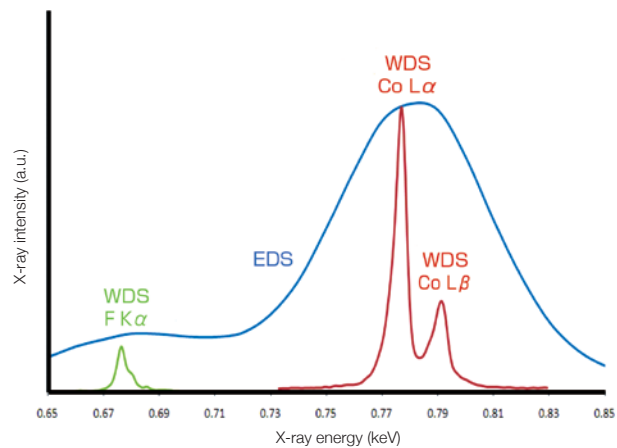
Analysis example

Qualitative analysis of positive electrode materials, Large area analysis

The spectra shown below on the right are the results of qualitative analysis for Co and F contained in a positive electrode material after a charge/discharge cycle. The EDS result shows a low energy resolution and a high background, and the F-K α line is influenced by the Co, so the peak is difficult to detect. With WDS, there is no Co-L α line effect, and the F-K α line can be detected.



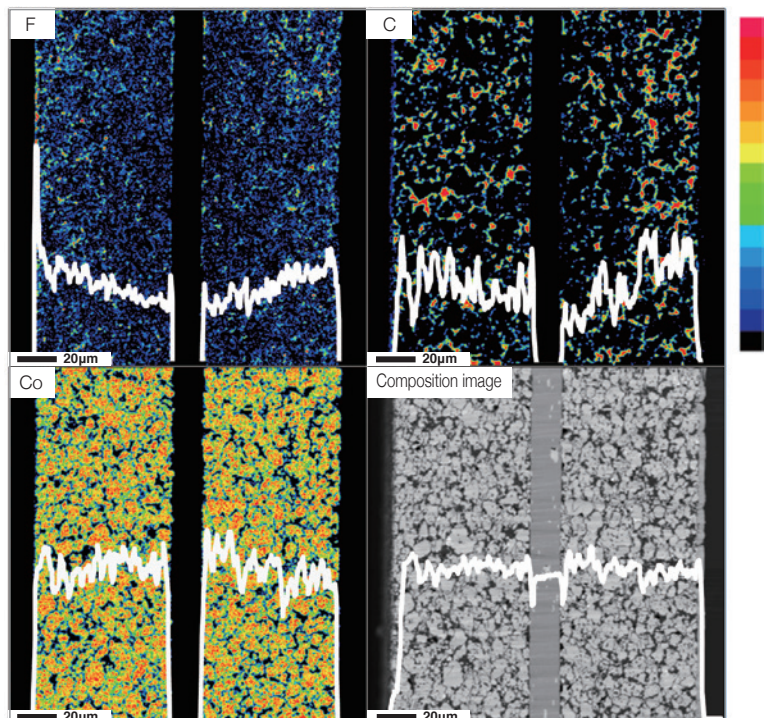
Positive electrode materials : LiCoO_2 , LiMn_2O_4 , LiFePO_4 , etc.
 Negative electrode materials : C, Si, SnO_2 , etc.
 Electrolyte : LiPF_6 , LiClO_4 , etc.



The images on the right show an example of element mapping with WDS for a cross section of Li-ion battery positive electrode material through repeated charge/discharge cycles. The signal intensity of the F and C that have migrated from the collector (Al) in the center portion increases.

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

A feature of EPMA is the ability to confirm minute changes in the element distribution. The analysis area is $180\ \mu\text{m} \times 180\ \mu\text{m}$.



1-5 Auger Electron Spectrometer (AES)

Auger electron spectroscopy, like XPS, is a method to directly detect Li. For Auger electron excitation, an electron beam is used as the excitation source, providing a high spatial resolution. The Li distribution in even a single particle of positive electrode material can be obtained.



JAMP-9510F

Li can be detected directly !

Features

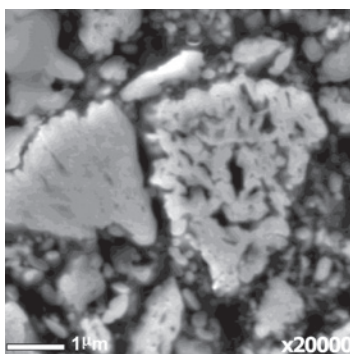
- High spatial resolution of Auger analysis: 8 nm
- Variable energy resolution: From 0.05% to 0.6%
- Analysis range: Up to 95 mm Φ with the large stage
- Insulating materials can be analyzed using the neutralizing gun and sample tilting method
- Wide range of options (BEI, EBSD, etc.)
- Depth profiling

Li sensitivity

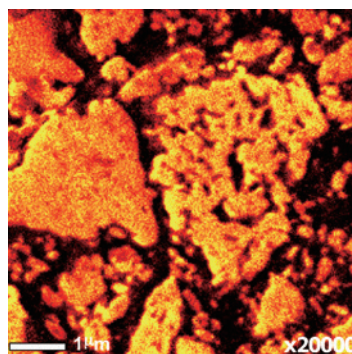
Because the JAMP-9510F uses a concentric hemispherical electrostatic analyzer, it is possible to obtain peaks even in low energy regions, such as those of Li, with high accuracy, high sensitivity and high energy resolution. The figure on the right below shows the analysis result with the JAMP-9510F for standard samples of Li, Li_2O , and Li_2CO_3 . This result clearly shows the changes in the peak position and shape for each of the different chemical bonding states.

· Auger map of Li in the positive electrode material particles

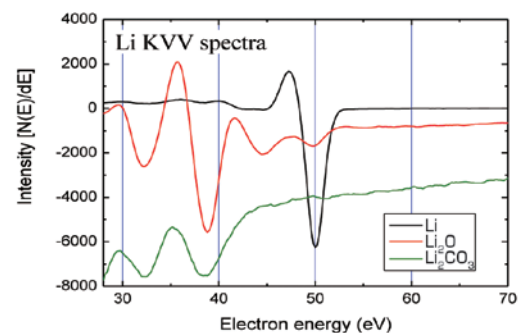
Since the Auger Electron Spectrometer uses an electron beam as the excitation source, it is possible to acquire element maps for micro areas corresponding to the secondary electron images and backscattered electron images.



SEI



Li



Comparison with other analysis methods (Li sensitivity, quantification)

• Li sensitivity

The Li sensitivity with Auger Electron Spectroscopy (AES) is higher than that of X-ray Photoelectron Spectroscopy (XPS). When assuming that the C sensitivity is about the same for AES and XPS, and the peak intensity of metallic Li is compared between AES and XPS using the peak intensity of C as the standard, the peaks obtained with AES are 70 times higher than those obtained with XPS.

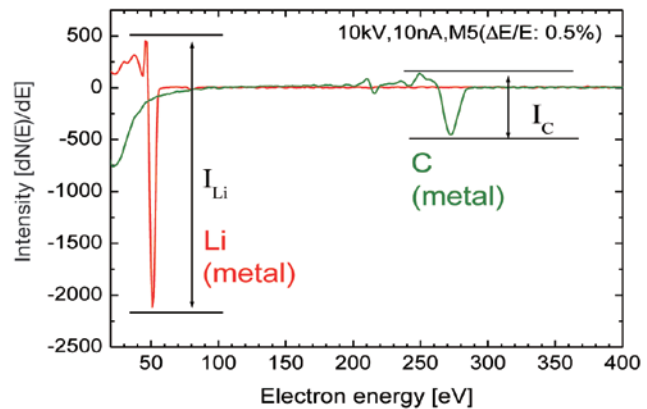
Comparison of ionization cross section (Al-K α) for Li and C with XPS

X-ray : Al K α (1487 eV)

Z	1s1/2
H	0.0002
He	0.0082
Li	0.0568
Be	0.1947
B	0.486
C	1.000
N	1.80
O	2.93
F	4.43
Ne	6.30

(Ref : J.Electron Spec, Relat.Phenom,8,129(1976))
 $I_{Li} / I_C \cong 1/18$
 (Li sensitivity is about 1/18 that of C)

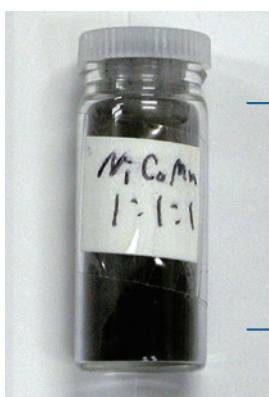
Comparison of peak intensities of Li and C measured with the same conditions using AES



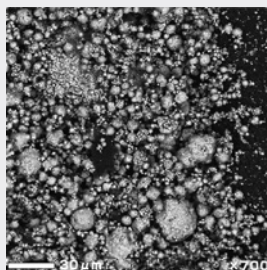
$I_{Li} / I_C \cong 4$
 (Li sensitivity is about 4 times greater than C)

• Comparison with quantification values acquired by other methods

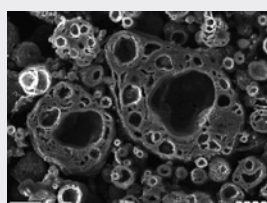
The quantitative analysis results obtained by various methods using positive electrode material particles containing Li (NMC particles) are shown in the table below. When AES is applied for analysis of a surface and analysis of a cross section prepared by CP, the absolute quantitative intensity obtained by AES is high. Comparison with other analysis methods shows that there is a difference of a few percent, and that comparable quantitative accuracy is obtained.



