

# 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



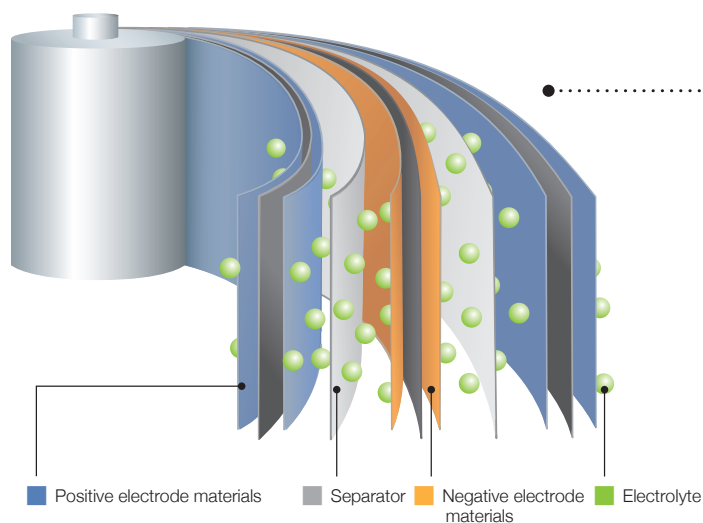
## Introduction

The applications for lithium ion batteries (LIB) cover a wide range, from power sources for personal computers and mobile devices to automobiles, and there is always a demand for even better performance and safety. In order to ensure the performance and quality of LIB, analysis and evaluation using high-performance assessment systems is necessary. JEOL offers a full line-up of equipment to support the development of new LIB technologies and to improve product quality, including instruments for morphology observation and surface analysis, chemical analysis systems to perform structural analysis on a molecular level, as well as fabrication 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 application.

## INDEX

Introduction	P01
Lithium Ion Battery Basic Structure & Fabrication Process	P02
<hr/>	
1.Morphology Observation & Surface Analysis Instruments	
1-1. Features to Consider for Instrument Selection	P03
1-2. XRF: X-ray Fluorescence Spectrometer	P04
1-3. XPS: X-ray Photoelectron Spectrometer	P05
1-4. EPMA: Electron Probe Micro Analyzer	P07
1-5. AES: Auger Electron Spectrometer	P09
1-6. SEM: Scanning Electron Microscope	P11
1-7. TEM: Transmission Electron Microscope	P17
1-8. CP: Specimen Preparation Equipment: Air Isolation & Cooling CP, FIB	P18
<hr/>	
2.Chemical Analysis Instruments	
2-1. GC-MS: Gas Chromatograph Mass Spectrometer	P20
2-2. NMR: Nuclear Magnetic Resonance Spectrometer	P21
<hr/>	
3.Fabrication Systems	
3-1. Roll to Roll Electron Beam Deposition Systems	P23
3-2. RF Induction Thermal Plasma System for Nano Particle Synthesis	P24
<hr/>	
Conclusion      Analysis Item and Applicable Instruments	P25

# Lithium Ion Battery Basic Structure & Fabrication Process

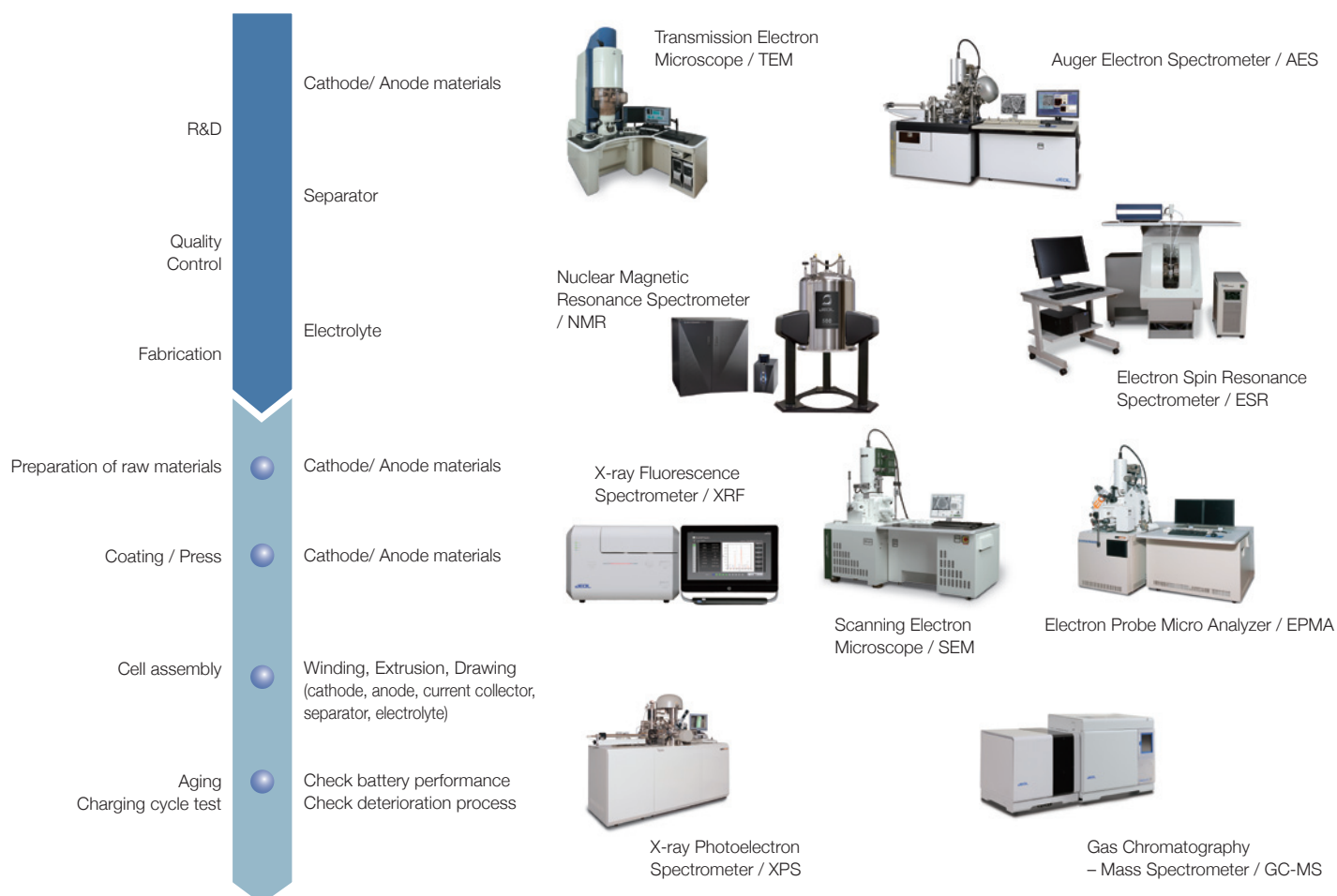


The basic structure of LIB consists of various components, as shown in the figure on the left.

These components have a variety of formats, powders, sheets, fluids, and there are different items to assess for the various material evaluations. It is also necessary to make assessments after assembly, and after repeating the charge/ discharge operations.

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

JEOL offers analytic instrument solutions for each process

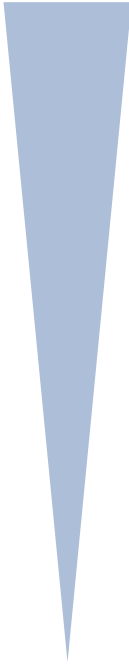








# 1. Morphology Observation & Surface Analysis Instruments

## 1 - 1 Features to Consider for Instrument Selection

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

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

	Instrument	Features
 <p>Micro scale</p> <p>Nano scale</p>	 XRF : X-ray Fluorescence Spectrometer	Suitable for rapid <u>specimen average composition analysis</u> (just a few minutes to obtain a result, including sampling and measurement). Measurements are possible for 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 cathode materials.
	 XPS : X-ray Photoelectron Spectrometer	Li is observable. <u>An ideal system for chemical bonding state analysis of the sample surface</u> . Chemical state analysis of the electrode interface is possible using Depth Profile.
	 EPMA : Electron Probe Micro Analyzer	<u>Multi-channel WDS allows micro area element analysis with a high energy resolution</u> . Secondary electron images and backscattered electron images make it possible to observe the surface morphology.
	 AES : Auger Electron Spectrometer	<u>Li is observable</u> . Depth profiling and <u>chemical bonding state analysis as well as surface analysis for micro area is possible</u> . 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 nano-level with low accelerating voltages. Available attachments include EDS and WDS, enabling element analysis.
	 TEM : Transmission Electron Microscope	Offers structural analysis <u>at atomic resolution</u> , element analysis with EDS, and chemical state analysis using EELS (a thin film specimen is required) <u>Can directly detect Li with EELS</u>
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 formats	Resolution guideline	Element analysis function			
						Analysis depth	Detectable element range	Energy resolution	Detection concentration limit <sup>*3</sup>
XRF	Vacuum <u>Normal atmosphere</u>	X-ray	Fluorescent X-ray	Bulk <u>Fluids</u>	1 to 12 mm $\Phi$ (analysis area)	1 mm <sup>*3</sup>	Na to U	About 150 eV (Mn K $\alpha$ )	Several ppm or more
XPS	Vacuum	X-ray	Photoelectron	Bulk	30 $\mu$ m to a few mm (analysis area)	6 nm	Li to U	About 0.1 eV	About 0.1% or more
EPMA	Vacuum	Electron beam	Secondary electron Backscattered electron Characteristic X-ray	Bulk	0.1 to 1 $\mu$ m <sup>*1</sup>	1 $\mu$ m	Be to U <sup>*2</sup>	About 10 eV	Tens of 10 ppm or more
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 % or more
SEM	Vacuum	Electron beam	Secondary electron Backscattered electron Characteristic X-ray	Bulk	1.2 nm or more <sup>*1</sup>	1 $\mu$ m	100 nm B to U	About 130 eV	About 0.1 % or more
							100 nm B to U	About 10 eV	Tens of 10 ppm or more
TEM	Vacuum	Electron beam	Transmission electron Characteristic X-ray	<u>Thin film</u>	0.1 nm or more <sup>*1</sup>	100 nm (sample thickness)	100 nm B to U	About 130 eV	About 0.1 % or more
							100 nm H to U	1.0 eV (Schottky) <sup>*4</sup> 0.50 eV (Cold-FEG) <sup>*4</sup>	About 0.1 % or more

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



# 1-2 Energy Dispersive X-ray Fluorescence Spectrometer (XRF)

The X-ray fluorescence spectrometer is an instrument for analyzing the types and concentrations of elements in a sample by irradiating the sample with X-ray and measuring the emitted fluorescent X-rays. It is mainly used for applications like assessing grades of steel, controlling product quality, and RoHS compliance (Cd, Pb, Hg, Cr, Br content). This instrument supports rapid analysis, with an extremely short time required from specimen preparation until a result is obtained.



