# Guest Forum

### Analytical Techniques Contributing to the Research and Development of All-Solid-State Batteries

### **TSUBOTA** Takayuki

Manager EV Battery Analysis & Evaluation section EV Battery Solution Center Kobelco Research Institute, inc. Doctor of Science



The worldwide shift to EVs in automobiles is accelerating in order to reduce  $CO_2$  during driving, and the demand for rechargeable batteries is increasing. Research and development of all-solid-state batteries using solid electrolytes that exhibit high Li ion conduction is underway, and this paper outlines the development trends and challenges. Analytical technology corresponding to non-atmospheric exposure is essential for the practical application of all-solid-state batteries. Comprehensive analytical evaluation and analysis techniques are important, including chemical state and structural analysis of solid electrolytes, observation techniques for the junction interface between solid particles in all-solid-state batteries.

### Introduction

Since the adoption of the Paris Agreement at COP21 (21st Conference of the Parties to the United Nations Framework Convention on Climate Change) in 2015, the world has taken a major step toward the realization of a decarbonized society. In Japan, "Achieving a carbon neutral, decarbonized society by 2050" was declared in October 2020. Carbon neutrality means that greenhouse gas emissions and sinks must be balanced and virtually zero. In December of the same year, the "Green Growth Strategy for Carbon Neutrality in 2050" was formulated.

Energy decarbonization includes electrification, hydrogenation, and the use of carbon-recycling fuels, but storage batteries are essential for promoting electrification. In the automotive industry, the European Union (EU) has agreed to effectively ban the sale of gasoline-powered and other internal combustion engine vehicles by 2035. In Japan, a policy to achieve 100% electric vehicles in new passenger car sales by 2035 was announced in 2021. The electric vehicles referred to here are electric vehicles (EV), hybrid vehicles (HV), plug-in hybrid vehicles (PHEV), and fuel cell vehicles (FCV). Against this backdrop of decarbonization, the shift to EVs is accelerating in the automotive industry.

Liquid-based Li ion batteries are mainly used in EVs.

Since battery performance has a large impact on vehicle performance, such as cruising range and acceleration, development of materials such as active materials for positive and negative electrodes, separators, and electrolyte is underway to achieve higher capacity, higher input/output, and improved durability. However, the energy density of liquid-based Li ion batteries is said to be limited at around 250 Wh / kg, and new batteries with even higher energy density are required. Sodium ion batteries as post Li ion batteries and multivalent cation batteries such as calcium ion batteries are being considered.

In recent years, the development of sulfide-based solid electrolytes, which are high Li ion conductors, has been actively pursued, and all-solid-state Li ion batteries have attracted attention as a new type of battery that is expected to have an energy density higher than that of liquid-based Li ion batteries.

Kobelco Research Institute. Inc (KRIJ) possesses technologies for prototyping and internal resistance analysis of Li ion rechargeable batteries, degradation analysis of components through battery disassembly and instrument analysis, computer simulation, and safety evaluation. Further to this, they have established comprehensive evaluation and analysis technologies for rechargeable batteries. In all-solid-state batteries, we have technologies ranging from the synthesis of solid electrolytes to battery prototyping and evaluation, and we are supporting research and development of all-solid-state batteries.

This paper reports on the analytical techniques required for the research and development of all-solid-state batteries, focusing on a case study in collaboration with HORIBA, Ltd.

### Features and Challenges of All-Solid-State Li ion Batteries

All-solid-state Li ion batteries are characterized by the fact that the electrolyte is replaced by a solid electrolyte that is a high ionic conductor, and the cathode composite layer, solid electrolyte layer, and anode composite layer are all composed of solid materials. Solid electrolytes are mainly classified into sulfide systems<sup>[1-7]</sup> represented by Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>, Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> (LGPS) and oxide systems<sup>[8]</sup> represented by Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZ). By selecting solid electrolytes, which have electrochemical stability at higher potentials compared to liquid electrolytes, it is possible to use 5V-class active materials such as LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> that have been difficult to apply in liquid-based batteries, thus increasing energy density.

