

Applications note Battery Note

Solutions for Innovation



Lithium Ion Batteries CP / XRF / SEM / AES / SXES / NMR / FIB / INFITOF MS / XPS Fuel Cells TEM Manufacturing Equipment Nanopowder Synthesis Systems





JEOL Ltd.

# **Battery**Note

# Introduction

Battery cells are essential in modern life as they are extensively used in mobile phones, personal computers, and even as the power source of some automobiles in recent years. In addition, the research and development of rechargeable batteries has become increasingly important in the endeavor to realize a low-carbon society. The demand for fuel cells as hydrogen-based generators is also expected to grow, as fuel cells have already been widely applied to household equipment and automobiles.

JEOL believes that analyses and evaluations by using various high-performance evaluation instruments are required to improve both the performance and quality of these battery cells.

JEOL offers a wide variety of analytical instruments available for morphological observations, surface analyses, structure analyses, and chemical analyses at micro- to nano-scales for the purposes of research, development, and quality improvement.

This Battery Note has been created to provide solutions and reference information for research and development activities focused on lithium ion batteries (LIBs).

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# **Features of Instruments**

	X-ray Fluorescence Spectrometer (XRF)	<ul> <li>Quick average composition evaluation with simple preparation</li> <li>High quantitative accuracy in ppm-order</li> <li>High-accuracy evaluations of composition ratio and impurities of products of positive-electrode active materials</li> </ul>
	X-ray Photoelectron Spectrometer (XPS: X-ray Photoelectron Spectroscopy)	<ul> <li>Top surface chemical state analysis</li> <li>Low specimen damage by X-ray irradiation</li> <li>Minimal effect of oxidation by ultra-high vacuum</li> <li>Li chemical state analysis</li> <li>Macro chemical state analysis of positive and negative electrodes</li> <li>Chemical state analysis by depth profiling from surface to inside</li> </ul>
	Auger Microprobe (AES: Auger Electron Spectroscopy)	<ul> <li>Top surface chemical state analysis</li> <li>Superior capability of local area analysis than XPS</li> <li>Li chemical state analysis</li> <li>Minimal effect of oxidation by ultra-high vacuum</li> <li>Chemical state analysis of micro regions of positive and negative electrodes</li> <li>Chemical state analysis by depth profiling from surface to inside</li> </ul>
	Scanning Electron Microscope (SEM)	<ul> <li>High-resolution morphological observations</li> <li>Compatibility with various attachments <ul> <li>Elemental analysis (Energy Dispersive X-ray Spectrometer: EDS)</li> <li>Orientation analysis (Electron BackScatter Diffraction: EBSD)</li> <li>Soft X-ray Emission Spectrometer (SXES)</li> </ul> </li> <li>Capability of low accelerating voltage observations of non-conductive macro-molecular materials such as separators</li> </ul>
	Electron Probe Micro Analyzer (EPMA)	<ul> <li>Morphological observations</li> <li>Quantitative analysis of trace elements in micro areas</li> <li>Soft X-ray Emission Spectrometer (SXES)</li> <li>Applicable to analysis of transition metals in positive-electrode active materials</li> </ul>
ler-	Transmission Electron Microscope (TEM)	<ul> <li>Morphological observations of nano-areas</li> <li>Atomic resolution image observation</li> <li>High spatial resolution elemental analysis</li> <li>Crystal structure analysis by electron diffraction</li> </ul>
	Nuclear Magnetic Resonance Spectrometer (NMR)	<ul> <li>Structure analysis</li> <li>Structure analysis and evaluation of positive-electrode active materials by solid-state NMR</li> <li>Structure evaluation of negative-electrode materials</li> <li>Lithium diffusion coefficient analysis based on magnetic gradient</li> </ul>
	Mass Spectrometer (MS)	<ul> <li>Mass spectrometry</li> <li>Hydrolysate analysis of electrolyte in combination with GC</li> <li>Evolved gas analysis of the inside of batteries</li> </ul>
	Cross-section specimen preparation equipment Cryo and Air-isolated CROSS SECTION POLISHER™ (CP)	<ul> <li>Cross-section specimen preparation equipment</li> <li>Specimen preparation for surface observation and analysis by SEM, EPMA, and AES, etc.</li> <li>Creating air-isolated interlock with other instruments by using holders applicable to air-isolation</li> </ul>
	MultiBeam System (Focused Ion Beam: FIB)	<ul> <li>Preparation of cross-section SEM specimen and thin film TEM specimen</li> <li>SIM and SEM image observations</li> <li>Air-isolated specimen preparation by using a transfer vessel</li> </ul>

Features and Applications



# Air-Isolated Transfer

Milling, Observation, and Analytical Instruments







Pickup system Glove box

Pickup

# **Basic Structure and Manufacturing Processes of** Lithium Ion Batteries



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

As LIBs contain highly-reactive lithium, they may not be properly evaluated due to alteration of lithium when it is exposed to the atmosphere. Thus, the evaluation of LIBs requires air-isolated pretreatment, observation, and analysis of specimens, as well as in-situ observation and analysis. For instruments applicable to air-isolation, please refer to the previous pages.

