

Solutions for Innovation

Solid-State Battery Note

Research on silicon negative electrode (Si anode)

CP / FIB / SEM / SXES / EBSD / TEM / AES

Physical property evaluation of solid electrolyte

MS / NMR

Operando evaluation of generated gas

MS



Solid-State Battery Note

Introduction

Battery cells are essential in modern life as they are extensively used in mobile phones, personal computers, and even in automobiles as the power source in recent years.

The shift to battery vehicles (BEV) is rapidly advancing worldwide in order to achieve carbon neutrality by 2050 which is to “reduce overall greenhouse gas emissions to zero”. The research and development on rechargeable battery cells that can be used repeatedly, are progressing for the use of power source of BEV and larger energy storage system (ESS). To improve both the performance and quality of these battery cells, analyses and evaluations by using various high-performance evaluation instruments are required.

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 purpose of research, development, and quality improvement.

This Solid-state battery Note has been created with the samples provided by Prof. Atsunori Matsuda, Toyohashi University of Technology (Department of Electrical and Electronic Information Engineering), to provide solutions and reference information for research and development of solid-state batteries evolving from the lithium ion batteries (LIBs).

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■ Features of Instruments

Instruments	Features and Applications
 <p>X-ray Fluorescence Spectrometer (XRF)</p>	<ul style="list-style-type: none"> • Quick average composition evaluation with simple preparation • High quantitative accuracy in ppm-order • High-accuracy evaluations of composition ratio and impurities of products of positive-electrode active materials
 <p>X-ray Photoelectron Spectrometer (XPS:X-ray Photoelectron Spectroscopy)</p>	<ul style="list-style-type: none"> • Top surface chemical state analysis • Low specimen damage by X-ray irradiation • Minimal effect of oxidation by ultra-high vacuum • Li chemical state analysis • Macro chemical state analysis of positive and negative electrodes and solid electrolyte • Chemical state analysis by depth profiling from surface to inside
 <p>Auger Microprobe (AES: Auger Electron Spectroscopy)</p>	<ul style="list-style-type: none"> • Top surface chemical state analysis • Superior capability of local area analysis than XPS • Li chemical state analysis • Minimal effect of oxidation by ultra-high vacuum • Chemical state analysis of micro regions of positive and negative electrodes • Chemical state analysis by depth profiling from surface to inside
 <p>Scanning Electron Microscope (SEM)</p>	<ul style="list-style-type: none"> • High-resolution morphological observations • Compatibility with various attachments <ul style="list-style-type: none"> • Elemental analysis (Energy Dispersive X-ray Spectrometer: EDS) • Crystal orientation analysis (Electron Back Scatter Diffraction: EBSD) • Soft X-ray Emission Spectrometer (SXES) • Capability of low accelerating voltage observations of non-conductive polymer materials such as separators
 <p>Electron Probe Micro Analyzer (EPMA)</p>	<ul style="list-style-type: none"> • Morphological observations • Quantitative analysis of trace elements in micro areas • Soft X-ray Emission Spectrometer (SXES) • Applicable to analysis of transition metals in positive-electrode active materials
 <p>Transmission Electron Microscope (TEM)</p>	<ul style="list-style-type: none"> • Structural observations of nano-areas • Atomic resolution observation and elemental analysis • Crystal structure analysis by electron diffraction • Chemical analysis by EELS
 <p>Nuclear Magnetic Resonance Spectrometer (NMR)</p>	<ul style="list-style-type: none"> • Structural analysis • Structural analysis and evaluation of positive and negative electrodes and solid electrolyte materials by solid-state NMR • Ion conductivity evaluation of materials by lithium diffusion coefficient evaluation
 <p>Mass Spectrometer (MS)</p>	<ul style="list-style-type: none"> • Mass spectrometry • Analysis of gas generated/evolved from inside the batteries • Evaluation of thermal property in combination with TG • Operando analysis during a charging-discharging cycle
 <p>Cross-section specimen preparation equipment Cooling CROSS SECTION POLISHER™ (CCP) (Air-isolated)</p>	<ul style="list-style-type: none"> • Cross-section specimen preparation instrument • Specimen preparation for surface observation and analysis by SEM, EPMA, and AES, etc. • Air-isolated transfer for atmosphere sensitive specimens • Linking air-isolation product family
 <p>MultiBeam System (Focused Ion Beam: FIB)</p>	<ul style="list-style-type: none"> • Preparation of cross-section SEM specimen and thin film TEM specimen • SIM and SEM image observations • Air-isolated specimen preparation by using a transfer vessel
 <p>Energy Dispersive X-Ray Spectrometer (EDS)</p>	<ul style="list-style-type: none"> • A device for spectroscopy of X-ray energy with semiconductor detector • Easy and fast elemental analysis of micro area and multi-elements at the same time (Analyzable Elements: Be to U) • Automatic elemental analysis function during observation (Live Analysis, Live MAP) • Time-shift visualization of focused data area in mapping data (Play back function) • Structural analysis by phase analysis function • Installable to a wide range of analytical instruments such as TEM, SEM, FIB, and EPMA.

Air-isolated Transfer

Air Isolation Cycle



Analysis



AES
Observation & Analysis



XPS
Observation & Analysis

Solid State Battery

n)



TEM
Observation & Analysis



Glove box



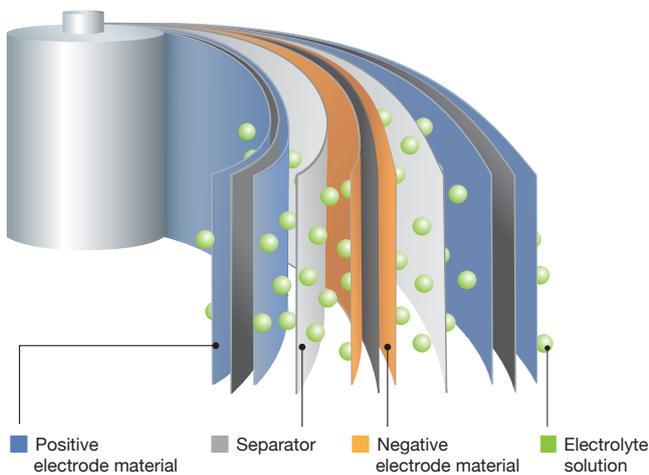
What is Solid-state battery

What is Solid-state battery

Lithium ion batteries (LIBs) are used for mobile batteries of mobile phones that are currently wide spread. LIBs are batteries that perform charging and discharging by making lithium ions move between positive and negative electrodes. They have separators of polymer between positive and negative electrodes to prevent short circuits and an electrolyte of organic solvent is used to conduct ions.

Solid-state batteries perform charging and discharging by using lithium ions, which is the same as with LIBs. However, instead of a separator and electrolyte solution located between positive and negative electrodes, a solid material electrolyte is used. Replacing with a solid electrolyte can reduce the risks of smoking and ignition caused by the electrolyte solution, expanding applications such as BEV and larger ESS. In recent years, lithium-based rechargeable batteries have been used due to the spread of BEVs. However, current LIBs have issues such as safety, cruising distance, and charging time. Solid-state batteries have high energy density and safety, and are expected to have long service life. Their expectations as next-generation batteries are high and are being developed for practical use by automakers and battery manufacturers.

Composition of Lithium Ion Battery (LIB)

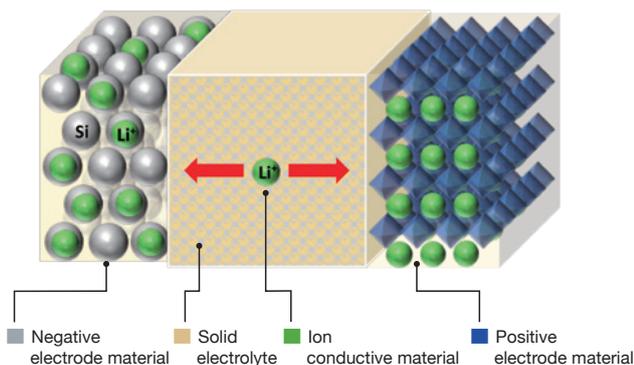


The basic structure of LIBs consists of components shown in the left figure.

For the positive electrode, a compound of oxidized material containing lithium is used as the main active material and created by kneading carbon materials as conductive assistant with polymer binders that bind them. For the negative electrode, graphite carbons that can intercalate lithium are used and created by kneading polymer binders.

Separator films for lithium ion batteries use porous polymers with narrow pores. Separator films have a shutdown function as a safety switch in case of thermal runaway by closing the pores, preventing short-circuits caused by contact between the positive and negative electrodes. The electrolyte solution is created by dissolving electrolyte containing lithium by an organic solvent. Since each material uses highly reactive lithium that alters in the air, it is inevitable to manufacture them in an air-isolation environment. In addition, for analysis of each material, specimen preparation, observation and analysis need to be conducted in an air-isolation environment, air-isolation instruments and those system shown in P. 3-4 are useful.

Composition of Solid-state Battery



The structure of solid-state battery (SSB) is composed as shown in the left figure.

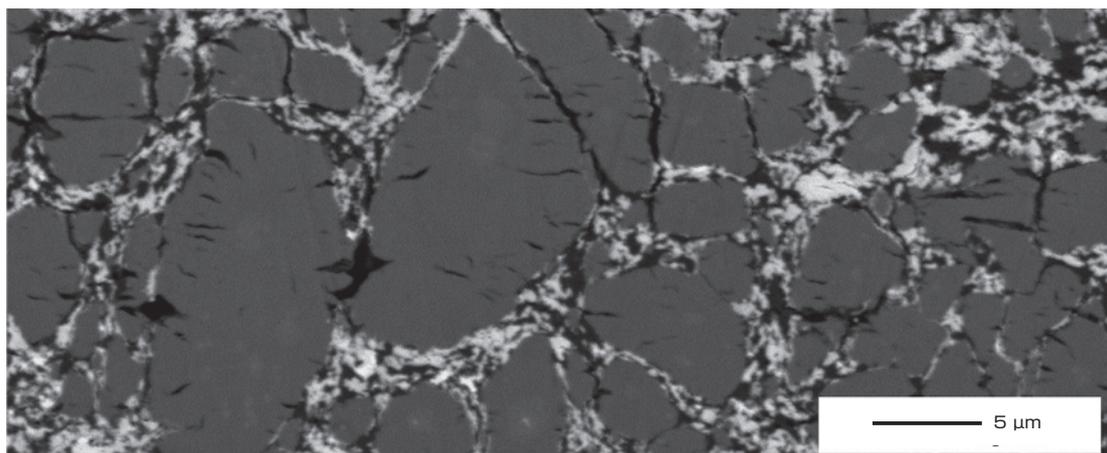
For solid-state battery, solid electrolyte is used to conduct ions, instead of a polymer material separator and electrolyte solution between positive and negative electrodes.

Same as LIBs, the positive electrode uses-lithium transition metal (TM) oxide materials and conductive assistants. Additional solid electrolytes are used in SSB. For the negative electrode, other than carbons used with LIBs, silicon materials have recently been attracting attention. Since they are expected to introduce nearly 10 times more lithium than carbon materials do, researches of silicon negative electrodes is progressing.

Silicon Negative Electrode and Solid Electrolyte

Silicon Negative Electrode (Si anode)

For rechargeable batteries that can be charged and discharged, anode materials that can store more Li by charging are desired. Carbon material(graphite) is mainly used in anodes of LIBs, with a theoretical capacity of 372 mAh/g. Si anodes have a theoretical capacity of 4200 mAh/g, which is approximately 10 times greater than graphite, so an increase in capacity can be expected. Silicon is attracting attention because of its relatively low action potential and abundant natural resources. On the other hand, silicon expands in volume nearly three times during charging, and has issue such as shorter life when used in LIBs. Use as complex with carbon material and silicon is proposed although theoretical capacity declines. Use of nano particle silicon are studied to improve both capacity and life for SSB.



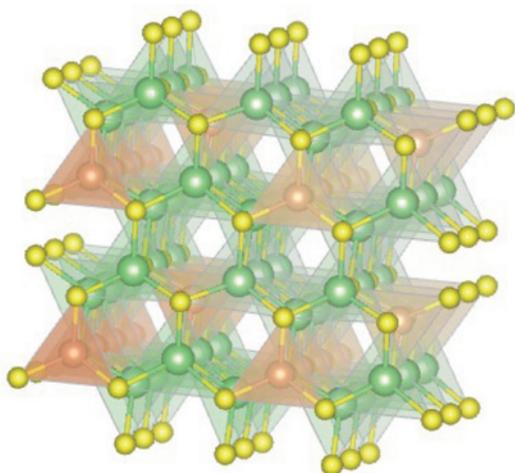
SEM backscattered electron image of Si anode complex: silicon particle (gray) solid electrolyte (white) and carbon (black) after charging

Solid electrolyte

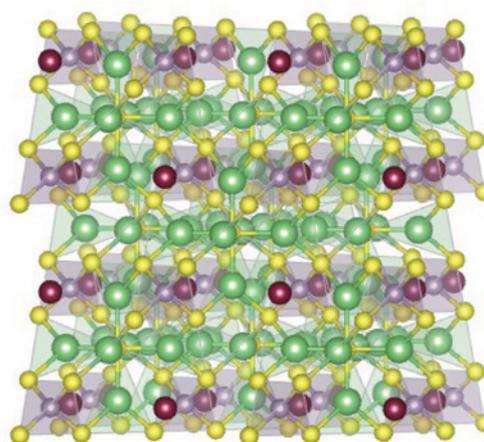
Solid electrolyte has the function of both an electrolyte solution to carry lithium ions between cathode and anode and a separator to prevent short circuiting. The material has high ion conductivity and electrochemical stability with wide potential window in CV (cyclic voltammetry), despite of its solid nature. In addition, since there are no anions other than lithium ions compared with electrolyte solution, side reactions do not happen, and a longer life of the battery is expected. At the moment, research is under way for mainly two kinds of materials, oxide based and sulfide based solid electrolytes. Oxide based solid electrolytes have lower ion conductivity than sulfide based but are more stable in the air. Sulfide based solid electrolytes have concerns over the generation of hazardous gas such as the generation of hydrogen sulfide. However, they are considered promising because they are soft and can suppress interface resistance.

