

Development of a compact all-solid-state lithium secondary battery using single-crystal electrolyte

—Towards realizing oxide-type all-solid-state lithium secondary batteries—

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All-solid-state lithium secondary batteries are attracting attention as a next-generation technology. To realize this technology, it is important to develop a new solid-state lithium-ion conductor. In this regard, we discuss the development of all-solid-state secondary lithium batteries using single-crystal solid electrolytes and the AD method.

Keywords : All-solid-state lithium battery, lithium-ion conductor, single-crystal, AD method, FZ method

1 Introduction

1.1 Current situation of next-generation lithium secondary battery

Lithium secondary batteries that possess high energy density are used in automobiles and various small electronic devices such as smartphones, and have become power source devices that cannot be separated from life in modern society. Recently, the required specifications for secondary batteries have shifted keeping balance with other electronic devices. The current liquid-state secondary batteries are running into problems that cannot be solved, such as high capacity, high voltage, long life, and high energy density. As post-lithium secondary batteries, there is R&D for various new secondary batteries such as lithium air batteries that use air for counter electrodes as well as secondary batteries that use sodium and magnesium as transfer ions. The most leading candidate for new secondary batteries is an all-solid-state lithium

secondary battery.^{[1]–[3]} According to the NEDO roadmap for FY 2013 in Japan, an all-solid-state battery is positioned as a product that fully covers the potential of a next-generation battery, and is set for practical utilization in 2030.^[4] The conventional lithium secondary battery is roughly composed of four parts: a positive electrode, a negative electrode, an electrolyte, and a separator that separates the positive and negative electrodes. On the other hand, an all-solid-state lithium secondary battery is composed of three parts: a positive electrode, a negative electrode, and a lithium solid electrolyte (a lithium ion conductor), and the lithium solid electrolyte plays the roles of both an electrolyte and a separator. Figure 1 shows a schematic diagram of a conventional liquid-state lithium secondary battery and an all-solid-state lithium secondary battery. While the materials for positive and negative electrodes in conventional liquid-state lithium secondary batteries can be used in all-solid-

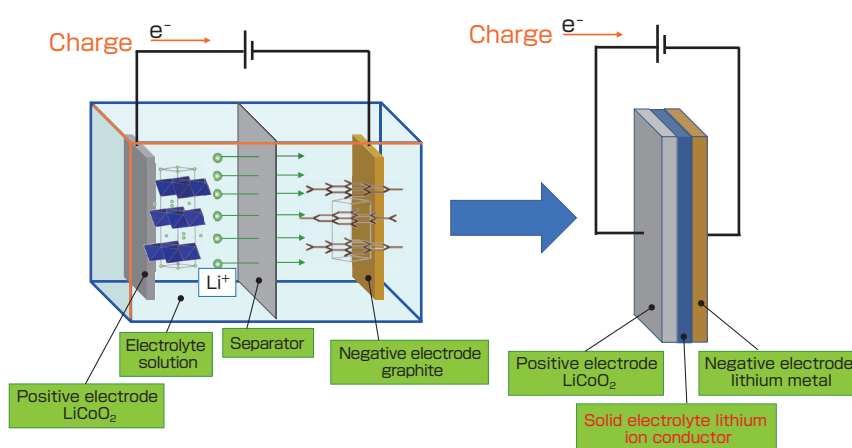


Fig. 1 Comparison of composition of current lithium secondary battery and all-solid-state lithium secondary battery

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Table 1. Reported representative examples of reported lithium solid electrolytes

	Chemical composition	Lithium ion conductivity (S cm ⁻¹)	Use of lithium metal negative electrode	Use of high-potential positive electrode	Formation of interface with electrode	Denseness as component material	Safety
Oxide	Li ₇ La ₃ Zr ₂ O ₁₂	3.0 × 10 ⁻⁴	Possible	Possible	Difficult	Difficult	Safe
	La _{0.57} Li _{0.29} TiO ₃	6.8 × 10 ⁻⁴	Impossible	Possible	Difficult	Difficult	Safe
	Li _{1.3} Al _{0.3} Ti _{1.7} (PO ₄) ₃	7.0 × 10 ⁻⁴	Impossible	Possible	Possible	Possible	Safe
	Li _{2.9} PO _{3.3} N _{0.46}	3.3 × 10 ⁻⁶	Possible	Possible	Possible	Possible	Safe
	Li _{1.5} Al _{0.5} Ge _{1.5} (PO ₄) ₃	4.0 × 10 ⁻⁴	Possible	Possible	Possible	Possible	Safe
Sulfide	Li ₁₀ GeP ₂ S ₁₂	1.2 × 10 ⁻²	Impossible	Possible	Easy	Easy	Hydrogen sulfide gas produced
	Li ₇ P ₃ S ₁₁	1.0 × 10 ⁻²	Impossible	Possible	Easy	Easy	Hydrogen sulfide gas produced
	Standard: Current organic electrolyte solution	10 ⁻²	Impossible	Impossible	Easy	-----	Flammable

state lithium secondary batteries, a lithium solid electrolyte must be newly developed. An all-solid-state lithium secondary battery that uses this lithium solid electrolyte is expected to have several advantages such as reduced internal resistance and operating voltage, and a bipolar all-solid-state lithium secondary battery that enables increased output is expected to have more advantages such as high voltage, high capacity, long life, simplified packaging, and possibility of using lithium metal negative electrodes. Currently, research institutions and companies around the world are engaging in the development of all-solid-state lithium secondary batteries. In this paper, a lithium solid electrolyte is defined as a solid-state electrolyte through which lithium ions move.