The figure below shows examples of instruments suitable for evaluation at each step of the process from evaluation and R&D of materials up to manufacturing.

JEOL's analytical instrument solutions offered for

each step of the process

#### Transmission Electron Auger Electron Spectrometer Microscope (TEM) (AFS) Positive electrode material Negative electrode material R&D Separator Quality control Nuclear Magnetic Resonance Spectrometer (NMR) Electrolyte Manufacturing Electron Spin Resonance Spectrometer (ESR) Positive electrode material Raw material preparation C Negative electrode material Positive electrode material Coating & pressing C Negative electrode material X-ray Fluorescence Scanning Electron Electron Probe Microanalyzer Spectrometer (XRF) Microscope (SEM) (EPMA) Winding, extrusion, and Cell assembly stretching (positive/negative electrodes, current collectors, separators, and electrolyte) Aging 0 Battery performance check Charge-discharge test Degradation process check X-ray Photoelectron Spectrometer (XPS) Gas Chromatograph Mass Spectrometer (GC-MS)

# 1 – 1 Lithium Ion Batteries Specimen Preparation: Air-isolated Transfer - Preparation of Specimen for TEM by FIB

## · Air-isolated transfer from FIB to TEM by using a glove box

Normally, transfer of specimens prepared by FIB thinning is performed in atmosphere. However, materials that alter when exposed to the atmosphere, such as battery materials, require a series of tasks to be performed without exposure to the atmosphere. FIG. 1 shows an example process of air-isolated transfer. In the process, a glove box (2) equipped with an inside manipulator (pickup system (1)) for thin film pickup is used. The built-in stage of the pickup system can be equipped with a slide cover holder (3) for air-isolated TEM observations. A specimen thinned by the Multi-Beam FIB JIB-4700F (5) equipped with a specimen exchange chamber compatible with the transfer vessel (4) is directly transferred to the slide cover holder by the pickup system within the glove box, and carried to the TEM JEM-ARM200F (6) without air exposure for TEM observation. Example images of preparation and TEM observation of a positive electrode specimen are shown in FIG. 2.

## FIG. 1 Air-isolated TEM specimen preparation process

Battery disassembly, specimen setup on a transfer vessel, and transfer of a FIB-thinned specimen to the slide cover holder are carried out within a glove box with a built-in pickup system.





FIG. 2 Air-isolated thin film milling

TEM images

a : SIM image

An FIB-milled thin film, with the top view.
SIM (secondary electron) image.

b : SEM image

An SEM (backscattered electron) image observed at a 53° tilt. FIB thinning at the center of a positive electrode material

**c** : BF-STEM image A BF-STEM image of a specimen transferred to TEM without air exposure.

Specimen: Positive-electrode active material Li(Co<sub>1/3</sub>,Mn<sub>1/3</sub>,Ni<sub>1/3</sub>)O<sub>2</sub>

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

# 1 - 2 Lithium Ion Batteries Specimen Preparation: Air-Isolated, Cryo Cross-Section Milling - Composite Material Evaluation

## · Cross section milling of assembled batteries - air-isolated, cryo cross section milling -

In order to analyze the positive electrode of the assembled battery after the charge-discharge cycle, air isolated specimen preparation is required. In addition, cryo cross-section ion milling methods are effective for polymer materials that are susceptible to damage by ion beams. Air-isolated Cryo CP can be used for specimen preparation with reduced exposure to air/thermal damage.

### Cross section of the assembled positive electrode using air-isolated, cryo CP.

A cross section SEM image of a current collector, a positive electrode, and a separator.





Air-isolated, Cryo CP IB-19520CCP

**——** 10 μm

#### Schematic diagram of a transfer vessel

Holders used for the air-isolated, cryo CP are designed with a removable cap in order to keep specimens air-isolated before and after milling. The cap can be removed within a compatible instrument for air-isolated observations and analyses. \* Compatible instruments: SEM, EPMA, and FIB

# EPMA analysis of a cross section using air-isolated, cryo CP. - An assembled battery material -

The assembled positive electrode after a charge-discharge cycle was milled by the air-isolated, cryo CP and elemental mapping of its cross section was conducted with EPMA. The images show distribution of the elements contained in the positive electrode and electrolyte in the separator.



## 1 - 3 Lithium Ion Batteries Positive Electrode Material Evaluation: Elemental Analysis of Active Materials

## · Elemental analysis

For positive electrode materials in LIBs, compounds of lithium and transition metals are used. Battery performance depends on elements contained in the positive electrode materials and their composition ratios. XRF is capable of quick qualitative and quantitative analyses of elements contained in a specimen by irradiating X-rays on the specimen and detecting fluorescent X-rays emitted from it. Therefore, identification of positive electrode materials and difference in composition ratios before and after a charge-discharge cycle can be done quickly with XRF.