Element Analyzer

*Excellent for element analysis of trace metals!*

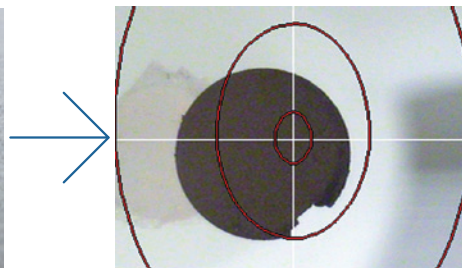
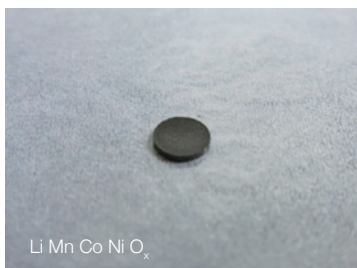
## Features

- Analysis elements: Na to U
- Analysis region: 1 to 12 mm $\phi$
- Specimen form: solid, powder, liquid
- Non-destructive analysis
- Detection lower limit: from several ppm

## Analysis example

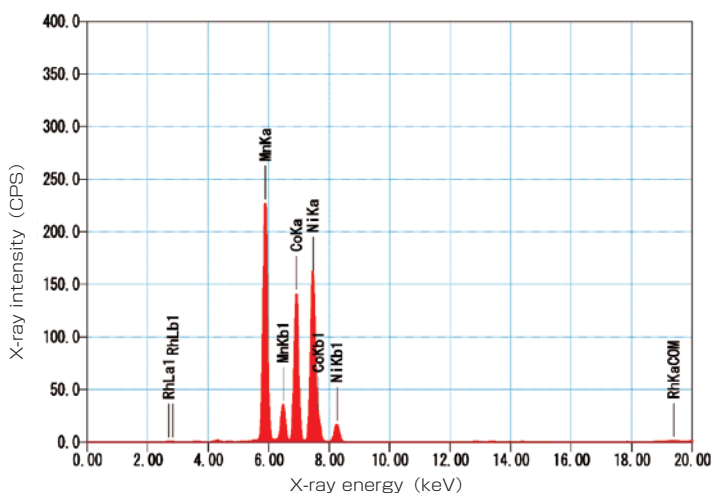
### Positive electrode material analysis (tablet of a powder sample)

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 specimen 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 $\phi$   
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

Quantification 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 the advantage of being able to analyze surface-sensitive solids with high energy resolution. 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.



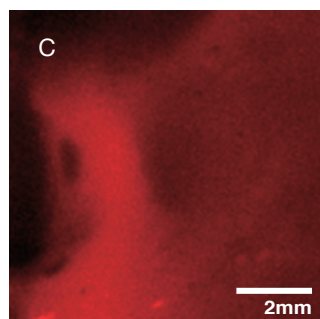
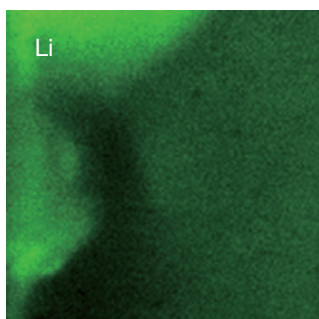
### Direct detection of Li !

#### 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

### Analysis example

### Photoelectron image, Analysis of chemical bonding state



#### • Li-ion battery cathode photo electron image (left)

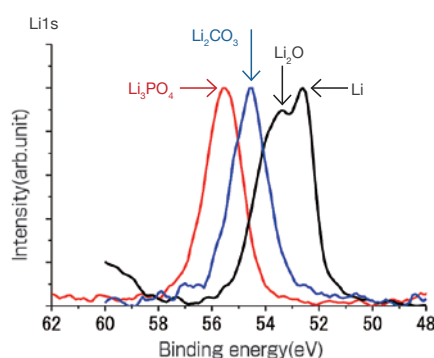
The stage scanning method makes it possible to acquire wide images of up to 50 mm x 18 mm. Performing photoelectron imaging is useful for identifying locations with different wettability due to differences in the chemical bonding state or sample contamination that cannot be determined from optical information.

#### • Identification of bonding state based on peak position differences

Since peak position differences occur due to variations in the chemical bonding state, it is possible to identify the chemical bonding state of the Li by interpreting the peak positions.



Metallic lithium



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

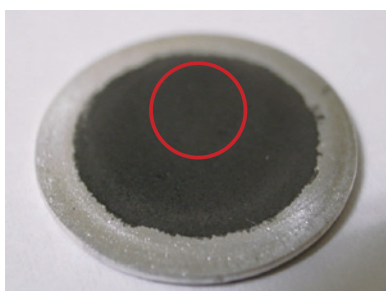
Standard sample

## Analysis example

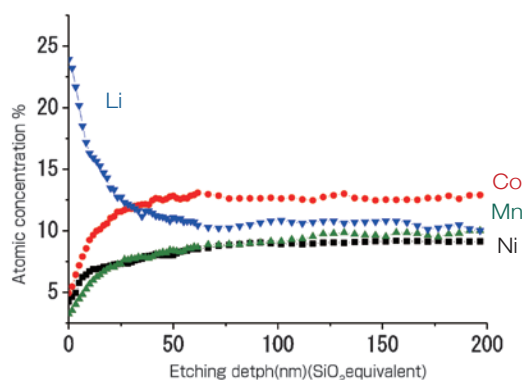
### Depth profile analysis of negative electrode material after charge/discharge

#### • 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 a region of about 30 nm on the surface, as shown in the graph on the right.

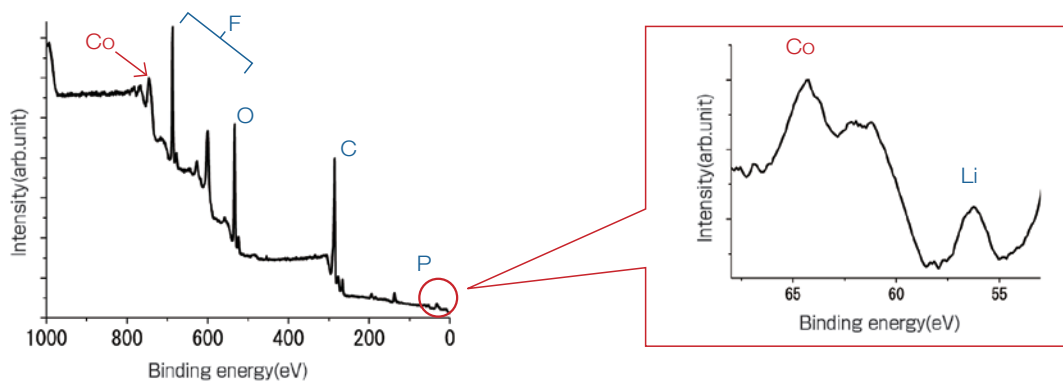


Analysis region : 1 mm  $\phi$

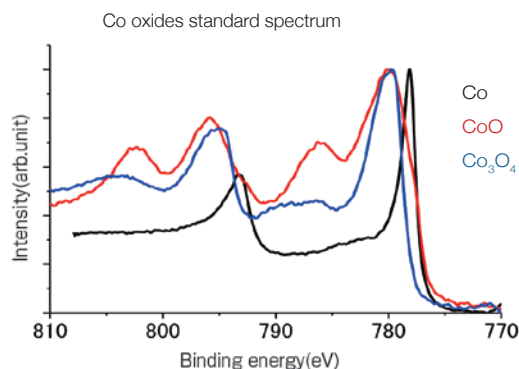
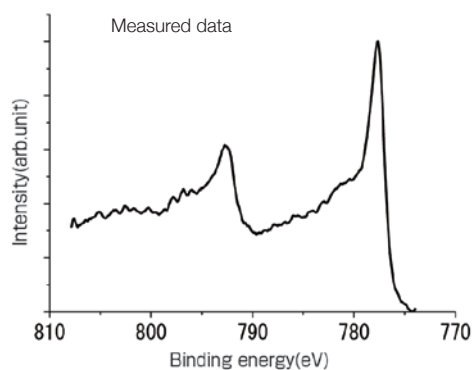


#### • Analysis of negative electrode material after charging/discharge cycle

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 simple 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 ionized, migrated to the negative electrode, and precipitated as metallic Co.



## 1-4 Electron Probe Micro Analyzer (EPMA)

EPMA using 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.

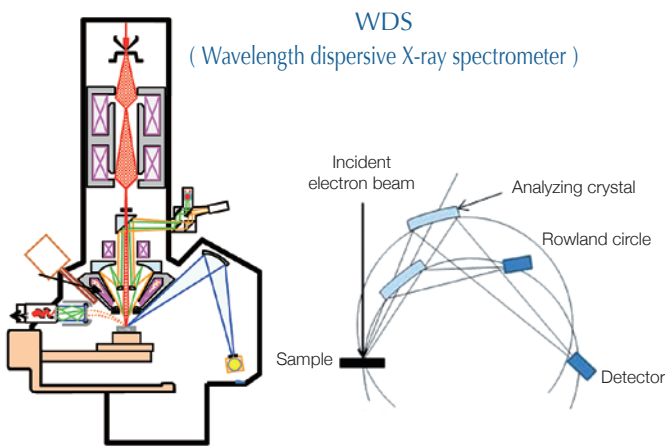


JXA-8530F

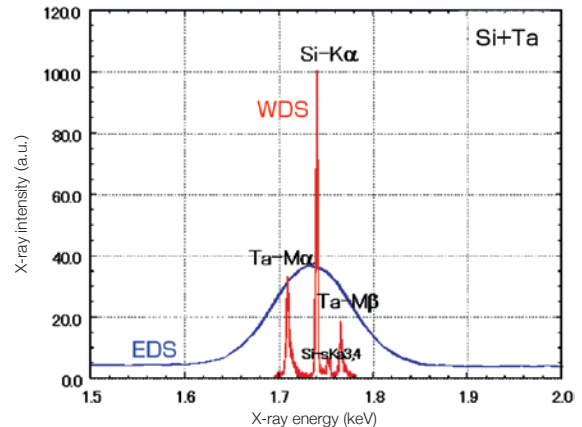
### Features

- Wavelength dispersive spectrometer (WDS), Max. 5ch
- Analysis elements: (Be) B to U
- Analysis region: several  $\mu\text{m}$  to several cm
- Analysis depth: up to about  $1\ \mu\text{m}$
- Detection lower limit: several 10 ppm

### Comparison of WDS and EDS

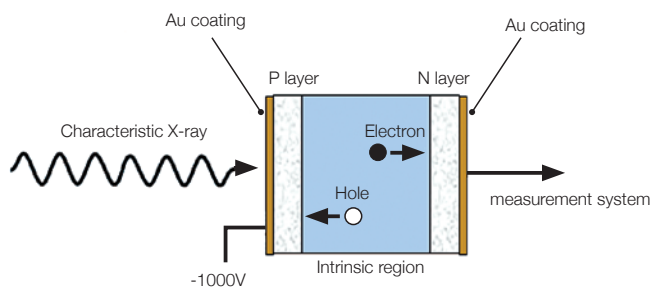


WDS principles



WDS-EDS spectra comparison

### EDS (Energy dispersive X-ray spectrometer)



EDS principles

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.