In sulfide based solid electrolyte, Thio-LISCON is one of the applied materials where the oxygen in the substance group called LISCON is replaced with the sulfur. LISCON is an oxide based, lithium ion conductor. Various other substances are being considered.

This application note is introducing an analysis example of sulfide based solid electrolyte $3\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{LiI}$ (LPSI) which can improve ion conductivity with the iodine included.



Thio-LISCON-based electrolyte Li_3SbS_4



Argyrodite-based solid electrolyte $\text{Li}_6\text{PS}_4\text{Cl}$

Battery Creation Process

and Evaluation & Analytical Instruments

Material development and manufacturing

- Positive electrode active material
- Negative electrode active material
- Solid electrolyte
- Binder
- Conductive assistant

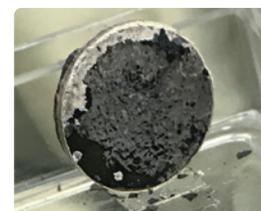


Electrode manufacturing

- Positive electrode (complex)
- Negative electrode (complex)
- Solid electrolyte



Battery creation



Evaluation content

Shape / composition / physical property / structure

Film thickness / material diffusion / void rate

Electric characteristic / structure / safety evaluation

Positive electrode material / negative electrode material / electrolyte / binder	
• Shape & Size	
Micrometer to millimeter order	SEM
Sub-micrometer to nanometer	TEM
Evaluation down to 1 micrometer by 3D	XCT, TEM
• Composition	
Solid ppb level measurement	XRF, LA-ICP-MS
Dissolution measurement	Ion Chromatography, ICP-MS
• Surface analysis	
Average rating in millimeter order	XPS
Local evaluation of tens of nanometers	Auger Microprobe (AES)
• Structural analysis	
Crystal/crystalline structure evaluation	XRD
Thermal property evaluation	TG-DTA, SEM, TEM, EPMA, ESR
Bonding state evaluation	Raman, NMR, XPS, TEM-EELS, SEM-SXES, AES, EPMA-SXES
Lithium diffusion coefficient (each material)	NMR
Chemical state evaluation	TEM-EELS, SXES, Raman, AES, XPS
Binder (SBR) evaluation	TG-MS (Negative ion measurement)
• Physical property analysis	
Specific surface area	Gas adsorption method
Zeta potential	Light scattering
Ion conductivity rate	AC impedance method
Electron conductivity rate	DC method
Potential area	Cyclic voltammetry
Evaluation for evolved gas from solid electrolyte	TG-MS
Electrode evaluation	
Film thickness	SEM
Dispersibility	SEM-EDS, Raman, AFM-IR, XCT
Void	Gas adsorption method, Mercury porosimetry, XCT
Evaluation of battery after assembly	
Charge-discharge capacity	Electric characteristic evaluation
Repeatability characteristic	Electric characteristic evaluation
Charge-discharge rate characteristic	Electric characteristic evaluation
Shape	SEM, TEM, AES, EPMA, XCT
Structural change during charge/discharge	XRD, SEM
Grain boundary structure / composition after charge-discharge cycles	Impedance measurement method, SEM, TEM, AES, EPMA
Dispersion evaluation of kneaded material	SEM-EDS, Raman, AFM-IR, TEM, AES, EPMA, XCT
Lithium diffusion coefficient	GITT method, Current pulse relaxation method, AC impedance method
Potential area confirmation	Cyclic voltammetry
Safety evaluation & Operando evaluation of generated gas	MS

*EPMA : Electron Probe Micro Analyzer

Analyses and Tools

-Solid-state battery-

What is needed for observation and analysis of solid-state battery

For batteries assembled with a positive electrode/negative electrode/solid electrolyte, it is also important to evaluate the composite-materials before and after assembly.

Disassembling the battery and using an electron microscope enables observation and analysis material property information. Batteries containing lithium and sulfur using sulfide based solid electrolyte should be handled in an air-isolated environment to suppress material alteration. These batteries require air-isolated transfer for specimen preparation and observation, JEOL's instruments are designed for air-isolated transfer to directly link specimen preparation and observation/analysis instrument.

Analysis case of this application note

In this application note, the silicon negative electrode and solid electrolyte taken out from an experimental coin-cell battery were used, and the cross section was processed, observed and analyzed under air-isolated conditions. For NMR analysis, each layer was stripped and extracted from a coin-cell battery in an air-isolated environment.

Silicon negative electrode	Processing / Observation / Analytical instrument
Air-isolated cross-sectioning / thin film milling for cross-section observation	CP, FIB
Chemical state of silicon / Lithium distribution evaluation in particle after charge	SEM-SXES/EDS, TEM-EELS, AES
Material distribution of negative electrode by phase analysis	EDS
Solid electrolyte	Processing / Observation / Analytical instrument
Evaluation of evolved gas and safety evaluation	MS (TG-MS)
Dynamics evaluation of lithium ion	NMR

Air-isolated transfer systems and tools

This application note is targeted at the analysis of silicon negative electrodes and solid electrolytes.

As they contain highly-reactive lithium and sulfide, analyses require minimizing reaction of oxygen and moisture in the air. JEOL's instruments are able to prepare systems in air-isolated environment as shown in P. 3, 4.

Specimen preparation and observations, analyses can combine instruments suitable for the evaluation purpose of the target material with air-isolated tools, based on the features of instruments as shown in P. 2.

Air-isolated tools available for each instrument are shown here:



Air-isolated processing / observation holder common for CP / FIB / SEM/EPMA¹



Air-isolated processing / observation holder common for CP / Auger Microprobe



TEM air-isolated observation / analysis holder

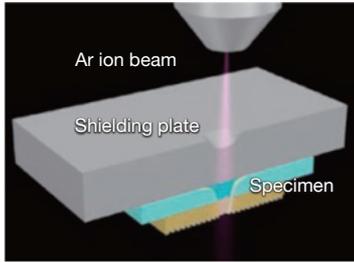


XPS air-isolated observation / analysis holder

1-1

Specimen Preparation

Air-isolated cross-section specimen preparation by CP



CROSS SECTION POLISHER™ : CP

Cross-section preparation device using Broad argon (Ar) Ion Beam (BIB). Specimen cross-section can be prepared by protruding the specimen from the shielding plate and irradiating argon ion beam to the protruded part for etching. Applicable materials vary including soft material, hard material, complex material, and polymer. Cooling CP (with air-isolation) can handle specimen transfer in air-isolated environment and cross-section milling while keeping the specimen cool. Specimen setting to the holder can be easily performed in a glove box.

Comparison of fracture surface and cross section by CP

Fig.1 shows the SEM image of the fracture surface and cross section by CP for solid-state battery. The fracture surface has roughness. On the other hand, the cross-section by CP is smooth, enabling clear observation of the boundary between the silicon anode and the solid electrolyte, and brightness information attributed to the materials inside silicon anode and solid electrolyte.

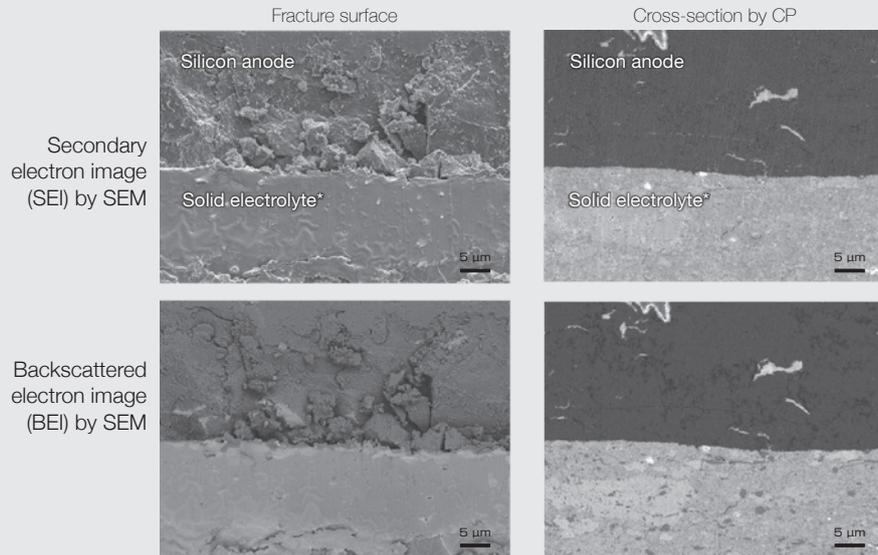


Fig.1 Fracture surface and cross-section by CP of solid-state battery silicon negative electrode(charged)

Effect of air-isolation

It is necessary to transfer a specimen in an air-to react with the air.

Fig. 2 shows the SEM images of a cross section before and after the exposure to the air. It can be and altered, after exposure to the air. (red circle

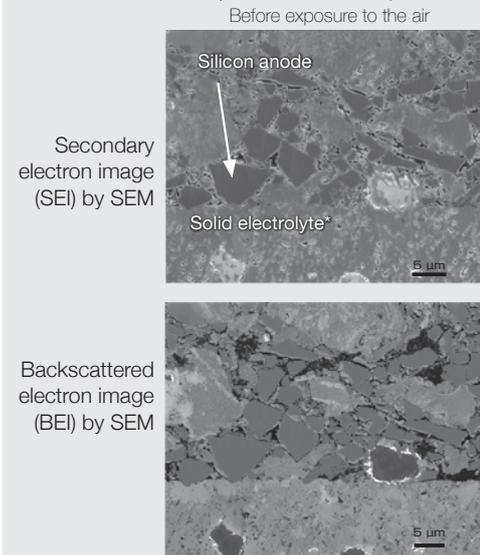


Fig.2 Cross-section of before and after air-exposure of

Specimen preparation flow

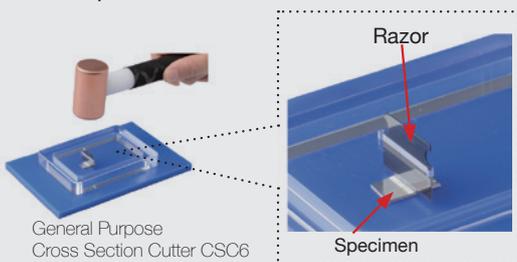


Set a specimen in Glove box

Transfer by transfer vessel



I. Cut a specimen

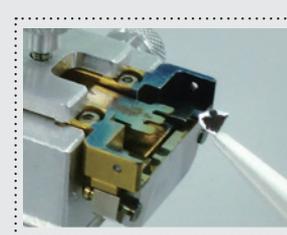


Specimen can be easily cut by a General Purpose Cross Section Cutter CSC6. Ceramic knife is also available.



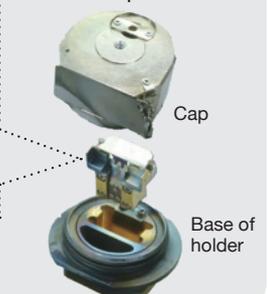
Cut battery specimen

II. Set the specimen to the holder



Specimen can be fixed by clamping.

III. Encapsulate the specimen by the base and the cap



Cap

Base of holder



Effect of CP cooling milling

CP can process the specimen while cooling, enabling suppression of the heat generated during milling. Milling while cooling is useful for thermally-labile material and material that may alter by heat. Fig.3 shows the SEM backscattered electron images of Sn-Pb solder milled by CP at room temperature and cooling temperature. At the room temperature, voids are confirmed in the boundary of Sn and Pb due to heat damage. On the other hand, at cooling temperature, a cross-section without voids is obtained.

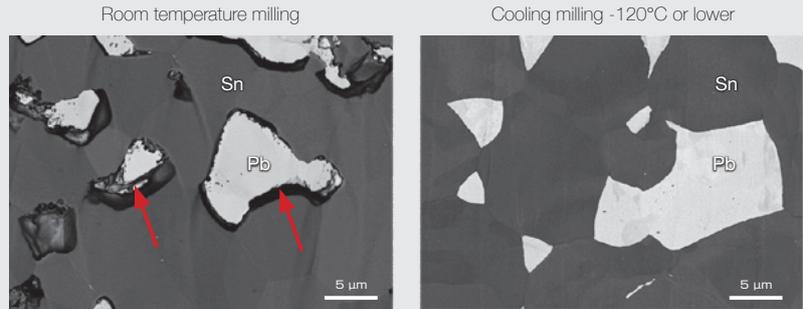


Fig.3 Cross-section of Sn-Pb solder milled at room and cooling temperatures by CP

Fig.4 shows the SEM BEI of a cross-section milled by cooling CP of solid-state battery in air-isolated environment. In the left image, nano silicon negative electrode material of several hundred nm size can be observed. The right image confirmed the difference in composition of solid electrolyte.

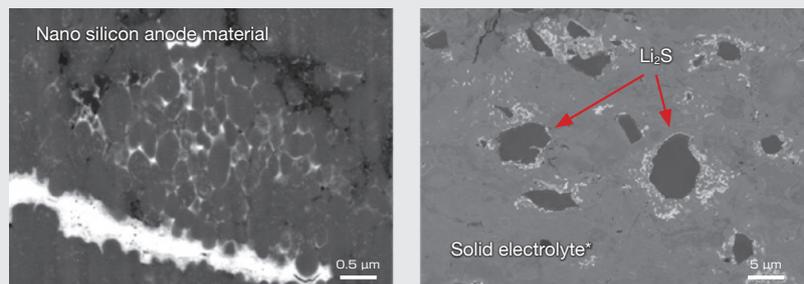


Fig.4 Cross-section of Nano silicon anode material and solid electrolyte* of solid-state battery (charged) by CP

isolated environment since battery materials tend to react with air by CP of silicon anode material containing sulfide, confirmed that the specimen reacted with the air area in the image).