#### Quantitative analyses before and after a chargedischarge cycle

Quantitative analyses of the positive electrode material (3) before and after a charge-discharge cycle were conducted to determine differences in Ni, Mn, and Co concentration. The quantification results showed that the atomic composition ratios of Ni, Mn, and Co varied before and after the charge-discharge cycle.

	Before a charge-discharge cycle	After a charge-discharge cycle
Ni	33.3	35.9 †
Mn	33.2	30.4 ↓
Со	33.6	33.7 →

Unit: atom%

# Lithium Ion Batterie Positive Electrode Material Evaluation: Shape and Size of Active Materials

## · Morphological observations

For evaluation of size and shape, the scanning electron microscope (SEM) is suitable.

SEM allows for evaluation in a wide area from nanometer- to micrometer-size, and is particularly effective for observing the shape of sintered primary particles and secondary particles of positive electrode active material, which greatly contributes to battery performance.

The cross section prepared using CP can be used for various evaluations such as the internal structure of secondary particles, voids, and cracks, to the distribution of particles after assembly.



Positive-electrode active material powder (raw material)

JSM-7900F



SEM image of positive-electrode active material powder (raw material)



Specimen: LiMn<sub>2</sub>O<sub>4</sub>

Scanning Electron Microscope (SEM)







**=** 1 µm

A cross section of a positive-electrode and an enlarged SEM image





Air-isolated, Cryo CP IB-19520CCP

# 1 - 5 **Lithium Ion Batteries** Positive-electrode Material Evaluation: Elemental Analysis

## · Elemental distribution

Element distribution in a wide area can be visualized by SEM.

For positive electrode active materials that are degraded due to repeated use, it is effective to evaluate element distribution by SEM/EDS (Energy Dispersive X-ray Spectrometer) mapping for the cross section prepared by CROSS SECTION POLISHER<sup>TM</sup> (CP).

SEM / EDS				
	Before a charge-discharge cycle (%)	After a charge-discharge cycle (%)		
Mn	34.1	34.5 †		
Со	32.8	31.9 ↓		
Ni	33.1	33.6 †		

Before the charge-discharge cycles: Resin-embedded active materials prepared to a cross section by CP.



After the charge-discharge cycles: Degraded active materials prepared to a cross section by Air-isolated CP.



Specimen: Li(Mn<sub>1/3</sub>Co<sub>1/3</sub>Ni<sub>1/3</sub>)O<sub>2</sub> (NMC)

#### EDS element mapping in an assembled state after degradation

Assembled positive electrode materials in degradation using EDS elemental mapping.

After Storage Degradation at High Temperature, positive electrode materials prepared to a cross section by Cryo and Air-isolated CP. The following element maps show the elements contained in the electrode / anode material / separator detected simultaneously using SEM/ EDS.



# Lithium Ion Batteries Positive Electrode Material Evaluation: Surface Elemental Analysis of Active Materials

## · Surface elemental distribution

Due to battery degradation after repeated use, nearsurface elemental distribution of active material particles significantly changes. Evaluation of elemental distribution over the specimen surface is important in understanding the degradation mechanism. Auger Microprobe is highly effective in surface elemental analyses.

## Chemical state analysis by depth profiling from surface to inside

Elements in positive electrode powder before and after a charge-discharge cycle were analyzed by etching in the depth direction of particles.



# Before a charge-discharge cycle



### After a charge-discharge cycle

16 nm

After a charge-discharge cycle, the elemental distribution in transition metals on the active material surface tends to be more heterogeneous in the depth direction than before the cycle. This suggests a change in composition due to lithium desorption and insertion.



## Cross section TEM/EDS analysis of positive electrode powder surface - before and after a charge-discharge cycle -

A cross section of a thinned particle surface was analyzed by TEM/EDS. The analysis result similar to that for the bulk surface using the Auger Microprobe was obtained.

40



#### Before a charge-discharge cycle

## After a charge-discharge cycle



# 1–7 **Lithium Ion Batteries** Positive Electrode Material Evaluation: Surface Elemental Analysis of Active Materials

## · Lithium analysis

Auger Electron Spectroscopy can directly detect Li and thereby obtain a Li elemental map, which represents Li distribution in a positive-electrode active material. Auger peaks and reflected EELS peaks, with high energy resolution (FWHM  $\leq 1.0 \text{ eV}$ ), can also be used for chemical state analyses of Li.



Elemental mapping of a positive-electrode active material (LiFePO<sub>4</sub>) by Auger electron spectroscopy



## Li absorption spectrum by the reflection EELS technique

With the reflection EELS technique, absorbed energy information from the inside of a specimen, which depends on accelerating voltage, can be obtained from greater depths than from Auger electron spectroscopy.