NMC particles used for the experiment
 (Mn : Co : Ni = 1:1:1)



Surface analysis	Standardized atomic concentrations, excluding carbon				
	Li	O	Mn	Co	Ni
AES (average of 50 μm ϕ)	19.6	55.0	8.5	8.5	8.4
XPS (average of 3 mm ϕ)	14.8	60.5	7.4	8.1	9.2



Bulk analysis	Standardized atomic concentrations, excluding carbon				
	Li	O	Mn	Co	Ni
AES	5.1	53.8	13.6	14.4	13.1
SEM-EDS	-	64.8	11.0	12.1	12.1
XRF	-	59.8	13.1	13.7	13.4

1-6 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) is suitable for observing fine structures on the surface of a specimen. SEM is especially useful for acquiring minute changes in the structure of electrode materials as the charge/discharge cycle is repeated. SEM system performance, such as spatial and lateral resolution, varies significantly depending on the electron gun and lens type. Here, we introduce the basic technology and application of the JSM-7900F, a high-end model SEM. The JSM-7900F utilizes a Super Hybrid Lens (SHL) combining superposed electrostatic and magnetic fields and provides a high-resolution image with the same operability as an out-lens SEM with almost no magnetic field influence. This field emission SEM (FE-SEM) that is equipped with a Schottky electron gun incorporates a wealth of the latest technologies, including a GENTLEBEAM™ mode for high-resolution image acquisition with a bias voltage applied to the specimen, and also various types of detectors.



JSM-7900F

Features

- In-lens Schottky Plus FEG
- Super Hybrid Lens (SHL) and TTL detector system
- GBSH-S (GENTLEBEAM™ Super High resolution Stage bias mode): specimen bias voltage 5 kV
- Wide range of options (EDS, WDS, EBSD, SXES, etc.)
- Neo Engine (New Electron Optical Engine)
- Low vacuum mode: Up to 300 Pa *Option

Arrangement of detectors

• Various types of detectors

The figure below shows the arrangement of the detectors that are incorporated in the JSM-7900F. The combination of the SHL and these detectors makes it possible to selectively detect the various kinds of information that are generated from the specimen.

UED (Upper Electron Detector)

Detection over a wide range is possible, from low energy secondary electrons to high energy backscattered electrons. Controlling the voltage that is applied to the electrode grid of the lower portion of the UED enables selection of the signals over a range from secondary electrons to backscattered electrons.

USD (Upper Secondary Electron Detector)

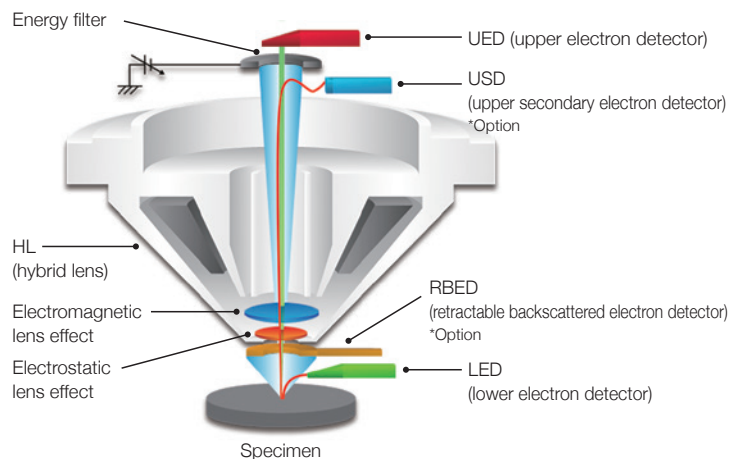
Detects the secondary electrons that have been eliminated with the grid voltage of the UED lower section. It is possible to simultaneously obtain 2 types of information; a backscattered electron image with the UED, and a secondary electron images with the USD.

LED (Lower Electron Detector)

The E-T detectors used for a wide range of SEM allow the use of a long working distance, unlike the UED and USD. Since a large number of backscattered electrons that have been generated at low angles are detected, this type of SEM image reflects the surface roughness and topology of the specimen.

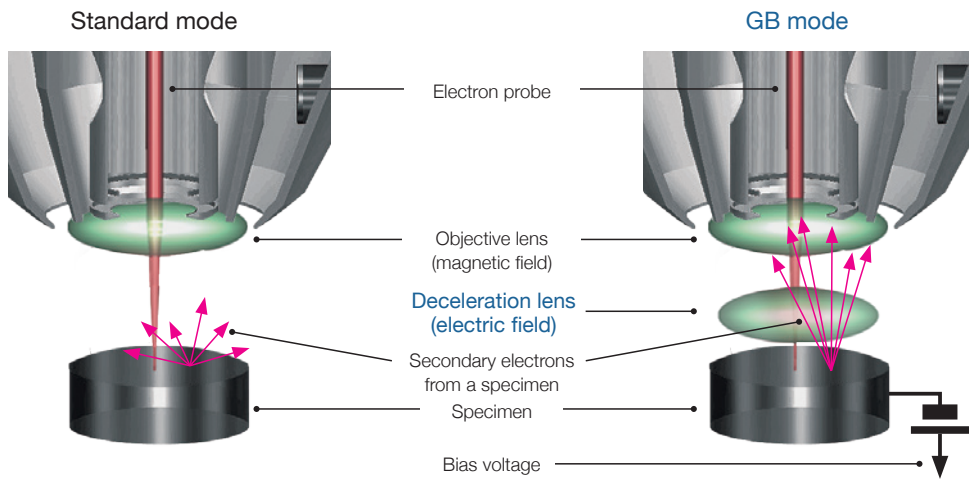
BED (Retractable Backscattered Electron Detector)

A detector mainly used to acquire backscattered electron images using a semiconductor detector.

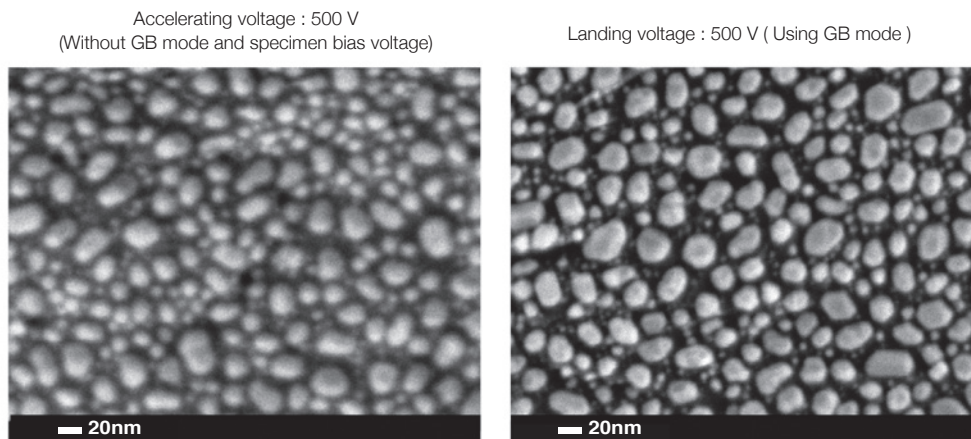


Principles of GENTLEBEAM™ mode

In GENTLEBEAM™ mode (GB mode), a voltage is applied to the specimen to reduce the landing voltage of the electrons just before they strike the specimen, enabling high-resolution observation with accelerating voltages as low as 100 V. Since the scattering region of the electron beam within the specimen is smaller, it is easy to observe fine structures on the surface, and the influence on specimens that are susceptible to heat damage can be reduced. Non-conductive specimens can be easily observed without pre-treatment. The new GBHS-S mode makes it possible to apply a bias voltage, up to 5 kV, to the specimen stage with no special holder.



A comparison of the resolution at low accelerating voltage for a conventional sample without any bias voltage (left) and for the GB mode (right) is shown in the image detected by the UED (Upper Electron Detector). The specimen is gold particles on carbon. For the specimen with no bias voltage (left), the image shows the gold particles observed with an accelerating voltage of 500 V. In the GB mode shown on the right, it is clear that the image is both sharper and that the fine details of the particles can be seen more clearly.