After exposure to the air for 15 seconds

silicon anode (uncharged) by CP

Cross-section by CP

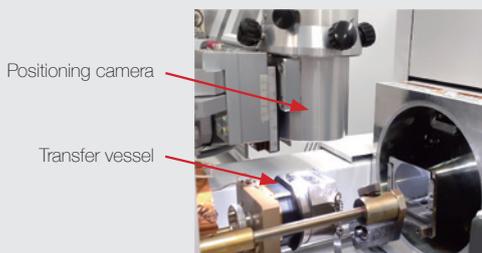
Transfer by transfer vessel

To each instrument



Confirmation of the position for milling

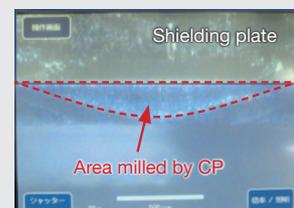
The milling position can be confirmed with the CP positioning camera through window of the cap. The camera image is displayed on the monitor of CP.



Milled area shown in CP monitor

Confirmation of cross-section during and after milling by CP

The cross section can be confirmed through the camera inserted in CP. The camera image is shown on CP monitor and can be confirmed in real-time during milling.



Solid electrolyte* Sulfide system solid electrolyte 3Li₂S-P₂S₅-LiI (LPSI)

1-1

Specimen Preparation

Air-isolated preparation of TEM specimen by FIB

Specimen Preparation Flow

Many battery materials can easily react with the atmospheric components, it is required to perform a series of tasks from preparation to observation of the specimen without exposure to the atmosphere. Fig.1 shows the flow of air-isolated TEM specimen preparation by using CP and FIB-SEM. The transfer vessel and the slide cover holder are used to transfer a specimen between instruments, and a specimen chamber manipulator is used during TEM specimen preparation process by FIB.

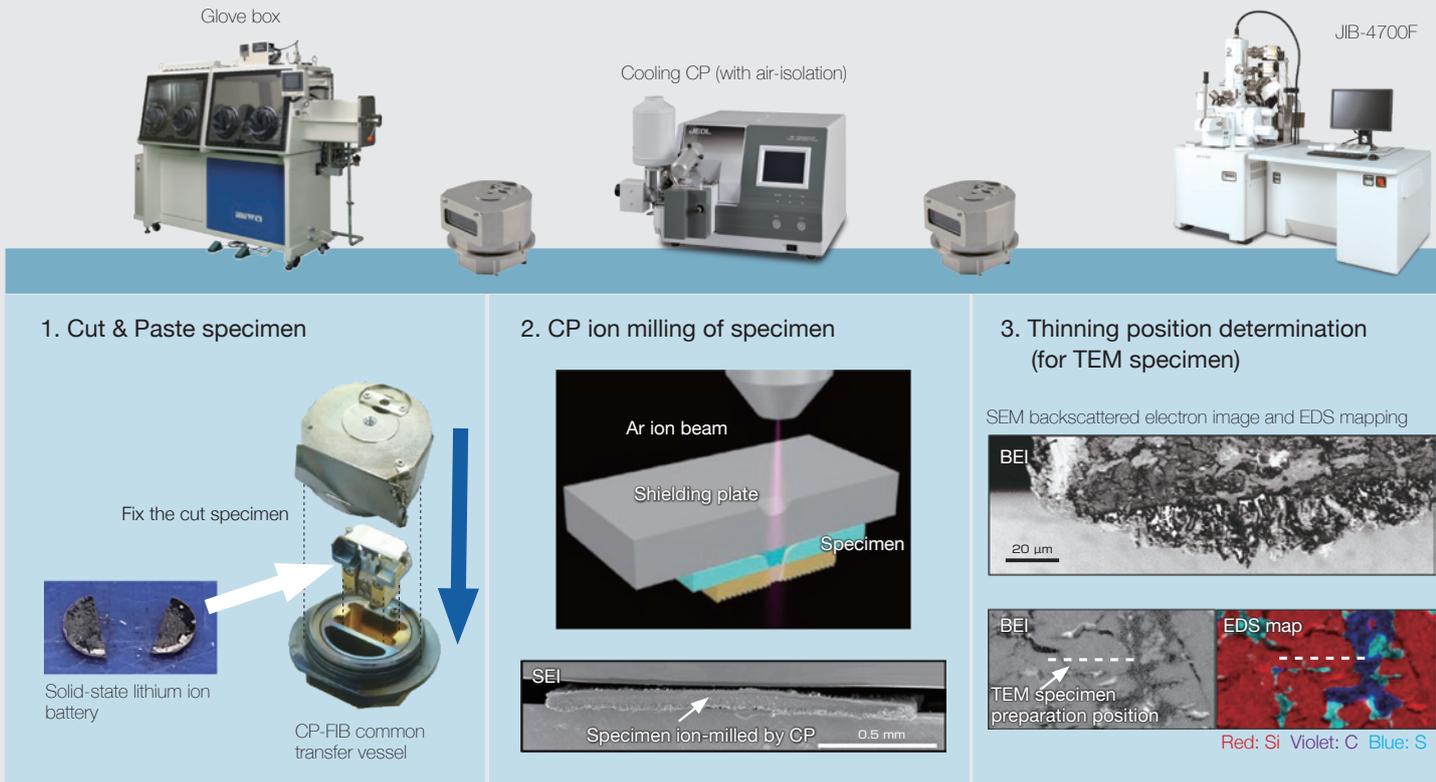


Fig. 1 Flow of Air-isolated TEM specimen preparation by CP and FIB-SEM

Instrument and Features

[Instrument]

FIB-SEM: Multi-Beam System JIB-4700F
 Manipulator: Specimen Chamber Nanomanipulator OmniProbe (OXFORD Instruments)
 EDS: Energy Dispersive X-ray Spectrometer
 Ultim[®] Max 170 (OXFORD Instruments)

[Features]

FIB is mainly used for TEM specimen preparation and fine milling for SEM. Since FIB is capable of for observation and processing, it enables high magnification observation of the area of interest for cross section and thin film as well as the subsequent processing by targeting a precise region.

The JIB-4700F is a FIB-SEM system equipped with both an SEM column and a FIB column in the chamber. It can provide high resolution SEM observation of a FIB-processed surface as well as monitor processes by SEM even during FIB milling. Moreover, attaching an OmniProbe to the JIB-4700F enables manipulating operations while observing SEM image and FIB image. Therefore, the specimen block processed in the FIB can be replaced on the FIB grid in an air-isolated environment.

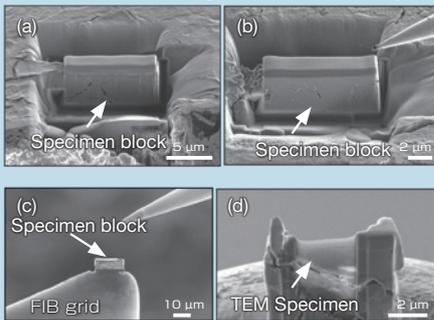


A specimen can be directly transferred from the CP to FIB-SEM in an air-isolated environment, enabling smooth and detailed SEM analysis of the CP cross section which is flat exposing inside of specimen. A TEM specimen can be then prepared from the same CP cross section. Lastly, the half-moon FIB grid (half-moon shape TEM grid) with a TEM specimen on it is transferred from the CP-FIB common transfer vessel to air-isolated TEM holder within a globe box, and transferred to a TEM for TEM observation/analysis.

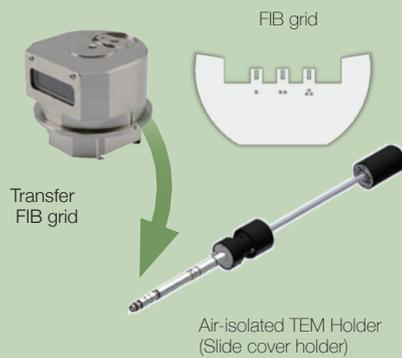


4. FIB thinning

Preparation of specimen block (a)
 Specimen fixation on FIB grid (b) to (c) and thinning (d)

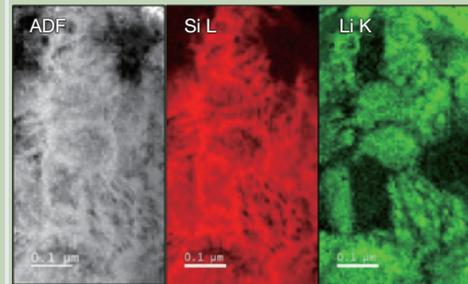


5. To TEM holder



6. TEM observation / analysis

ADF-STEM image and EELS mapping



Air-isolation

The transfer vessel specimen holder provides mechanism to prevent exposure of specimens to the air with a cap that can be sealed and unsealed with the instruments. A CP-FIB common transfer vessel is compatible with our air-isolated Cooling CP and JIB-4700F. Thus, a CP ion-milled specimen can be directly transferred to the JIB-4700F (Fig. 2), enabling SEM observation and FIB processing of CP ion-milled surfaces in air-isolated environment.



Fig. 2. Examples of air-isolated CP-FIB common transfer vessel attached to Cooling CP and JIB-4700F.

1-2

Structural Analysis

Structural analysis of silicon anode by SEM

Purpose

Crystalline state and physical property evaluation are conducted by SEM for silicon anodes in the charged state which is expected to be used in solid-state battery. Silicon anodes are expected to be applied to solid-state batteries. Crystalline state and physical property of silicon anodes in the charged state are evaluated by SEM.

Content

Silicon anodes are expected to be applied to solid-state batteries. Since Li is introduced to silicon anode after charging, air-isolated transfer is required. The results of several observations and analytical methods including SEM backscattered electron image observation, EDS, EBSD and SXES are shown here, for silicon negative electrodes after introduction of Li through charging to understand how the crystalline state and physical property changed.



Instrument and Features

【Instrument】

SEM: JSM-IT800 <HL/SHL>

EDS: JED-2300, Ultim Extreme
(OXFORD Instruments)

SXES: SS-94000SXES(SXES-LR)

EBSD: Symmetry (OXFORD Instruments)

【Features】

The JSM-IT800 incorporates our "In-lens Schottky Plus field emission electron gun" for high resolution imaging and an innovative electron optical control system "Neo Engine", as well as a system of seamless GUI "SEM Center", as a common platform.

The JSM-IT800 series offers a choice of objective lenses to suit the user's purpose.

The HL version and SHL version (including SHLs version) are equipped with an electromagnetic/electrostatic field superposed objective lens developed from the versatile out-lens. The high resolution observation and analysis of a wide variety of specimens from metals to nano materials are possible. By combining it with SXES and EBSD, analysis of chemical state and crystalline state are available.

Observation, analytical method by instruments

- SEM Observation method to utilize secondary electrons and backscattered electrons generated by the electron beam irradiated to the specimen. → Observations of morphology and composition distribution of specimen and channeling contrast by crystal orientation are possible.
- EDS Analytical method to detect the characteristic X-ray generated by the interaction with electron beams and easily perform distribution measurement, qualitative and quantitative analyses of composing elements of a specimen. → Used for qualitative, quantitative analyses of elements in a specimen
Detection of metal Li is possible by a windowless EDS.
- SXES High energy resolution X-ray spectroscopy to obtain spectrum reflecting chemical state by analyzing the characteristic X-rays in soft X-ray range (X-ray of very low energy less than 2keV) by diffraction grating. → Used for analysis of chemical state of element in a specimen. Detection of metal Li and its chemical state analysis are possible by SXES-LR.
- EBSD Analytical method to measure crystal orientation at the electron beam irradiation point, from the electron backscatter diffraction pattern generated from the specimen, by irradiating the electron beam to the bulk crystal specimen greatly tilted (approx. 70°) against the horizontal plane. → Used for analysis of crystal orientation and crystal grain size of a specimen.

Observation and analysis - cross section of 90% SOC silicon anode -

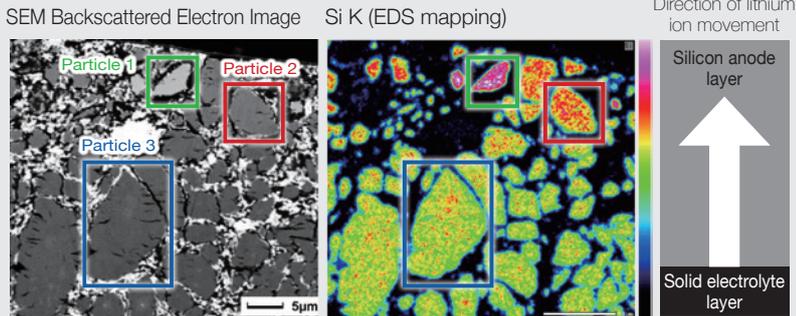


Fig.1 SEM backscattered electron image and Si elemental map by EDS

The SEM backscattered electron image shows different contrasts between Si particles in different location in electrode and the distribution of Si K intensity of EDS elemental analysis corresponds to the contrast difference.

The SXES analysis showed that the particles with lower Si L intensities had higher Li content due to the higher intensity per unit area of Li K. The chemical state of silicon also differs, and spectra are obtained that suggest Li-Si alloying for particles 2 and 3.

The distribution of lithium intensity according to the direction of lithium ion movement during charging was confirmed. In addition, the chemical state of the silicon negative electrode particles was also found to change.