Auger electron spectroscopy enables acquisition of information from a depth of about 2 nm from the surface, whereas the reflection EELS technique at an accelerating voltage of 2 kV can obtain information from a depth of about 6 nm. Therefore, this EELS technique allows for a more detailed analysis when combined with Auger electron spectroscopy, which provides the specimen's top surface information.



Distribution of the energy of electrons generated from the surface

Standard spectra of lithium compound

Chemical state analysis for lithium can be performed with the use of a high energy resolution standard spectra library.



The Li absorption spectra obtained by the reflection EELS technique contain information about Li amounts on the active material surface before and after the chargedischarge cycle as well as changes in chemical states. Variations in the Li amount are obtained from peak intensities. To analyze chemical states of Li, additional tasks such as peak deconvolution from transition metals are required.



Absorption spectra by the reflection EELS technique

# 1 - O Lithium Ion Batteries Soft X-ray Emission Spectrometer (SXES)

## · SXES system

An SXES, installed on SEM or EPMA (Electron Probe Microanalyzer) can measure ultra soft X-ray emission spectra.



## · Comparison of SXES, WDS, and EDS spectra

While EDS or conventional WDS has difficulty in peak deconvolution of Ti L $\ell$  and N K lines overlapping in titanium nitride, SXES is able to distinguish the spectra because of a clear Ti-L $\ell$  shoulder peak.



#### Overview

This spectrometer can obtain high energy resolution soft X-ray emission spectra with parallel signal detection. This instrument detects X-rays dispersed by a diffraction grating arranged at a fixed position by using a high-sensitivity CCD camera. We have two types of spectrometers, SXES and SXES-ER, which are designed for measuring energy regions of 50-210 eV and 100-2300 eV, respectively.

# Measurement of changes in the chemical bonding states in the depth direction

This spectrometer enables changing the effective X-ray detection depth with variations of accelerating voltage.

Further, the GENTLEBEAM™ (GB) method can be used to finely adjust the landing voltage between several 100 V to 5 kV, which enables measuring the chemical state depth profile in the range of several nm to several 100 nm.

## Detection of lithium

SXES can detect the Li K line signal of Li metal or Li alloy, while signal emission almost does not occur at Li oxide, because most of the valence electrons of Li are occupied by the oxygen atoms.

However, for sulfur-lithium compounds used in solid electrolytes, measurement in an airisolated environment may lead to SXES detecting the S L line signal together with the Li K line signal.

Chemical bonding state behaviors can be evaluated measuring the O-K emission spectrum (for compound elements other than lithium).

	SXES	SXES-ER	EPMA(WDS)	EDS
Resolution	< 0.3 eV (Fermi edge Al L)	< 5 eV (FWHM@Fe L)	8 eV (FWHM@Fe K)	130 eV (FWHM@Mn K)
Chemical bond state analysis	Yes	Yes	Yes (mainly light elements)	No
(Spectrum)Parallel detection	Yes	Yes	No	Yes
Optical element & detector	Diffraction grating + CCD	Diffraction grating + CCD	Analyzing crystal + Proportional counter	SDD
Detector cooling	Peltier cooling	Peltier cooling	Not needed	Peltier cooling
Detection limit (reference value with B)	20 ppm	B:20 ppm S:30 ppm	100 ppm	5000 ppm

# 1 – O **Lithium Ion Batteries** Positive Electrode Material Evaluation: Soft X-ray Emission Spectroscopy

## · Analysis of changes in chemical bonding states of the transition metals in the positive electrode material - Soft X-ray emission spectroscopy -

SXES can analyze changes in the chemical states of positive electrode active materials that have cycled through chargingdischarging several times.

One of the prominent features of SXES is that it is easy to measure the chemical bonding states of transition metals, with detectors attached to SEMs and EPMAs.

The results show an SXES-ER analysis example of the positive electrode active materials that have cycled through charging and discharging.



Soft X-ray Emission Spectrometer (SXES) EPMA / JXA-8230

A cross section of a positive electrode in LiB, after six charging and discharging cycles. This specimen was prepared by air-isolated cryo CP techniques.



Specimen: Li(Mn<sub>1/3</sub>Co<sub>1/3</sub>Ni<sub>1/3</sub>)O<sub>2</sub> (NMC)

SXE spectrum of a positive electrode active material. (diffraction grating: JS2000)



### L-line spectrum comparison of transition metals between particle surface and cross section of the positive electrode material after six charging and discharging cycles.

The detection depth of Ni L in the positive electrode active material is estimated about 40 nm at an accelerating voltage 2 kV. SXES can obtain depth information in the bulk of the specimen rather than the surface sensitive AES. We found that there is a large difference at Mn L line between the particle surface and inside, while no significant difference in the Co L and Ni L lines.



# 1 – 1 O **Lithium Ion Batteries** Positive Electrode Material Evaluation: State Analysis of Active Materials

## Analyses of chemical bonding states of transition metals inside active materials

Active-material degradation, due to charge-discharge cycles, arises for the surface and bulk of the material. Also, changes in surface and bulk states of the material particles can change composition ratios and chemical bonding states.