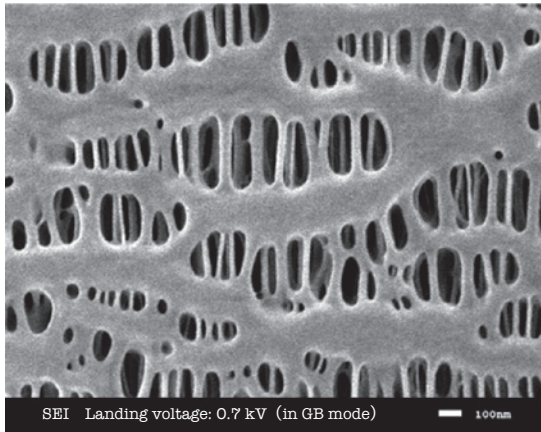
Specimen : Gold particles on carbon

1-6 Scanning Electron Microscope (SEM)

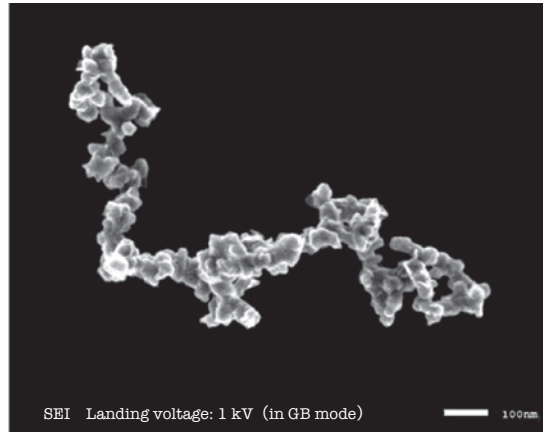
Observation example

Observation of battery materials

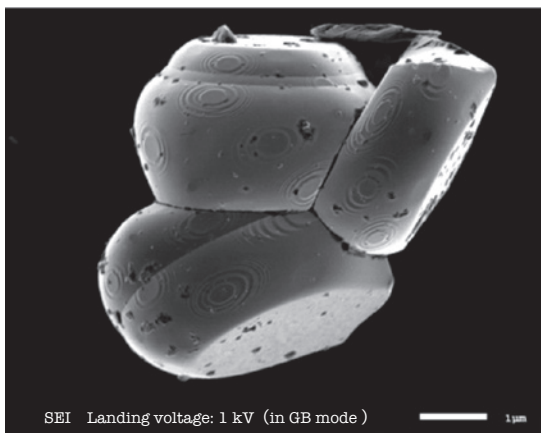
SEM is highly suitable for observing the morphology of various types of battery materials. Several examples are shown below.



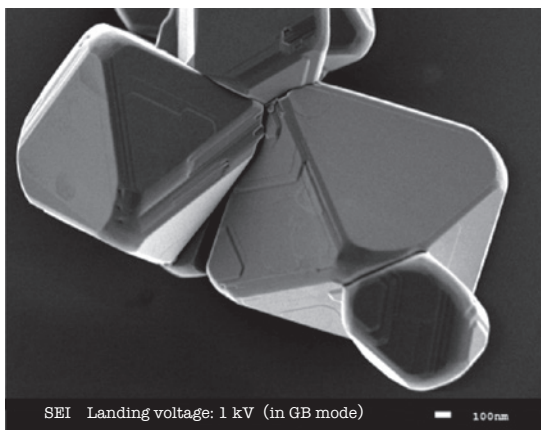
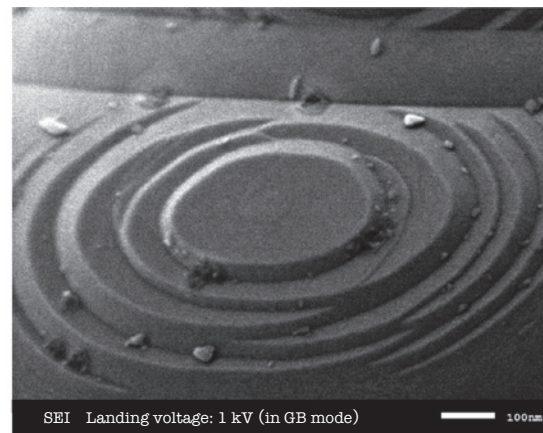
Separator (polyethylene)



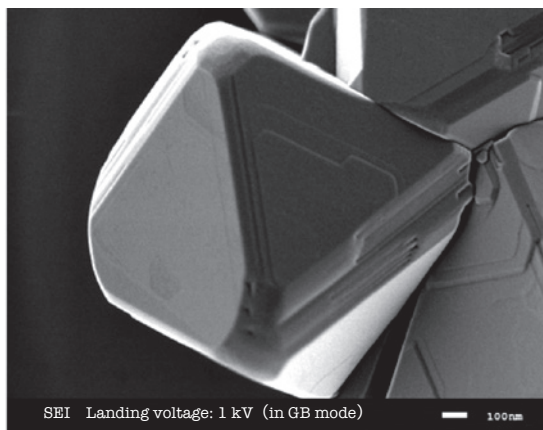
Conductive additive (Acetylene black)



Positive electrode active material : LiCoO_2



Positive electrode active material : LiMn_2O_4 (Spinel)

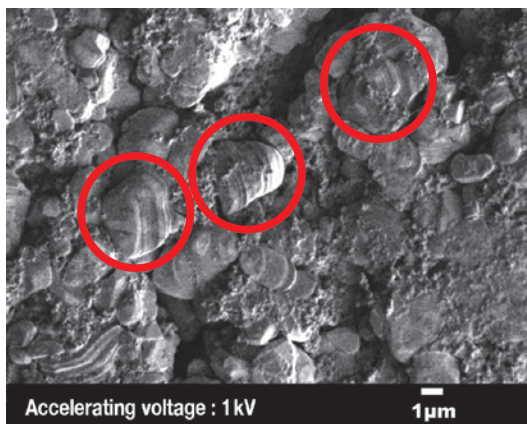


Observation example

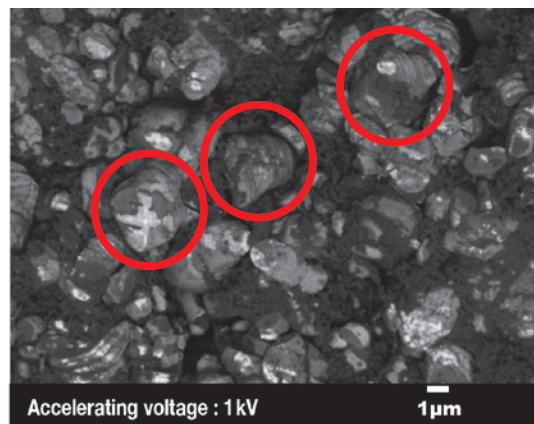
Imaging with various detectors and EDS analysis at ultra-low accelerating voltage

- Li ion battery positive electrode material
(Simultaneous acquisition of surface topography and composition information using a low accelerating voltage)

With the JSM-7900F, it is possible to acquire a variety of information about the surface of a specimen by selectively using the various detectors. The two micrographs below show an example of the simultaneous observation with the USD (left) and UED (right) of a lithium-ion battery positive electrode. With the USD, information about the surface roughness and topology is obtained, while composition information for the specimen is acquired with the UED.



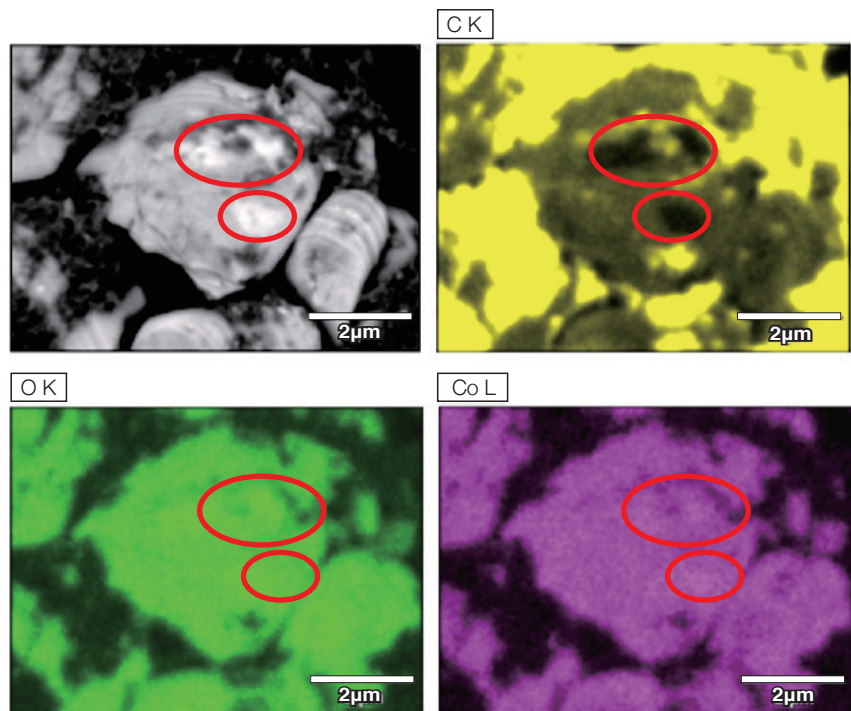
USD: surface information (mainly topography)



UED: Composition information

- EDS analysis with low accelerating voltage

The images on the right show EDS analysis results of the surface of a positive electrode material for Li ion batteries at a low accelerating voltage of 1 kV. It is possible to reveal the carbon distribution in an extremely thin film layer on the uppermost surface, which cannot be detected under ordinary acquisition conditions. Even at an accelerating voltage of 1 kV, the JSM-7900F can deliver a sufficient probe current (25 nA) for EDS analysis. This is quite useful for both image observation and EDS analysis.



Sample : Li-ion battery positive electrode material (Accelerating voltage:1 kV, Probe current:15 nA)

1-6 Scanning Electron Microscope (SEM)

Transfer Vessel

The transfer vessel is a device for transferring a specimen that has been prepared in an inert gas environment (such as in a glove box) to the specimen exchange chamber without exposing the specimen to the atmosphere, so that it can be observed using the FE-SEM. This is especially useful for handling specimens that alter rapidly when exposed to air.