1.2 Problems of all-solid-state lithium secondary battery and all-solid-state lithium secondary battery that Advanced Coating Technology Research Center has in view

Various kinds of R&D are being actively conducted for all-solid-state lithium secondary batteries, from component development for lithium solid electrolytes to battery design of all-solid-state lithium secondary batteries.^[5] Table 1 summarizes the characteristics of the main lithium solid electrolyte for which development is being currently conducted. Sulfide solid electrolytes have high lithium ion conductivity and plasticity. While these characteristics are advantageous in battery fabrication, they are disadvantageous from a safety perspective as harmful hydrogen sulfide gas is produced when many of the component materials used react with water. Since lithium secondary batteries are familiar devices used in everyday life, safety must be guaranteed, and the Advanced Coating Technology Research Center (hereinafter, the Center) engages in the development of all-solid-state lithium secondary batteries that use oxide solid electrolytes with high safety, although there are still issues. Figure 2, an overview of the current situation of

lithium secondary batteries and future prospects, shows the positioning of the all-solid-state lithium secondary battery that the Center sets as the goal. Although it is still difficult to achieve high capacity and high output with oxide all-solid-state lithium secondary batteries because large surface area is needed, it is thought to excel in higher safety, longer life, and better environmental resistance compared to sulfide all-solid-state lithium secondary batteries. It is thought that the goal should be the creation of small all-solid-state lithium secondary batteries that take advantage of these characteristics and can be used in the Internet of Things (IoT), wearable devices, and medical use.

1.3 Problems and solutions for garnet-type lithium solid electrolyte

The Center has been engaging in the development of oxide materials for positive and negative electrodes used in conventional lithium secondary batteries, before starting

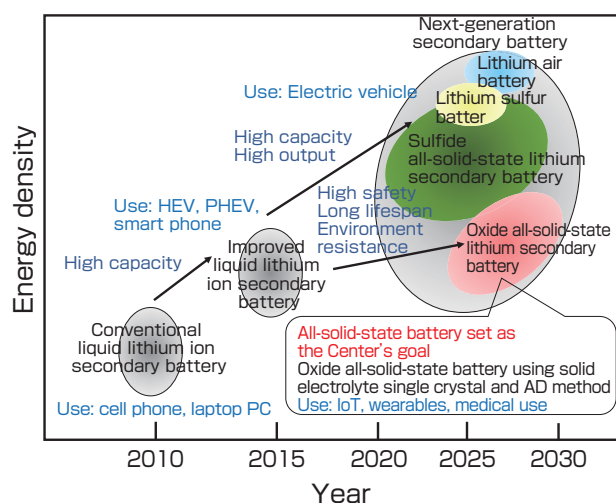

Fig. 2 Overview of current situation of lithium secondary battery and future prospects

Table 2. Fabrication methods of major oxide all-solid-state lithium secondary battery and their characteristics

Fabrication method of all-solid-state battery	Film thickness of electrode layer	Degree of freedom of material selection	Fabrication temperature
Integral sintering method	Bulk-type battery	Low	Approx. 1000 °C
Sol-gel method	Thin film battery	Low	Approx. 800 °C
PLD method	Thin film battery	High	Approx. 400 °C
AD method	Bulk-type battery	High	Approx. 25 °C

the research for all-solid-state lithium secondary batteries. Recently, we have become more involved in R&D for all-solid-state lithium secondary batteries, and we have concentrated our R&D on a garnet-type among the oxide lithium solid electrolytes. Research of garnet-type lithium solid electrolytes is being conducted at research institutes and companies around the world. In general, the bulk body is fabricated by a sintering method, but garnet-type lithium solid electrolytes are broken down by high temperature, and there are disadvantages that lithium evaporates, and sintered density of the sintered body cannot be increased. The sintered density has been increasing every year though low-temperature sintering achieved by densification of garnet-type lithium solid electrolytes and the spark plasma sintering (SPS) method. However, grain boundaries are always present in the sintered body, and grain boundary resistance when lithium ions pass between the grains is large, so it is difficult to bring out the original performance of the bulk body. Therefore, it may be possible to bring out the original lithium ion conductivity performance of the bulk body if one large grain without any granular boundaries is used, that is, by growing a large single crystal solid electrolyte. In an oxide all-solid-state lithium secondary battery that uses a sintered body of the garnet-type lithium solid electrolyte, there is the problem that lithium metal needles grow like dendrites in the solid electrolyte during precipitation of lithium metal. In papers, it is reported that lithium metal dendrites may cause short-circuits in all-solid-state lithium secondary batteries.^[6] To solve this issue, we thought it was necessary to create a single crystal of a lithium solid electrolyte that is a bulk body without any grain boundaries.

To overcome the issues of garnet-type lithium solid electrolytes, the Center started development of large garnet-type lithium solid electrolytes without grain boundaries by utilizing a single crystal growing technology that it has been developed over the years. If the disadvantage of a garnet-type lithium solid electrolyte could be overcome by obtaining a single crystal, it was expected to be a breakthrough technology as a component for oxide all-solid-state lithium secondary batteries. There had been no successful growth of single crystals for large lithium solid electrolytes, including garnet-type lithium solid electrolytes.