Below are the results of chemical state analyses by AES. A cross section of NMC prepared by CP and the surface of NMC were analyzed.



Auger Microprobe (AES) JAMP-9510F



Positive-electrode active materials after a charge-discharge cycle - chemical bonding state analysis of transition metals - Differences in chemical bonding states of NMC at its surface and bulk (cross section) were analyzed.



47%

47%

33%

33%

100%

100%

100%

100%



25%

34 %

(28%)

10%

(29%)

18%

(72%)

24% (71%)

28%

33 %

(25%)

14%

(42%)

21%

(75%)

19%

(58%)



In the active material after a chargedischarge cycle, the MnO-MnO<sub>2</sub> ratio varied between the specimen's surface (25%/75%) and bulk (42%/58%).

Surface

Cross section

# 1 – 1 1 **Lithium Ion Batteries** Positive Electrode Material Evaluation: Structure Analysis of Active Materials

## Structure analysis

Positive-electrode active materials are known to vary in their structures through charge-discharge cycles due to desorption, insertion, and transfer of lithium and the inability to recover lithium ions thereafter. Accordingly, analysis of such structural change is important in investigating mechanisms and degrees of battery performance degradation. The structure analysis requires both comprehension of overall structures by XRD and analysis of local structural changes by a transmission electron microscope (TEM). Electron diffraction and atomic resolution images of nano-areas provided by TEM allows for comprehension of changes in a specimen's crystal structure.

The crystal structure of positive-electrode active materials - precession electron diffraction - Specimer

Specimen: Li (Co1/3, Mn1/3, Ni1/3) O2

Precession electron diffraction (PED) is a technique used to obtain an electron diffraction pattern under less dynamical diffraction effects by precessing the incident electron beam under a certain tilt angle with respect to the optical axis. Orientation and phase separation maps can be created from electron diffraction patterns over a scanned area.





A phase map of particles of a positive-electrode active material. Surface and internal structures are distinguishable by different coloration. Red: laminar rock salt structure, Green: cubic rock salt structure



Schematic of precession electron diffraction



Particle surface after a charge-discharge cycle - nano-beam electron diffraction (NBD) -

NBD patterns were obtained from the top surface and the inside of a particle



Inside NBD pattern: A laminar rock salt structure [11-20] was observed.



Atomic resolution image observation of a particle's surface before and after a charge-discharge cycle - HAADF-STEM -

The atomic-resolution HAADF-STEM observations showed a change in the lithium-occupied site on the active material particle surface after a charge-discharge cycle; bright points that were only visible on the top surface before a chargedischarge cycle were observed inside the particle after the cycle. These bright points were identified to be caused by cation mixing, i.e. inclusion of a compound's transition metals into a lithium site. The results were also consistent with the analysis results from an Auger Microprobe (P.11).



🗕 2 nm

Top layer NBD pattern: A structural change was observed on the particle's top surface.





2 nm

# 1 – 1 2 Lithium Ion Batteries Positive Electrode Material Evaluation: Structure Analysis of Active Materials

## · Solid-state NMR - Chemical state analysis of lithium -

NMR is a technique for analyzing the surrounding structures and environments of a target element in a substance. This is one of few LIB analysis techniques that enable direct observations of Li nuclei to reveal local structural defects from the chemical states of lithium in a positive electrode.

For samples containing paramagnetic ions such as LIB positiveelectrode materials, a solid-state NMR probe with a small diameter of 1 mm or below, which allows for ultra-high speed spinning around 100 kHz, is desirable in order to avoid the spinning side band (SSB) effect. Ultra-high speed spinning can force the SSB to move away from the center bands and thereby allows the center bands to be identified. Furthermore, the stateof-the-art pulse technique called MATPASS can eliminate the SSB effect and provides quantitative <sup>7</sup>Li NMR spectra, which allows for observations of structural degradation such as cation mixing in a cycle from the lithium side.



Nuclear Magnetic Resonance Spectrometer (NMR) JNM-ECZ500R

### MAS-frequency dependency of <sup>7</sup>Li NMR spectra



HAADF-STEM image of an area near the particle surface of  $LiMn_2O_4$ 



Manganese substitution occurred at the lithiumoccupied site due to cation mixing. This is consistent with the lithium state in the NMR observation.

#### <sup>7</sup>Li MATPASS spectra before and after LiMn<sub>2</sub>O<sub>4</sub> degradation



2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200 -400 <sup>7</sup>Li chemical shift / ppm





# 1–13 **Lithium Ion Batteries** Positive Electrode Material Evaluation: Structure Analysis of Active Materials

## · 3D-FIB - void rate evaluation -

Some positive-electrode active materials exhibit changes in the number of voids and cracks in particles before and after a charge-discharge cycle. Three-dimensional imaging is effective for quantitative evaluation of voids and cracks in cross section observations of such materials. The Slice & Observation FIB function, which automatically performs slicing and cross section observation, helps three-dimensional imaging by automatic serial cross-section observations.