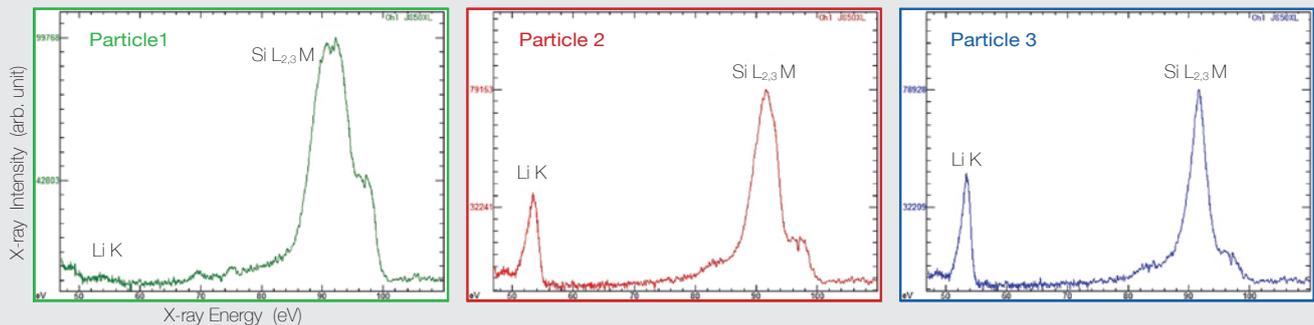


Fig.2 SXES spectra obtained for each particle

Observation and analysis - cross section of 90% charged silicon negative electrode particle -

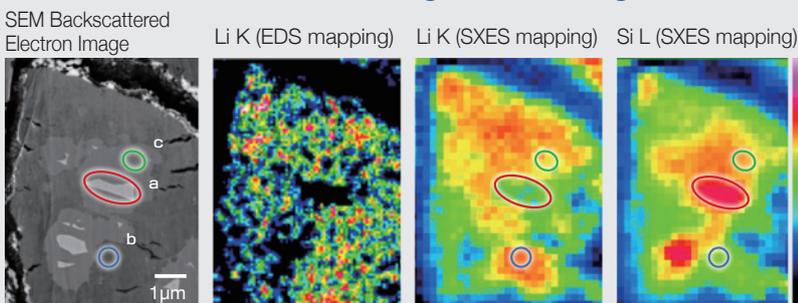


Fig.3. SEM BSE image and elemental mapping by EDS and SXES

SEM backscattered electron image shows different information parts a & b & c in Si particle. The SXES elemental mapping confirms that Li K and Si L intensities are different. Comparing the SXES spectrum of each point, a spectrum corresponding to crystal Si is obtained in a, while a spectrum suggesting the Li-Si alloying is obtained in b. Considering the EBSD results, crystalline Si remains in a, indicating that it is not charged. In b, since Li is inserted, it is charged and existing as $\text{Li}_{15}\text{Si}_4$ alloy. On the other hand, in c, Li was detected in the SXES analysis, but no EBSD pattern was obtained. It suggests that it is in a charged state but not yet alloyed, in an amorphous state, or in a mixture of amorphous and Li-Si alloys.

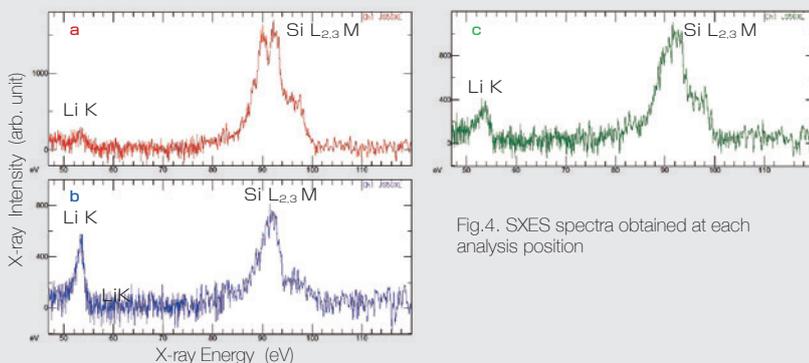


Fig.4. SXES spectra obtained at each analysis position

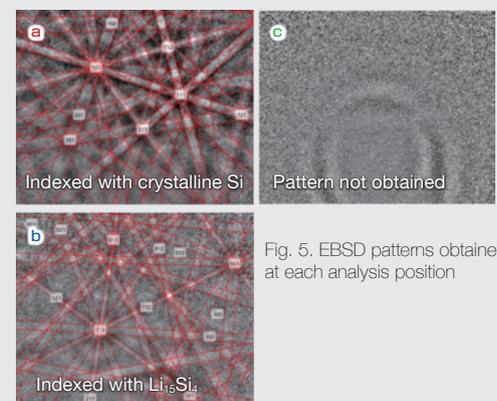


Fig. 5. EBSD patterns obtained at each analysis position

Summary

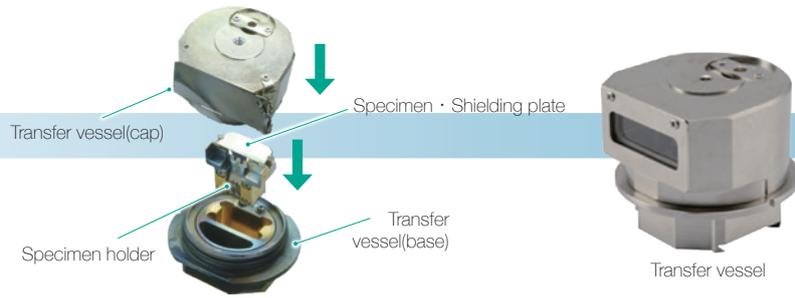
The combination of observation by SEM in air-isolated environment, SEM-SXES method and EDS analysis, and EBSD analysis, provided the information of crystal structure and chemical state of charged silicon anode, suggesting the effectiveness of this method in analysis of Li battery.

Sample Courtesy:
Prof. Atsunori Matsuda,
Department of Electrical and Electronic Information Engineering,
Toyoashi University of Technology,

1-2 Structural Analysis EDS phase analysis



Solid-state lithium ion battery

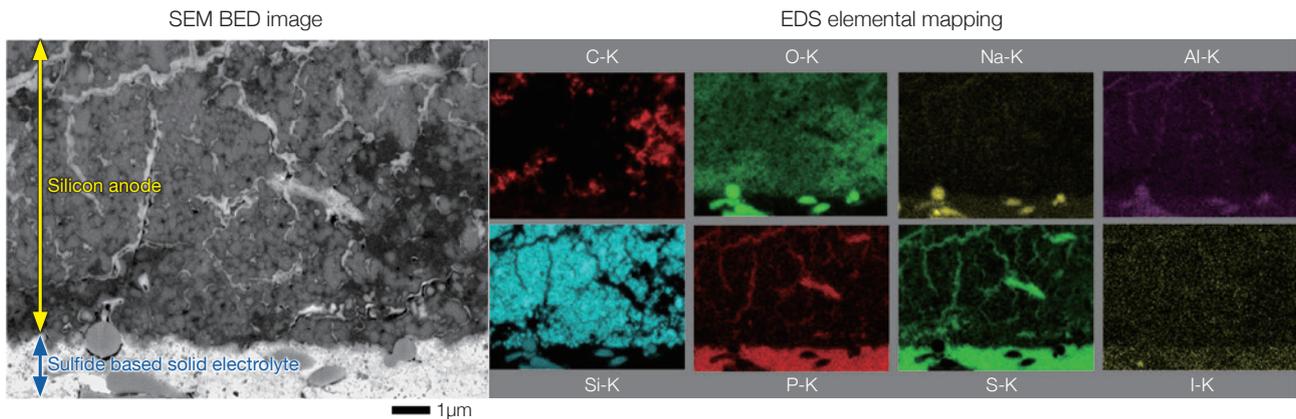


EDS phase analysis

The EDS phase analysis function can analyze a combination of multiple elements and a distribution of compounds. When compounds are distinguished by conventional EDS elemental mapping, characteristic X-ray intensities and concentrations of each element are mapped for comparison and study. EDS phase mapping automatically calculates the characteristic compositions (=phases) by applying multivariate analysis to the spectra of all points, and maps the distribution of each phase.

An analysis example of a silicon anode by EDS phase analysis

A cross section was prepared for a half cell composing of silicon anode that was changed once and sulfide based solid electrolyte $3\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{LiI}$ (LPSI) in air-isolated environment by Cooling CROSS SECTION POLISHER™. The cross section was observed and analyzed by SEM/EDS.



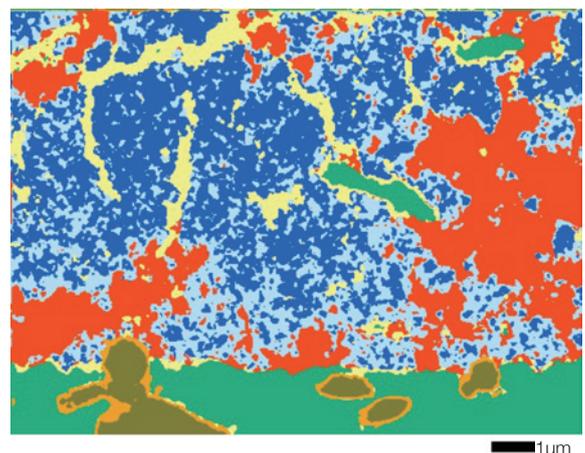
EDS elemental mappings of elements in the cross section of silicon negative electrode and solid electrolyte, detected and visualized by SEM/EDS are shown in the above figure. Normal EDS elemental mapping shows that the conductive assistant is localized in the silicon negative electrode in C-K map and that the solid electrolyte is localized in the silicon negative electrode in P-K, S-K map.

EDS phase mapping

EDS phase maps are created by running multivariate analysis to the spectra of all points obtained by EDS map acquisition. The cross section of silicon negative electrode and solid electrolyte is automatically separated into 7 phases and displayed in different colors (right figure). Each phase is labelled based on the result obtained by the analysis of EDS phase spectra.

- Silicon negative electrode
- Si poor phase (vs. silicon negative electrode phase)
- Conductive assistant phase
- Solid electrolyte phase
- P, S poor, Si rich phase (vs. solid electrolyte phase)
- Additive phase
- P, S rich phase (vs. additive phase)

EDS phase mapping (composite image)



Sample Courtesy:
 Prof. Atsunori Matsuda,
 Department of Electrical and Electronic Information Engineering,
 Toyohashi University of Technology,



Cooling CROSS SECTION POLISHER™
 IB-19520CCP



Scanning Electron Microscope
 JSM-IT800<SHL>



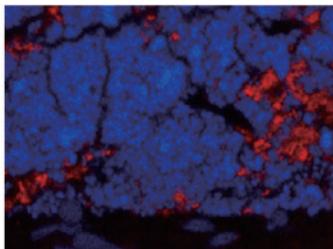
Energy Dispersive X-ray Spectrometer
 EX-74720U1L5Q

EDS phase analysis can distinguish the regions that are difficult to judge by EDS elemental mapping, such as a region that contain elements with different composition ratios and voids. In analyzing battery material, it automatically identifies the characteristic phases such as active material regions and electrolyte regions, and supports the structural analysis.

The figures below are superimposed images of the normal EDS elemental mapping and superimposed images and spectra of the phases of interest in EDS phase mapping. In EDS elemental mapping, distribution of Si is shown in both silicon negative electrode and additive of solid electrolyte which are different in structure. On the other hand, in EDS phase mapping, it is easy to distinguish the difference in structure, as it judges and separates silicon negative electrode particle and additive of solid electrolyte as different phases, based on the difference of contained elements and the composition ratio.

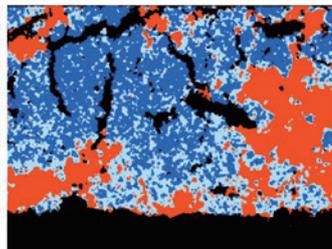
In addition, it can confirm regions where the intensities of composing elements are slightly different, such as the Si poor phase in silicon negative electrode (light blue) and P,S poor phase in solid electrolyte (yellow). The difference in types and intensity ratios of composing elements in each phase is known from the EDS phase spectrum.

