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Design and Microstructural Observation of Composite Electrodes in All-Solid-State Rechargeable Li/S Batteries with High Capacity

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Doctoral Thesis at Osaka Prefecture University
Design and Microstructural Observation of Composite Electrodes in All-Solid-State Rechargeable Li/S Batteries with high capacity

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1. General introduction

Realization of sustainable low-carbon society is desired because environmental issues such as global warming and depletion of energy resources have been growing. Development of large-scale applications in green-cars and smart grids has been accelerated toward realization of low-carbon society. Along with this situation, expectation for energy storage technologies, which store renewable energy such as sunlight, water and biomass, has been increasing. Lithium-ion batteries have several advantages such as lightweight, no memory effect, high operating voltage and high energy density compared with other energy storage technologies. In order to realize those large-scale applications, there are two important factors such as safety and energy density of lithium-ion batteries. Commercialized lithium-ion batteries have risks of ignition and explosion because of using a volatile and flammable organic liquid electrolyte. Moreover, an increase in energy density accelerates a possibility of sudden rise of internal temperature in the battery after unexpected short circuit and overcharge, which may cause more serious accidents [1]. In fact, a series of incidents in lithium-ion batteries took place in the last couple of years, indicating that the improvement of the safety and reliability of the batteries is a critical issue to be solved.

An effective way to improve the safety issues of lithium-ion batteries is to replace organic liquid electrolytes with inorganic solid electrolytes. All-solid-state lithium secondary batteries using the inorganic solid electrolytes are expected to be ultimate batteries from the viewpoint of safety issues because the solid electrolytes are nonflammable and nonvolatile [2,3]. As well as enhancement of battery’s safety, all-solid-state lithium batteries have several superior properties to the batteries with liquid electrolytes: no fluidity in solid electrolytes allows bipolar stacking of cells in a packaged battery, resulting in enhancement of operating potential of the battery and then simplifying its packaging. Furthermore, there is a potential for application of electrode materials which are difficult to be used in current batteries to all-solid-state batteries. Two types of all-solid-state batteries have been reported so far: one is thin-film-type battery and the other is bulk-type battery. This thesis focuses on
bulk-type solid-state batteries.

Bulk-type solid-state batteries are composed of composite electrodes having active material powders (for lithium store), solid electrolyte powders (for lithium ion conducting paths) and conductive additive powders (for electron conducting paths). The key material for bulk-type solid-state batteries is inorganic solid electrolytes. They are desired to have the following properties: high lithium ion conductivities, transference number of lithium ion close to 1, and high chemical stability in contact with lithium metal, etc. The inorganic solid electrolytes, which have been studied extensively, are classified into two categories: one is oxide-based solid electrolyte and the other is sulfide-based solid electrolyte.

Oxide-based solid electrolytes such as Perovskite-type $\text{La}_{3x}\text{Li}_{2/3-x}\text{TiO}_3$ ($0<x<0.16$) [4-8], NASICON-type $\text{LiAl}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ [9,10] and Garnet-type $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M}=\text{Nb}, \text{Ta}$) [11-15] have been reported to exhibit ambient temperature conductivities from $10^{-6}$ to $10^{-3}$ S cm$^{-1}$. Oxide-based solid electrolytes require sintering process at high temperatures over 1000 $^\circ$C to reduce the resistance at grain boundaries. This sintering process would trigger side-reactions at the interface between active materials and solid electrolytes. To achieve the bulk-type batteries with high performance, there are several attempts to lower the sintering temperature and construct the favorable solid-solid interface: the addition of the sintering additives $0.44\text{LiBO}_2\cdot0.56\text{LiF}$ [16] or Ag [17] to the electrolytes, the use of co-sintering process of the electrode and the electrolyte by hot pressing [18,19] or spark plasma sintering [20] and the filling of $\text{LiMn}_2\text{O}_4$ sol (active material) into three-dimensionally ordered macroporous (3DOM) $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ and $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ [21-23]. Although these cells operated at limited current densities, the interfacial resistance between electrodes and electrolytes still remains high.