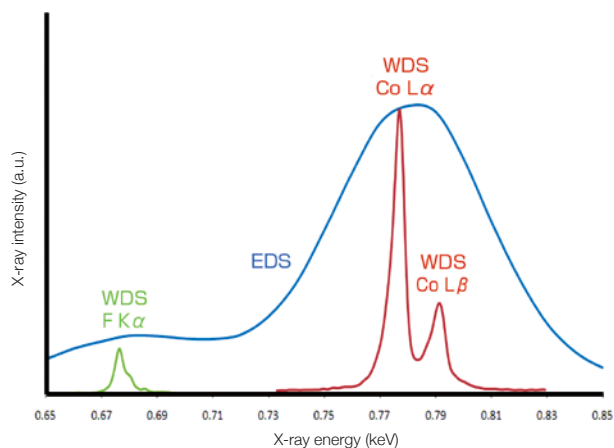
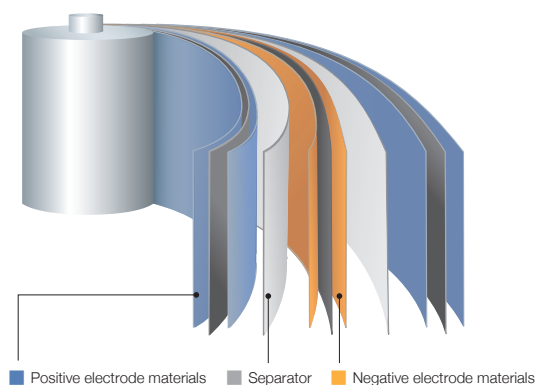
The figure on the above right shows a comparison of the EDS and WDS analyses of Si oxides and Ta oxides in multi-layer films. The Si and Ta peaks are overlapped in the EDS spectrum, but are separated in the WDS spectrum, demonstrating the high energy resolution attainable with WDS.



### Analysis example

### Qualitative analysis of positive electrode materials, Wide region 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 has a low energy resolution and a high background level, and the F-K $\alpha$  line is influenced by the Co, so the peak is difficult to detect. With WDS, there is no Co-L $\alpha$  line effect, and the F-K $\alpha$  line can be detected.

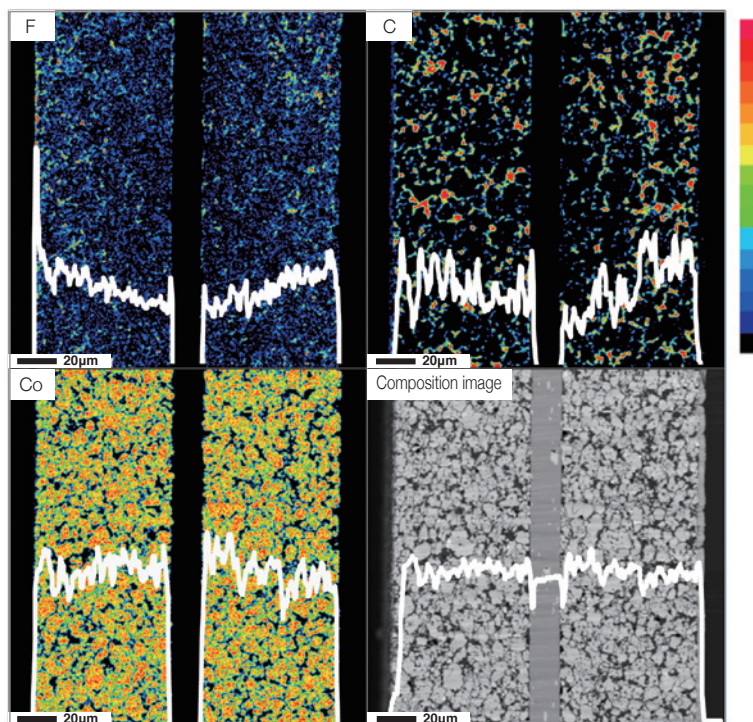


The images on the right show an example of element mapping with WDS for a cross section of Li-ion battery positive electrode material through repeated charge/discharge cycles. The signal intensity of the F and C that have migrated from the collector (Al) in the center portion increases.

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 be one of the factors in 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, are one way 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

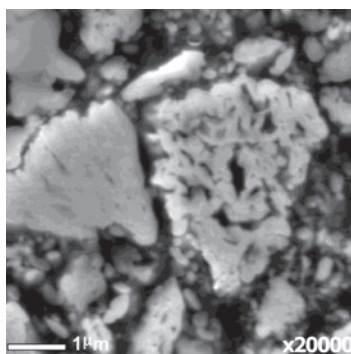
- High spatial resolution of Auger analysis: 8 nm
- Variable energy resolution: From 0.05 % to 0.6 %
- Analysis range: Up to 95 mm $\Phi$  with the large stage
- Insulating materials can be analyzed using the neutralizing gun and sample tilting method
- Wide range of options (BEI, EBSD etc.)
- Depth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

### Li sensitivity

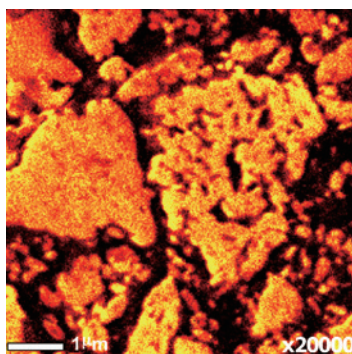
Because the JAMP-9510F uses a concentric hemispherical electrostatic analyzer, it is possible to obtain peaks even in low energy regions, such as those of Li, with high precision, high sensitivity and high energy resolution. The figure on the right below shows the results of measurements with the JAMP-9510F for standard samples of Li, Li<sub>2</sub>O, and Li<sub>2</sub>CO<sub>3</sub>. This clearly illustrates the changes in the peak position and shape for each of the different chemical bonding states.

#### • Auger map of Li within the positive electrode material particles

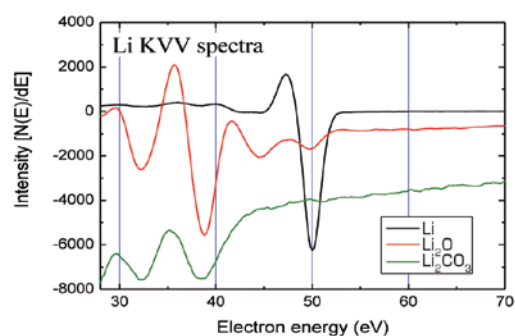
Since the Auger Electron Spectrometer uses an electron beam as the excitation source, it is possible to acquire element maps for micro areas corresponding to the secondary electron images and backscattered electron images.



SEI



Li



## Comparison with other analysis methods (Li sensitivity, quantification)

### • Li sensitivity

The Li sensitivity with Auger Electron Spectrometry (AES) is higher than that of X-ray photoelectron spectrometry (XPS). Assuming that the C sensitivity is about the same for AES and XPS, using the C peak as the base line, and comparing the peak intensities for metallic Li, the peaks from AES are 70 times higher than those from XPS.

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

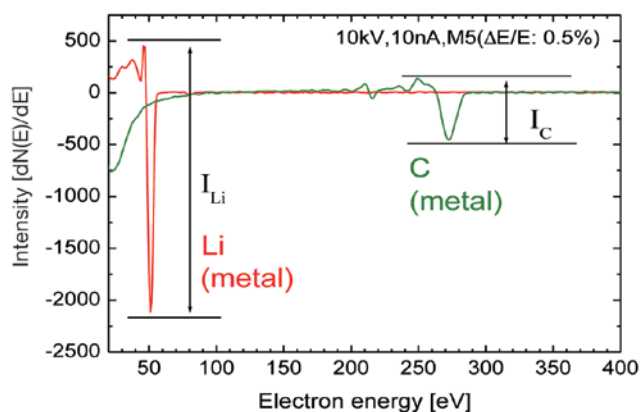
X-ray : Al K $\alpha$  (1487 eV)

	Z	1s1/2
H	1	0.0002
He	2	0.0082
Li	3	0.0568
Be	4	0.1947
B	5	0.486
C	6	1.000
N	7	1.80
O	8	2.93
F	9	4.43
Ne	10	6.30

(Ref : J.Electron Spec, Relat.Phenom,8,129(1976))

$I_{\text{Li}} / I_{\text{C}} \approx 1/18$   
(Li sensitivity is about 1/18 that of C)

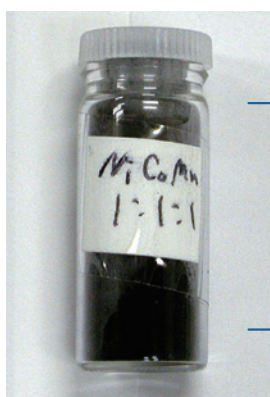
Comparison of peak intensities of Li and C measured with the same conditions using AES



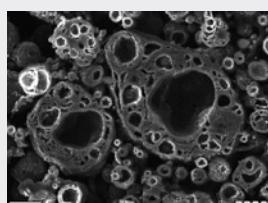
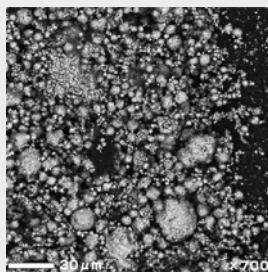
$I_{\text{Li}} / I_{\text{C}} \approx 4$   
(Li sensitivity is about 4 times greater than C)

### • Comparison with quantification values from other methods

The quantitative analysis results from various methods using positive electrode material particles containing Li (NMC particles) as the specimen are shown in the table below. Even for analysis from the surface, and analysis of a CP cross-section, comparing the results from the other methods to the values for the absolute intensity quantification from AES, shows that there is a difference of a few percent, and that comparable quantitative accuracy is obtained.