### Sliced section observation images of a lithium-cobalt oxide particle (SIM images)



	Before a charge-discharge cycle	After a charge-discharge cycle
Particle volume ( µm³)	1321.08	2298.26
Void volume ( µm³)	0.35	26.86
Void rate(%)	0.03%	1.17%



**1**0 µm

Before a charge-discharge cycle

# 1 4 Lithium Ion Batteries Measurement of Compounds Generated within Degraded Lithium Ion Batteries

#### Features

#### · Small and lightweight console

The JMS-MT3010HRGA has similar dimensions to a standard desktop PC, thus making it easy to transport and install.

#### · High mass resolution

Despite its compact size, the instrument has a maximum mass resolution as high as 30,000 (FWHM) due to its advanced Multi-Turn technology, thus making it easy to perform the mass separation of gas components such as  $N_2^{+}(m/z \ 28.0062)$  and CO<sup>+</sup> ( $m/z \ 27.9949$ ), which is difficult with conventional compact mass spectrometers.



## Gas generated within a fully-charged lithium ion battery that has been stored at high temperature

Multi-Turn Time-of-Flight Mass Spectrometer JMS-MT3010HRGA INFITOF

Gas generated within a fully-charged lithium ion battery stored at high temperature was introduced into a gas chromatograph and analyzed with high mass-resolution by the JMS-MT3010HRGA. Nitrogen (N<sub>2</sub>), presumably from an air leak, and carbon monoxide (CO) were successfully observed separately through the use of high resolution with accurate mass, extracted ion chromatogram (EIC) data. Also, peaks appearing in the total ion current chromatogram (TICC) were estimated to represent the compounds indicated in the figures below based on elemental composition estimation results. These compounds are thought to be products from the electrolyte.



Appearance of JMS-MT3010HRGA connected with a gas chromatograph



TICC and EIC of the gas generated within a fully-charged lithium ion battery having been stored at high temperature



Mass spectra and enlarged spectra of the m/z 28 section of Peak 1, 2, and 3

# 1 – 1 5 **Lithium Ion Batteries** Electrolyte Analysis

GC-MS is a combination of a gas chromatograph (GC) and mass spectrometer (MS). In GC-MS, a substance is separated into its components by a GC capillary column and then introduced into the MS for ionization and mass analysis. This instrument is suited for the analysis of volatile organic compounds consisting of multiple components and is widely used for a variety of quantitative and qualitative studies.

## Features

- Capable of measuring gases, liquids, and solids in combination with relevant pretreatment equipment.
- · Compatible with various ionization methods (EI, FI, PI, and CI).





High Performance Gas Chromatograph Time-of-Flight High Resolution Mass Spectrometer JMS-T200GC AccuTOF™GCx-plus

# Identification of electrolyte products using deuterium labeled materials - electrolyte with deuterated EC (EC-d4) -

Electrolyte components that have degraded due to charge-discharge cycles can be detected and identified by extracting the electrolyte from the lithium ion battery (LIB) after a charge-discharge cycle and evaluating the electrolyte by high resolution time-of-flight mass spectrometry.

- Extractant (acetone), electrolyte, and electrolyte-derived peaks
- Degradation component peaks
- The peaks for any deuterated degradation components were presumably influenced by EC-d4

Among all degraded components, EC-d4 was related to only three components. Therefore, it is estimated that most degraded components are generated from the DMC.



# 1 – 1 6 Lithium Ion Batteries Electrolyte Analysis: Diffusion Behavior of Lithium Ion Batteries

Nuclear Magnetic Resonance (NMR) is a useful method for analyzing the surrounding structures and environments of a target element in a substance. Owing to improved instrument performance and the invention and advancement of analysis techniques in recent years, its applications in the battery field now extends beyond electrode and electrolyte structure analysis and includes analyses such as charge-discharge dynamics, as well as similar studies.

## · Diffusion measurement by a high field-gradient probe

JEOL's GR probes can create a very high magnetic field gradient in a sample and measure the Li ion diffusion coefficient in solid-state electrolyte, which is difficult to measure with a normal liquid NMR probe.

#### Features of the GR probe

- · Capable of generating a magnetic field gradient over 1200 G/cm
- · Applicable to diffusion measurement of liquid, gel, and solid electrolyte



GR probe

JNM-ECZR series FT NMR (compatible with the GR probe)



Analysis of Li diffusion coefficient in solid-state electrolyte



D : Self-diffusion coefficient

Data courtesy: Yasuhiro Hashimoto, Noriko Horiike, and Hitoshi Shobukawa of Asahi Kasei Corporation

## · Electric field application to a liquid sample by an electric field cell

In combination with an appropriate field-gradient probe, JEOL's electric field cell can be used to measure diffusion behaviors of ions in an electrolyte specimen under an electric field.