Good input/output characteristics are also expected. In electrolyte, anions in addition to Li ions contribute to conduction, resulting in low transfusion rate, but anions in solid electrolyte only form the framework and do not contribute to conduction. In other words, solid electrolyte is a single conductor of Li ion and the transporter ratio is 1, resulting in high ionic conductivity. Sulfide-based solid electrolytes, such as glass sulfide electrolyte  $\text{Li}_{7}\text{P}_3\text{S}_{11}$ ,<sup>[1,2]</sup> the crystalline electrolyte  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS),<sup>[3-5]</sup> and the argyrodite-type  $\text{Li}_6\text{PS}_5X$  (X=Cl, Br, I),<sup>[6,7]</sup> have excellent ion conductivity. Solid electrolytes with ion conductivities of the order of  $10^{-2}$  S/cm, exceeding that of organic electrolytes, have been reported. Figure 1(a) shows the ionic conductivity of solid electrolytes synthesized by our company.<sup>[9]</sup> The crystal structure of  $\text{Li}_6\text{PS}_5\text{Cl}$ , an argyrodite-type sulfide solid electrolyte, is shown in Figure 1(b) as a representative crystalline electrolyte. The chloride ions form a face-centered cubic (FCC) lattice (4a, 4c) and the Li ions are randomly distributed in tetrahedral positions; P occupies the tetrahedral site (4b) and S forms a  $\text{PS}_4^{-3^-}$  tetrahedral unit in the structure.

While all-solid-state Li ion batteries are expected to have high energy density and high input/output characteristics, there are challenges in materials and manufacturing processes for practical use, and research and development is being conducted from this perspective. Since all the components of an all-solid-state battery are solid, it is required to form and maintain a good bonding interface between the solid electrolyte and the active material interface. It is crucial to monitor the battery's deformation during molding as well as the active material's expansion and contraction due to charging and discharging. For this reason, the development of all-solid-state batteries with flexible deformation capabilities using sulfide-based solid electrolytes is primarily being supported for automotive applications. Solid sulfide electrolytes are highly reactive and easily hydrolyzed by moisture in the atmosphere to generate hydrogen sulfide, so they must be handled in a low



Figure 1 (a) Ion conductivity of sulfide-based solid electrolytes. (b) Crystal structure of Li<sub>6</sub>PS<sub>5</sub>Cl solid electrolytes.

Development issues		Focus points	Analytical methods
Optimization of solid-state electrolytes	Improvement of ionic conductivity	Crystal structure     Chemical state	• XRD, in-situ XRD • Raman, in-situ Raman
Optimization of the coating layer	Improvement of stability Improvement of coverage Homogenization of the coating	Atmospheric stability     Coverage, uniformity	Exposure test + Gas analysis     XPS, TOF-SIMS
Optimization of electrode and cell structures	Improvement of the dispersibility of materials	Dispersion state, unevenness	SEM + image analysis
	Improvement of the flowability of materials	Flowability, adhesion	Flowability test
	Understanding of material and electrode strengths	Crushing strength, hardness     Modulus of elasticity	Crushing test, Nanoindentation     SPM, Nanoindentation
	Improvement of the adhesion of each layer	Interface adhesion	SAICAS, peel test
	Optimization of Li ion and electron paths	<ul> <li>Electrode structure observation</li> <li>Effective conductivity analysis</li> </ul>	<ul> <li>3D-FIB-SEM</li> <li>Image analysis</li> <li>Symmetric cells + resistance analysis</li> </ul>
Battery characteristics Optimization of battery characteristic control and management	Understanding of battery characteristics	Cycle characteristics, temperature characteristics	Creating prototype cells     + charge/discharge test
	Clarification of the degradation mechanism	<ul> <li>Composition distribution in the electrode</li> <li>Chemical state distribution in the electrode</li> <li>Reaction phase at the interface between solid electrolyte and active material</li> <li>Valence and local structure of active material</li> <li>Morphological changes during charge/ discharge</li> </ul>	<ul> <li>GD-OES</li> <li>Diagonal cutting XPS</li> <li>Cryo biaxial Cs-STEM</li> <li>XAFS/Synchrotron radiation</li> <li>In-situ SEM</li> </ul>
	Understanding of thermal properties	Thermal conductivity     Specific heat	<ul> <li>Hot disk method, heat transfer analysis</li> <li>DSC, external heating evaluation of cells</li> </ul>
	Understanding of safety	Reaction heat evaluation	DSC     Safety test

#### Table 1 Analysis technology for secondary batteries

dew point Ar atmosphere glove box with strict moisture control.<sup>[10]</sup> In various types of analysis, it is essential to handle the materials in a non-exposed atmosphere throughout the entire process from sampling, transportation to the analysis equipment, and measurement. Table 1 shows a list of analytical techniques required for research and development of all-solid-state batteries.