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



Surface analysis	Standardized atomic concentrations, excluding carbon				
	Li	O	Mn	Co	Ni
AES (average of 50 $\mu\text{m}\Phi$ )	19.6	55.0	8.5	8.5	8.4
XPS (average of 3 mm $\Phi$ )	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 tracking minute changes in the structure of electrode materials as the charge/discharge 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-7800F, a high-end model SEM. The JSM-7800F 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 Gentle Beam mode for high-resolution image acquisition with a bias voltage applied to the specimen, and also various types of detectors.



JSM-7800F

### Features

- In-lens Schottky electron gun
- Super Hybrid Lens (SHL) and TTL detector
- Specimen bias (Gentle Beam (GB)) function
- Wide range of options (EDS, WDS, EBSD, etc.)

### Arrangement of detectors

#### · Various types of detectors

The figure below shows the arrangement of the detectors that are incorporated in the JSM-7800F. 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.

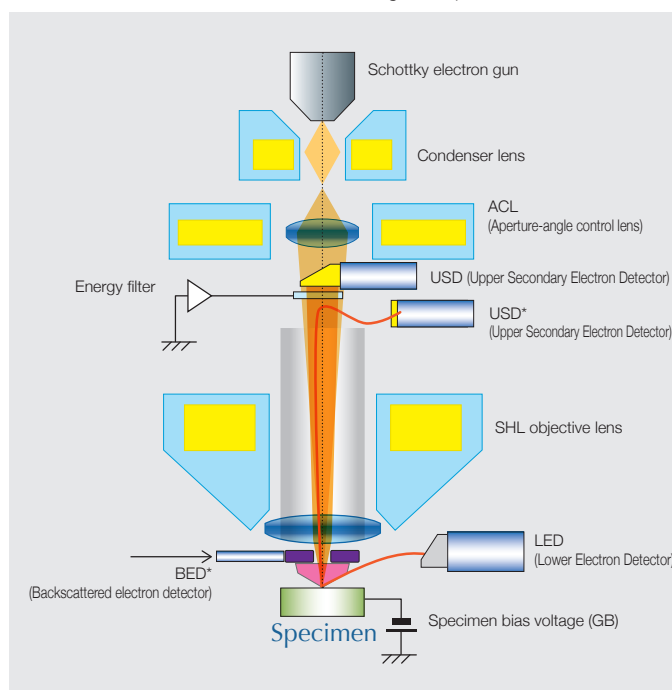
#### LED ( Lower Electron Detector )

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.

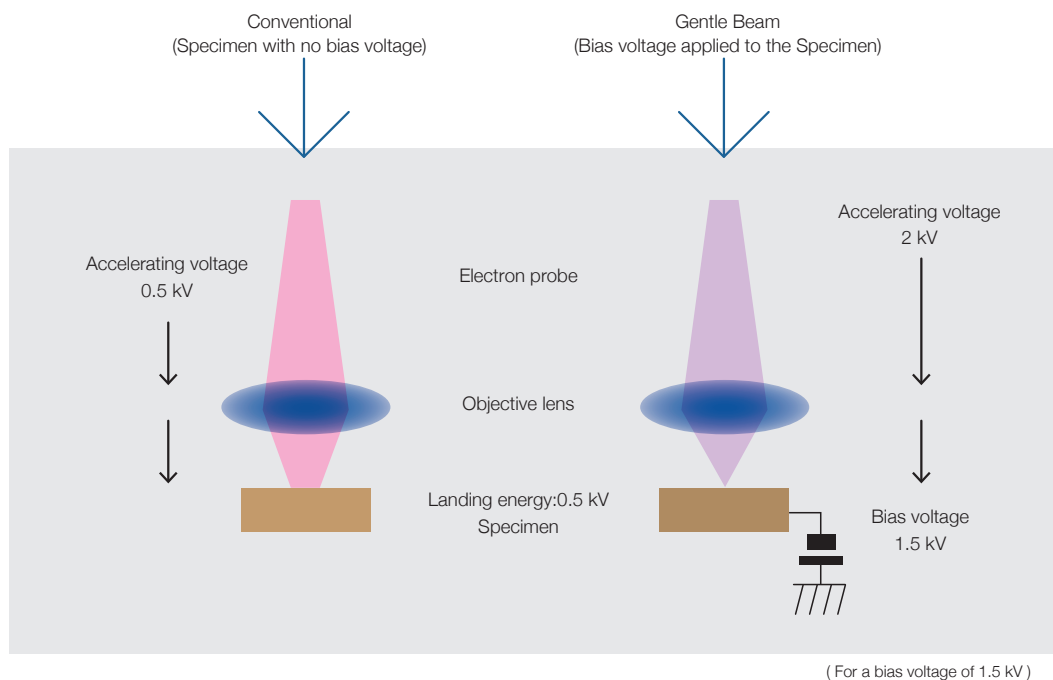
JSM-7800F structural diagram \*Option



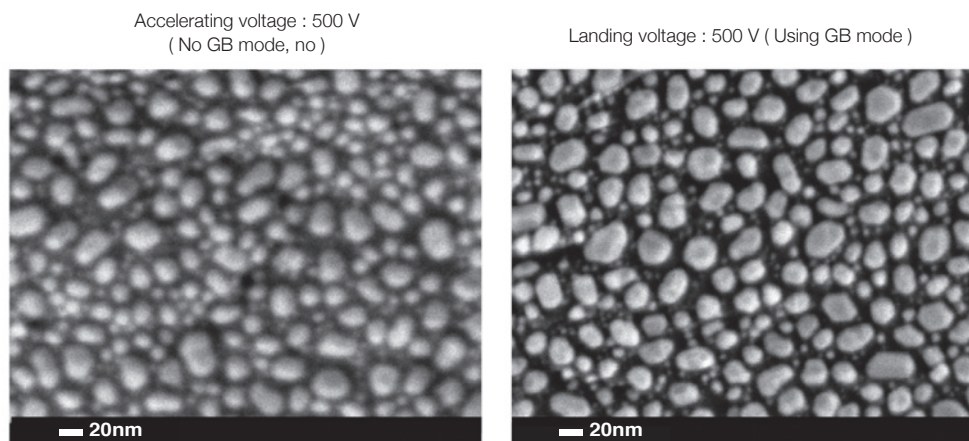


## Principles of Gentle Beam mode (GB)

In the Gentle Beam (GB) mode when the electron probe with a high accelerating voltage passes through the objective lens, the landing energy of the electron probe on the specimen is reduced by a bias voltage that is applied to the specimen. This is an effective method for obtaining high resolution with extremely low accelerating voltages.



A comparison of the resolution with a low accelerating voltage for a conventional sample without any bias voltage (left) and for the GB mode (right) is shown. 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.



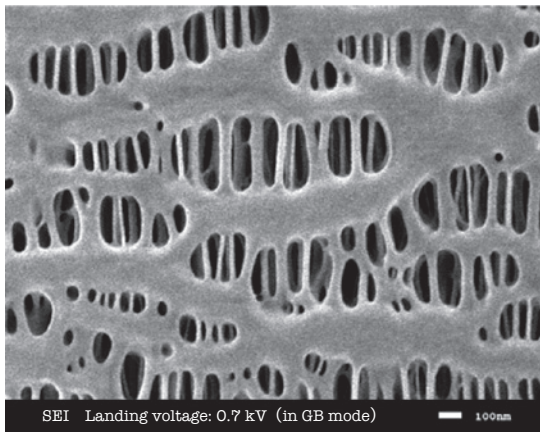
Specimen : Gold particles on carbon

# 1-6 Scanning Electron Microscope (SEM)

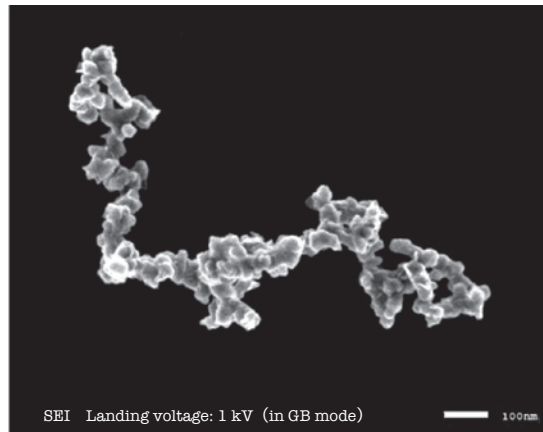
Observation  
example

### Observation of battery materials

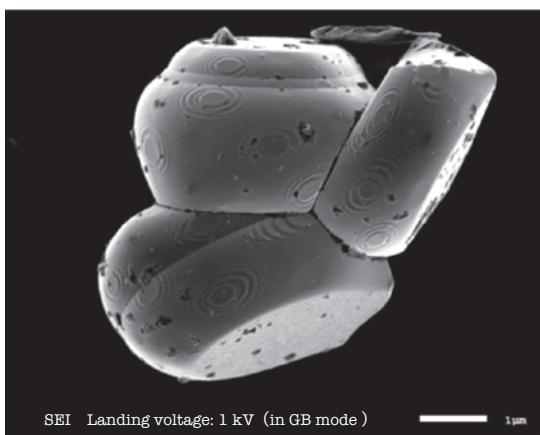
SEM is highly suitable for observing the morphology of various types of battery materials. Several examples are shown below.