### Features of electric field cells

- · Equipped with electrodes in its sample tube and capable of applying an electric field to a sample
- $\cdot$  Adjustable distance between electrodes



# 1 – 1 7 **Lithium Ion Batteries** Negative Electrode Material Evaluation: Foreign Materials

## · X-ray photoelectron spectroscopy - top surface chemical bonding state analysis -

X-ray photoelectron spectroscopy (XPS) is a technique of dispersing energies of photoelectrons emitted through X-ray irradiation and is used for surface analysis and chemical bonding state analysis. This technique is applicable to air-isolated analyses with use of a transfer vessel, and thus effective in macro surface analysis of materials that should not be exposed to air, e.g. LIBs. In addition, abundant standard spectra are available, facilitating chemical bonding state analysis, which was difficult before.



The result of a qualitative analysis of positive- and negativeelectrode material surfaces



sed Very set of the s

Co\_metal

CoO

 $CO_3O_4$ 

A spectrum of cobalt detected from the negative electrode material surface (integral)



The result of a peak deconvolution calculation based on the standard cobalt spectrum (differential)



### Twin anode

With a twin anode, two different X-ray targets can be instantly switched. Changing the X-ray type to be used for irradiation is effective in avoiding overlapping of photoelectron peaks with Auger peaks.





Fe and Ni photoelectron peaks and Auger peaks can be separated by changing the X-ray source to Mg-Ka line. Cobalt spectra with Mg-Ka line and Al-Ka line source irradiation.

found to be metal.

Negative-electrode surface measurement spectrum

Performing a peak deconvolution calculation based on the standard spectrum enables evaluation of the state of detected transition metals. With this, the detected Co was

Standard spectrum



# 2-1 **Fuel Cells** Carbon-supported Platinum Catalyst: 3D Observation

## · 3D microstructure observation

Electron tomography is a 3D microstructure imaging technique that obtains transmission images at different angles by tilting the specimen stage and then reconstructs a three-dimensional image from the sequential tilt-series images. The technique allows for observations at nm-order three-dimensional resolution, which is effective in 3D structure analysis of carbon-supported platinum catalyst.

Sequential tilt-series imaging



Sequential tilt-series images of a platinum catalyst



Transmission Electron Microscope (TEM) JEM-2100Plus



3D reconstruction of a platinum catalyst



Volume rendering image



Digital slice (Z-view)

# 2-2 Fuel Cells Catalyst Particle Analysis

Solid-state polymer electrolyte fuel cells (PEFCs) exhibit degradation of their electrode catalysts through generation-stop cycles, which entails changes in morphology and composition distribution of catalyst particles.

For observations and analyses of nano-order particles, imaging by a scanning transmission electron microscope (STEM) equipped with an aberration corrector is useful.

7.0



JEM-ARM200F NEOARM

	Before the cycle	After the cycle
Mean particle diameter *	4.6 nm	6.1 nm
Standard deviation (SD)	2.2 nm	2.6 nm

Circle-equivalent diameter

Circle-equivalent diameter



Before the cycle

After the cycle

#### Relation between particle diameter and Pt/Co concentrations before and after the cycle

Before degradation, the composition ratio of Pt was higher with larger particle diameters, whereas that of Co was lower with smaller diameters. After degradation, however, the ratios of Pt/Co were both substantially constant regardless of particle diameters.

This is because the amount of Pt contained in a particle is constant regardless of particle sizes before degradation; i.e., the ratio of Pt against Co is necessarily smaller in larger particles. After degradation, sintering among particles has occurred and made the Pt-Co ratio substantially constant despite certain variations.



# Particle diameter measurement





#### Particle diameter/ composition analysis

EDS/area analysis



Particle diameter measurement



# 2-3 Fuel Cells Catalyst Particle Analysis

In order to identify the element distribution in a nanopowder, e.g. trace catalyst particles, it is essential to perform measurements by using TEM, which is capable of nano-area analyses. EDS analysis using a scanning transmission electron microscope (STEM) equipped with an aberration corrector allows for measurement of element distribution in a particle.

#### Evaluation of particle composition distribution

#### Before an accelerated degradation test (EDS mapping)





The catalyst particles before the degradation test exhibited a core-shell structure with more Pt on their surfaces and Co concentrated inside. (EDS/mapping and line analysis)

HAADF-STEM EDS line analysis





Semi-quantitative line profile (atom %)

#### After an accelerated degradation test

#### HAADF-STEM



EDS/Map Red: Co Green: Pt Yellow: Pt+Co



EDS mapping of the degraded catalyst particles showed a sintering effect among particles. The particles after degradation were larger due to sintering and some of them had more than one Co core.



JEM-ARM200F NEOARM

# 2-4 Fuel Cells Carbon Carrier and Catalyst Particle Analysis

A secondary electron (SE) detector equipped on a TEM can detect a specimen's near-surface information. The instrument is also effective in the evaluation of morphology and the distribution of catalysts distributed over a carbon carrier surface of PEFC. Also, a scanning transmission electron microscope (STEM) equipped with an aberration corrector can be used to visualize monoatoms distributed over a carbon carrier surface and this is expected to contribute to elucidation of degradation mechanisms.