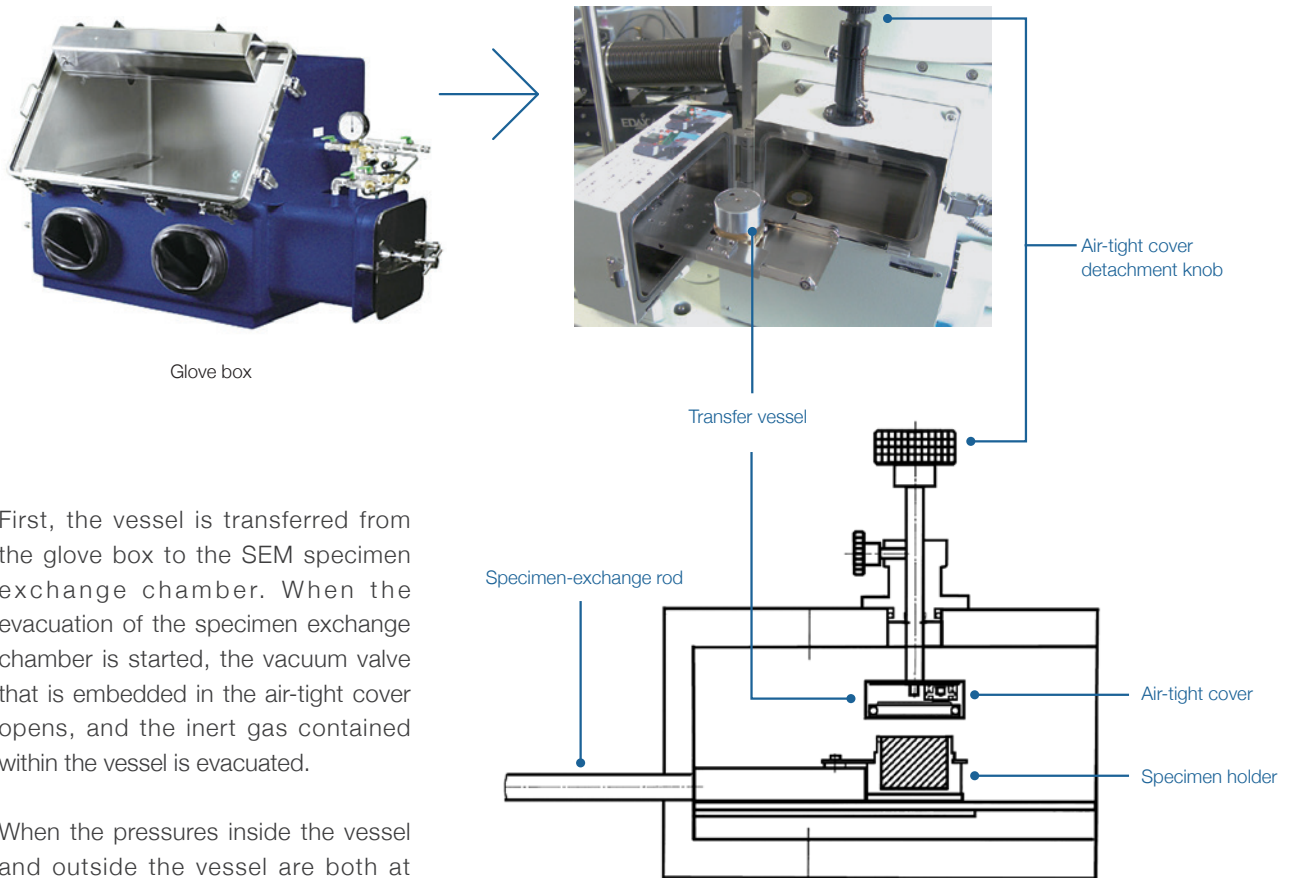
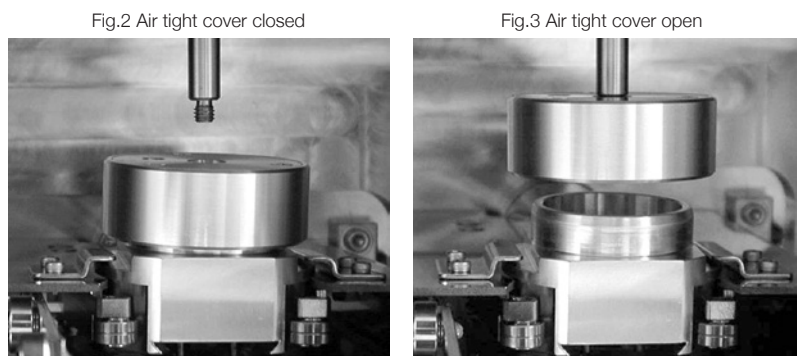


Fig.1 Cross section view of the specimen exchange chamber with the transfer vessel mounted

First, the vessel is transferred from the glove box to the SEM specimen exchange chamber. When the evacuation of the specimen exchange chamber is started, the vacuum valve that is embedded in the air-tight cover opens, and the inert gas contained within the vessel is evacuated.

When the pressures inside the vessel and outside the vessel are both at atmospheric pressure, this valve is designed to maintain the air-tight seal by the force of a spring. When the pressure outside the vessel is reduced, the force of the pressure inside the vessel pushes the valve open.

As shown in Fig. 1, there is an “air-tight cover detachment knob” on the top of the specimen exchange chamber. When evacuation is completed, the threaded rod on the end of this knob is screwed into the tap in the air-tight cover and used to pull it up. Fig. 2 and 3 show this knob being used.



Specimen size : Φ 25.4 mm X 20 mm h

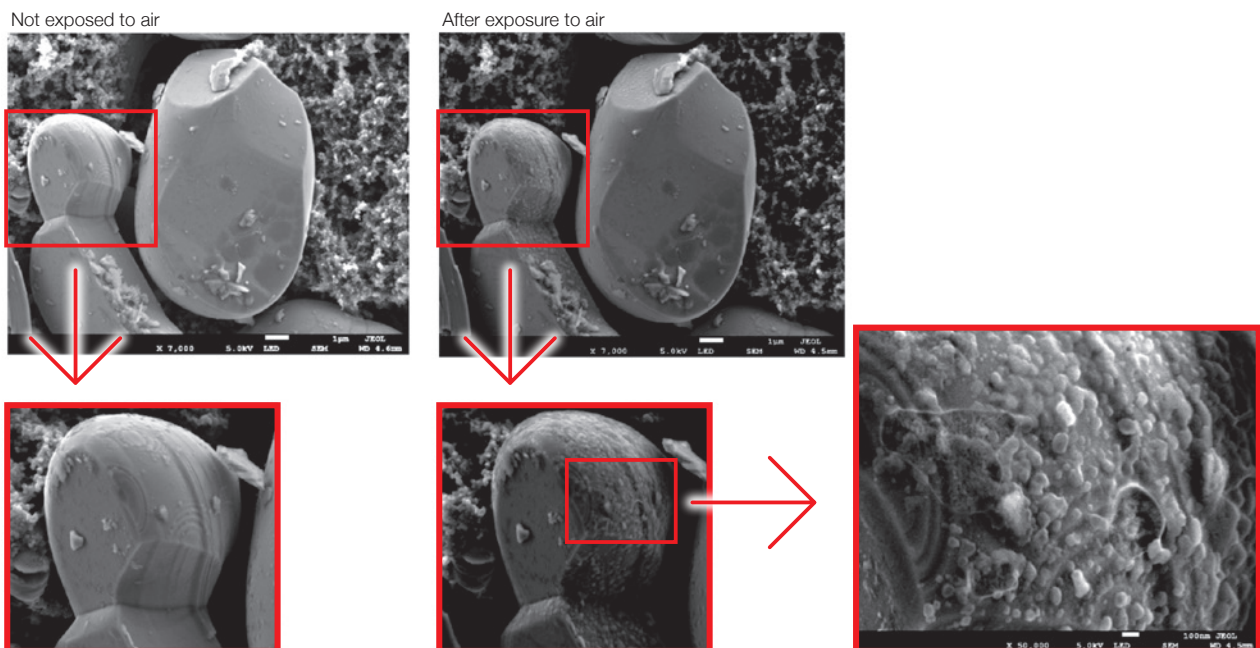
Effect of Preventing Air Exposure using the Transfer Vessel

For the evaluation of lithium ion battery materials that react with air, it is indispensable to have techniques to prevent the exposure of the specimen to the atmosphere. Data demonstrating the effect of the transfer vessel is shown below.

In the example here, specimens of a lithium-ion battery positive electrode material containing LiCoO_2 are first observed without being exposed to the atmosphere, and then the same location is observed after exposing the specimen to air. A comparison is made between a specimen that has never been charged/ discharged and a specimen that has been subjected to a charge/discharge cycle 5 times. There are no deposits observed on the unexposed specimens, but when the same locations are observed after exposure to air, the deposits are observed. This demonstrates the effect of the transfer vessel for preventing specimen exposure to the air.

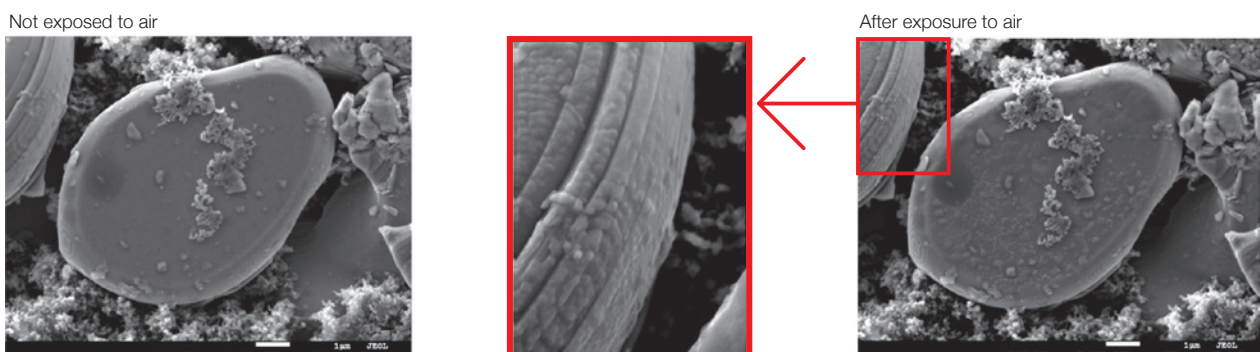
• Battery that has never been charged

Precipitates that are not observed on the LiCoO_2 particles that have not been exposed to the atmosphere are seen here and there after exposure to the air.