Therefore, the growth of single crystals for lithium solid electrolytes was a meaningful research topic as an academic elemental technology for solid-state ionics that investigates the movement of lithium ions in solids, as well as for the field of all-solid-state lithium secondary batteries. Also, an ideal interface could be created by using single crystals of lithium solid electrolytes, and it was thought possible to clarify the interface structure that could not be shown in a sintered body.

1.4 Problems and solutions for formation of solid-solid interface

In fabricating an oxide all-solid-state lithium secondary battery, we worked on the issue of how to bond single crystals of garnet-type lithium solid electrolytes and the electrode layer. For the fabrication of an electrode for all-solid-state lithium secondary batteries, an integral sintering method, fabrication of thin film batteries by a sol-gel method, and pulse laser deposition (PLD) methods have been reported. Table 2 summarizes the methods and characteristics of major fabrication methods of oxide all-solid-state lithium secondary batteries. In all methods, it is necessary to form a strong boundary surface between the lithium solid electrolyte and the electrode layer. In the garnet-type lithium solid electrolyte, integral sintering at high temperature is difficult because of formation of different phases, which is a reactive product at solid interfaces between electrodes and solid electrolytes due to the mutual diffusion of electrodes and solid electrolytes at high temperature. Therefore, we focused on the development of an electrode layer fabrication technology by the aerosol deposition (AD) method that uses a room-temperature impact consolidation (RTIC) that was researched and developed over the years as a thick film ceramics coating technology at the Center. We thought the problem could be solved by applying a room-temperature bonding technology using the AD method that is a film forming process at room temperature. While various cases of usage are considered for all-solid-state lithium secondary batteries, we are aiming for the fabrication of a bulk-type all-solid-state lithium secondary battery that has high battery capacity. Therefore, to fabricate a bulk-type all-solid-state lithium secondary battery, we thought an all-

solid-state lithium secondary battery could be fabricated at room temperature, by combining with the AD method, which enables strong film forming at room temperature and is a technology to form strong interfaces for lithium to move between single crystals of garnet-type lithium solid electrolytes and solid-state interfaces.

1.5 Research goal for this paper

In the process of conducting R&D for oxide all-solid-state lithium secondary batteries at the Center, we felt there were two issues that were important in realizing all-solid-state lithium secondary batteries: short-circuits inside batteries and interface formation between solids. Particularly, short-circuits inside batteries have been taken up as a problem widely, and a solution has not been found by any other method. In this paper, we describe the current situation of the R&D for all-solid-state lithium secondary batteries and lithium solid electrolytes, the electrode formation technology using the AD method that is a room-temperature film forming technology, and achievement of single crystals for garnet-type lithium solid electrolytes. The research currently being conducted at the Center is described to solve the aforementioned two issues of oxide all-solid-state lithium secondary batteries.

2 All-solid-state lithium secondary battery and lithium solid electrolyte

As mentioned in the previous chapter, an all-solid-state lithium secondary battery is composed of three main parts: a positive electrode, a negative electrode, and a lithium solid electrolyte. In all-solid-state lithium secondary batteries, oxide lithium solid electrolytes in which anions are composed of oxygen and sulfide lithium solid electrolytes in which anions are composed of sulfur are widely researched. A sulfide lithium solid electrolyte has the advantage that interface formation with electrodes is easy since it has excellent plasticity, and there are reports of a solid electrolyte that has high lithium ion conductivity of 10^{-2} S/cm order that surpasses the existing organic electrolyte solutions.^{[7][8]} On the other hand, there is the danger of harmful hydrogen sulfide gas being generated. An oxide lithium solid electrolyte is superior in safety aspects, but has issues in solid-solid interface formation and lithium ion conductivity. In the current situation of development of all-solid-state lithium secondary batteries, research of sulfide all-solid-state lithium secondary batteries that use sulfide lithium solid electrolytes is taking the lead and approaching realization, and time is necessary for the realization of oxide lithium solid electrolytes. However, the Center is engaging in R&D of oxide all-solid-state lithium secondary batteries, looking at the superior safety performance of oxide lithium solid electrolytes. Oxide solid electrolytes include poly-anion-type lithium solid electrolytes represented by NASICON-type structure material,^[9] perovskite-type

lithium solid electrolytes,^[10] and garnet-type lithium solid electrolytes.^{[4][11]-[19]} The Center reported a relatively high lithium ion conductivity (10^{-4} S/cm) among oxide lithium solid electrolytes. We focused on garnet-type lithium solid electrolytes in which metallic lithium can be used as high-potential positive and negative electrode active material, which cannot be used in organic electrolyte solutions since it has a wide potential window, and have been conducting R&D for oxide all-solid-state lithium secondary batteries since 2009.

3 Garnet-type lithium solid electrolyte

A garnet-type lithium solid electrolyte possesses, as the name implies, a very similar crystal structure as garnet used as a precious stone, or yttrium-aluminum-gallium (YAG) garnet used as optical crystals. The original garnet is expressed by the general equation $C_3A_2B_3O_{12}$, in which the C site has oxygen and dodecahedral coordination, the A site has oxygen and octahedral coordination, and the B site has oxygen and tetrahedral coordination. On the other hand, in garnet-type lithium solid electrolytes, lithium is present in the interspace where oxygen and octahedral coordination are present in an ordinary garnet structure. Figure 3 shows the crystal structure of a garnet-type lithium solid electrolyte.