## Application of Raman Spectroscopy (RS) in Solid Electrolyte Synthesis

The synthesis of solid electrolytes can be roughly divided into solid-phase and liquid-phase processes. Mechanical alloying (MA), which is typical of solid-phase processes, is a method used to obtain solid electrolytes in amorphous or thermodynamically metastable phases by mechanically applying energy to accelerate chemical reactions. The liquid phase procedure involves submerging the starting material in an organic solvent, speeding up the chemical reaction through shaking or stirring, and then volatilizing the organic solvent through heating to produce solid electrolytes. In this study, we employed the solid-phase process to synthesize an argyrodite-type sulfide solid electrolyte, Li<sub>6</sub>PS<sub>5</sub>Cl, which is being considered for application in all-solid-state batteries for automotive use. After mixing the starting materials in an Ar atmosphere glovebox with a dew point of -70°C or lower in a molar ratio of Li<sub>2</sub>S:  $P_2S_5$ : LiCl = 0.625: 0.125: 0.25 at.%, the precursor was prepared by the MA process using a planetary ball mill.

Figure 2(a) shows the results of crystal structure analysis by X-ray diffraction (XRD). As the precursor synthesis progresses, the peaks of Li<sub>2</sub>S and LiCl derived from raw materials decrease, but amorphization also progresses, making it difficult to attribute the state by XRD. In other words, evaluation is done by XRD and ion conductivity measurement after crystallization by heat treatment following the MA process since XRD, which is good at evaluating crystallinity, cannot identify the development of chemical processes. If the chemical reaction is subsequently found to be insufficient during the MA process, a large amount of man-hours is required to redo the process, which reduces productivity at the manufacturing site.

Therefore, KRIJ and HORIBA have been studying a compact Raman spectrometer that enables in-line evaluation of solid electrolytes after MA. RS is an oscillatory spectroscopy method that uses Raman scattered light to evaluate materials. The scattered light includes Rayleigh scattered light with the same wavelength as the incident light and Raman scattered light with a different wavelength from the incident light due to the interaction between the incident light and the material. The wavelength difference corresponds to the energy of the molecular vibration of the target material. The chemical bonding state can be obtained from the peak position, molecular structure information and crystal structure from the spectral shape, crystallinity from the peak half-width, and physical property information such as stress and strain from the peak position shift.

Figure 2(b) shows the results of crystal structure analysis using a compact laser Raman spectrometer manufactured by HORIBA, Ltd. The laser wavelength was 532 nm and the laser power was 3 mW. It was confirmed that the peaks derived from  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$ , which are raw materials, decrease as the precursor synthesis proceeds by MA, and the peaks derived from  $\text{PS}_4^{3-}$  tetrahedral unit of  $\text{Li}_6\text{PS}_5\text{Cl}$  appear and become sharp. Thus, RS can capture the progress of chemical reactions in MA and is a useful analytical technique in solid electrolyte synthesis.

### Observation Technique for Solid Electrolytes

The crystal structure of solid electrolytes is observed using a spherical aberration corrected scanning transmission electron microscope (Cs-STEM). Since the state of solid electrolytes easily changes due to reactions with moisture, they are sampled in a glove box with a low dew point Ar atmosphere, inserted into a focused ion beam (FIB) machine while maintaining an inert gas atmosphere, and TEM samples are extracted by the cross-sectional microsampling method. The TEM sample is then thinned by FIB processing. Figure 3 shows the Cs-STEM observation results of LLZ, an oxide-based solid electrolyte. Although LLZ is an oxide, it is susceptible to electron beam damage and is easily altered, making observations at room temperature difficult. We have succeeded in taking atomic column images of LLZ by using an atmospheric non-open-cooled biaxial holder that enables

crystal band axis observation by biaxial tilting, in addition to reducing thermal damage by cooling during observation.

### All-solid-state Battery Electrode Prototyping and Electrode Structure Evaluation Technology

In liquid-based Li ion batteries, the electrolyte soaks into the porous electrode and an active material/electrolyte interface is formed spontaneously. In sulfide-based allsolid-state batteries, the solid electrolyte, active material, and conductivity aid must be pre-mixed and uniformly



Figure 2 (a) Ion conductivity of sulfide-based solid electrolytes. (b) Crystal structure of  $Li_6PS_5CI$  solid electrolytes.