EDS elemental map
 (superimposed image)



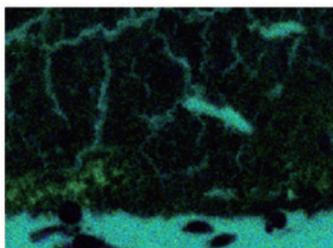
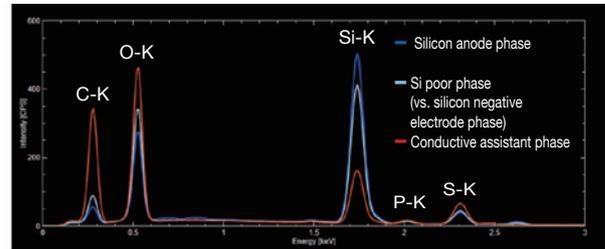
■ C-K ■ Si-K

EDS phase map
 (phase of interest)

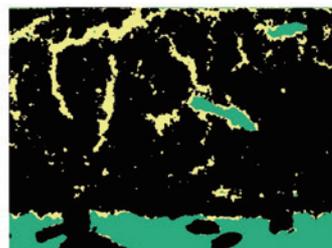


■ Silicon anode phase ■ Si poor phase (vs. silicon negative electrode phase) ■ Conductive assistant phase

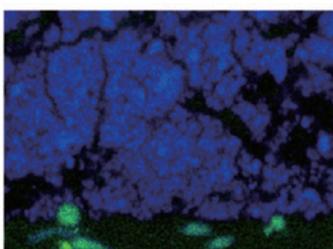
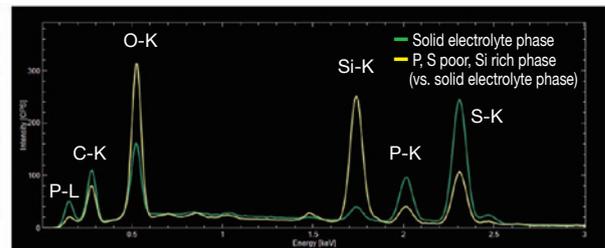
EDS phase spectra
 (phase of interest)



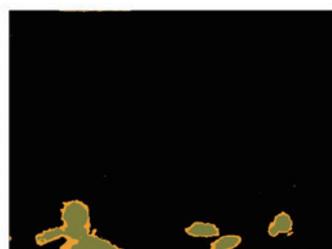
■ P-K ■ S-K



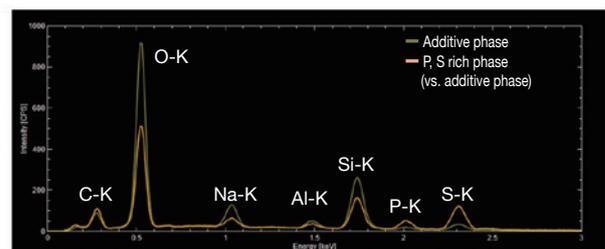
■ Solid electrolyte phase ■ P, S poor, Si rich phase (vs. solid electrolyte phase)



■ Na-K ■ Si-K



■ Additive phase ■ P, S rich phase (vs. additive phase)



1-2 Evaluation of Physical Property Analysis of silicon anode by TEM

Purpose

Transmission electron microscopy is used to evaluate crystalline state and physical properties for the state of charge of silicon negative electrode, which is expected to be applied to solid-state batteries.

Content

The application of silicon negative electrode to solid-state battery has been expected. However, as Li is introduced after charging, it is necessary to transfer silicon negative electrodes in an air-isolated environment. In addition, the results of multiple observation and analysis methods are shown including TEM, electron diffraction, STEM, EDS, and EELS, to understand the changes of crystalline state and physical property with the introduction of Li during the charging process.

Instrument and Features

[Instrument]

TEM: JEM-ARM300F2 (GRAND ARM™2)
EDS: JED-2300
EELS: ContinuumER (GATAN)

[Features]

JEM-ARM300F2 (GRAND ARM™2) is an atomic resolution electron microscope with a maximum accelerating voltage of 300 kV incorporating a JEOL-designed aberration corrector. It is not only capable of achieving the highest level imaging resolution in the world, but also of atomic resolution analysis by the combination of EDS and/or EELS.

Moreover, in the event that beam to the specimen is a concern, the acceleration voltage can be reduced down to 40 kV, enabling the observation and analysis with reduced electron beam damage.

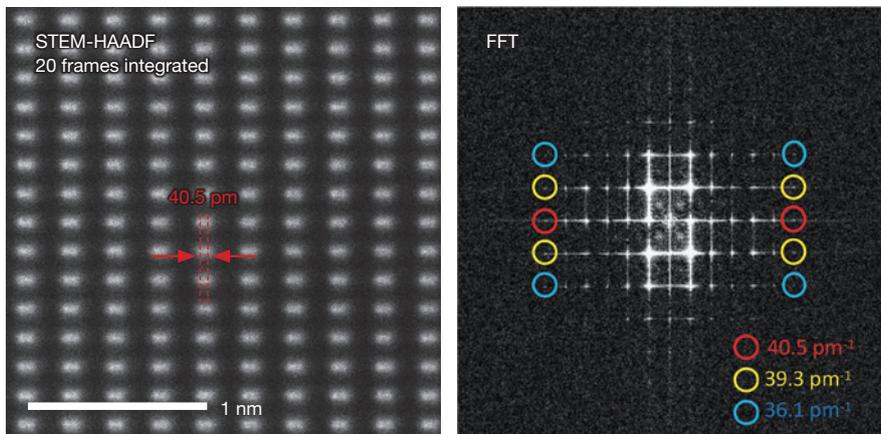


Fig.1 STEM-HAADF image and its FFT pattern. Highest level STEM resolution in the world. Accelerating voltage 300 kV, Specimen GaN[212]

Observation, analytical method by instruments

- | | | |
|-----------------------------|---|---|
| • TEM | The TEM images are magnified with magnetic field lens formed by electrons transmitted through the specimen. |▶ Even the atomic level structure can be observed. |
| • Electron Beam Diffraction | A diffraction pattern corresponds to electrons elastically scattered in a specific direction at a crystal plane. |▶ It can be used to evaluate crystallinity and other properties. |
| • STEM | The STEM images are obtained by scanning a converged probe on a specimen and plotting the intensity of transmitted (or diffracted) waves excited from the irradiated point.
With the STEM-HAADF imaging mode, Z contrast corresponding to the atomic number is obtained. |▶ Used to confirm the composition of a specimen. |
| • EDS | An analytical method to detect the characteristic X-rays generated by the interaction of the electron beams with the specimen, qualitative and quantitative analyses and position-sensitive distribution of composing elements within a specimen can be obtained. |▶ Used for qualitative, quantitative analyses of elements in a specimen |
| • EELS | A method of spectroscopy for energy loss of electrons scattered by Coulomb interactions with electrons and nuclei in a substance after the electron beam has transmitted through it. |▶ Used for analysis of bonding states of composing elements and for qualitative and quantitative analyses. |



— Solid electrolyte
 — Carbon black
 — Silicon

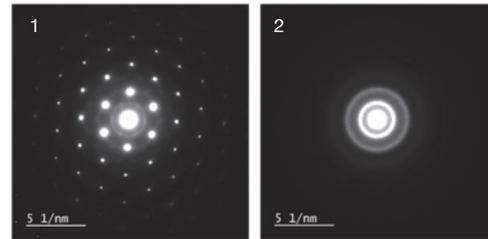


Fig.2 TEM image and diffraction patterns taken at the indicated positions (1,2)

Observation and analysis of silicon anode by TEM image and electron diffraction

The TEM image shows dramatically different contrast for the same silicon region indicated by positions 1 and 2. Diffraction patterns were obtained from each position; position 1 is demonstrated to be highly crystalline, whereas position 2 is amorphous. Thus, the same silicon anode exists in different crystalline states.

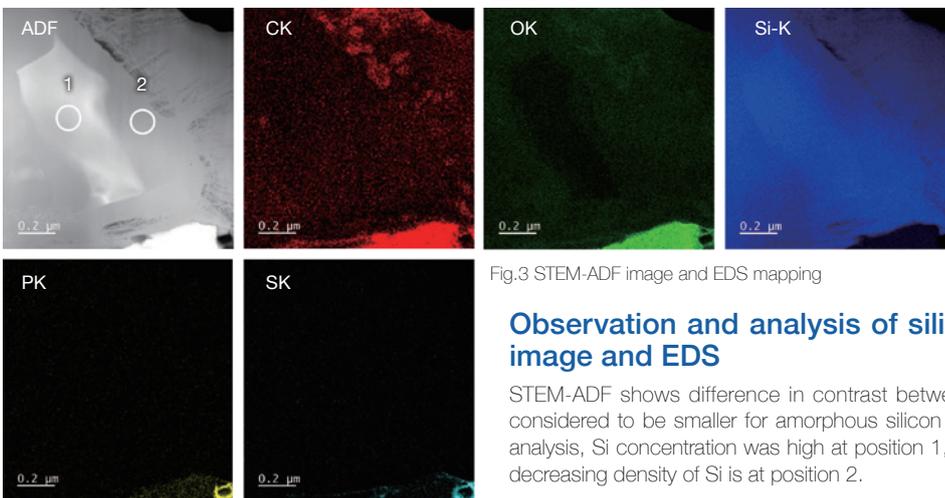


Fig.3 STEM-ADF image and EDS mapping

Observation and analysis of silicon anode by STEM-ADF image and EDS

STEM-ADF shows difference in contrast between positions 1 and 2. The density is considered to be smaller for amorphous silicon at position 2. Also, as a result of EDS analysis, Si concentration was high at position 1, and it was slightly lower, indicating the decreasing density of Si is at position 2.

Analysis of silicon anode by STEM-EELS

STEM-EELS mapping shows that the Li concentration is higher at position 2 compared to position 1. It was assumed that the introduction of Li by charging would promote amorphization process of the silicon. In EELS, it was observed that Si $L_{2,3}$ edge peak shifted due to the introduction of Li. It is considered that Li was inserted to the Si crystal by charging, causing it to change from a crystalline state to an amorphous state; the bonding state was also changed.

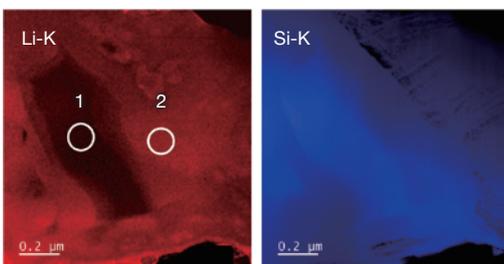


Fig.4 EELS mapping of Li and Si by STEM-EELS

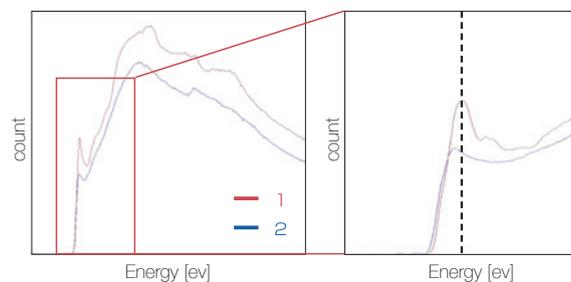


Fig.5 EELS obtained from positions 1 and 2

Summary

Changes in the silicon anode after charging were confirmed by the multifaceted observation and analysis methods of TEM in an air-isolated environment, demonstrating the effectiveness of TEM in analyzing Li batteries.

1-2 Structural Analysis Lithium analysis in charged anode



Introduction

Lithium is a key element in an ion battery. Analysis of this element is considered important. Auger electron spectrometer (AES) is an instrument which can detect lithium, and perform surface analysis and chemical state analysis as well as qualitative and quantitative analysis. It is used in a wide range of uses from development to failure analysis of lithium ion battery. This example of Auger analysis shows quantification of lithium in silicon anode particles for each state of charge and visualized lithium by chemical state in a silicon active material and a solid electrolyte.

Air-isolated transfer using an inert transfer vessel

Lithium is easily reacted with the atmosphere. Therefore, a series of processes from specimen preparation to transferring needs to be performed in an air-isolated environment. In addition to the existing air-isolated transfer system from the CROSS SECTION POLISHER™ (CP) to SEM, EPMA, and FIB, a new transfer vessel that directly connects the Auger Electron Microprobe Spectrometer to the CP has been added to the lineup. Smooth transfer between instruments is possible without the need for complicated work in the glove box.

Specimen preparation



Glove box (made by Miwa Manufacturing Co., Ltd.)

Cross section preparation

Cooling CROSS SECTION POLISHER™ (IB-19520CCP)



Observation/Analysis

Auger Microprobe (JAMP-9510F)



AES-CP compatible holder for transfer vessel

Once the specimen is placed in this holder, specimen transferring is possible from the cross section preparation to AES in an air-isolated environment without removal of specimen.



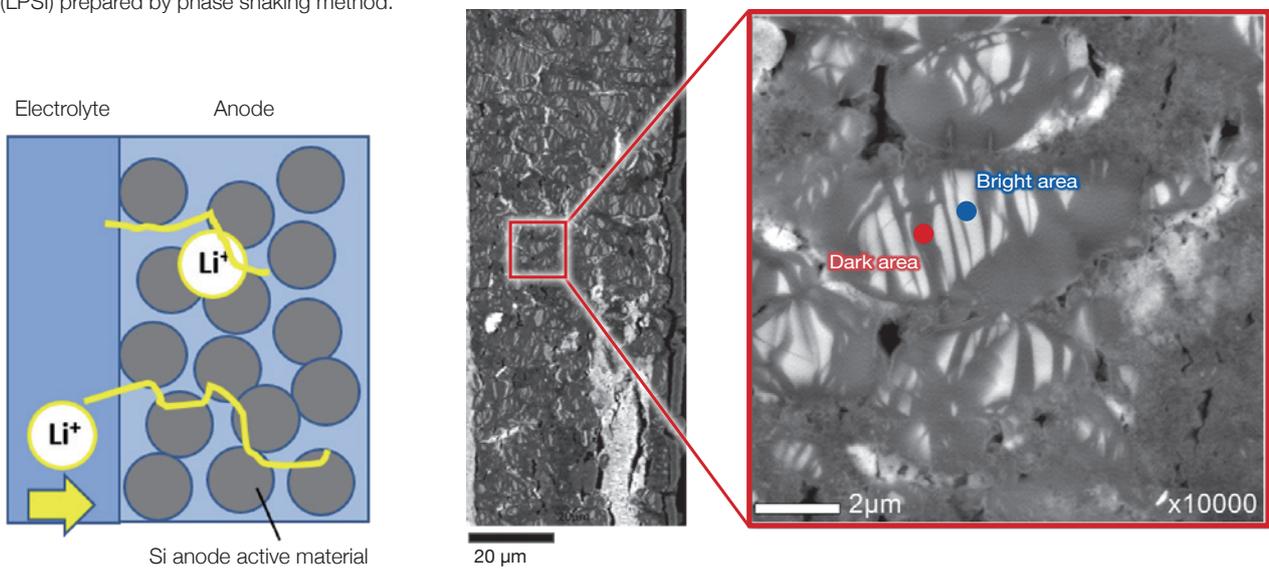
Fig.1 Schematic diagram of the air-isolated transfer system of the glove box-CP-AES

1. Quantitative analysis of lithium in active material in charged anode

As a result of BSE images for the CP cross section of a 38% charged anode, vertical stripe patterns with different brightness were observed in the Si active material. Quantitative analysis by AES was performed for the bright and dark areas in the particle. There was no significant difference in concentration of Li and Si between them. It is assumed that the brightness information obtained by the BSE image is attributed to the structure such as crystalline difference and density difference. The relative sensitivity coefficient method is used to calculate the quantitative values here, with the use of the chemical state quantification method¹⁾ using reference spectra that is expected to improve the quantitative accuracy.