For example, in a garnet-type lithium solid electrolyte with $Li_7La_3Zr_2O_{12}$ composition, the C site is occupied by lanthanum, the A site by zirconium, and the B site and interspace are occupied by lithium.

For a garnet-type lithium solid electrolyte, it is known that various elements are substituted, and it has been reported that at the C site calcium, strontium, barium substitute; at the A site, niobium, tantalum, tin, and hafnium; and at the B site, aluminum and gallium.^{[11]-[15]} The amount of lithium changes according to the substituent element, and lithium ion conductivity changes with the changes of arrangement and occupancy rate of lithium. For garnet-type lithium solid

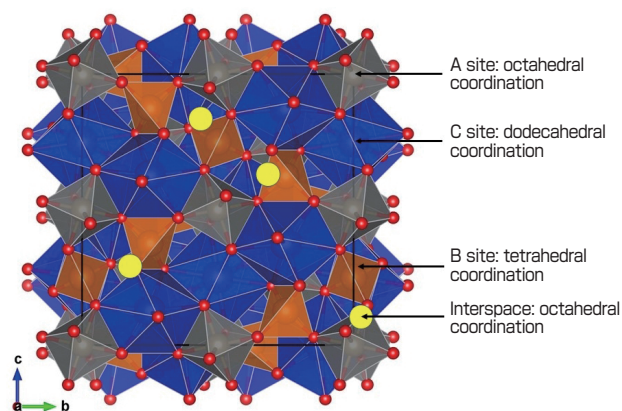


Fig. 3 Crystal structure of garnet-type lithium solid electrolyte

by the FZ method, and, as the FZ method is a so-called melting method, if single crystals can be grown, there are possibilities of improving and adapting large single crystal growth methods to industrial purpose for use in production by companies. There is a path for joint development with companies that already own facilities for growing and manufacturing single crystals. In fact, there is an example of pulling single crystals by the Czochralski (CZ) method using an iridium crucible in our published patent.^[25]

In fact, we faced hardship when we started the actual investigation of single crystal growth of garnet-type lithium solid electrolytes. We did not know whether single crystals of garnet-type lithium solid electrolytes could be grown by a melting method. In addition, generally in single crystal growth by a melting method, one often considered issues while looking at phase diagrams, but in garnet-type lithium solid electrolytes, composition was complicated and there was no phase diagram. Therefore, in our R&D, various single crystal growth parameters were changed, analysis of the coagulated material was done after actual growth to achieve single crystal growth, and this was conducted by trial-and-error. Four years after starting the investigation of single crystal growth of garnet-type lithium solid electrolytes, we found the conditions for single crystal growth. Some of the characteristics of growth conditions are as follows: to excessively add about 1.2 times of lithium carbonate that will be the lithium source when preparing the raw material; to remove gas derived from evaporating lithium by passing about 7 L/min of dried air during single crystal growth; to remove air bubbles by rotating the supplied multi-crystal sample at about 40 rpm; and to keep the growth rate of single crystal growth to about 10 mm/h. Figure 6 shows the conditions of the growth in this study. Particularly, the part about the growth rate is interesting. Regarding single crystal growth using a general FZ method, the growth rate is kept at about 1–2 mm/h, but concerning garnet-type lithium solid electrolytes, single crystals could not be obtained at a generally-used growth rate, and were obtained at a fast rate of about 5–10 times. Using this method, we grew single crystals of garnet-type lithium solid electrolytes with various chemical compositions using the melting method for the first time in the world, and after organizing the patent application and the know-how, we published an academic paper.^{[26][27]} In this paper, we describe the evaluation result of $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Nb}_x\text{O}_{12}$ in which part of zirconium was substituted by niobium in a garnet-type lithium solid electrolyte as described in Reference [26]. Please refer to this reference for the experimental method and details of the result.

Figure 7 shows a single crystal rod of a garnet-type lithium solid electrolyte $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12}$ that was grown in this study, and a single crystal plate that was cut and surface polished. As shown in Fig. 7, we were able to grow a large single crystal with length of 8 cm and diameter of 8 mm for the first time in the world.

4.2 Crystallographic and electrochemical evaluation of garnet-type lithium solid electrolyte

The first evaluation conducted was on the correlation of lithium ion conductivity by substitution amount of Nb. Since higher lithium ion conductivity will be advantageous for battery action, this is the most important property. Looking at the correlation between the amount of Nb substitution and lithium ion conductivity using an AC impedance method, the lithium ion conductivity was maximum when Nb substitution was 0.5, and the value, as shown in Fig. 8, was 1.39×10^{-3} S/cm at 298 K. This value was higher than the conventionally reported value for a sintered body sample, and it is thought to be because there is no grain boundary effect. As a result of X-ray diffraction