Figure 3 Cs-STEM images of Li7La3Zr2O12 solid electrolyte.



Figure 4 Depth profile analysis of cathode by GD-OES.

dispersed. In order to improve the utilization of active materials and obtain high input/output characteristics, an electrode structure with optimized electron and ion conduction pathways, respectively, is required. Therefore, the electrode is comprehensively evaluated using various analyses such as elemental analysis in the depth direction of the electrode, visualization of the three-dimensional (3D) structure of active material, solid electrolyte, and conductivity aid, and conductivity mapping.

On the other hand, from the battery point of view, small all-solid-state batteries are often used, which are made by dry mixing, pressing, and stacking of powders due to their easy manufacturing and handling methods. However, in order to conduct evaluations that more closely resemble actual use, such as cycle degradation analysis and safety evaluation, a large-capacity battery that simulates actual equipment is required. One method to fabricate large-area electrodes for high-capacity batteries is to slurry and wet-coat the electrode composite; a process similar to that used for liquid-based Li ion secondary batteries. We have fabricated a prototype of a coated sulfide all-solid-state battery by slurrying the electrode composite, coating, drying, adjusting the density by pressing, and lamination. The weight ratio of Li (Ni<sub>1/3</sub>  $Mn_{1/3}$  Co<sub>1/3</sub>) O<sub>2</sub> cathode active material with LiNbO<sub>3</sub> coating on its surface, synthesized Li<sub>6</sub>PS<sub>5</sub>Cl solid electrolyte, conductive aid, and binder is 74:23:3:3 wt.%. The binder and solvent were mixed, slurried, and then the coated cathode was coated and dried on the current collecting foil.

Depth elemental analysis of the coated cathode was performed by high-frequency glow discharge optical emission spectroscopy (GD-OES) using the GD-Profiler2 using a GD-Profiler2 manufactured by HORIBA, Ltd. In scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX), which is used to evaluate electrodes, it is difficult to detect Li, which is a light element, but GD-OES can detect Li emission with high sensitivity, making analysis possible. GD-OES has unique features such as a wide analysis area (e.g.,  $\Phi$ 4 mm) and the ability to measure depths from the surface layer to 100 µm by Ar sputtering, making it a useful analysis method for depth analysis of electrodes. Electrodes were sampled in a glove box with a low dew point Ar atmosphere, transported in a transfer vessel for non-exposure to air, and set in the GD-OES. Figure 4 shows the results of elemental analysis of the coated cathode in the depth direction. For electrodes with a coating thickness of approximately 100 µm, the constituent elements Li, P, S, Cl, C, Ni, Co, Mn, and Al are captured from the surface layer to the current collecting foil, allowing evaluation of the mixing state of active materials, solid electrolytes, and binders.

manufactured by HORIBA, Ltd. GD-OES was performed

The 3D structure of the electrode is analyzed using Focused Ion Beam Scanning Electron Microscopes (FIB-SEM). Across-sectional machining is performed by FIB and a cross-sectional SEM image is acquired. Then, the machined surface is further shaved and a new cross-sectional SEM image is repeatedly obtained, and a 3D construction image is obtained from multiple two dimensional (2D) cross-sectional images. The structure is further optimized by evaluating the volume ratio of each component and the contact area between components through image analysis. Since solid electrolytes are easily altered by heat during cross-sectioning, cooling processing (cryo-processing) is required to minimize thermal effects. Cross-sectional observation of all-solid-state batteries is possible only by optimizing the observation conditions, such as low acceleration voltage and cryo-processing, in order to minimize damage to the sample.

On the other hand, from the manufacturing process perspective, it is important to understand the behavior of particles during the electrode formation and powder filling processes. The flowability and adhesiveness of solid electrolytes are very important parameters in the design of electrode mixtures and manufacturing processes. The higher the fluidity of a solid electrolyte, the better the dispersibility of the electrode during the electrode composite fabrication process. On the other hand, the higher the fluidity, the lower the adhesion required to form and maintain an interface between particles, so appropriate powder design is necessary. We have installed a powder rheometer in a dry room where flowability and shear tests can be evaluated with the same device and a relatively small amount of sample can be measured.<sup>[11]</sup>

The elastic modulus of a solid electrolyte is an important property to evaluate the ease of active material/solid electrolyte interface formation. However, it is sometimes difficult to measure the elastic modulus of the solid electrolyte itself due to the influence of the macroscopic structure of the solid electrolyte pellet by different measurement methods. We have evaluated the elastic modulus of the solid electrolyte itself by mapping the elastic modulus in a small area using scanning probe microscopy (SPM) in a low dew point Ar atmosphere glove box.