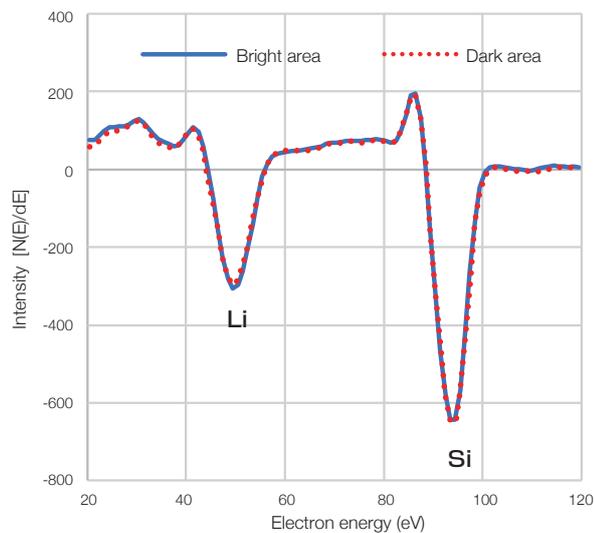
[Anode] is a mixture of silicon particles and sulfide-based solid electrolyte $3\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{LiI}$ (LPSI) prepared by phase shaking method.

1) K. Tsutsumi, Hyomen Kagaku Vol.33, No.8, pp.431-436, 2012



(a) Schematic diagram

(b) BSE composition image of CP cross section of 38% charged anode material



	(atm%)	
	Li	Si
Bright area	56.5	43.5
Dark area	56.9	43.1

(c) AES quantitative analysis of the Si active material (quantification by relative sensitivity coefficient method)

Fig.2 Cross section and surface analysis of Si anode / Si particle (charged)

1. Research on Silicon Negative Electrode (Si anode)

Evaluation of lithium insertion volume in anode materials of different SOC

Comparison of Lithium (Li) atomic concentration inserted into the Silicon (Si) active material between particles was conducted for the 38% and 66% SOC anode materials (Fig.3). As shown in Fig.4, there is a difference of lithium atomic concentration in silicon between particles from the anode material of 38% and 66% SOC. In addition, there was a tendency for there to be a difference in the lithium atomic concentration ratio to silicon particles depending on the distance from the interface of the solid electrolyte and the anode.

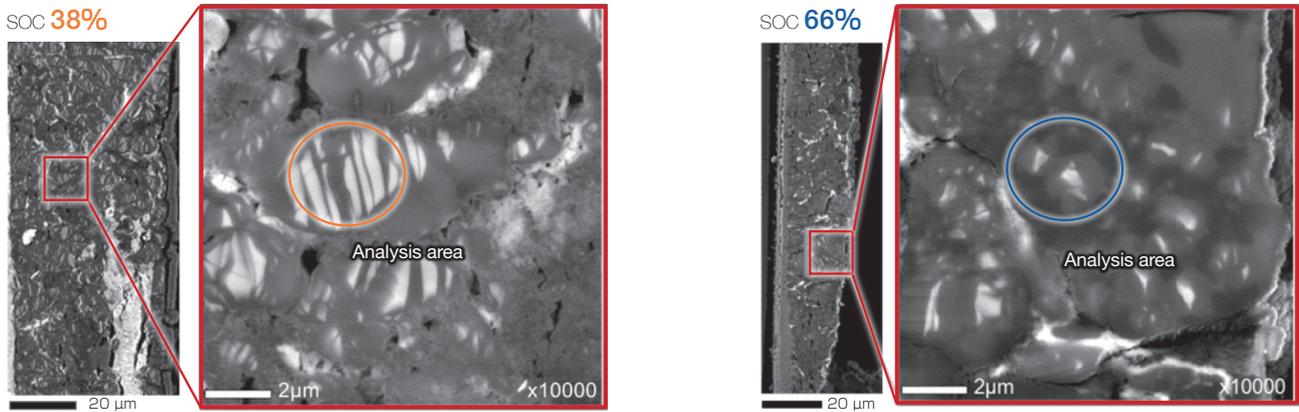


Fig.3 BSE images of anode material in different SOC

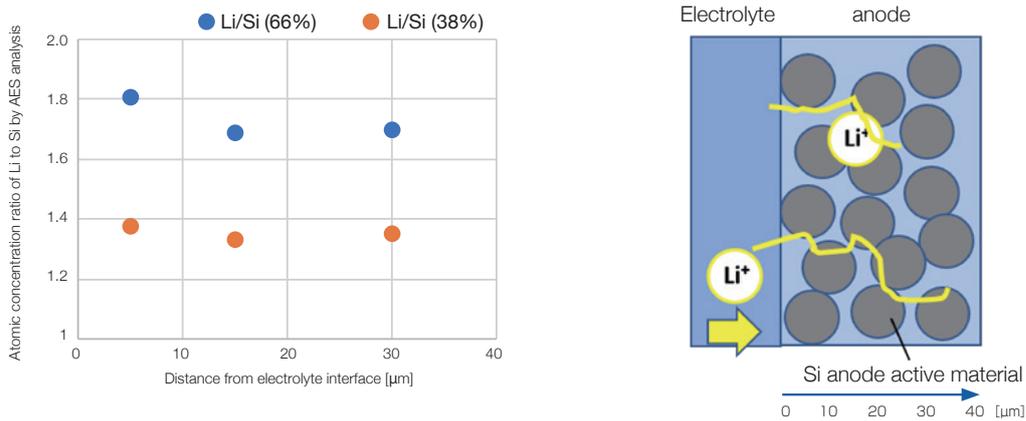


Fig.4 Distance from electrolyte interface vs. Li atomic concentration ratio to Si in active material (quantification by relative sensitivity factor method)

2. Chemical state maps by AES-Spectrum imaging method

AES-Spectrum imaging is a method to obtain hyperspectral data by storing high energy resolution spectrum pixel by pixel (Fig.5). Compared to the conventional AES mapping method, it can simplify the setting and shorten the acquisition time and realize the expandability in analysis after data acquisition. Not only element maps but also chemical state maps using chemical shift difference can be visualized by AES-Spectrum imaging. It is also possible to visualize an energy filtered SEM image with various energy bands selected such as secondary electron and backscattered electrons.

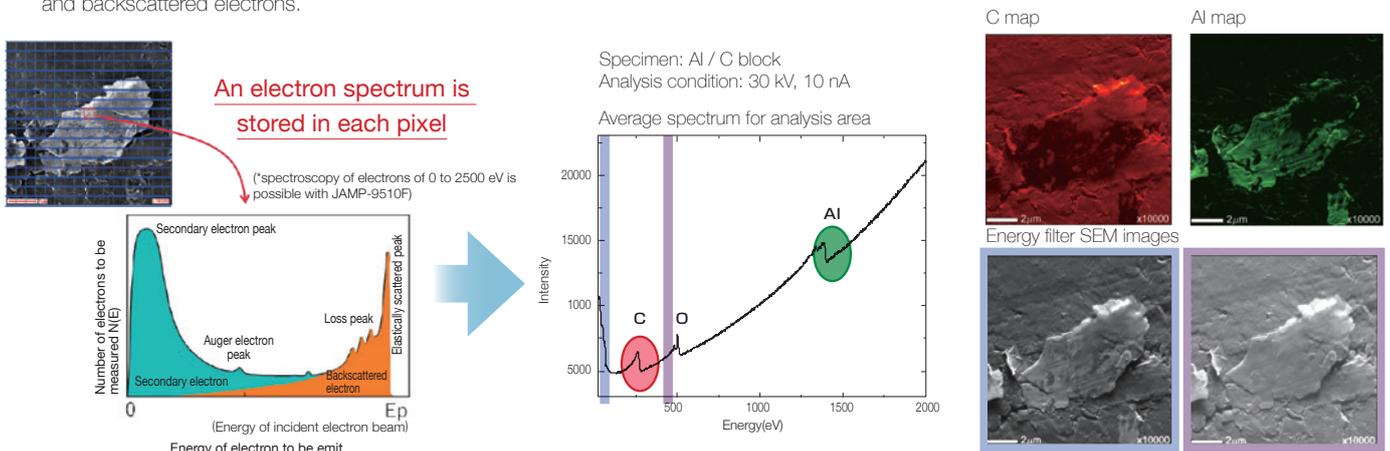
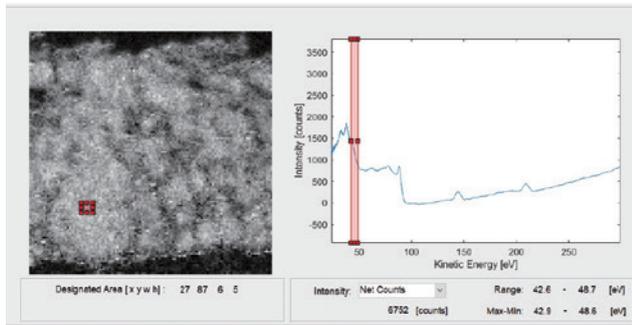


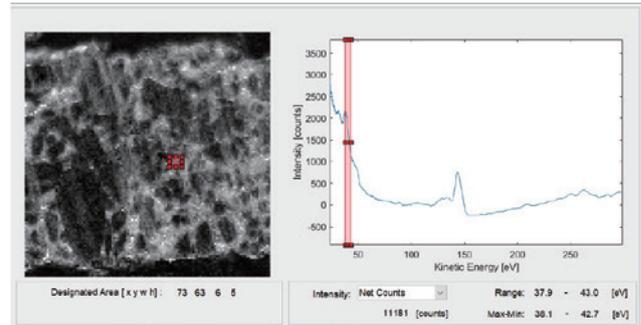
Fig.5 Electron spectroscopic images with AES-Spectrum imaging method

(*spectroscopy of electrons of 0 to 2500 eV is possible with JAMP-9510F)

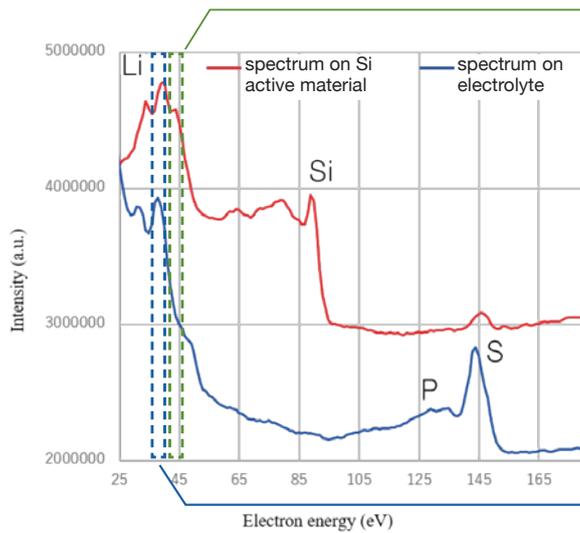
AES-Spectrum imaging was performed for the CP cross section of a solid-state lithium ion battery anode material of 100% SOC. As a result, lithium distributions in different chemical states in the silicon particles and electrolyte were obtained from the spectrum extracted after mapping. Even small energy differences by chemical peak shift were able to be reconstructed.



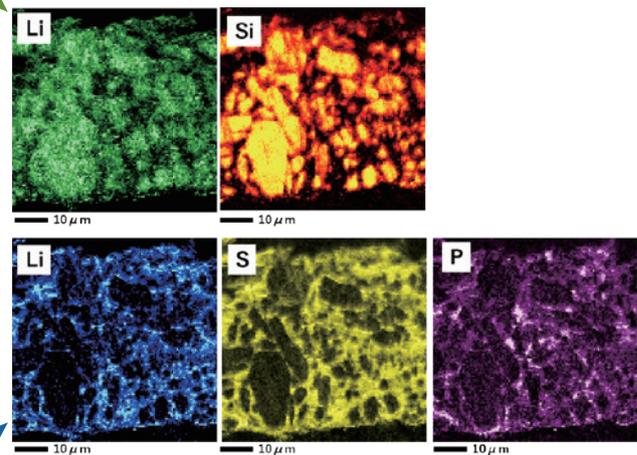
(a) Extraction of a spectrum on a Si active material



(b) Extraction of a spectrum on an electrolyte



(c) Comparison of spectra extracted



(d) Reconstructed Auger maps

Fig.6 Spectra and maps of each area obtained by AES-Spectrum imaging

2-1 Safety Evaluation Evolved gas analysis-Mass Spectrometry

Purpose

To understand the thermal properties of sulfide-based solid electrolyte and the evolved gases during charging and discharging.

Content

Due to the risk for sulfide-based solid electrolytes to evolve hazardous gases such as hydrogen sulfide, there is a need to test these materials for both safety and quality control concerns. In order to understand the thermal properties for these solid electrolyte, thermogravimetry combined with mass spectrometry (TG-MS) can be used to test for hazardous gases (i.e. hydrogen disulfide) evolved during thermal decomposition. Additionally, halogen materials which are added to improve ion conductivity are difficult to evaluate using positive-ion MS measurements. Consequently, negative-ion measurements should be used to evaluate their decomposition as shown below.