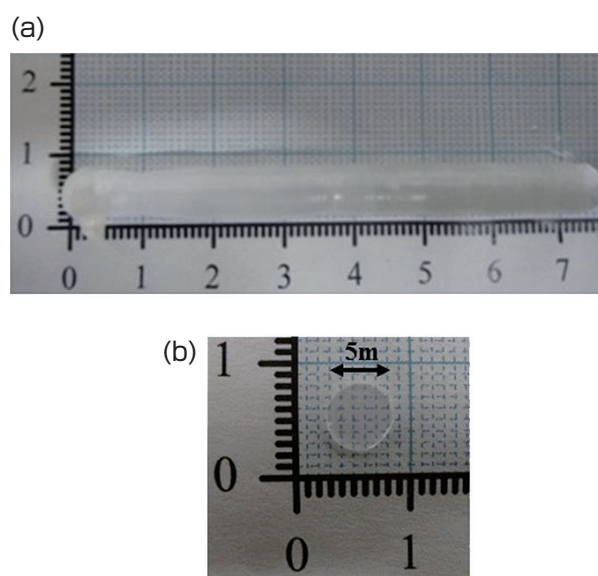


Fig. 7 (a) Grown single crystal of garnet-type lithium solid electrolyte $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12}$; (b) cut and polished single crystal plate

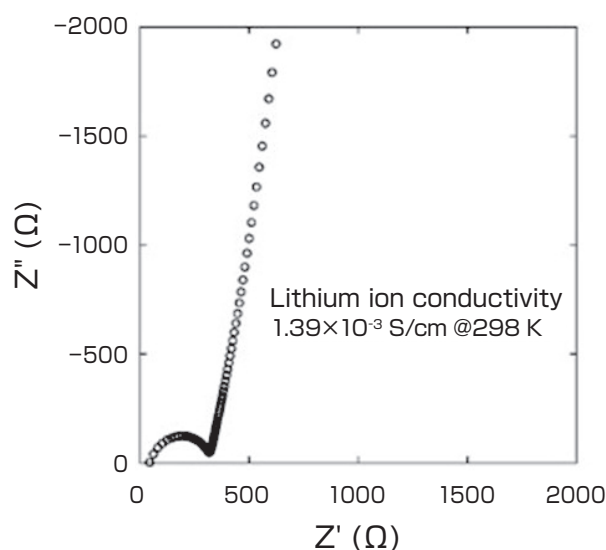


Fig. 8 Lithium ion conductivity and Nyquist plot at 298 K of garnet-type lithium solid electrolyte obtained by AC impedance measurement

and neutron diffraction measurements, as shown in Fig. 9, it was confirmed that the arrangement of lithium differed from the crystal structure of a conventionally reported garnet-type lithium solid electrolyte. In a conventionally reported garnet-type crystal structure, lithium was dominant at the 24*d* site, while in our crystal structure analysis result, lithium occupied the 96*h* site where the 24*d* site was split into four. As a result, the distance between lithium became shorter compared to the garnet-type crystal structure, and this is thought to have led to the increased lithium ion conductivity.

To see whether the problem was solved by achieving single crystals for garnet-type lithium solid electrolytes, we conducted internal short-circuit tests by dendrite growth of lithium metal. For the short-circuit test, we used symmetric batteries to which lithium metal was attached, and confirmation was made by applying constant current and repeating melting and precipitation of lithium metal. Figure 10 shows the results of internal short-circuit tests. From these results, it was confirmed that the battery operated without short-circuiting at current density of 0.5 mA/cm². The lithium ion conductivity calculated from the results of internal short-circuit tests was 1.0×10^{-3} S/cm, and there was no major difference compared to the measurement results of

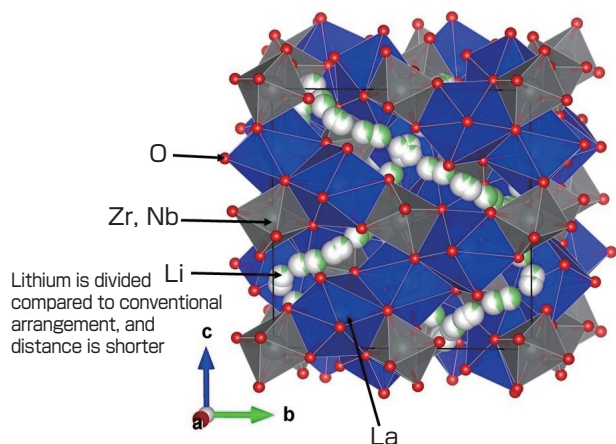


Fig. 9 Crystal structure of grown garnet-type lithium solid electrolyte

1.39×10^{-3} S/cm obtained by an AC impedance method. From the above results, we believe the problem of short-circuiting that was the issue of garnet-type lithium solid electrolytes was solved using single crystals.

5 Electrode formation by aerosol deposition method

Another issue was the interface formation between solids of electrodes and single crystals of garnet-type lithium solid electrolytes. We attempted to solve this issue by using the aerosol deposition (AD) method to create the electrodes. The AD method is a technology for forming a film by mixing fine particles with gas, and shooting this mixture from a nozzle in a decompressed condition as an aerosol jet onto a substrate.

Using the “room-temperature impact consolidation (RTIC)” (in which high-density solidification occurs at room temperature without heating by applying high pressure or mechanical impact to fine particle materials such as ceramics with particle diameter of around 1 μm) that was discovered by Akedo, one of the authors of this paper, dense and highly adhesive ceramic films were formed on substrates of various materials such as metal, glass, and plastic, at room temperature. This is a film forming process for which AIST has the know-how.^[28] This film forming process is a technology that is already utilized by companies and has high versatility. Please refer to Reference [28] published in *Synthesiology* for detailed explanation and past efforts on the AD method.