• Battery after being charged and discharged 5 times

Significantly different from a battery that has never been charged. After exposure to air, precipitates appear across the surface of the LiCoO_2 particles.



1-7 Transmission Electron Microscope (TEM)

The transmission electron microscope (TEM) is essential to capture the charge-and-discharge induced changes of a lithium ion battery at the atomic level. TEM observation requires preparation of a thin-film specimen. But in addition to morphological observation, TEM provides elemental analysis by EDS and EELS. In particular, EELS enables chemical-state analysis and direct analysis of Li.

Further, instruments with a STEM function to acquire transmission images by scanning the surface with a focused electron beam, can be used to obtain a variety of images, such as BF (bright field), ABF (annular bright field), and HAADF (high angle annular dark field), by capturing electrons with different scattering angles. ABF is useful for direct observation of the atomic column sites of light elements such as oxygen and lithium. Even more detailed characterization of the mechanisms of the lithium ion battery can be expected by using a JEM-ARM200F equipped with a spherical aberration corrector. The main performance of the JEM-ARM200F is as follows.

NEOARM
JEM-ARM200F

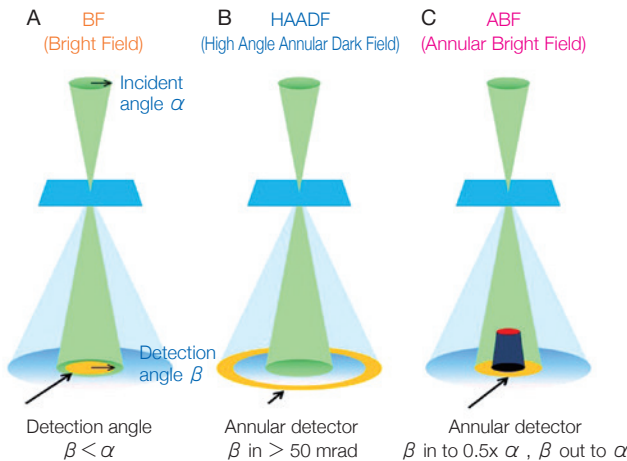


Features

- Advanced STEM Corrector (ASCOR)
- Accelerating voltage 30 to 200 kV (30, 60*, 80, 120*, 200 kV)
- STEM HAADF image resolution (UHR)
70 pm (200 kV), 100 pm (80 kV), 160 pm (30 kV)
- Aberration correction software JEOL COSMO™ (Corrector System Module)
- New Annular Bright Field (ABF) detector system
- Dual-SDD*
Solid angle UHR: 1.24 sr/HR: 1.75 sr *Option

Observation example

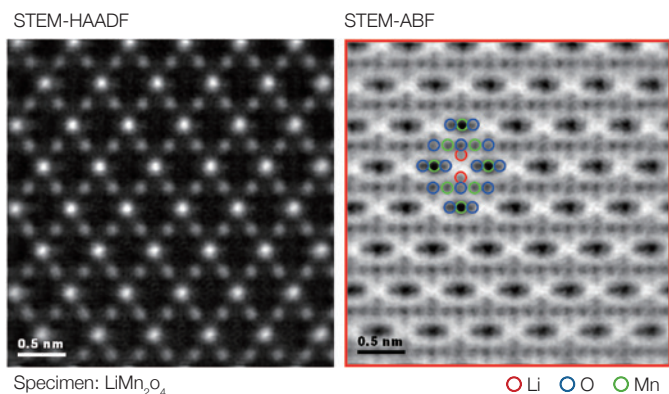
Li column observation using ABF



For an aberration-corrected STEM system, the angle of the incident electron beam onto the specimen is 20 to 25 mrad. The STEM detector detects the electrons that pass through the specimen and are scattered.

As shown in Figure A, a BF image can be obtained by detecting electrons at angles lower than the incidence angle. Figure B illustrates acquisition of an HAADF image by detecting electrons scattered at larger angles than the incidence angle, 50 mrad or more. The ABF image is obtained using a detector with a beam stopper to detect electrons scattered at about 10 to 25 mrad.

This figure shows high-resolution STEM images of LiMn_2O_4 positive electrode materials for a lithium-ion battery. In the HAADF image shown on the left, only Mn can be seen, while in the ABF image on the right it is possible to directly observe the column sites of the light elements such as lithium and oxygen. This allows evaluation of the lithium-ion battery material at the atomic level.



Specimen: LiMn_2O_4

○ Li ○ O ○ Mn

1-8 Specimen Preparation Equipment: Air Isolation & Cooling CROSS SECTION POLISHER™

We introduce the CROSS SECTION POLISHER™ IB-19520CCP with the added functionality to cool the specimen and prevent exposure to the air. This is the optimal instrument for preparing cross sections as SEM specimens of low-melting point metals, like solder, which are easily deformed by heat, materials with a low glass-transition temperature, like resins, and battery materials that react with air.



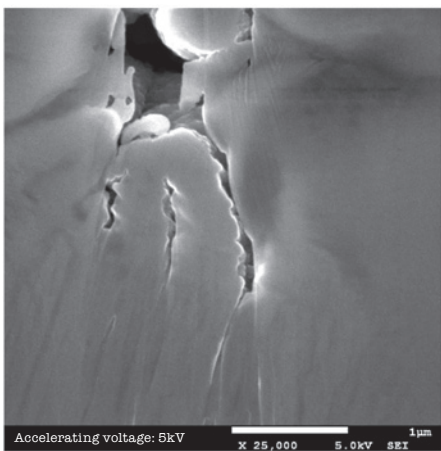
- Features**
- Special transfer vessel can be used to transfer a specimen between a glove box, CP, SEM, EPMA, FIB without exposure to the air
 - Cooling the specimen during ion milling reduces thermal damage
 - Thermal damage can also be reduced by using intermittent milling
 - Milling is possible with the temperature controlled in the range from 0 to -120 °C

Observation example

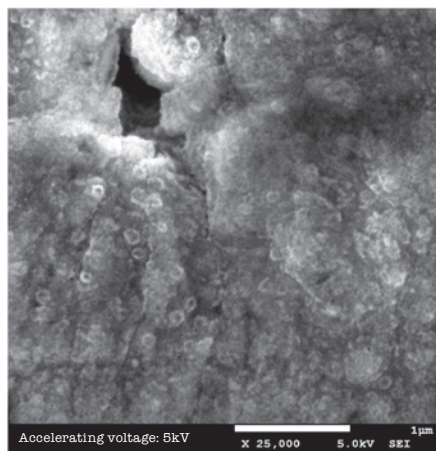
Metallic lithium processing and observation

• Processing without exposure to air and the effects

The image on the left below is a SEM image of a cross section of metallic lithium processed without being exposed to the atmosphere. The image on the right shows the SEM image of the same location on the same sample after it was exposed to air for 2 minutes. The reaction products caused by the exposure to air are clearly seen covering the entire sample. This also demonstrates the value of transferring the specimens without exposure to air.



Processed without exposure to the air



Appearance after exposure to the air for 2 minutes

1-8 Specimen Preparation Equipment: FIB (Focused Ion Beam)

The FIB system is an instrument with an electrostatic lens system to focus a Ga ion beam and scan the beam across a specimen surface. Utilizing Ga sputtering effects, the system has functions to process box shapes, allow observation of scanning ion microscope (SIM) images from the secondary electrons generated by exposure to the Ga ion beam, as well as creating the coating films of carbon, tungsten or platinum by organic metal gas irradiation. Recently, the Multi-Beam system allows immediate SEM observation and EDS analysis of specimen surfaces that have been processed with FIB. This system extends its applications to micro-fabrication, TEM sample preparation, and 3D structure analysis from 3D sample information obtained by automatic repetition of FIB processing & SEM imaging at fixed intervals. Available attachments include a specimen cooling system and a transfer vessel system.



JIB-4700F

Features

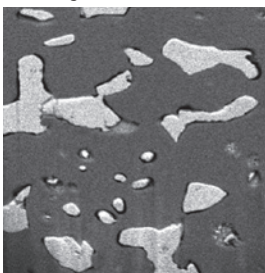
- High resolution at low accelerating voltage
Combination of a hybrid conical objective lens and GENTLEBEAM™ achieves high resolution at low accelerating voltage (1.6 nm at 1 kV).
- Supporting not only 3D analysis of the morphology, but also EBSD (crystal orientation analysis), and EDS (element analysis)

Observation example

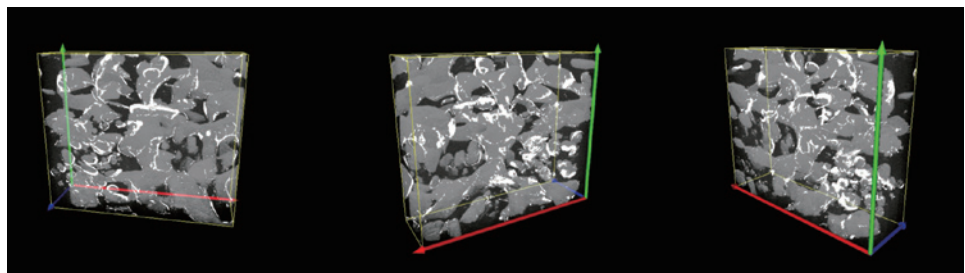
Solder Cold processing, 3D analysis

An example of using the cooling stage to process lead solder is shown below. At the upper left is an example of lead solder cross section that was processed at 25°C (room temperature). Voids can be clearly seen at the boundary. The image that was reconstructed using 3D analysis shows that these voids are distributed quite uniformly. In comparison, in the cross section that was processed at -50°C voids are not seen (bottom left). When the 3D reconstruction image is checked, the contrast of voids cannot be recognized. This indicates that the voids at the interface found in lead solder that was processed at room temperature are the result of thermal damage during the processing.