Method (NEG_Ion)

In order to gain a comprehensive understanding for the gases evolved from these materials, the accepted practice is to measure both positive and negative ions separately. Using negative ionization enables the high-sensitivity observation of sulfide and halogen compounds while using positive ionization provides information for the other evolved gases. As a result, the qualitative analysis of evolved gas components is complemented by the measurement of both positive and negative ions. In particular, Fig.1 shows the results for halogen compound identification, which is remarkably more selective and sensitive using negative-ion measurements versus positive-ion measurements.

Measurement result comparison of sulfide based solid electrolyte by TG-MS system

TG Approx. 300 °C Spectrum m/z 70-180 enlarged display

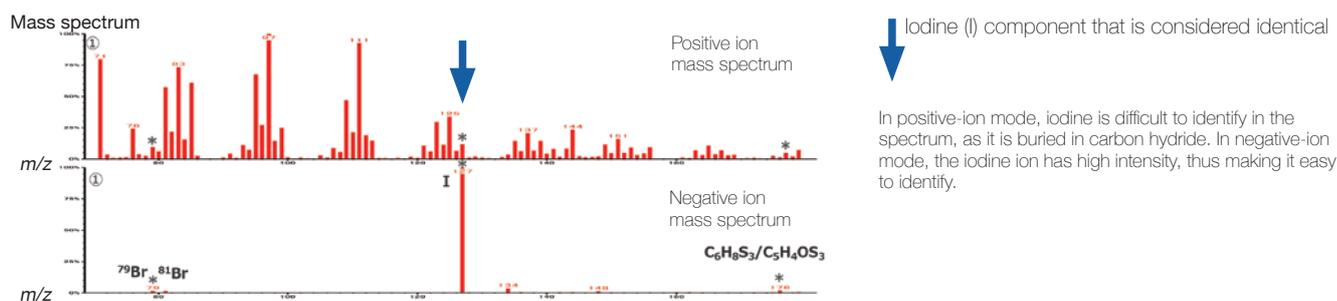
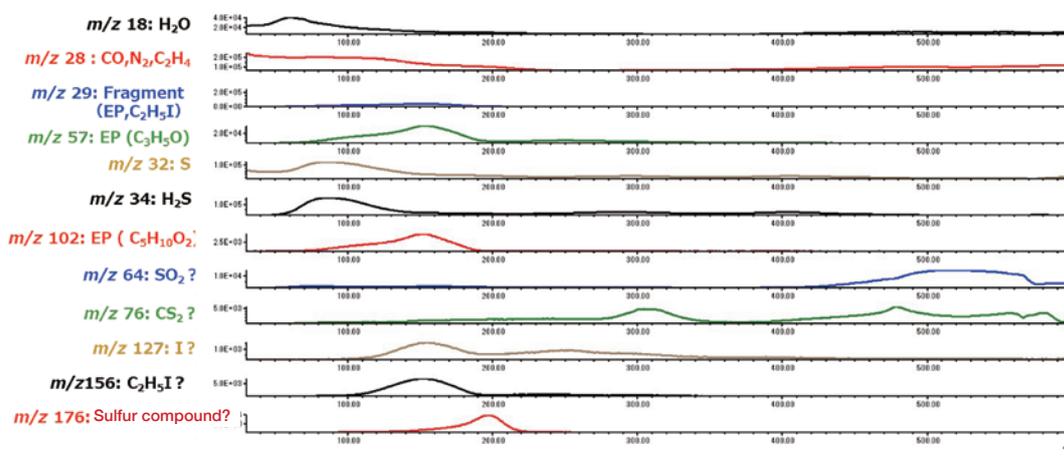


Fig.1 Positive-ion mass spectrum (top), and negative-ion mass spectrum (bottom).

Major evolved gases and hazardous gases by TG-MS

Positive ion profile (Maximum intensity at each mass is shown)

Sample: $3Li_2S \cdot P_2S_5 \cdot LiI$ (LPSI) Solid electrolyte



Notes: The substance name indicates the names for major components. Because the mass resolution is low, molecular structure determination by estimated composition is not possible.

Positive-ion measurement confirmed that hydrogen sulfides were evolved when the system was near to room temperature. Negative-ion measurement confirmed that highly-toxic ethanethiol and highly-inflammable ethanedithiol were evolved in addition to hydrogen sulfide. Halogens resulting from impurities were also identified with negative ion mode.

Sample Courtesy:
 Prof. Atsunori Matsuda,
 Department of Electrical and Electronic Information Engineering,
 Toyohashi University of Technology,

Instrument and Features

【Instrument】

TG: Thermogravimetry analyzer
 STA 449 F1 Jupiter (NETZSCH)

MS: Mass spectrometer
 JMS-Q1600GC(JEOL)



【Features】

In TG-MS system, the thermogravimetry system (TG) is combined with mass spectrometer (MS).

This is a system for real-time analysis of gas component evolved from the sample heated in the furnace of TG while the sample weight declines. Data analysis with the TG-MS system shows mass and temperature (or time) on the horizontal axis and weight and intensity on the vertical axis, allowing analysis of the gas components evolved at different times.(Fig.2)

Thermogravimetry - Mass Spectrometry

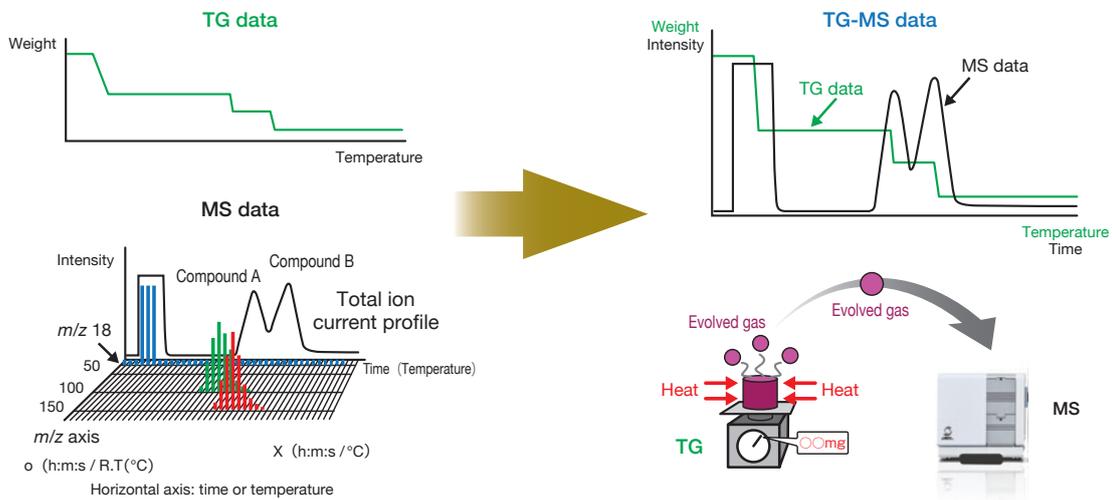
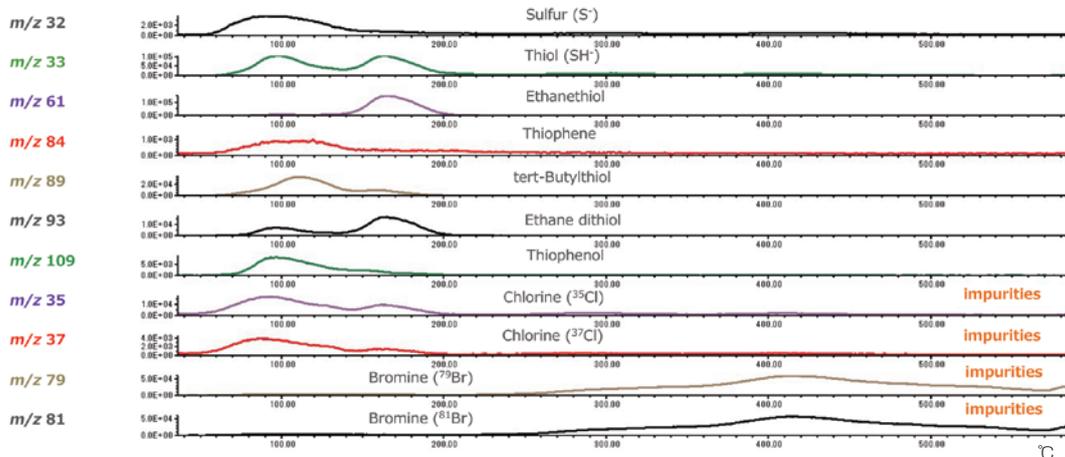


Fig.2 TG-MS system data and schematic diagram

Negative ion profile (Maximum intensity at each mass is shown)

Sample: $3\text{Li}_2\text{S}\cdot\text{P}_2\text{S}_5\cdot\text{LiI}$ (LPSI)Solid electrolyte



Notes: The substance name indicates the names for major components. Because the mass resolution is low, molecular structure determination by estimated composition is not possible.

With a TG-MS system, evolved gas components can be monitored and confirmed while the sample is being heated. As shown here, sulfide-based solid electrolytes evolve hazardous gases such as hydrogen sulfide and chlorine. Because a TG-MS system can directly monitor for these types of compounds, it is an effective tool for evaluating product safety and quality control.

2-2

Ion Dynamics Evaluation

Lithium ion dynamics evaluation by NMR diffusion and solid-state NMR relaxation time

Purpose

Lithium ion dynamics in solid electrolyte is analyzed by diffusion NMR and solid-state NMR relaxation time.

Content

Nuclear magnetic resonance spectrometry (NMR) method is one of the analytical methods that enables direct observation of properties of lithium. It can provide not only structural analysis of solid electrolyte, but also the evaluation of ion dynamics which largely contribute to ion conductivity. It is possible to identify whether differences in conductivity can be attributed to the characteristics of material, or to the other factors such as electrode interface, by comparing with the conductivity measurement results of devices. Typical NMR methods for analyzing ion dynamics are introduced with examples of diffusion NMR and solid-state NMR relaxation time measurements.

Analytical Method

Diffusion NMR Method:

A method to obtain the self-diffusion coefficients, a velocity index of translational motion (self-diffusion) of molecules and ions.

The positions of molecules and ions are encoded with magnetic field gradient pulses. The diffusion of the molecules and ions over time is recorded as an attenuation of the signal intensity.

Solid-state NMR Relaxation Time Method:

A method to analyze kinetic states of molecular or ion motion by using NMR relaxation time. A wide range of motions from kHz to 100 MHz can be analyzed by utilizing multiple magnetic fields and measurement methods.

T_1 measurements sensitive to motions on the order of MHz and $T_{1\rho}$ measurements sensitive to motions on the order of kHz are available.

Instrument and Features

[Instrument]

NMR spectrometer: JNM-ECZ-500R

Diffusion measurement: Diffusion probe

Solid relaxation time measurement: AUTOMAS probe

[Features]

• Diffusion probe

The new generation diffusion probe is a specialized NMR probe for diffusion applications that require large magnetic field gradients. The new gradient coil design results in improved gradient recovery times compared to older gradient coil designs. This probe is best used for the analyses of dynamics of high molecular weight polymer solutions with small diffusion coefficients, nuclei with small gyromagnetic ratios, and ions in solid electrolytes. Using 50A magnetic field gradient power supply a magnetic field gradient of 2000 G/cm can be generated, allowing measurement of diffusion coefficients as small as 10^{-14} m²/s.

• AUTOMAS Probe

JEOL AUTOMAS using an Auto Sample Changer with ROTORCARRIER™ and Auto Tune Unit allows for fully automated solid NMR measurements including sample load/eject, magic angle spinning (MAS) control, and temperature control. It enables automated data collection for structural analysis and ion dynamics measurements of various solid-state battery materials, including positive and negative electrodes, and solid electrolytes.



Lithium ion dynamics analysis of inorganic oxide solid electrolytes by diffusion measurement

NMR diffusion experiments can measure the self-diffusion coefficients of ions in a solid electrolyte. Self-diffusion coefficients are a measure of translational motion (self-diffusion) of molecules and ions when the chemical potential gradient equals zero.

Positions of molecules and ions are coded by magnetic field gradient pulses, and the diffusion of molecules and ions over time is observed as an attenuation in signal intensity.