The reason why we used the AD method as the technology for electrode formation was because there was a technological merit as a technology that was already being used in the industrial world. The representative characteristics of the AD method are as follows: it is a room-temperature film forming process that does not require heating; it does not require binders such as a coating film; adhesion between substrate materials and films is strong; and a composite film can be created by utilizing multiple types of fine particles together.

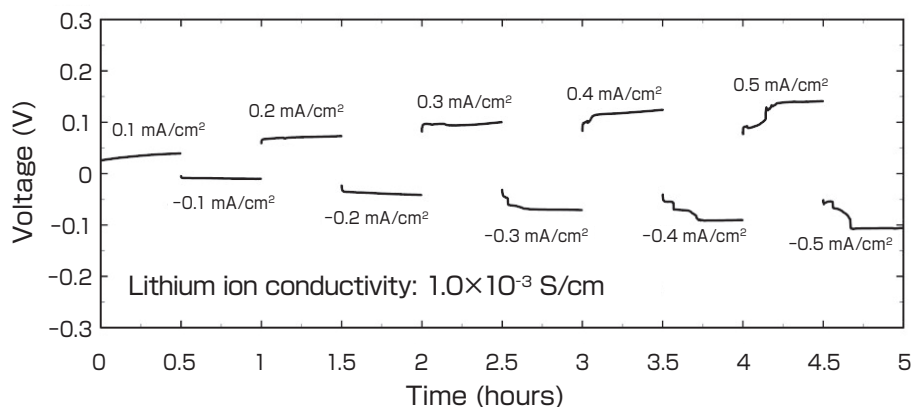


Fig. 10 Result of internal short-circuit test

In forming electrodes on single crystals of garnet-type lithium solid electrolytes, we thought that the AD method was appropriate due to the facts that it is a room-temperature film forming process and that there is strong adhesiveness between the substrate and the film. The first reason for the decision is because a garnet-type lithium solid electrolyte is a material with relatively high reactivity. When a film forming process requiring heating is used, a garnet-type lithium solid electrolyte which is the substrate and an electrode may react, a different substance may be formed at the interface, and it will not function as an all-solid-state lithium secondary battery. The second reason is that because lithium ions move on the interface of the garnet-type lithium solid electrolyte and the electrode, strong interface adhesiveness is required. In the actual film forming maneuver, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), which is the positive electrode active material of current lithium secondary batteries, was used along with dry air, and film forming was done by spraying an aerosol jet onto a single crystal of a garnet-type lithium solid electrolyte placed in a decompression chamber. Figure 12(a) shows a film-formed product of an NCA electrode on a single crystal of a garnet-type lithium solid electrolyte as the substrate, using the AD method.

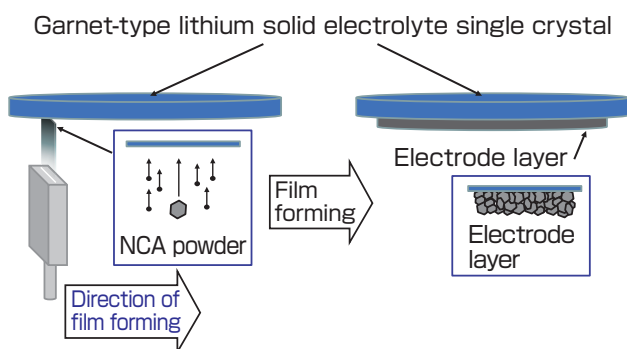


Fig. 11 Schematic diagram of NCA electrode film forming onto garnet-type lithium solid electrolyte single crystal substrate using the AD method

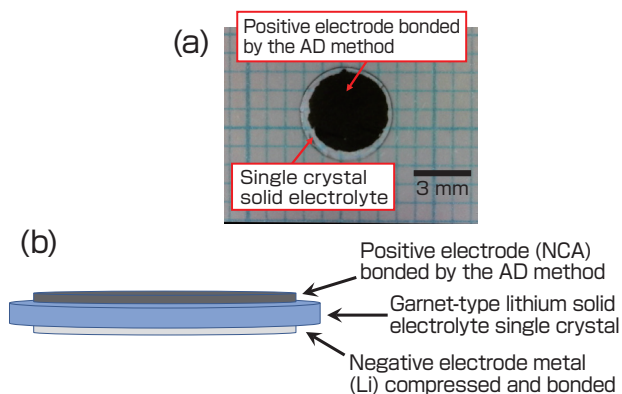


Fig. 12 (a) NCA electrode film formed on garnet-type lithium solid electrolyte single crystal substrate using the AD method; (b) schematic diagram of developed all-solid-state lithium secondary battery