SIM image

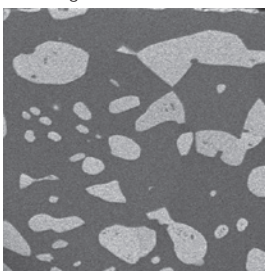


3D reconstruction

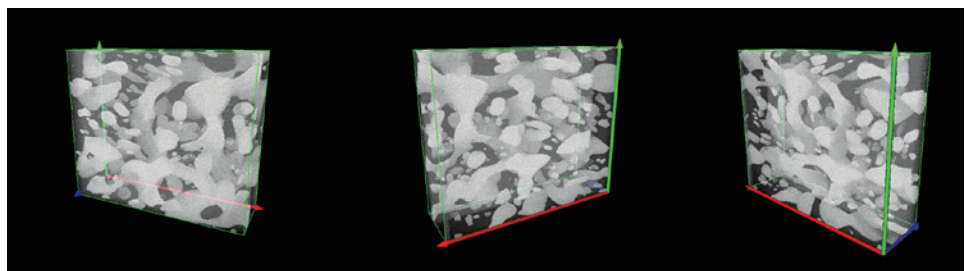


Processing temperature 25 °C (Lead portions are gray, voids shown in white)

SIM image



3D reconstruction



Processing temperature -50 °C (no apparent voids)

2-1 Gas Chromatograph - Mass Spectrometer (GC-MS)

GC-MS is a combination of a gas chromatograph (GC) and a mass spectrometer (MS). With a GC-MS, a sample is separated into its components by a GC capillary column and then introduced into the MS for mass analysis. This technique is highly suited for analyzing complex organic mixtures and is widely used for both qualitative and quantitative analysis.



JMS-TQ4000GC

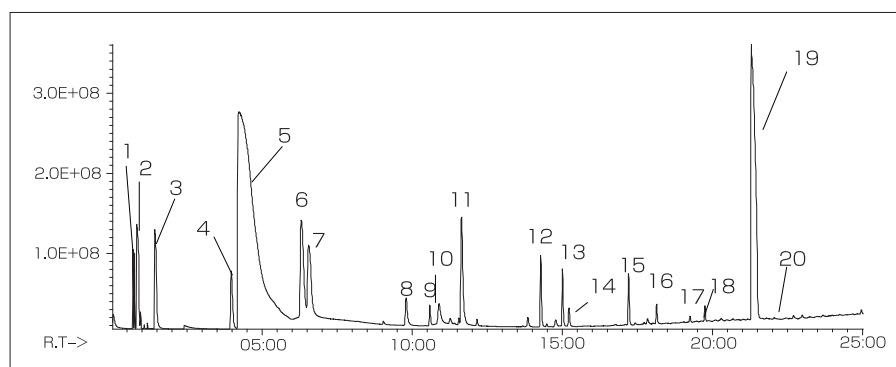
Features

- Selected Reaction Monitoring (SRM) mode enables high sensitivity analysis.
- Various ionization methods can be used (EI, CI, PI).
- The range of applications can be expanded through combination with other techniques.
 - Thermal analysis: Pyrolyzer and TG/DTA
 - Volatile compound analysis from liquids and solids: Head space autosampler.

Analysis example

Evolved gas in a over-discharged Lithium ion battery cell

The following example shows a measurement made using a gas chromatograph quadrupole mass spectrometer to identify the evolved gas components from an over-discharged lithium ion battery cell. A variety of components were detected, including ethylene carbonate (EC, Peak No.20) and diethyl carbonate (DEC, Peak No.19), which are widely used as electrolyte solvents, as well as lower level hydrocarbons, fluorinated compounds, and silicone compounds.



TIC chromatogram of evolved gas from over-discharged LIB cell

Peak No.	Component	Peak No.	Component	Peak No.	Component
1	Air (N ₂ , O ₂)	8	2-fluoropropane	15	Ethyl acetate
2	Methane	9	Methyl formate	16	Hexane
3	Carbon dioxide (CO ₂)	10	Difluorodimethylsilane	17	Ethyl methyl carbonate
4	Fluoroethane	11	Butane	18	Ethyl propionate
5	Trifluoromethylsilane	12	Ethyl formate	19	Diethyl carbonate (DEC)
6	Propane	13	Ethyl ether	20	Ethylene carbonate (EC)
7	Cyclopropane	14	Pentane		

2-2 Nuclear Magnetic Resonance Spectrometer (NMR)

NMR is a technique that focuses on specific atoms in a material and analyzes molecular structures and states of the peripheral regions for relevant atomic nuclei. For LIB analysis in particular, it is one of the few valuable methods to directly observe and measure the Li nuclei, enabling the acquisition of various information, such as the quantity, chemical state and mobility of the Li in a sample, regardless of the location, or whether it is a positive electrode, negative electrode or electrolyte material.

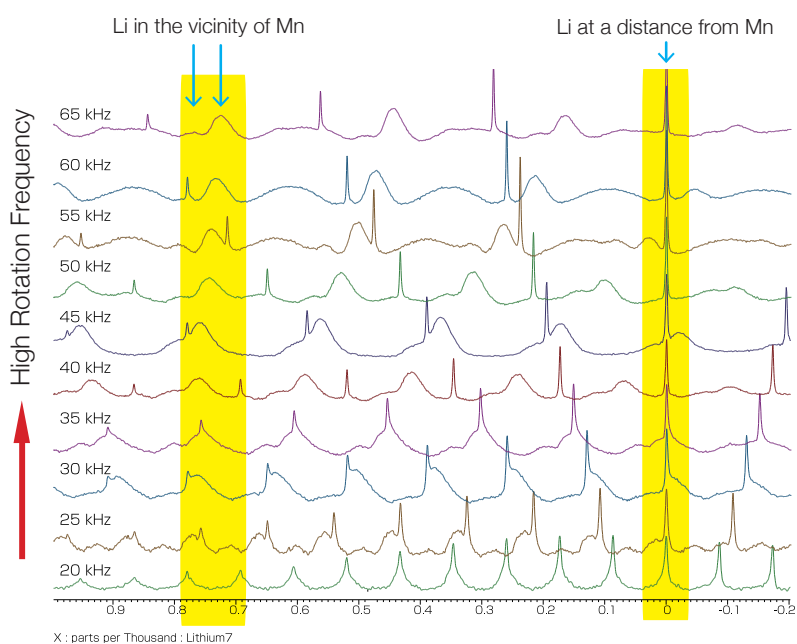


Nuclear Magnetic Resonance spectrometer / JNM-ECZ500R

Analysis example

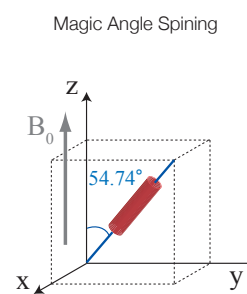
Positive electrode material analysis with ultra high-speed MAS measurement

Solid state NMR is a powerful tool for analysis of the physical properties and structure of solid materials because it allows us to observe the chemical state of different nuclei (ions) as different signals. In solid state NMR, in order to obtain high-resolution spectra, measurements are performed with the samples tilted relative to the external magnetic field at a magic angle (54.74°) and rotated at high speed (Magic Angle Spinning, hereafter abbreviated to MAS). However, for LIB electrodes, many spinning side bands (SSB) are generated in the observation range due to the influence of paramagnetic ions, which makes the analysis difficult. For this kind of sample, it is possible to force the SSB to move away from the true peaks by using a 1 mm or 0.75 mm MAS probe and spinning at extremely high speeds (up to 110 kHz), which allows the true peaks to be identified. The ^7Li spectrum for positive electrode material for a manganese dioxide lithium battery below clearly shows that there are 2 kinds of Li in the vicinity of Mn around 800 ppm, and 1 type of Li distant from Mn at 0 ppm.