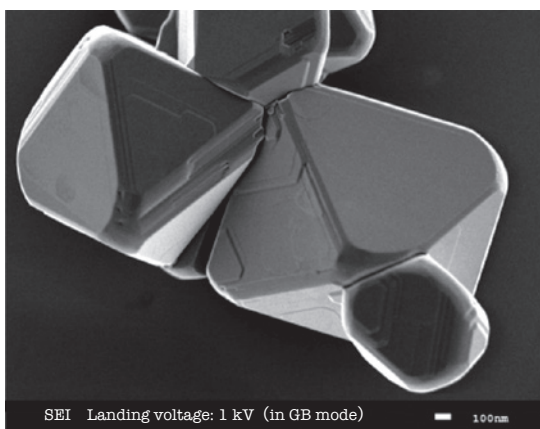
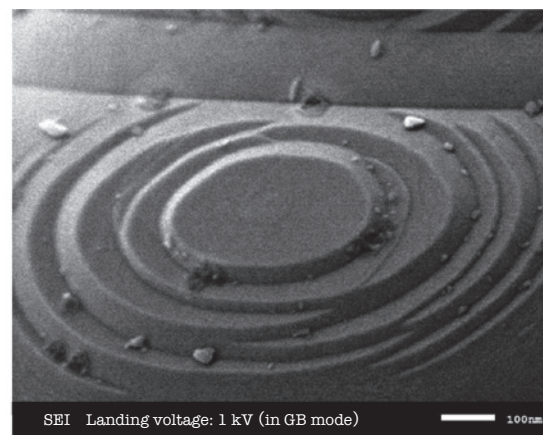
Separator ( polyethylene )



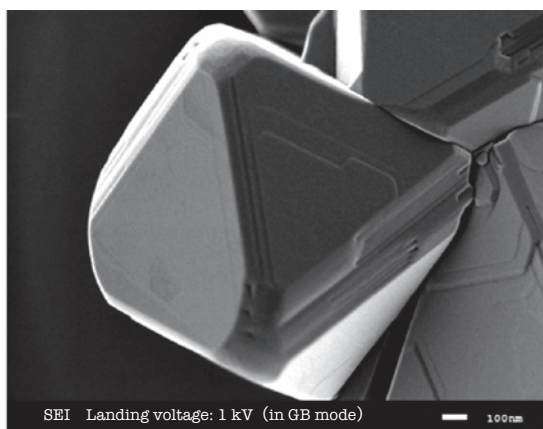
Conductive additive ( Acetylene black )



Cathode active material :  $\text{LiCoO}_2$



Cathode active material :  $\text{LiMn}_2\text{O}_4$  ( Spinel )



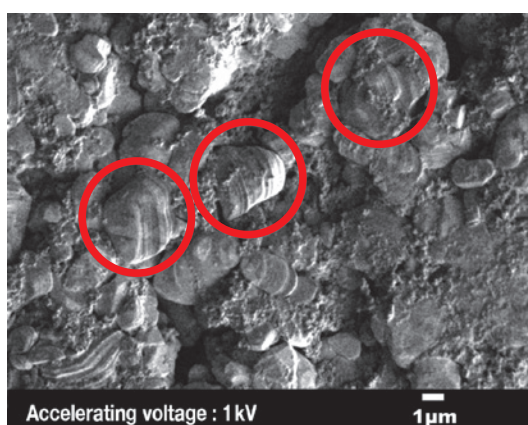
## Observation example

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

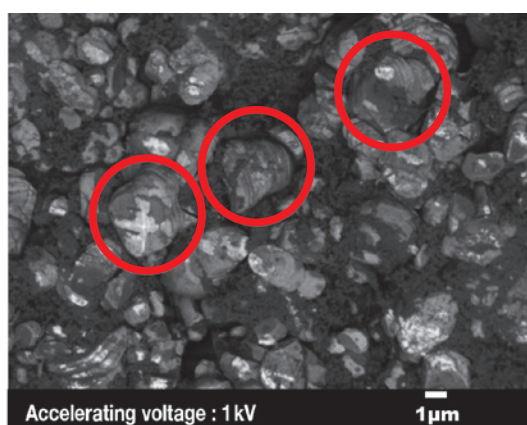
#### • Li ion battery positive electrode material

(Simultaneous acquisition of surface topography and composition information using a low accelerating voltage)

With the JSM-7800F, it is possible to acquire a variety of information about the surface of a specimen by selectively using the various detectors. The two photos 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)



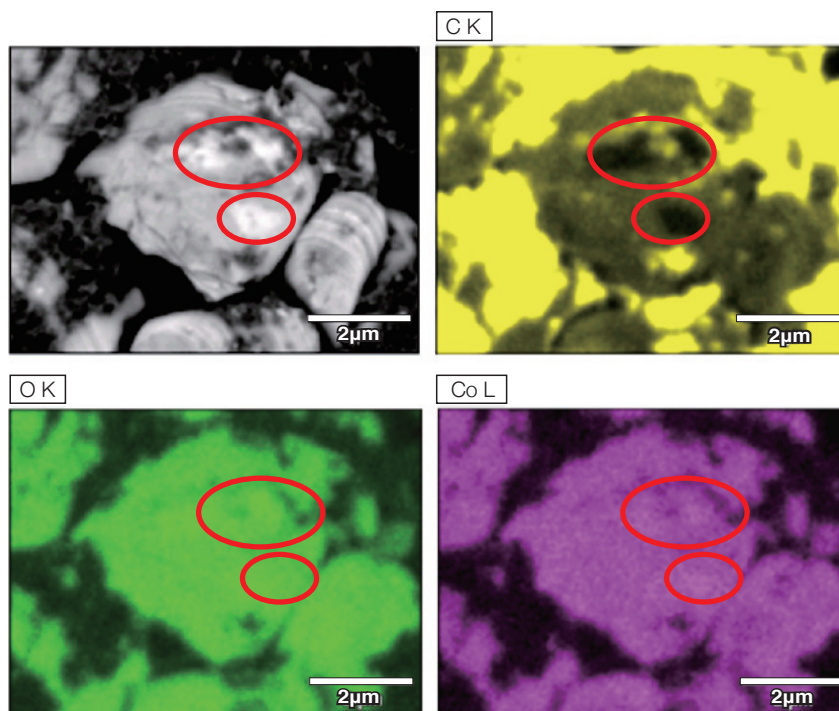
UED: Composition information

#### • EDS analysis with low

#### accelerating voltage

The photo on the right shows an example of EDS analysis of the surface of a positive electrode material for Li ion batteries at a low accelerating voltage of 1 kV. It is possible to observe 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-7800F can deliver a sufficient probe current (15 nA) for EDS analysis. This is quite useful for both image observation and EDS analysis.



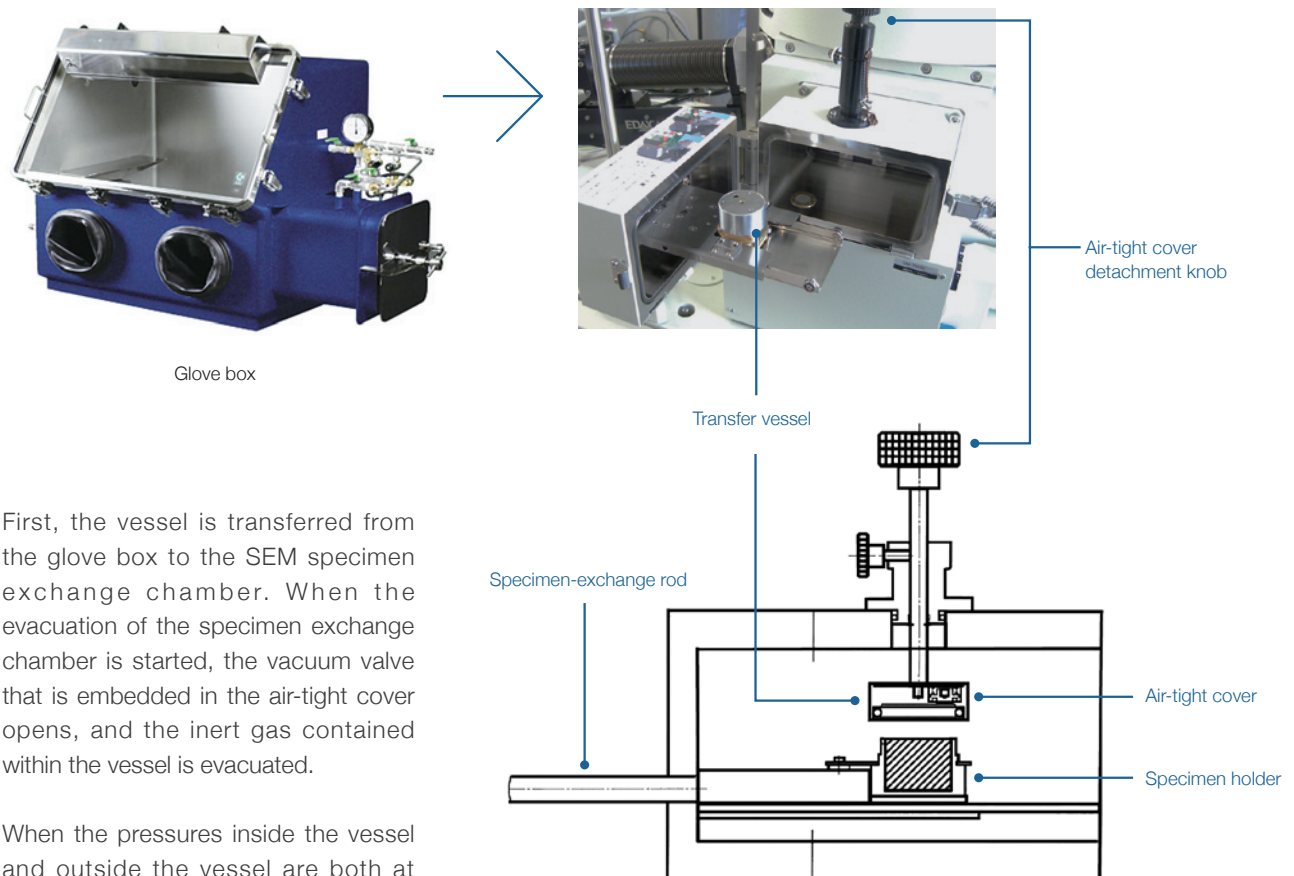
Sample : Li-ion battery cathode material ( V<sub>acc</sub>: 1kV, Probe current: 15 nA )



## 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.

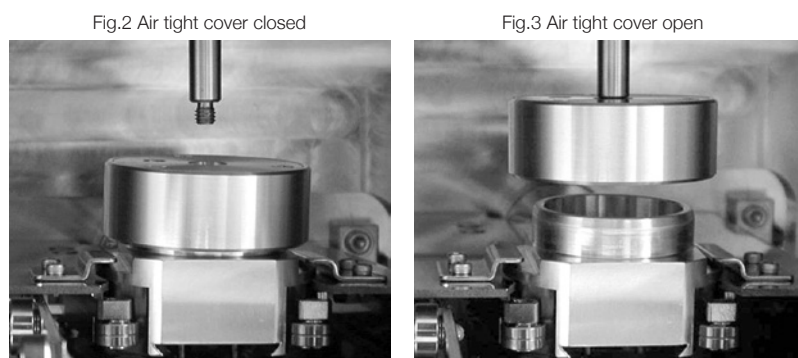


First, the vessel is transferred from the glove box to the SEM specimen exchange chamber. When the evacuation of the specimen exchange chamber is started, the vacuum valve that is embedded in the air-tight cover opens, and the inert gas contained within the vessel is evacuated.

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.