6 Evaluation of all-solid-state lithium secondary battery

Using single crystals of garnet-type lithium solid electrolytes and the AD method as explained above, the Center created an original prototype of an oxide all-solid-state lithium secondary battery. As a negative electrode active material, to utilize the merit of single crystals of garnet-type lithium solid electrolytes, metallic lithium was crimped. Figure 12(b) shows a schematic diagram of an all-solid-state lithium secondary battery that was developed. For evaluation tests, five cycles of charge/discharge were repeated at voltage range 3.0 V–4.2 V, 0.5 μA , and at 60 $^{\circ}\text{C}$, and then five more cycles of charge/discharge were done at 25 $^{\circ}\text{C}$. Figure 13 shows the results of the charge/discharge test at 60 $^{\circ}\text{C}$, and Fig. 14 shows the result at 25 $^{\circ}\text{C}$. As shown in Fig. 14, although it does not reach the logical volume of NCA, it was confirmed that reversible charge/discharge was accomplished in a room-temperature environment. That is, it was confirmed that the interface formation of the solids of a garnet-type lithium solid electrolyte formed by the AD method and the positive electrode film was sufficiently strong. Also, it was clarified

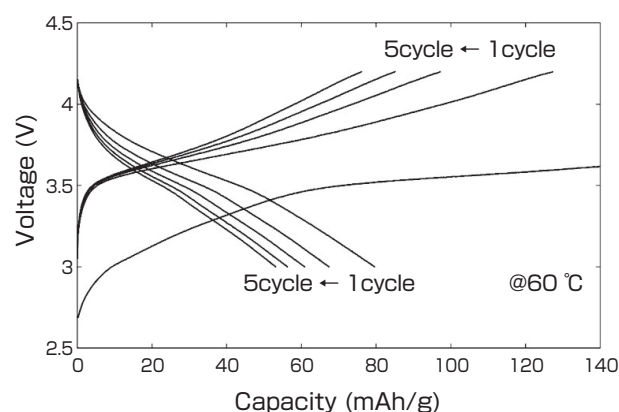


Fig. 13 Charge/discharge property of Li / garnet-type lithium solid electrolyte / NCA all-solid-state lithium secondary battery at 60 $^{\circ}\text{C}$

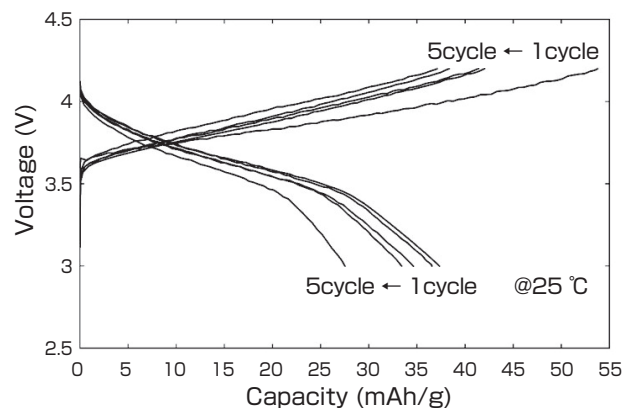


Fig. 14 Charge/discharge property of Li / garnet-type lithium solid electrolyte / NCA all-solid-state lithium secondary battery at 25 $^{\circ}\text{C}$

that a single crystal of a garnet-type lithium solid electrolyte possessed the functions of an electrolyte solution and a separator as in conventional lithium secondary batteries.

7 Future prospects

There are still several issues for an oxide all-solid-state lithium secondary battery that is a prospective candidate for a next-generation secondary battery. In this research, it was found that the issues could be solved by combining single crystals of garnet-type lithium solid electrolytes and the AD method.

Single crystals of garnet-type lithium solid electrolytes, which we succeeded in growing for the first time in the world, has drawn interest of many research institutions and companies academically as well as industrially. Academically, there was hardly any research on garnet-type lithium solid electrolytes because a large bulk body of single crystals of lithium solid electrolytes did not exist. Currently, we are engaging in research on solid dispersal of lithium ions in a single crystal with solid ionics researchers, as well as conducting joint research with various institutions on the measurement of basic properties. Moreover, we are conducting research on the interface structure between solid electrolytes and electrodes to enable fabrication of an ideal electrode interface using single crystals. Industrially, we are conducting joint development with companies for single crystal growth toward achieving high quality, mass production, and large size, for single crystals of garnet-type lithium solid electrolytes.

The Center currently engages in research to clarify the mechanism with which single crystals of garnet-type lithium solid electrolytes are grown in a melting method, search for new garnet-type lithium solid electrolytes by element substitution to increase lithium ion conductivity, fabrication of a composite electrode film consisting of an electrode active substance and a lithium solid electrolyte, and achievement of a thick electrode film. While there are many issues to be overcome, we have succeeded in growing single crystals of high quality solid electrolytes, and we aim for practical realization of an all-solid-state lithium secondary battery by around 2030.

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Discussions with Reviewers

1 Overall

Comment (Haruhiko Obara, AIST)

This paper describes a highly original research on electrolytes using oxide single crystals and on electrode formation using the AD method for realization of all-solid-state lithium secondary batteries, and I think it is valuable as a paper for *Synthesiology*.

Comment (Masahiko Makino, AIST)

I think the social demand for lithium secondary batteries will continue to increase in the future. It is expected that the technology developed in this paper will be the core as its usage expands to “IoT, wearables, and medical use” as aspired by the authors. This paper provides a detailed explanation on the hardships met in growing single crystals of garnet-type lithium solid electrolytes. I think it is appropriate as a paper of *Synthesiology* as it contains valuable information.