In contrast, sulfide-based solid electrolytes exhibit higher lithium ion conductivity compared with oxide-based ones due to higher polarizability of sulfide ions. Three types of sulfide-based solid electrolytes such as crystalline, glassy and glass-ceramic materials have been reported. Crystalline electrolytes in the system of $\text{Li}_{4-x}\text{M}_{1+y}\text{M'}_y\text{S}_4$ ($\text{M}=\text{Si}, \text{Ge}$ and $\text{M'}=\text{P}$, Al, Zn, Ga) has high lithium ion conductive crystalline phase named thio-LISICON [24,25],
and among them, Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ has so-called thio-LISICON II crystalline phase and showed high lithium ion conductivity of $2.2 \times 10^{-3}$ S cm$^{-1}$ [26]. Recently, Kanno et al. reported a lithium superionic conductor, Li$_{10}$GeP$_2$S$_{12}$ that has a new three-dimensional framework structure [27]. It exhibited an extremely high lithium ion conductivity of $1.2 \times 10^{-2}$ S cm$^{-1}$, which exceeds the conductivity of organic liquid electrolytes [27]. Glassy solid electrolytes were prepared by melt quenching and mechanical milling. The pelletized Li$_2$S-Si$_2$S$_3$-Li$_x$MO$_y$ (Li$_x$MO$_y$ = Li$_x$SiO$_4$, Li$_3$PO$_4$, Li$_3$BO$_3$, etc.) or Li$_2$S-P$_2$S$_5$ glasses prepared by pressing the glass powder at room temperature exhibited high conductivities over $10^{-4}$ S cm$^{-1}$ [28-32]. In these glassy electrolytes, glass transforms into supercooled liquid and softens at around glass transition temperatures. The supercooled liquid of a glassy electrolyte flows onto active material particles and liquid-solid interface would be formed. After cooling the liquid-solid interface, the favorable electrode-electrolyte solid-solid interface would be obtained, which resulted in a decrease in grain boundary resistance and an increase in contact area between them. Glass-ceramic solid electrolytes were prepared by crystallization of the corresponding glasses at around their crystallization temperatures [33,34]. The 80Li$_2$S·20P$_2$S$_5$ (mol%) and 70Li$_2$S·30P$_2$S$_5$ (mol%) glass-ceramics exhibited much higher lithium ion conductivities than the glasses due to precipitation of highly conductive crystals of a thio-LISICON II analogous crystal [35] and Li$_7$P$_3$S$_{11}$ crystal [36,37], respectively. Especially, 70Li$_2$S·30P$_2$S$_5$ glass-ceramic having Li$_7$P$_3$S$_{11}$ crystal showed the extremely high conductivity of $3.2 \times 10^{-3}$ S cm$^{-1}$ [36,37]. In addition, substitution of a small amount of P$_2$O$_5$ [38,39] or P$_2$S$_3$ [40] for P$_2$S$_5$ enhanced electrochemical stability and lithium ion conductivity, and the glass-ceramics with 1 mol% P$_2$S$_3$ exhibited ambient temperature conductivity of $5.4 \times 10^{-3}$ S cm$^{-1}$ [40]. As described above, these glass-ceramics show lithium-ion conductivities comparable to liquid electrolytes. These electrolytes have a wide electrochemical window over 5 V and high chemical stability against lithium. They have the lithium ion transference number close to 1. In the case of using above glasses or glass-ceramics as an electrolyte, sintering process is not indispensable for fabrication of the bulk-type solid-state batteries. The formation of relatively intimate contacts between electrodes and electrolytes is achieved
by only pressing at room temperature. It is thus considered that sulfide-based solid electrolytes are promising materials for all-solid-state batteries.