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

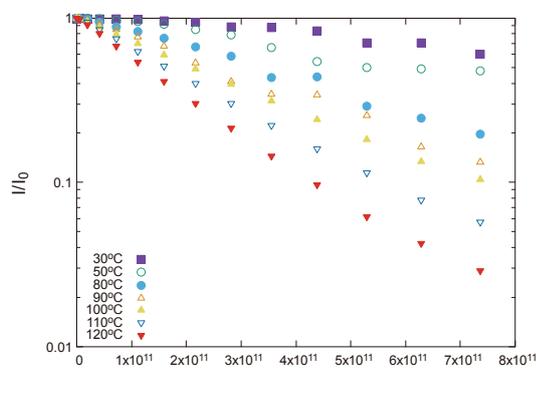
$$I(g, \delta, \Delta) = I_0 \exp(-D(\gamma g \delta)^2 (\Delta - \delta/3))$$

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

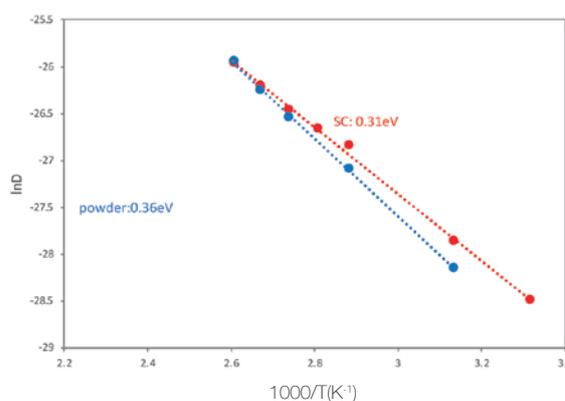
The temperature dependent diffusion plot for the oxide solid electrolyte LLTZO (left below) provides the diffusion coefficient at each temperature. The activation energy of diffusion motions can be obtained with an Arrhenius plot (right below). Comparison of single crystal (SC) and powder samples (Powder)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

Measurement method: ^7Li Stimulated Echo LED
Sample: LLTZO(Single crystal, powder)

Sample : Courtesy of Dr. Naoaki Kuwata (NIMS)
Dr. Junji Akimoto (AIST)



Temperature dependence of ^7Li diffusion

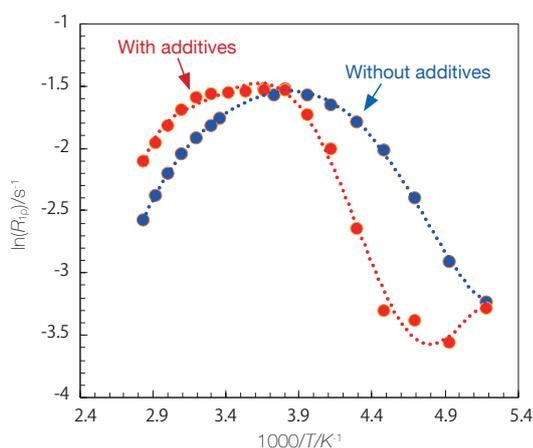


Activation energy of diffusion motion of Li ions
(Arrhenius plot of the diffusion coefficients)

Lithium ion dynamics analysis of sulfide based solid electrolytes by solid-state NMR relaxation time

NMR relaxation is caused by the time variation of NMR interactions that nuclear spins undergo due to the motion of molecules and ions. Measuring relaxation times indirectly reveals information about the motion. The relaxation time is associated with the correlation time which is an index of the dynamics of molecules and ions. The correlation time and activation energy of hopping motion can be obtained from an Arrhenius plot. Here we present the results from $T_{1\rho}$ (spin-lock method) relaxation time measurements in the rotating frame that are sensitive to motions on the order of several 10's of kHz.

Measurement method : Spin-lock method (^7Li $T_{1\rho}$)
Spin-lock frequency : 50 kHz
Sample : Sulfide based solid electrolyte
: Without additives / With additives



Plotting the relaxation rate ($R_{1\rho} = 1/T_{1\rho}$) of ^7Li against temperature in an Arrhenius plot, we can calculate the correlation time of the ion hopping motion from the temperature at which $R_{1\rho}$ reaches its maximum value and the activation energy from the slope.

The temperature at the maximum $R_{1\rho}$ value means that the hopping motion has matched the spin-lock frequency (50 kHz in this measurement). The lower the temperature at which the $R_{1\rho}$ maximum peak shows up, the higher ion hopping rate in the materials. Comparing the temperatures at $R_{1\rho}$ maximum with and without additives indicate that the additives inhibit the ion hopping motion.

Sample Courtesy:
Prof. Atsunori Matsuda,
Department of Electrical and Electronic Information Engineering,
Toyoashi University of Technology,

3-1

Operando Evaluation of Generated Gas Evaluation of generated gas and safety evaluation

Purpose

To analyze gases generated during the first charge/discharge cycle inside the cell of a solid-state lithium-ion battery made of sulfide-based solid electrolyte.

Content

Understanding the gas generated inside when rechargeable battery is used, is being studied in performance maintenance and quality control aspects. Use of test cell where generated gas inside can be taken out, allows for identification of the generated gases and estimation of generation volume, although the actual battery works in a closed space. We are introducing an analysis example focusing on the gas generated during charge-discharge cycle of the solid-state battery by using mass spectrometer.

Instrument

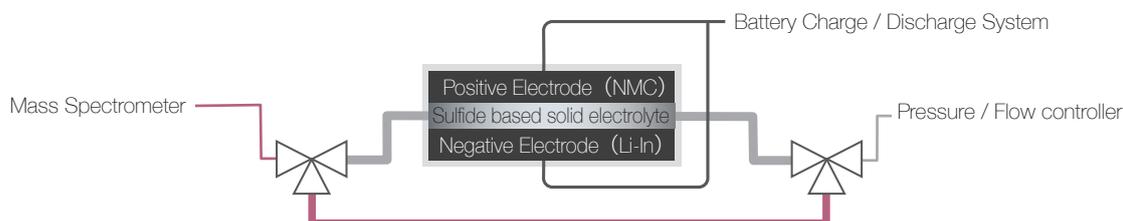
A high-resolution gas chromatograph time-of-flight mass spectrometer JMS-T2000GC AccuTOF™ GC-Alpha was used to identify gases generated from the cell using accurate mass measurements, and the change in gas volume was measured by using our gas chromatograph mass spectrometer JMS-Q1600GC UltraQuad™ SQ-Zeta.



High performance gas chromatograph time-of-flight mass spectrometer JMS-T2000GC AccuTOF™ GC-Alpha

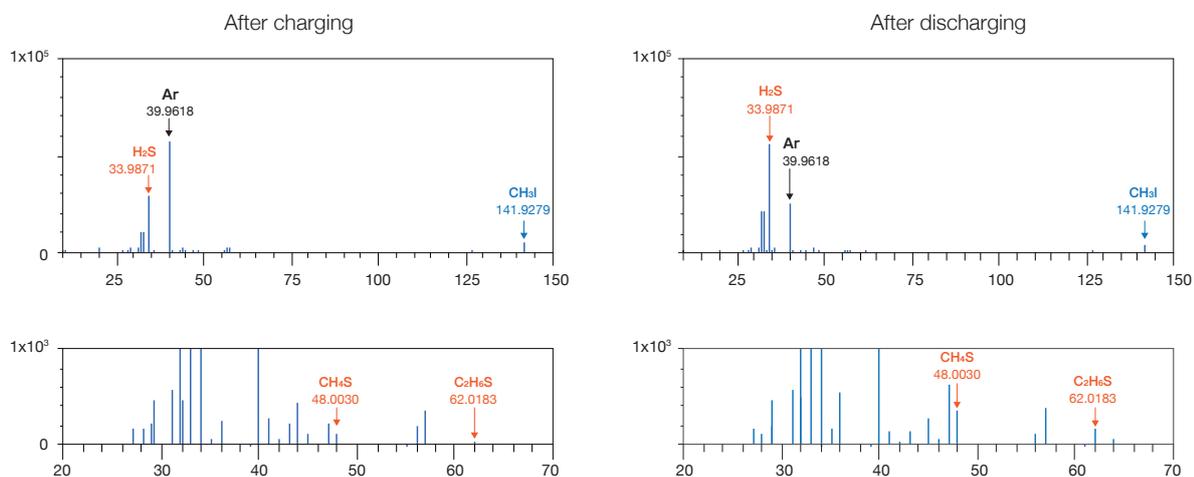
Analytical Method

The gases generated during and after a charge/discharge cycle were measured by connecting the mass spectrometer to a test cell that allows a supply gas flow that pushes the generated gases into the instrument. A schematic of the test cell connection to the mass spectrometer is shown below.



Identification of gas generated-inside cell after charge-discharge cycle

The gases generated inside the cell were measured with high resolution MS, and analyte compositions were calculated using the accurate mass for the major peaks in the extracted mass spectra. The results below show that sulfide gases (H_2S , CH_4S , C_2H_6S) and iodomethane (CH_3I) appear to be generated in the cell during a charge/discharge cycle. Among the detected components, an increase in volume of hydrogen sulfide (H_2S) was confirmed after battery discharge.



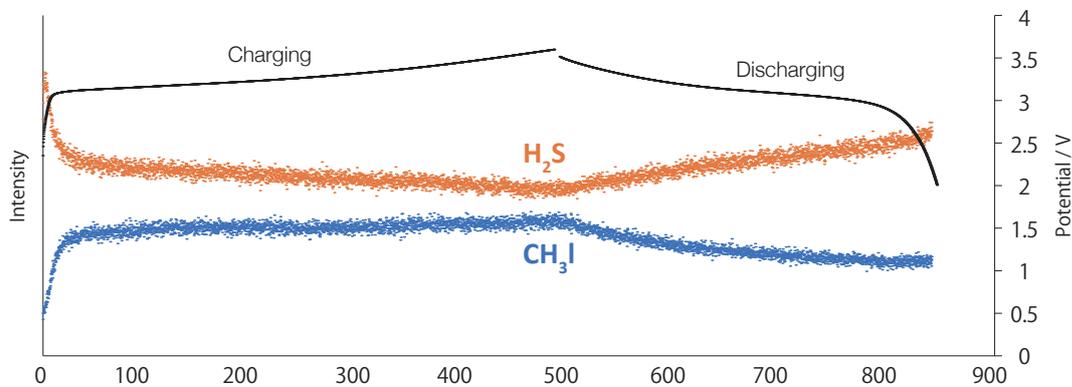
Sample Courtesy:
 Prof. Atsunori Matsuda,
 Department of Electrical and Electronic Information Engineering,
 Toyohashi University of Technology,

Confirmation of volume of gas generated inside cell during charge-discharge cycle

The results below show the real-time measurement of gas generated inside the battery while it is being charged and discharged. The graph shows the volume changes of hydrogen sulfide and iodomethane gases generated inside the cell. Hydrogen sulfide showed a significant decrease immediately after a charge/discharge cycle started, and then a continued slow decrease until the cell started to discharge and generate more hydrogen sulfide. A converse pattern was observed for iodomethanes, where an exponential increase was noted during the charging cycle, and then a slow decrease when discharging.

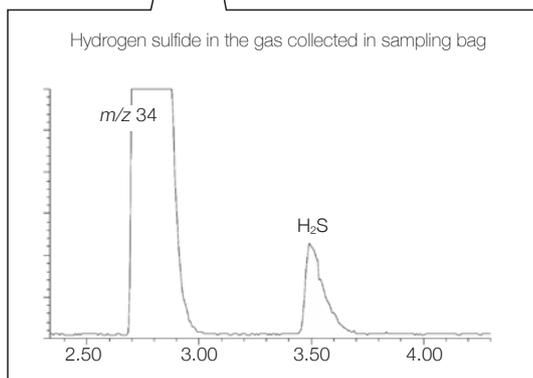
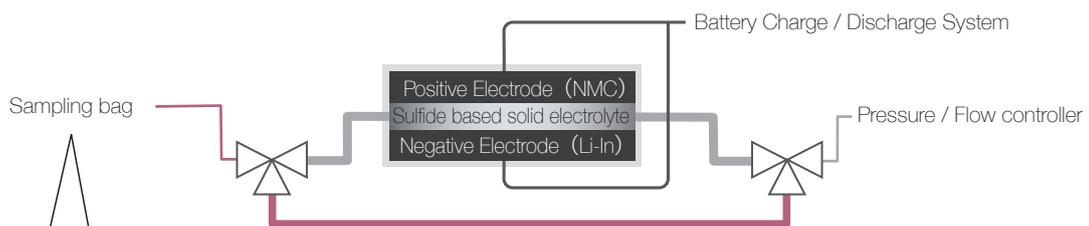


Gas Chromatograph Mass Spectrometer
 JMS-Q1600GC UltraQuad™ SQ-Zeta



Quantification of hydrogen sulfide inside cell

Gas generated inside the cell can be quantified by GC-MS when collected in a sampling bag.



GC/MS Condition

Column	: DB-1 (Agilent Technologies, Inc.), 60 m × 0.32 mm id, 5 μm film thickness
Column flow rate	: 2 mL/min
Oven	: 30 °C (5 min)
Injection temperature	: 200 °C
Injection method	: Split (1/5)
Ion source temperature	: 250 °C
GC Interface temperature	: 250 °C
Ionization energy	: 70 eV
Ionization current	: 50 μA
Acquisition mode	: Scan (<i>m/z</i> 10 to 150)

Solid State Battery Note

Conclusion



Transmission Electron Microscope



Scanning Electron Microscope



Auger Electron Spectrometer

Materials	Analysis items	TEM	SEM	AES
Positive electrode material Negative electrode material Solid electrolyte Binder	• Morphological observation			
	Millimeter to Micro order		○	○
	Micro to submicron order	○	○	○
	submicron to nanometer order	○		
	down to 1 micrometer in 3D	○		
	• Composition			
	PPB level analysis in solid material			
	Solubility test			
	• Surface analysis			
	Average evaluation in millimeter order			
	Local area in tens of nanometers			○
	• Structural analysis			
	Crystal structure/Crystalline property	○	○	
	Thermal change	○	○	
	Bonding state	○		○
	Lithium diffusion coefficient (each material)			
	Chemical state analysis			○
	Binder (ex. SBR)			○
Residual gas evaluation				
Battery after assembly	Charge-discharge capacity			
	Cycle characteristics			
	Charge-discharge cycle characteristics			
	Potential window			
	Shape	○	○	○
	Structural change during charge or discharge		○	
	Grain boundary structure/composition after charge-discharge	○	○	○
	Diffusion of kneaded material	○	○	○
	Lithium diffusion coefficient			
Operando analysis of generated gas				

Solid-State Battery Analysis Items and Corresponding Instruments of JEOL

Application examples of solid-state battery analysis and evaluation are presented in this Solid-State Battery note using representative JEOL's instruments and their features.

The table below JEOL's instruments for the application of solid-state batteries.

For more information on their applications, please refer to catalogs, and specifications of respective instruments or contact JEOL.



EPMA	XPS	XRF	NMR	ESR	MS	XCT
○						
○						
						○
		○				
	○					
○			○	○		
○ sxes	○		○	○		
○	○		○			
					○	
					○	
○						○
○						
○						○
			○			
					○	

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