Battery Note

Lithium Ion Batteries
CP / XRF / SEM / AES / SXES / NMR / FIB / INIFTOF
MS / XPS
Fuel Cells
TEM
Manufacturing Equipment
Nanopowder Synthesis Systems
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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<td>- High quantitative accuracy in ppm-order</td>
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<td>X-ray Photoelectron Spectrometer (XPS: X-ray Photoelectron Spectroscopy)</td>
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<td>- Cross-section specimen preparation equipment</td>
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<td></td>
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<td>Thin film preparation equipment Cryo ION SLICER™ (CIS)</td>
<td>- Thin film preparation equipment for TEM observations and analysis</td>
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<td></td>
<td>- Low-damage specimen preparation by the cooling function</td>
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<tr>
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<td>- Cross-section thin film preparation of particles such as positive-electrode active materials</td>
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Air-Isolated Transfer
Milling, Observation, and Analytical Instruments

SEM/EPMA Observation & Analysis

Transfer vessel

Air-Isolated, Cryo CP

Cryo CP Cross Section Milling

Transfer vessel

FIB Thin Film Milling

Transfer vessel
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

1. Lithium Ion Batteries

Basic Structure and Manufacturing Processes of Lithium Ion Batteries
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

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

Specimen: Positive-electrode active material
Li(Co1/3,Mn1/3,Ni1/3)O2
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.

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

![Schematic diagram of a transfer vessel](image)

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. 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.

Identification of positive electrode materials and quantitative analyses before and after a charge-discharge cycle

Three different positive electrode materials (before a charge-discharge cycle) were measured for 60 seconds each. Differences in elemental concentrations can be identified through qualitative analysis.

- Iron phosphate
- Ni-Co based system
- Ni-Mn-Co based system

Identify the positive electrode materials

Positive electrode material (1)

Positive electrode material (2)

Positive electrode material (3), before a charge-discharge cycle

Quantitative analyses before and after a charge-discharge 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.

<table>
<thead>
<tr>
<th>Element</th>
<th>Before a charge-discharge cycle</th>
<th>After a charge-discharge cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>33.3</td>
<td>35.9</td>
</tr>
<tr>
<td>Mn</td>
<td>33.2</td>
<td>30.4</td>
</tr>
<tr>
<td>Co</td>
<td>33.6</td>
<td>33.7</td>
</tr>
</tbody>
</table>

Unit: atom%
1 - 4  Lithium Ion Batteries
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.

SEM images of a positive-electrode active material
Specimen: Li(Mn\textsubscript{1/3}Co\textsubscript{1/3}Ni\textsubscript{1/3})O\textsubscript{2}

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

Air-isolated, Cryo CP
IB-19520CCP

SEM image of positive-electrode active material powder (raw material)
Specimen: LiMn\textsubscript{2}O\textsubscript{4}
**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\textsuperscript{TM} (CP).

<table>
<thead>
<tr>
<th>SEM / EDS</th>
<th>Before a charge-discharge cycle (%)</th>
<th>After a charge-discharge cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>34.1</td>
<td>34.5 (^\uparrow)</td>
</tr>
<tr>
<td>Co</td>
<td>32.8</td>
<td>31.9 (^\downarrow)</td>
</tr>
<tr>
<td>Ni</td>
<td>33.1</td>
<td>33.6 (^\uparrow)</td>
</tr>
</tbody>
</table>

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

![Before the charge-discharge cycles](image)

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

![After the charge-discharge cycles](image)

**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.

![EDS element mapping](image)
1 Lithium Ion Batteries

- Positive Electrode Material Evaluation:
  Surface Elemental Analysis of Active Materials

· Surface elemental distribution

Due to battery degradation after repeated use, near-surface 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

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.

Before a charge-discharge cycle

After a charge-discharge cycle
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 eV), can also be used for chemical state analyses of Li.