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



Specimen size :  $\Phi 25.4$  mm X 20 mm h



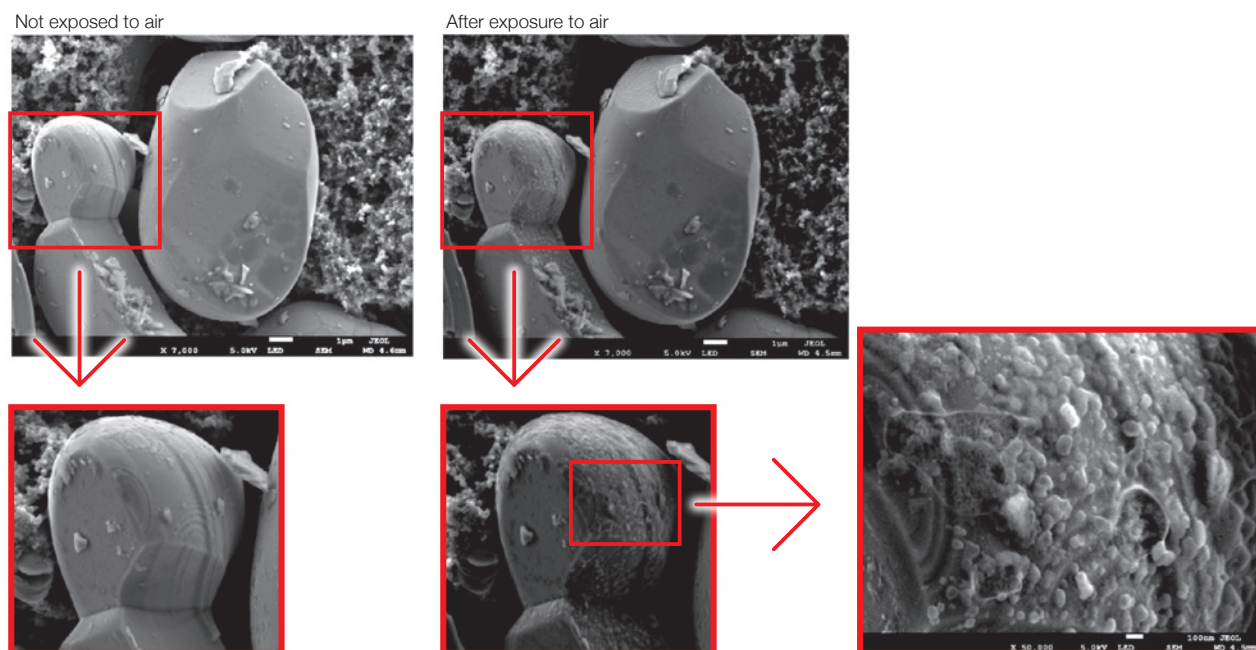
## Effect of Preventing Air Exposure using the Transfer Vessel

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  $\text{LiCoO}_2$  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.

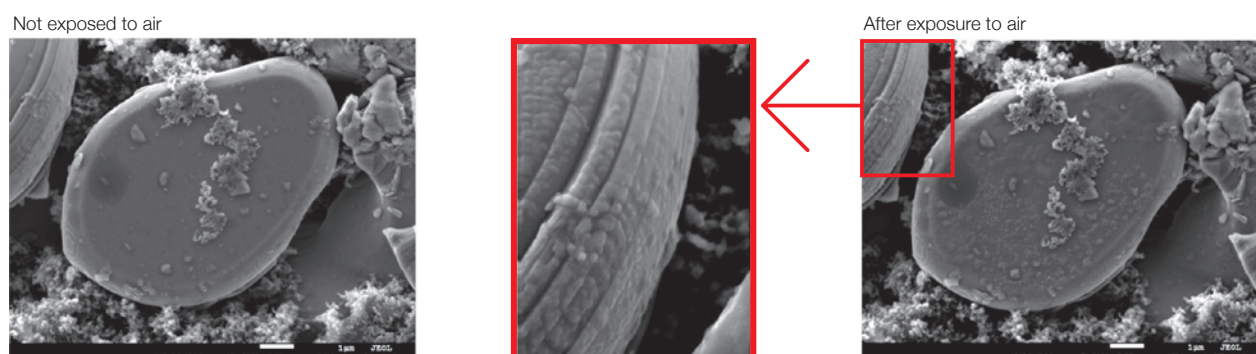
### • Battery that has never been charged

Deposits that are not observed on the  $\text{LiCoO}_2$  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, deposits appear across the surface of the  $\text{LiCoO}_2$  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 table below shows the main performance of the JEM-ARM200F.

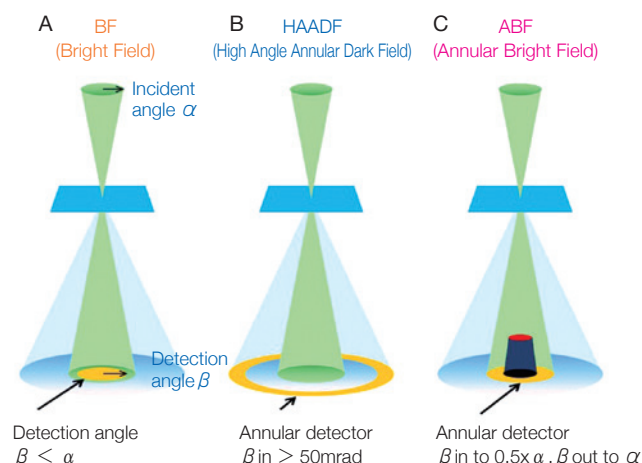


JEM-ARM200F external appearance

Pole piece type	URP	HRP
Guaranteed resolution:	82 $\mu\text{m}$	100 $\mu\text{m}$
STEM-HAADF images	78 $\mu\text{m}$ (with CFEG)	100 $\mu\text{m}$ (with CFEG)
TEM image (point-to-point)	110 $\mu\text{m}$	120 $\mu\text{m}$
With aberration corrector	100 $\mu\text{m}$ (with CFEG)	120 $\mu\text{m}$ (with CFEG)
Solid angle (EDS) (*With 100 mm <sup>2</sup> SDD mounted)	0.8 sr	0.98 sr

## Observation example

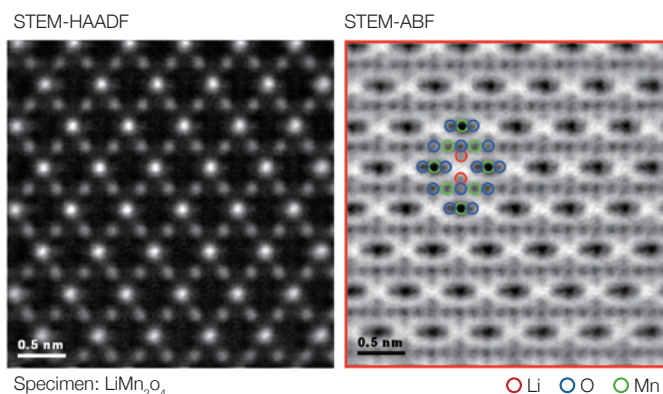
### Li column observation using ABF



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  $\text{LiMn}_2\text{O}_4$  positive electrode materials for a lithium-ion battery obtained with the JEM-ARM200F. 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.



# 1-8 Specimen Preparation Equipment: Air Isolation & Cooling Cross Section Polisher

We introduce a cross section polisher IB-19510 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.



Air Isolation + Cooling Cross Section Polisher



Transfer vessel

## Features .....

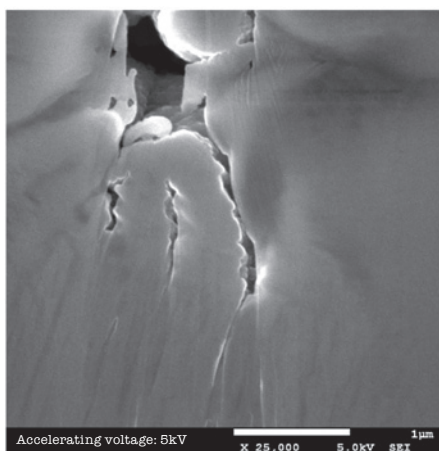
- Special transfer vessel can be used to transfer a specimen between a glove box, CP and SEM without exposure to the air
- Cooling the specimen during ion milling reduces thermal damage
- Thermal damage can also be reduced by using intermittent milling

## Observation example

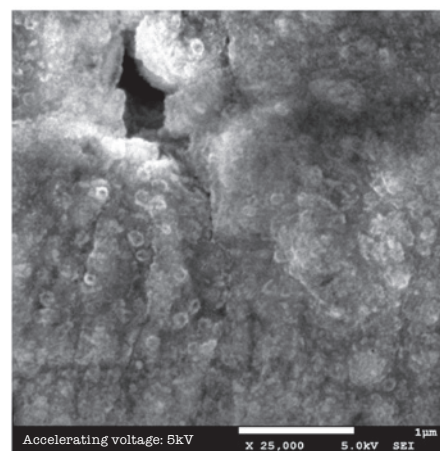
### Metallic lithium processing and observation

#### • Processing without exposure to air and the effects

The photo 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.



### Features

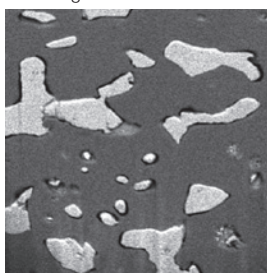
- For SEM, a Schottky electron gun (JIB-4601F) and the LaB<sub>6</sub> (JIB-4501F) are available
- Supporting not only 3D analysis of the morphology, but also EBSD (analysis of crystal orientation) and EDS (element analysis)

### Observation example

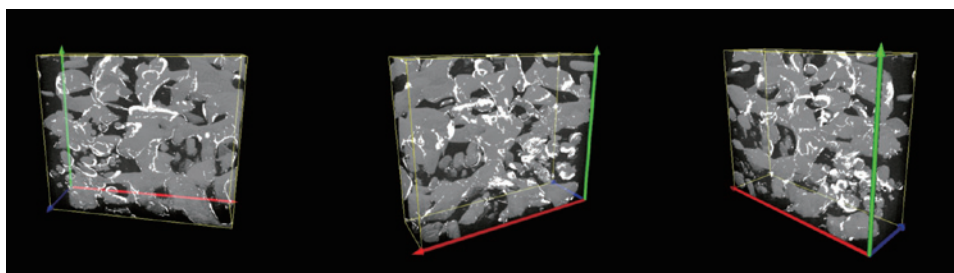
### Solder Cold processing, 3D analysis

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

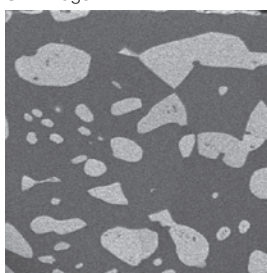


3D reconstruction

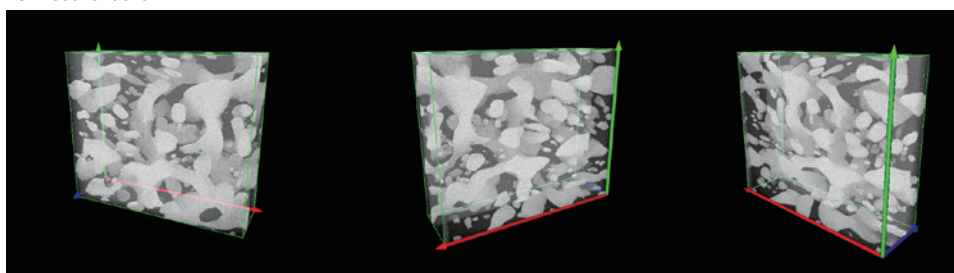


Processing temperature 25°C (Lead portions are gray, voids shown in white)

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).