2 Expectation for oxide all-solid-state lithium secondary battery and issues for its R&D

Comment (Haruhiko Obara)

There is a possibility that the readers may become excessively concerned about the danger of sulfide all-solid-state lithium secondary batteries, on which many companies and research institutes are working, as you indicate the safety issues of sulfide solid electrolytes that are your competing technology. I think you should reconsider the expression in the paper in making comparison with oxide batteries.

Answer (Kunimitsu Kataoka)

I am not criticizing sulfide all-solid-state batteries. The issue of production of hydrogen sulfide gas when sulfide solid electrolytes react with water has been discussed for a long time in academic societies and papers, and is common knowledge among researchers and developers of all-solid-state lithium secondary batteries. However, with sulfide material large surface area and excellent interface formation can be achieved, and many institutes and companies are moving to realize sulfide all-solid-state lithium secondary batteries first. Since the generation of hydrogen sulfide gas by water reaction cannot be avoided due to the nature of the material, institutes and companies are currently doing R&D by devising packaging. On the other hand, it has also become common knowledge among researchers and developers that there is no safety issue for oxide all-solid-state lithium secondary batteries.

Comment (Haruhiko Obara)

In general, the FZ method is used in crystal growth in places where a crucible cannot be used, and therefore, I feel there is a large gap in using it for large single crystal growth. If you have any clues on large multiple crystal growth, I think you should explain them to a degree that you are allowed to disclose, to make your claims more convincing.

Answer (Kunimitsu Kataoka)

For achieving large crystals, we submitted evidence for large single crystal growth for garnet-type solid electrolytes by the Czochralski (CZ) method using an iridium crucible in the published patent No. WO2016017769A1 for which we submitted a patent application. Based on this fact, I added the following text.

“In fact, there is an example of pulling single crystals by the Czochralski (CZ) method using an iridium crucible in our published patent.”

Comment (Haruhiko Obara)

You write, “There is a difference in lithium arrangement between the crystal structure and the garnet-type lithium solid electrolyte that have been reported.” I think you should add some discussion about why you obtained such a crystal structure and how it affects the physical properties (such as conductivity).

Answer (Kunimitsu Kataoka)

It is still unknown why the lithium arrangement changed. There is a possibility that we were able to confirm the original crystal structure through neutron diffraction that uses a single crystal with abundant diffraction data. Although this may be a problem of interpretation, the crystal structure obtained in this study has shorter distance between lithium compared to the conventional garnet-type crystal structure, and we think the ion conductivity increased as a result.

Therefore, I added the following text:

“In a conventionally reported garnet-type crystal structure, lithium was dominant at the 24d site, while in our crystal structure analysis result, lithium dominated the 96h site where the 24d site was split into four. As a result, the distance between lithium became shorter compared to the garnet-type crystal structure, and this is thought to have increased lithium ion conductivity.”

Comment (Haruhiko Obara)

You write, “The problem of internal short-circuiting that was the issue of a garnet-type lithium solid electrolyte was solved by using a single crystal.” I think it is apparent that dendrites do not form because there is no grain boundary. Or, is there a basic mechanism that prevents dendrite growth when a single crystal is used?

Answer (Kunimitsu Kataoka)

While it may seem obvious, this is not so clear and is a theme that is discussed to this day. There is a report that dendrite growth is a phenomenon that occurs regardless of the presence or absence of grain boundaries. However, in our research, we were able to prevent dendrites in the single crystal solid electrolyte. One factor is thought to be, as shown in Fig. 4, that the lithium metal precipitates homogeneously since the surface of a single crystal is flat. In fact, we confirmed the phenomenon in which dendrites grew in single crystal solid electrolytes with rough surfaces and caused cracks.

3 Expectation for room-temperature bonding technology using AD method

Comment (Haruhiko Obara)

You mention that the difficult issue of sintering integrally could be solved by room-temperature bonding technology using the AD method, but I cannot judge objectively whether the problems such as interface resistance and prevention of dispersal were actually solved. Do you have any evidence of the problems being solved?

Answer (Kunimitsu Kataoka)

Since the AD method is a film forming technology at room temperature, it does not require a heating process. In the integral sintering method, heating is necessary to assure sintering. If heating is required, thermal dispersion occurs mutually at the interface of different solids, and there is high possibility of formation of different phases. On the other hand, the fact that the AD method is a technology of film forming at room temperature is evidence of being a solution above all else.

4 Expansion of use to “IoT, wearables, and medical use”

Comment (Masahiko Makino)

For the “link between research goal and society,” you tend to concentrate on technical descriptions. How about addressing “high safety,” “long lifespan,” “environmental resistance,” or “Usage: IoT, wearables, medical use” that are listed in “Figure 2.

Overview of the current situation of lithium secondary battery and its future prospect” in this paper? I think there is particularly great expectations from society for secondary batteries of medical use.

Answer (Kunimitsu Kataoka)

I added the following text.

“Although it is still difficult to achieve high capacity and high output with oxide all-solid-state lithium secondary batteries because a large surface area is needed, it is thought to excel in higher safety, longer lifespan, and better environmental resistance compared to sulfide all-solid-state lithium secondary batteries. It is thought that the goal should be the creation of small all-solid-state lithium secondary batteries that take advantage of such characteristics and can be used in the Internet of Things (IoT), wearable devices, and medical use.”