## Observation of carbon carrier surface (simultaneous STEM-SEM observations)



# Observation of monoatoms on a carbon carrier

In combination with a relevant image processing technology, quantification of monoatoms per carbon carrier can be made.

Number of atoms	Number of atoms per carbon carrier
332 atoms	1.286 atoms/nm <sup>2</sup>





**2** nm

# **S-1** Manufacturing Equipment RF Induction Thermal Plasma for Nanopowder Synthesis

RF Induction Thermal Plasma concentrating the high-frequency power at inert gases such as argon gas to spontaneously generate plasma of approximately 10,000 °C using electromagnetic induction. Materials (fine powder, liquid, and gas) can be introduced into the plasma to induce melting, vaporization, chemical reactions, and dissociation. Possible applications of the plasma include preparation of nanopowder and composite compounds from electrodes and electrolyte materials of all-solid lithium ion batteries and alteration.



TP-40020NPS (6 kW experiment system)



Ar+H2 plasma

#### Features

- Plasma can vaporize or melt raw materials while floating in the air, enabling high-purity synthesis of materials.
- Ultra-high temperature of the plasma can induce instantaneous flash evaporation of heterogenous materials with different boiling points.
- Various gases can be processed to generate the plasma, inducing chemical reactions and alteration such as oxidation, reduction, nitriding, and carbonization in a high-radical reaction field.
- A base material or a base plate can be placed at the distal end of the plasma to form a coating (plasma spraying).



Ar plasma

## Schematic of hybrid plasma



Appearance of 100 kW hybrid plasma torch

### Features of hybrid plasma

The hybrid plasma consists of a DC (direct current) plasma jet superimposed on RF (radio-frequency) plasma. With preheating and the rapid cooling effects of DC plasma, the hybrid plasma can induce vaporization (nano-particalization) for more efficient and sharper particle distribution than with RF plasma only.

#### Hybrid plasma system (RF 100 kW + DC 8 kW)



## Example of system configuration

# **3-2** Manufacturing Equipment Nanopowder Synthesis Systems

# • An application example of Si nanopowder preparation: silicon nanopowder for negative-electrode materials

100 kW hybrid



#### 100 kW hybrid





Core: crystalline silicon (approx. 30-40 nm) / Shell: amorphous carbon (approx. 2-3 nm) Core material: small silicon particles (approx. 10 µm crashed powder) / Shell material: methane gas



Fig.4 Changes in charge-discharge energy density with different CH<sub>4</sub> additive concentrations



Data courtesy: Kambara Laboratory, Department of Materials Engineering, University of Tokyo Fig.1/Fig.2 Reproduced with permission from J. Appl. Phys. 155, 143302(2014). Fig.3/Fig.4 Sci. Technol. Adv. Mater. 15 (2014) 025006

## Features

- · Compatible with metallurgy silicon (up to 99.5%)
- High throughput (up to 360 g/h)
- Higher-order composite structure (higherorder nano-composites composed of primary particles of tens of nanometers in size)
- Synthesis of composite particles, e.g. core-shell and supported particles

# BatteryNote







Transmission Electron Microscope

Scanning Electron Microscope

Auger Electron Spectrometer

Material	Analysis item	ТЕМ	SEM	AES
Positive-electrode	Morphological observation	0	0	0
material	Element composition analysis	0	0	0
	Element distribution analysis	0	0	0
	Crystal structure analysis	0	0	
	Active material valance identification	0		0
	Current collector passive film analysis	0		0
	Chemical state analysis	0		0
	Binder qualitative analysis			
	Impurity evaluation			
Negative-electrode	Morphological observation	0	0	
material	Element composition analysis	0	0	0
	Element distribution analysis	0	0	0
	Carbon crystal state analysis	0		
Separator	Morphological observation	0	0	0
	Element composition analysis	0	0	0
	Chemical structure analysis			
	Thermal degradation mechanism			
Electrolyte	Component and impurity analysis			
	Diffusion coefficient evaluation			
Production	Gas composition analysis			
atmosphere gas	Continuous component monitoring			
Overall	Defect and failure analysis	0	0	0

# Compatibility of Lithium Ion Battery Analysis Items and JEOL Instruments

In this Battery Note, we have introduced JEOL's representative instruments and their features, and application examples for different LIB analyses and evaluations. The table below indicates a compatibility reference of JEOL instruments and different applications including those not covered in this document. For more information on their applications, please refer to catalogs, specifications, and other technical materials of respective instruments or contact JEOL.















Electron Probe Microanalyzer

Photoelectron Spectrometer

X-ray Fluorescence Spectrometer

Nuclear Magnetic

Electron Spin Resonance Spectrometer Resonance Spectrometer

Gas Chromatograph Mass Spectrometer

EPMA	XPS	XRF	NMR	ESR	MS
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