Organic components in a mixture sample are separated by using a capillary column in the GC and introduced into the MS for mass analysis.

It is highly suited for analyzing a complex mixture of volatile organic compounds and widely used for both qualitative and quantitative analysis.



JMS-Q1500GC

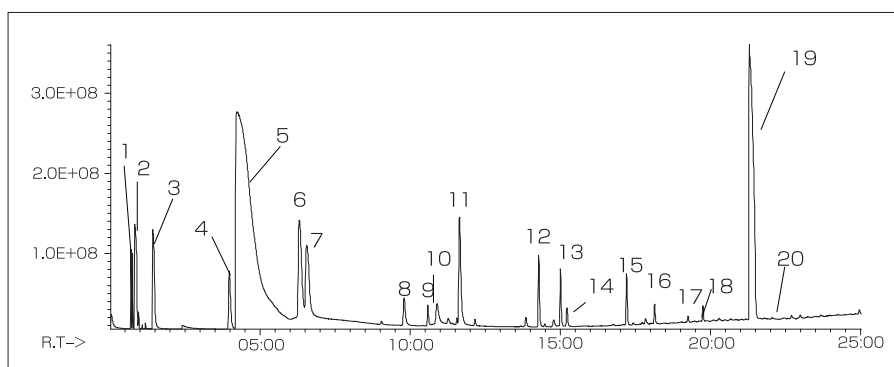
## Features .....

- Supports analysis of volatile and semi-volatile compounds via GC and solids via direct insertion probe (DIP)
- Can use a variety of ionization methods (EI, CI, PI)
- Applications can be expanded by combining other techniques.
  - Thermal analysis : Pyrolyzer and TG/DTA
  - Volatile components in liquids and solids: head space autosampler
  - Odor analysis : GC-Olfactometry-MS

## 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 components of the evolved gas in a over-discharged lithium ion battery cell. Many components have been detected, including ethylene carbonate (EC, Peak No.20) and diethyl carbonate (DEC, Peak No.19), 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 <sub>2</sub> , O <sub>2</sub> )	8	2-fluoropropane	15	Ethyl acetate
2	Methane	9	Methyl formate	16	Hexane
3	Carbon dioxide ( CO <sub>2</sub> )	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 cathode, anode or electrolyte material.

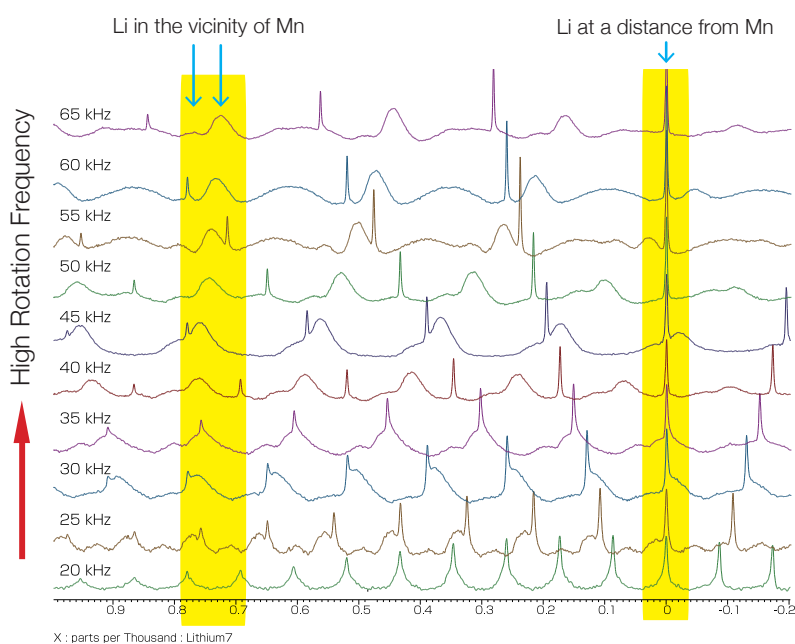


Nuclear Magnetic Resonance spectrometer / JNM-ECZ500R

### Analysis example

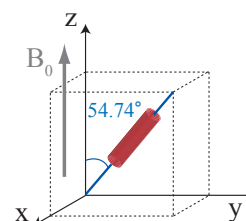
#### Positive electrode material analysis with ultra high-speed MAS measurement

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 ( $54.74^\circ$ ) 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  $^7\text{Li}$  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.



$^7\text{Li}$  spectra of positive electrode material for manganese dioxide lithium battery

#### Magic Angle Spinning



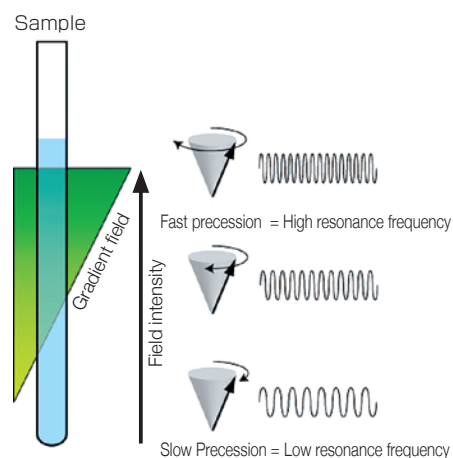
#### Ultra high speed MAS sample tubes



## 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 $^7\text{Li}$ 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.

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

$I$  : Signal intensity

$G$  : Magnetic field gradient strength

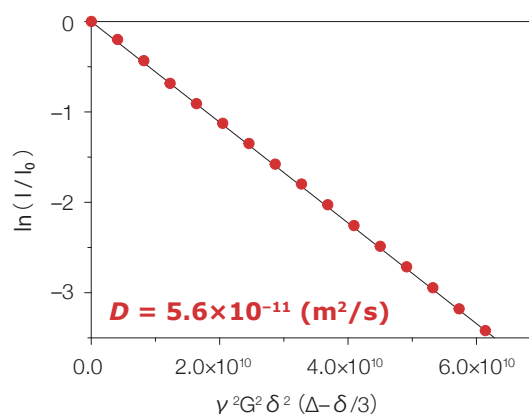
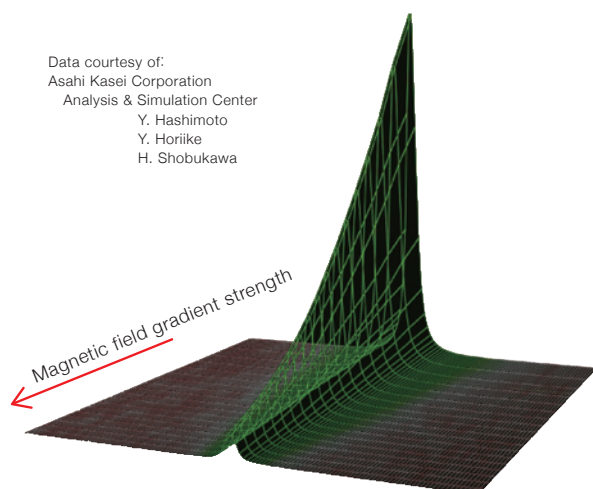
$\Delta$  : Diffusion time

$\gamma$  : Nuclear gyromagnetic ratio

$\delta$  : 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



# 3-1 Roll to Roll Electron Beam Deposition Systems

This instrument can provide 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 with the electron beam heating. Applications include electrode films for lithium-ion batteries.

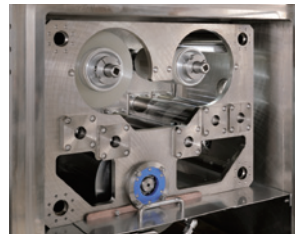
### Features

- 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 rates an order of magnitude higher than those from sputtering or CVD methods.
- The use of a dedicated controller enables co-deposition from 2 or 3 sources.

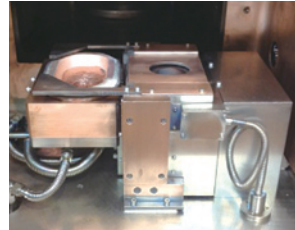


Roll to Roll electron beam deposition system for R&D  
(Made by M-TECHNOLOGIES Corp.)

Roll section



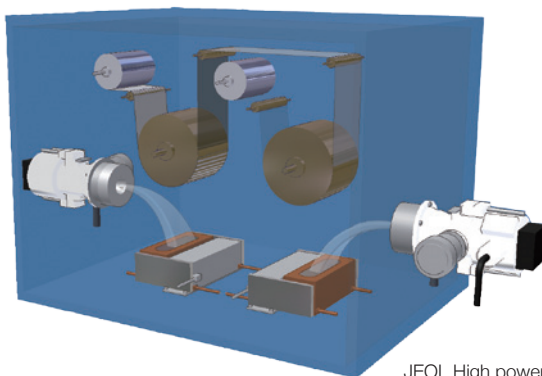
JEOL deflection beam type electron beam source (16 kW)



Copper film deposited onto aluminum foil

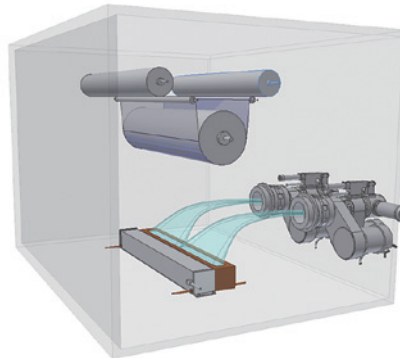


Example of double-side deposition configuration



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

Example of parallel electron beam source configuration



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

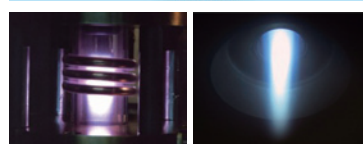
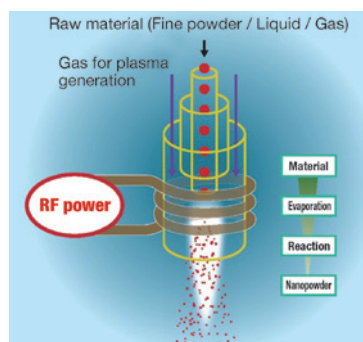
The plasma is generated using high frequency power and an inert gas like Ar to create a plasma state with an ultrahigh temperature of nearly 10,000 degrees, called RF induction thermal plasma.