### Prototyping and Evaluation Technology for All Solid-State Batteries

A coated cathode consisting of a composite of cathode active material Li (Ni<sub>1/3</sub> Mn<sub>1/3</sub> Co<sub>1/3</sub>) O<sub>2</sub>, synthesized solid electrolyte Li<sub>6</sub>PS<sub>5</sub>Cl, conductivity aid, coated anode consisting of graphite (anode active material), and solid electrolyte Li<sub>6</sub>PS<sub>5</sub>Cl, were placed facing each other with the

solid electrolyte in between. The coated all solid-state battery was densified and an interface was formed by warm isostatic pressing (WIP).

Figure 4(a) shows the results of the discharge rate characteristic test. The voltage range was 2.0 V to 4.2 V. After constant-current and constant-voltage charging at an ambient temperature of 25°C, discharge was performed at different C rates. The output characteristics were good, with a high capacity retention rate even at 5C discharge.

Figure 4(b) shows the results of a charge-discharge cycle test at 1 C. 300 cycles resulted in a capacity retention rate of 98% and a charge-discharge efficiency of approximately 100%. Thus, 300 cycles of repeated charge-discharge at 1 C are possible, and long-term durability evaluation is possible.

### Conclusion

Analytical techniques contributing to the development of materials and processes for all-solid-state batteries, which are expected to become the next-generation batteries, were introduced. Compared to liquid-based Li ion batteries, sulfide-based all-solid-state Li ion batteries are expected to have higher energy density and superior input/output characteristics. Research and development for their practical application is accelerating, especially for automotive applications. Solid electrolyte, a key material for all-solid-state batteries, requires an analysis technique for non-atmospheric exposure according to the synthesis process, and we introduced an example of evaluation using a compact Raman spectrometer in the MA process. Since all solid-state batteries are composed entirely of solid particles, the formation and maintenance of solid/solid interface and the formation of conductive paths and Li ion paths in the electrode are necessary to obtain good battery characteristics, directional analysis and depth analysis of electrode by GD-OES. Thus,



Figure 5 Electrochemical performances of solid-state battery. (a) Discharge rate performance. (b) Charge-discharge cycle performance.

evaluation of electron conduction path by SPM, etc., should be combined and evaluated comprehensively.

We will contribute to the research and development of rechargeable batteries, including all-solid-state batteries, through prototyping of rechargeable batteries, disassembly investigations using physical and chemical analysis, safety testing, and combined analyses with computational science.

#### References

- [1] F. Mizuno, A. Hayashi, K. Tadanaga, and M. Tatsumisago: Adv. Mater. 17, 918 (2005).
- [2] M. Tatsumisago, M. Nagao, and A. Hayashi, J. Asian Ceram. Soc., 1 (2013) 17-25.
- [3] R. Kanno, Jpn. J. Appl. Phys., 90 (1), (2021) 6-23.
- [4] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, and R. Kanno: *Nat. Energy*, 1 (2016) 16030.
- [5] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, and A. Mitsui, *Nature Materials*, **10**, (2011), 682-686.
- [6] S. Boulineau, M. Courty, J.-M. Tarascon and V. Viallet, Solid State Ionics, 221 (2012) 1-5.
- [7] H.J. Deiseroth, S.T. Kong, H. Eckert, J. Vannahme, C. Reiner, T. Zaiss, and M. Schlosser, *Angew. Chem.*, Int. Ed., 47 (2008) 755.
- [8] R. Murugan, V. Thangadurai, and W. Weppner, Angew. Chem. Int. Ed., 46 (2007) 7778.
- [9] K. Momma and F. Izumi, J. Appl. Cryst., 44 (2011) 1272
- [10] H. Muramatsu, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, Solid State Ionics, 182 (2011)116.
- [11] T. Achiha, J. Soc. Powder Technol. (Jpn.), 59 (11), (2022) 575-581.