To date, the electrochemical properties of bulk-type lithium secondary batteries using sulfide-based solid electrolytes have mainly been examined in Japan. Takada’s group has explored the properties of all-solid-state batteries using a number of active materials such as TiS$_2$ [41], LiCoO$_2$ [42-45], In [43], LiNiO$_2$ [45], Li$_2$FeS$_2$ [46-49], LiVS$_2$ [48], Li$_2$FeP$_2$S$_6$ [49], C [44,50,51], FeS [46,52], LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ [53], 0.5LiVO$_2$·0.5Li$_2$TiO$_3$ [54] and Li$_2$SiS$_3$ [55] for about 20 years. Machida et al. have reported cell performance of LiCo$_{0.3}$Ni$_{0.7}$O$_2$ [56], S-Cu-C [57-59], Li$_{4.4}$Si [60], Li$_{4.4}$Si$_x$Ge$_{1-x}$ [61] and LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ [62] in the bulk-type batteries using the Li$_2$S-SiS$_2$ glassy electrolytes. Kanno et al. have examined the performance of the all-solid-state batteries in combination with the Mo$_6$S$_8$ [63-65], Al [65], Ni$_3$S$_2$ [66], S-C [67] or LiCoO$_2$ [27] active materials and the Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ [26] or Li$_{10}$GeP$_2$S$_{12}$ [27] crystalline electrolytes. Tatsumisago et al. have examined the charge-discharge performance of all-solid-state batteries using Li$_2$S-P$_2$S$_5$ glass or glass-ceramic solid electrolytes. A variety of positive and negative electrode materials such as LiCoO$_2$ [68], S-Cu [69], LiNi$_{0.5}$Mn$_{0.5}$O$_2$ [70] LiCoPO$_4$ [71], a-V$_2$O$_5$ [72, 73], Li$_4$Ti$_3$O$_{12}$ [72, 73], SnS-P$_2$S$_5$ [74-76], SnO-P$_2$O$_5$ [76], Li$_2$S-Cu [77, 78], a-Fe$_2$O$_3$ [79], NiP$_2$ [80], NiS [81], LiMn$_2$O$_4$ [82], LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ [83] and LiFePO$_4$ [84] have been applied to the batteries. Figure 1 shows the voltage versus capacity for some positive and negative electrode materials in bulk-type solid-state batteries reported so far. Most of the bulk-type solid-state batteries exhibit long cycle life. For example, the batteries In / LiCoO$_2$ [85], Li-In / Li$_4$Ti$_3$O$_{12}$ [85] and Li-In / V$_2$O$_5$ [86] using Li$_2$S-P$_2$S$_5$ glass-ceramics were reversibly charged and discharged for several hundred cycles at current densities less than 1 mA cm$^{-2}$. There are two key factors such as rate performance and energy density toward the practical use of all-solid-state batteries for large-scale applications. An important clue to enhance electrochemical performance is a solid / solid interface between electrodes and electrolytes. The electrochemical reactions proceed at the solid / solid interface in the all-solid-state batteries. The batteries with solid electrolytes possess smaller contact area at the electrode-electrolyte
Figure 1  Voltage versus capacity for some positive and negative electrode materials in bulk-type solid-state batteries reported so far.
interface than the batteries with liquid electrolytes. This small contact area results in poor electrochemical performance. To overcome this issue, several approaches such as the application of mechanochemistry [87], the softening of Li$_2$S-P$_2$S$_5$ glass electrolytes [88] and the coating of lithium ion conducting solid electrolytes using pulsed laser deposition [89,90] have been carried out. These approaches are highly effective in enhancing rate performance of all-solid-state batteries using sulfide-based solid electrolytes, and thus power density equivalent to the batteries using organic liquid electrolytes has almost been achieved [91].