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 is expected to be useful for processes like complex composition, nanoparticulation and reforming of fine powders for lithium-ion battery electrodes.



6 kW experiment system



Ar plasma

Ar + H<sub>2</sub> plasma

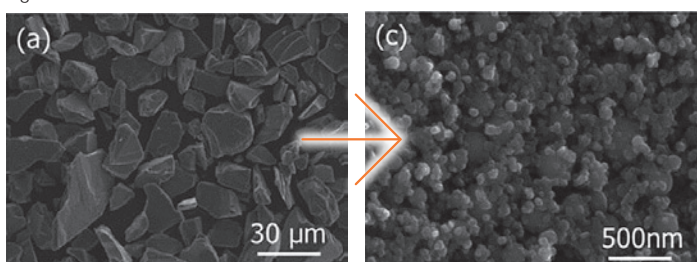
### Features

- 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

Fig.1



### <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.)

Fig.2

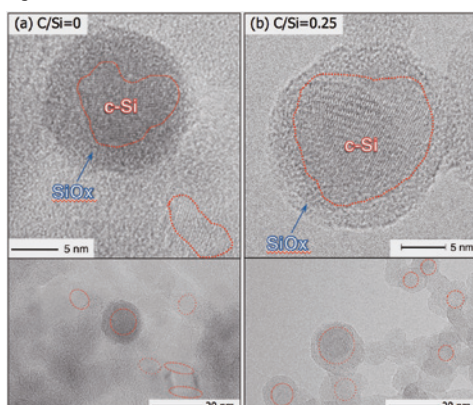
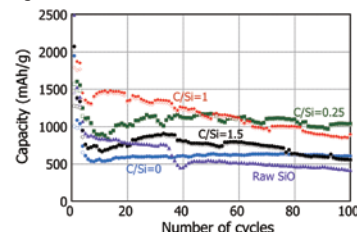
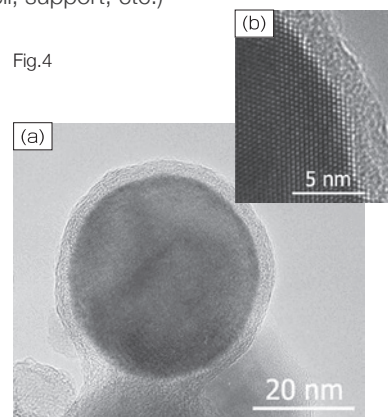


Fig.3



Charge-and-discharge energy density variations depending on CH<sub>4</sub> doped concentrations

Fig.4



Core shell nanoparticle composed of silicon core and carbon shell

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



Transmission Electron  
Microscope



Scanning Electron  
Microscope



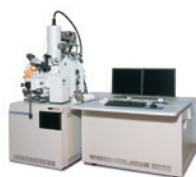
Auger Electron  
Spectrometer

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			
	Assessment 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			
	Thermo degradation mechanism			
Electrolyte	Component / Impurity analysis			
	Assessment of diffusion coefficient			
Fabrication atmosphere gas	Gas composition analysis			
	Continuous monitoring			
General	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

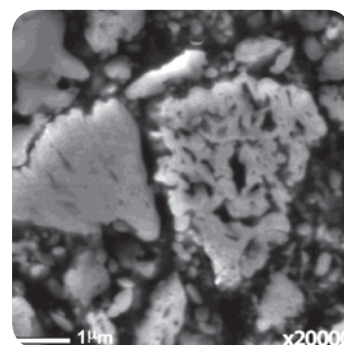
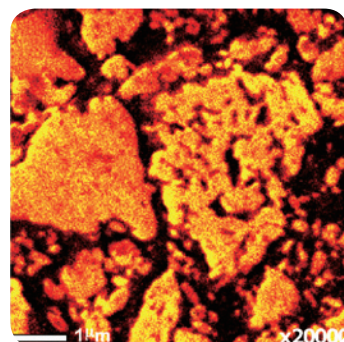
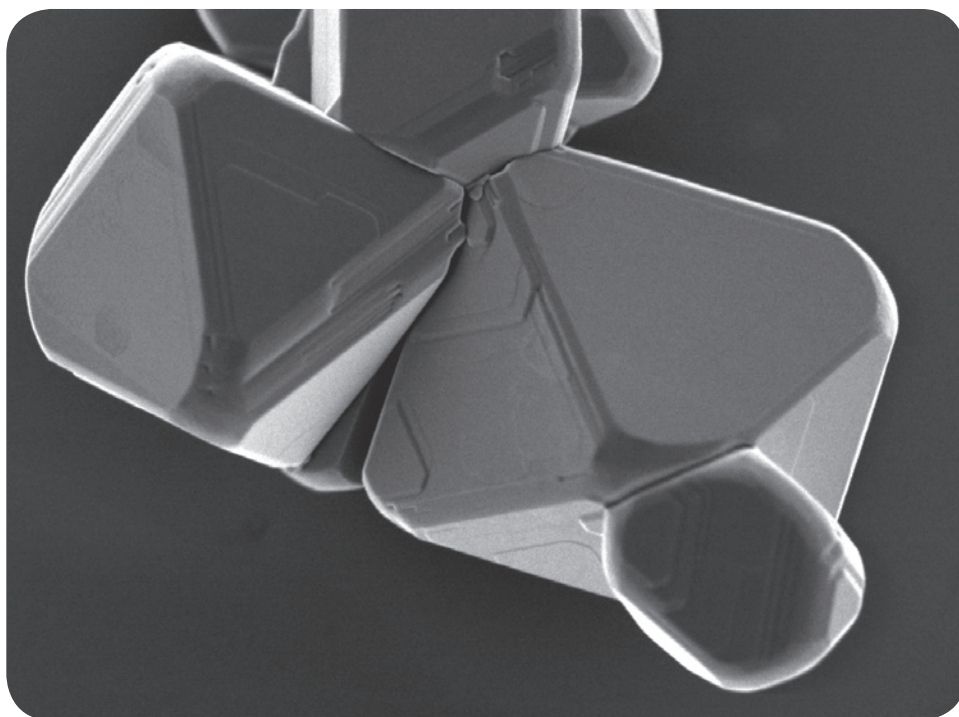


Electron Spin Nuclear Magnetic Resonance



Gas Chromatograph Mass Spectrometer

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



Certain products in this brochure are controlled under the "Foreign Exchange and Foreign Trade Law" of Japan in compliance with international security export control. JEOL Ltd. must provide the Japanese Government with "End-user's Statement of Assurance" and "End-use Certificate" in order to obtain the export license needed for export from Japan. If the product to be exported is in this category, the end user will be asked to fill in these certificate forms.



3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577  
www.jeol.com ISO 9001 • ISO 14001 Certified

• **AUSTRALIA & NEW ZEALAND** /JEOL(AUSTRALASIA) Pty.Ltd, Suite 1, L2 18 Aquatic Drive - Frenchs Forest NSW 2086 Australia • **BELGIUM** /JEOL (EUROPE) B.V. Planet II, Gebouw B Leuvensesteenweg 542, B-1930 Zaventem Belgium • **BRAZIL** /JEOL Brasil Instrumentos Científicos Ltda. Av. Jabaquara, 2958 5º andar conjunto 52 ; 04046-500 Sao Paulo, SP Brazil • **CANADA** /JEOL CANADA, INC. 3275 1ere Rue, Local #8 St-Hubert, QC J3Y-8Y6, Canada • **CHINA** /JEOL(BEIJING) CO., LTD. Zhongkeziyuan Building South Tower 2F, Zhongguancun Nansanjie Street No. 6, Haidian District, Beijing, P.R.China • **EGYPT** /JEOL SERVICE BUREAU 3rd Fl. Nile Center Bldg., Nawal Street, Dokki, (Cairo), Egypt • **FRANCE** /JEOL (EUROPE) SAS Espace Claude Monet, 1 Allée de Giverny 78290, Croissy-sur-Seine, France • **GERMANY** /JEOL (GERMANY) GmbH Gute Aenger 30 85356 Freising, Germany • **GREAT BRITAIN & IRELAND** /JEOL (U.K.) LTD, JEOL House, Silver Court, Watchmead, Welwyn Garden City, Herts AL7 1LT, U.K. • **ITALY** /JEOL (ITALIA) S.p.A. Palazzo Pacinotti - Milano 3 City, Via Ludovico il Moro, 6/A 20080 Basiglio(MI) Italy • **KOREA** /JEOL KOREA LTD, Dongwoo Bldg, 7F, 1443, Yangjae Daero, Gangdong-Gu, Seoul, 134-814, Korea • **MALAYSIA** /JEOL(MALAYSIA) SDN.BHD, 506, Block A, Level 5, Kelana Business Center, 97, Jalan SS 7/2, Kelana Jaya, 47301 Petaling Jaya, Selangor, Malaysia • **MEXICO** /JEOL DE MEXICO S.A. DE C.V. Arkansas 11 Piso 2 Colonia Napoles Delegacion Benito Juarez, C.P. 03810 Mexico D.F., Mexico • **RUSSIA** /JEOL (RUS) LLC, Krasnoproletarskaya Street, 16, Bld. 2, 127473, Moscow, Russian Federation • **SCANDINAVIA** /SWEDEN JEOL (Skandinaviska) AB Hammarbacken 6A, Box 716, 191 27 Sollentuna Sweden • **SINGAPORE** /JEOL ASIA PTE.LTD, 2 Corporation Road #01-12 Corporation Place Singapore 618494 • **TAIWAN** /JIE DONG CO., LTD, 7F, 112, Chung Hsiao East Road, Section 1, Taipei, Taiwan 10023 Republic of China • **THE NETHERLANDS** /JEOL (EUROPE) B.V. Lireweg 4, NL-2153 PH Nieuw-Vennep, The Netherlands • **USA** /JEOL USA, INC. 11 Dearborn Road, Peabody, MA 01960, U.S.A.