Features of Auger Microprobe (JAMP-9510F)

- High-sensitivity elemental mapping and chemical state mapping
- Auger chemical state analysis
- Powerful insulator analysis functions

Elemental mapping of a positive-electrode active material (LiFePO$_4$) 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.

The Li absorption spectra obtained by the reflection EELS technique contain information about Li amounts on the active material surface before and after the charge-discharge 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.

Standard spectra of lithium compound

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

Distribution of the energy of electrons generated from the surface

Absorption spectra by the reflection EELS technique
1. Lithium Ion Batteries

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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 Lℓ and N K lines overlapping in titanium nitride, SXES is able to distinguish the spectra because of a clear Ti-Lℓ 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 air-isolated 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).

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

SXES can analyze changes in the chemical states of positive electrode active materials that have cycled through charging-discharging 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 EPMA.

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

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.

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.
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.

Before a charge-discharge cycle

After a charge-discharge cycle

The results show changes in composition ratios up to a depth of about 16 nm after a charge-discharge cycle.

Specimen: Li(Mn_{1/3}Co_{1/3}Ni_{1/3})O_2 (NMC)

Auger Microprobe (AES)
JAMP-9510F

Active materials - element concentration analysis from surface to a depth of 70 nm -

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.

In the active material after a charge-discharge cycle, the MnO-MnO_2 ratio varied between the specimen’s surface (25%/75%) and bulk (42%/58%).

<table>
<thead>
<tr>
<th></th>
<th>MnO</th>
<th>MnO_2</th>
<th>CoO</th>
<th>Co_3O_4</th>
<th>NiO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>7%  (25%)</td>
<td>21%  (75%)</td>
<td>18%  (72%)</td>
<td>7%  (28%)</td>
<td>47%</td>
<td>100%</td>
</tr>
<tr>
<td>Cross section</td>
<td>14%  (42%)</td>
<td>19%  (58%)</td>
<td>24%  (71%)</td>
<td>10%  (29%)</td>
<td>33%</td>
<td>100%</td>
</tr>
</tbody>
</table>
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 -

Specimen: Li(Co$_{1/3}$Mn$_{1/3}$Ni$_{1/3}$)O$_2$

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.

1. Lithium Ion Batteries

Positive Electrode Material Evaluation: Structure Analysis of Active Materials

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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

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 charge-discharge 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 (P11).
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 positive-electrode 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 state-of-the-art pulse technique called MATPASS can eliminate the SSB effect and provides quantitative $^7\text{Li}$ NMR spectra, which allows for observations of structural degradation such as cation mixing in a cycle from the lithium side.

After degradation, disordered spinel structure and octahedral Li were observed, which suggest the occurrence of cation mixing.

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

<table>
<thead>
<tr>
<th>Image</th>
<th>Before a charge-discharge cycle</th>
<th>After a charge-discharge cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>40th</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
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<tr>
<td>95th</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
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<td><img src="image5.png" alt="Image" /></td>
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<tr>
<td>205th</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
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<td>260th</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
</tbody>
</table>

### Table

<table>
<thead>
<tr>
<th></th>
<th>Before a charge-discharge cycle</th>
<th>After a charge-discharge cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle volume</td>
<td>1321.08 (µm³)</td>
<td>2238.26 (µm³)</td>
</tr>
<tr>
<td>Void volume</td>
<td>0.35 (µm³)</td>
<td>26.86 (µm³)</td>
</tr>
<tr>
<td>Void rate(%)</td>
<td>0.03%</td>
<td>1.17%</td>
</tr>
</tbody>
</table>
1. Lithium Ion Batteries

1. 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 \( \text{N}_2^+ (m/z \ 28.0062) \) and \( \text{CO}^+ (m/z \ 27.9949) \), which is difficult with conventional compact mass spectrometers.

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

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 (\( \text{N}_2 \)), presumably from an air leak, and carbon monoxide (\( \text{CO} \)) 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.