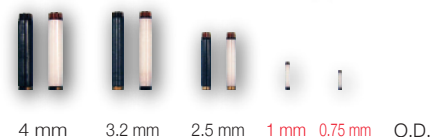


X : parts per Thousand : Lithium7

^7Li spectra of positive electrode material for manganese dioxide lithium battery



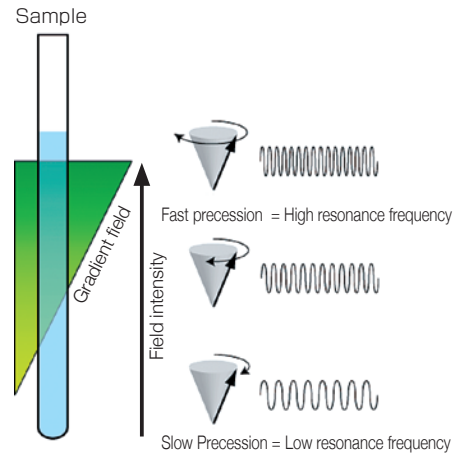
Ultra high speed MAS sample tubes



2-2 Nuclear Magnetic Resonance Spectrometer (NMR)

Measurement of self-diffusion coefficients using NMR

NMR system is an instrument for observing the absorption and emission processes of the electromagnetic waves that correspond to the energy differences arising from nuclear spin in a magnetic field. The resonance frequency (precession frequency of the nuclear spin) depends on the intensity of the magnetic field and the type of nucleus (nuclear gyromagnetic ratio). Therefore, by using magnetic field gradient pulses it is possible to obtain the position information for the atoms in a sample, and to obtain self-diffusion coefficients (of molecules and ions). Since there is a strong correlation between the self-diffusion coefficient of ions and the ion conductivity in an electrolyte, this can be used as a method for evaluating electrolytes. Furthermore, since the diffusion coefficients of the cations and anions can be obtained separately, it is possible to obtain information about the ion conduction mechanisms.



Effect of field gradient pulse relative to sample position

Analysis example

Analysis of ^7Li nuclear diffusion coefficient in solid electrolyte

Here is an example of self-diffusion coefficients obtained for Li ions in a solid electrolyte. When the intensity of the applied magnetic field gradient is varied, the attenuation of the signal intensity obtained from the Li ion is described by the equation below.

Accordingly, by plotting the signal intensity obtained (lower right figure), the self-diffusion coefficient ($D = 5.6 \times 10^{-11} \text{ m}^2/\text{s}$) of Li ion in the electrolyte can be obtained as an indicator of the ionic conductivity.

$$I_G/I_0 = \exp[-(\gamma \cdot G \cdot \delta)^2 D (\Delta - \delta/3)]$$

I : Signal intensity

G : Magnetic field gradient strength

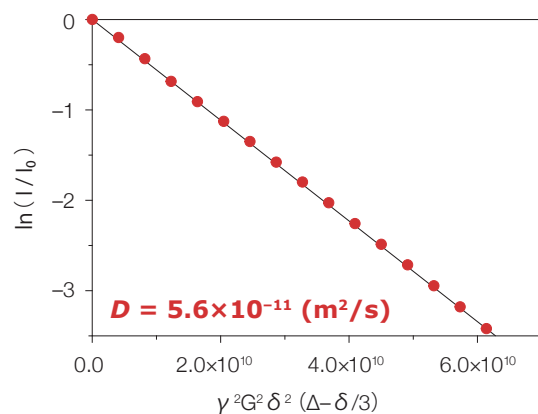
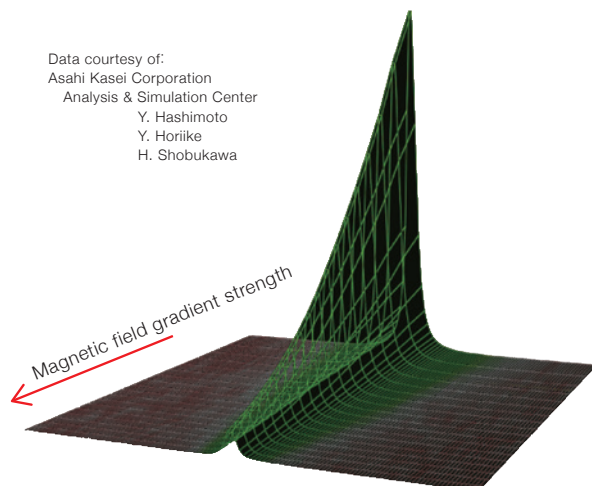
Δ : Diffusion time

γ : Nuclear gyromagnetic ratio

δ : Magnetic field gradient pulse width

D : Self-diffusion coefficient

* For the measurement of electrolytes with small self-diffusion coefficients, or nuclei with a small gyromagnetic ratio, a system that can apply a large magnetic field gradient is required.



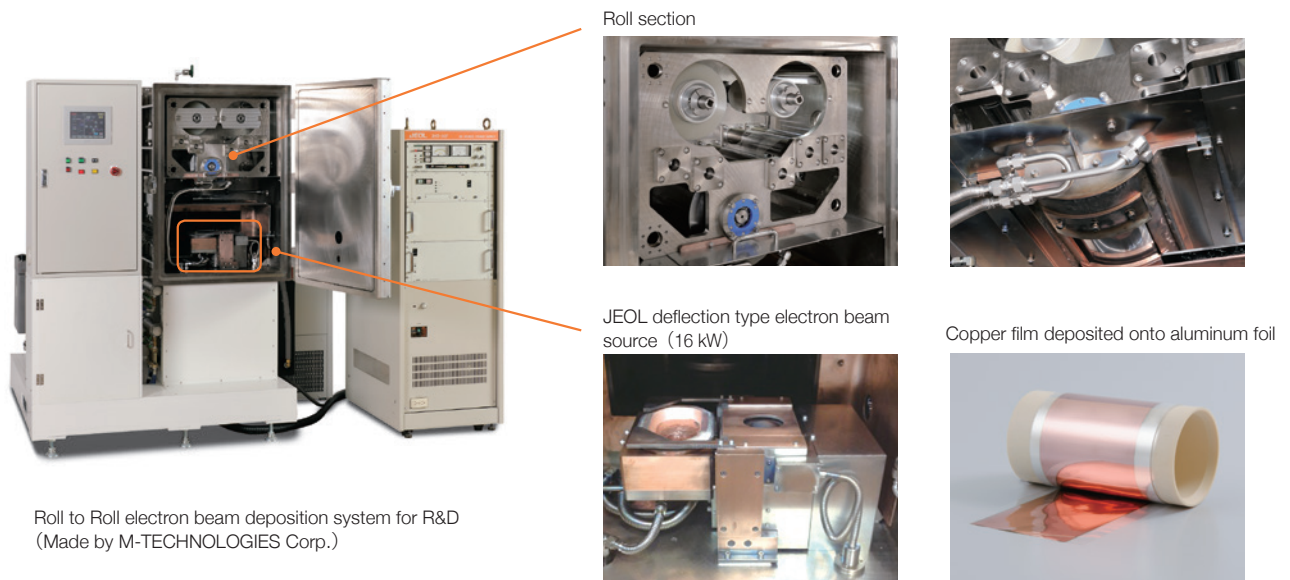
3. Fabrication Systems

3-1 Roll to Roll Electron Beam Deposition Systems

This system creates thin films using electron beam evaporation technique while the substrate of a wide metal foil or film is passed through in a vacuum chamber. Deposition of a variety of inorganic materials, including both metallic and oxide materials, is possible by heating with an electron beam. Applications include formation of electrode films for lithium-ion batteries.

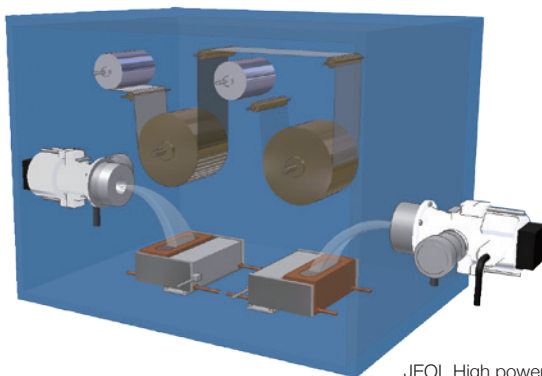
Features

- High-frequency sweep system can control the electron beam irradiation and heating within a specified range of deposition material.
- The high-speed output control enables precise control of the film thickness and deposition rate.
- Deposition rate: an order of magnitude higher than those from sputtering or CVD methods.
- The use of a dedicated controller enables simultaneous deposition using 2 or 3 deposition materials.



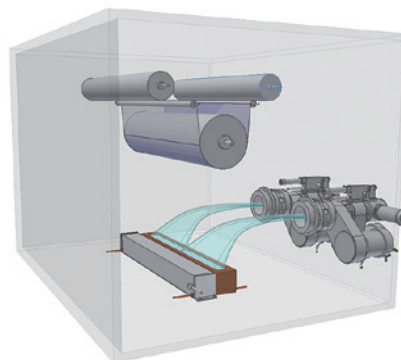
Roll to Roll electron beam deposition system for R&D
(Made by M-TECHNOLOGIES Corp.)

Example of the configuration of double-side deposition



JEOL High power type electron beam source
(30 kW, 100 kW, 300 kW)

Example of the configuration of a parallel electron beam source

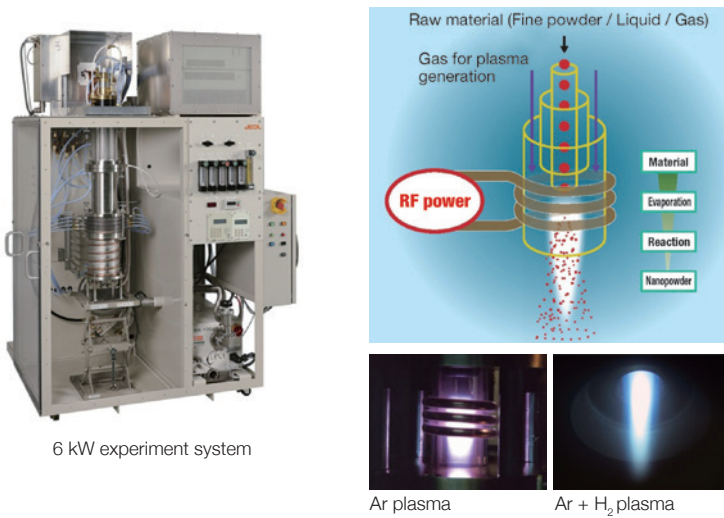


JEOL High power type electron beam source
(100 kW)

- * Deposition width of 500 to 1,000 mm is possible with a single unit (depending on the electron beam source specifications and layout).
- * Arranging multiple High power type electron beam sources in parallel allows deposition of films with widths of more than 1 m.