![Image of JMS-MT3010HRGA connected with a gas chromatograph](image)

**Analysis example**

**Introduction of sample gas**

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

![Graph showing TICC and EIC](graph)

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

![Graph showing mass spectra](mass_spectra)

**Note:**

- Lithium Ion Batteries
- Measurement of Compounds Generated within Degraded Lithium Ion Batteries
1-15 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).

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.

- 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.

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.

The degradation product methyl ethyl carbonate (MEC) is formed by the reaction of the reactant of EC-d4 with DMC.
1. 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 extend beyond electrode and electrolyte structure analysis and include 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

  **Analysis example**
  Analysis of Li diffusion coefficient in solid-state electrolyte

  \[
  D = 5.6 \times 10^{-11} \text{ (m}^2/\text{s)} \]

  \[
  \ln(l_i) = \exp\left(- \frac{B \cdot G \cdot \Delta \cdot (\Delta - \delta/3)}{\gamma^2 \cdot \delta^3 \cdot \Delta}ight)
  \]

  \[
  \begin{align*}
  I & : \text{Signal intensity} \\
  \gamma & : \text{Gyromagnetic ratio} \\
  G & : \text{Magnetic field gradient intensity} \\
  \delta & : \text{Magnetic field gradient pulse width} \\
  \Delta & : \text{Diffusion time} \\
  D & : \text{Self-diffusion coefficient}
  \end{align*}
  \]

  Data courtesy: Yasuhiro Hashimoto, Noriko Horike, 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
  - Adjustable distance between electrodes
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.

An example in which trace transition metals in a used carbon negative electrode material were detected

The result of a qualitative analysis of positive- and negative-electrode material surfaces

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-Kα line.
2. Fuel Cells

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

Transmission Electron Microscope (TEM)
JEM-2100Plus

Sequential tilt-series images of a platinum catalyst

3D reconstruction of a platinum catalyst

Volume rendering image
Digital slice (Z-view)
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.

**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.
2. 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)

After an accelerated degradation test

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.
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)

<table>
<thead>
<tr>
<th>Magnification: x800,000</th>
<th>Magnification: x2,000,000</th>
<th>Magnification: x8,000,000</th>
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<tr>
<td>HAADF</td>
<td>BF</td>
<td>SE</td>
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<td></td>
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<tr>
<td>2 nm</td>
<td>20 nm</td>
<td>20 nm</td>
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</table>

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

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>Number of atoms per carbon carrier</th>
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<tbody>
<tr>
<td>332 atoms</td>
<td>1.286 atoms/nm²</td>
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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.

**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 heterogeneous 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).

**Example of system configuration**

**Schematic of hybrid plasma**

**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.
3-2 Manufacturing Equipment
Nanopowder Synthesis Systems

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

100 kW hybrid
Fig.1  Si fine powder
   Si nanopowder

Fig.2  Core-shell synthesis

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

100 kW hybrid
Fig.3  Core-shell synthesis

Fig.4  Changes in charge-discharge energy
density with different CH₄ additive concentrations

Data courtesy: Kambara Laboratory, Department of Materials Engineering, University of Tokyo
Fig.1-Fig.2 Reproduced with permission from J. Appl. Phys. 115, 143502 (2014).
Fig.3-Fig.4 Sci. Technol. Adv. Mater. 15 (2014) 025006.
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<th>SEM</th>
<th>AES</th>
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<td>Continuous component monitoring</td>
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<td>Overall</td>
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## 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.

### JEOL Instruments
- Electron Probe Microanalyzer
- X-ray Photoelectron Spectrometer
- X-ray Fluorescence Spectrometer
- Nuclear Magnetic Resonance Spectrometer
- Electron Spin Resonance Spectrometer
- Gas Chromatograph Mass Spectrometer

### Application Examples

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<th>XPS</th>
<th>XRF</th>
<th>NMR</th>
<th>ESR</th>
<th>MS</th>
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