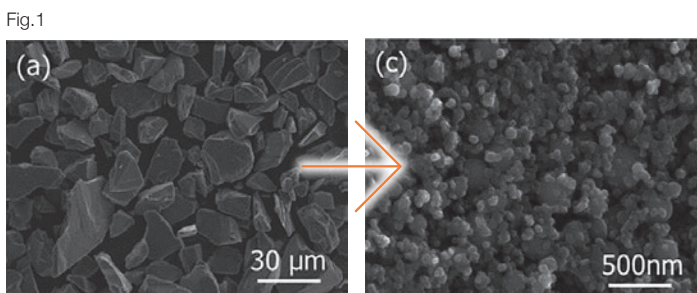
3-2 RF Induction Thermal Plasma System for Nano Particle Synthesis

Plasmas are generated using high frequency power and an inert gas like Ar to create a plasma state with an ultrahigh temperature of nearly 10,000 degrees, called RF induction thermal plasma. Raw materials (fine powder / liquid / gas) can be introduced into this RF induction thermal plasma and instantaneously evaporated or melted to induce reactions or decomposition. This plasma system is expected to be useful for processes like complex composition, nanoparticulation and reforming of fine powders for lithium-ion battery and all-solid-state lithium-ion battery electrodes.

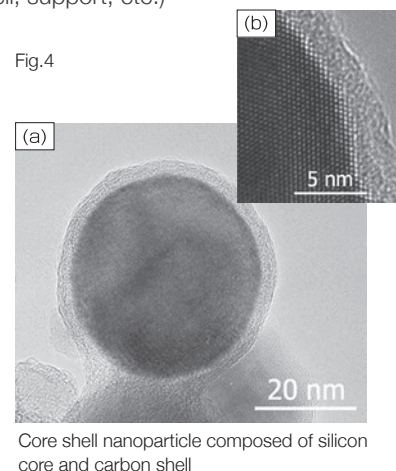
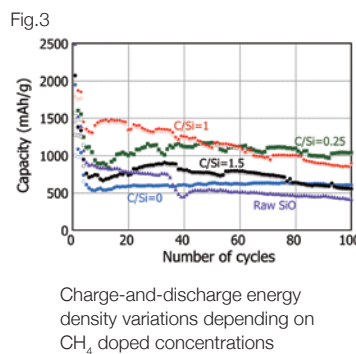
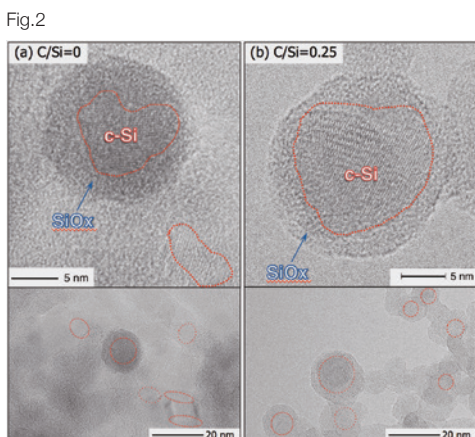


- Features**
- Since there is no electrode, it is possible to melt or evaporate the raw material as is.
 - The ultra-high temperature enables instantaneous flash evaporation, even for heterogeneous materials with different boiling points.
 - A variety of gases can be used to generate the plasma, making it possible to induce reforming and chemical reactions such as carbonization, nitriding, reduction, and oxidation in high-radical reaction field.
 - Raw materials are rapidly cooled after passing through the ultra-high temperature region of the plasma (nucleation and condensation from the rapid cooling process).

Application example: Silicon nanoparticles for negative electrode materials



- <Advantages and Features>**
- Possible to use metallurgy silicon (~ 99.5%)
 - High throughput (~ 360 g/h)
 - Higher-order composite structure (higher-order nano composites formed by a few 10-nm primary particles)
 - Possible to synthesize composite particles (core shell, support, etc.)



Data courtesy: Kambara Laboratory, Department of Materials Engineering, The University of Tokyo
 Fig.1, 4 : Reproduced with permission from J. Appl. Phys. 115, 143302 (2014). Copyright 2014, AIP Publishing LLC.
 Fig.2, 3 : Sci. Technol. Adv. Mater. 15 (2014) 025006

LIBnote

Lithium Ion Battery

Conclusion



Transmission Electron Microscope



Scanning Electron Microscope



Auger Electron Spectrometer

Material	Analysis item	TEM	SEM	AES
Positive electrode material	Morphology observation	○	○	○
	Element composition analysis	○	○	○
	Element distribution analysis	○	○	○
	Crystalline structure analysis	○	○	
	Active material valance identification	○		○
	Collector passive film analysis	○		○
	Chemical state analysis	○		○
	Binder qualitative analysis			
	Examination of impurities			
Negative electrode material	Morphology observation	○	○	
	Element composition analysis	○	○	○
	Element distribution analysis	○	○	○
	Carbon crystallization analysis	○		
Separator	Morphology observation	○	○	○
	Element composition analysis	○	○	○
	Chemical structure analysis			
	Thermal degradation mechanism			
Electrolyte	Component / Impurity analysis			
	Examination of diffusion coefficient			
Fabrication atmosphere gas	Gas composition analysis			
	Continuous monitoring			
Overall	Defect failure analysis	○	○	○

JEOL Instruments Best Suited to Lithium Ion Battery Analysis Tasks

Here, we introduce the features and application examples for the representative instruments in the JEOL line up for the LIB analyses and evaluations. The table indicates the instruments suited to each of various tasks, including those that were not introduced in previous sections.

For more detailed information, please refer to the catalogs, specifications and data sheets for each instrument, or contact a JEOL representative.



Electron Probe Micro Analyzer



X-ray Photoelectron Spectrometer



X-ray Fluorescence Spectrometer



Nuclear Magnetic Resonance Spectrometer

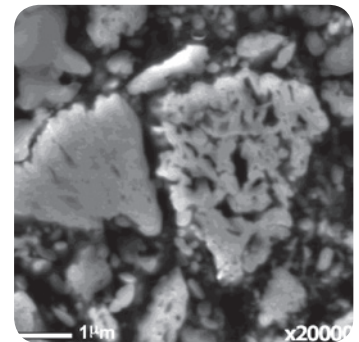
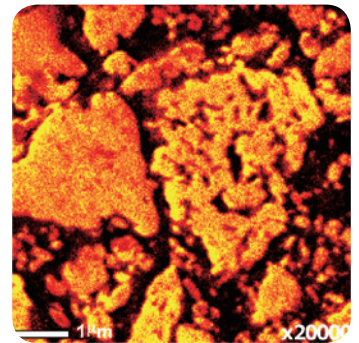
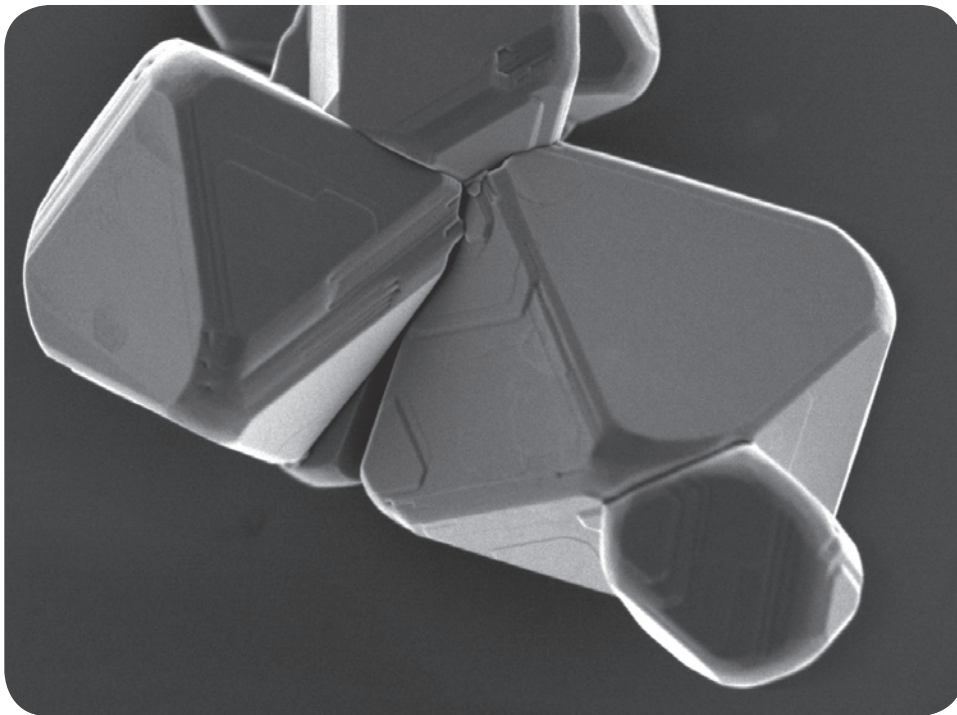


Electron Spin Resonance Spectrometer



Gas Chromatograph Mass Spectrometer

EPMA	XPS	XRF	NMR	ESR	MS
○					
○	○	○			
○	○				
				○	
○	○				
	○				
○	○		○		
			○		
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○					



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