Further improvement of energy densities of rechargeable batteries in various fields of applications is increasingly needed. For example, new generation lithium-ion batteries require five times higher energy densities than the current lithium-ion batteries to build electric vehicles with a driving range of 300-400 miles on one full charge [92]. It would be difficult to achieve this goal by using the current electrode materials such as LiCoO$_2$ positive electrodes and graphite negative electrodes, and thus construction of innovative rechargeable batteries with extremely high capacity is one of the urgent tasks. There are several rechargeable battery systems as prospective candidates for future generation rechargeable batteries [93,94]. Among them, much attention has been focused on Li/S batteries [95,96].

Sulfur and Li$_2$S positive electrodes have several challenges in Li/S batteries with organic liquid electrolytes to achieve excellent battery performance. The main cause for their poor cycle performance is the high solubility of polysulfide ions formed during charge-discharge cycles, which results in degradation of capacity with cycling. The recent approaches focus on confining sulfur and Li$_2$S active materials in porous nanostructures to capture the polysulfide ions [97-102], leading to enhancement of the cycle performance. There are still a few soluble species escaping from the nanostructures over numerous cycles, resulting in a consecutive capacity fading with cycling. On the other hand, there would be no or less dissolution of lithium polysulfide into sulfide-based solid electrolytes. The all-solid-state Li/S batteries are expected to show little capacity fading for a long cycle test. Several attempts have been made to enhance utilization of sulfur and Li$_2$S active materials. For instance, composites of sulfur and electrically conducting materials such as copper [103-105]
or nanocarbon [106,107] were prepared by mechanical milling [103-105], gas-phase mixing [106] and spark plasma sintering [107]. In these papers, the batteries exhibited very high capacity per gram of sulfur, but there are at least two major issues to be solved: one is the increase in the weight ratio of sulfur in electrodes and the other is the improvement of rate performance. The particle size and the dispersion of sulfur or Li$_2$S active materials in the electrodes and the construction of both favorable electron and lithium ion conduction paths to active materials would be key factors to resolve these issues in all-solid-state Li/S batteries.

To achieve higher energy density of all-solid-state batteries, researching high-capacity negative electrodes is very important. As alternative high-capacity negative electrodes for traditional graphite electrodes, metals and semimetals which can electrochemically form alloy with lithium (alloy materials) [108,109] have been investigated. Typical alloy materials, silicon and tin electrodes, have the significantly high theoretical capacity. However, they undergo huge volume changes during the reaction, leading to a pulverization of active materials, a progressive decohesion and a capacity loss [110,111]. In order to solve this problem, various approaches have been done: the use of nanostructured alloy materials [112-114] and active-inactive or active-active binary alloys [115-117]. Although significant progress has been made, further improvements in cycling stability are required to make them commercially viable. In all-solid-state batteries, there are some reports about the charge-discharge properties of batteries using alloy materials [43,55,60,65] and conversion reaction materials [46,52,66,79-81], and even the batteries using these micrometer-sized active materials exhibited relatively good cycle performance with high capacity. Although there is an interest in observing how large volume changes of these active materials could be accommodated in all-solid-state batteries, the morphological changes in an electrode or at an electrode-electrolyte interface have not been reported in the batteries. Understanding of the morphological changes in the alloy materials would provide the strategies to improve battery performance such as cyclability and utilization of these active materials.

Lithium metal, which is a negative electrode in the Li/S battery system, is the ultimate negative electrode material having the highest theoretical capacity and the lowest reaction
potential. Despite its superior advantages, the rechargeable batteries using lithium metal negative electrodes have some concerns about safety and cyclability [118]. This is because the dendritic growth of lithium metal occurs in liquid electrolytes [119], leading to an internal short circuit of the batteries and resulting in their fire and explosion. Meanwhile, suppression of the dendritic growth is anticipated by the use of inorganic solid electrolytes as a separator in bulk-type solid-state batteries. However, charge-discharge properties in rechargeable bulk-type solid-state batteries with lithium metal electrode and sulfide-based solid electrolytes have been hardly studied. Formation of a favorable interface between lithium electrodes and Li$_2$S-P$_2$S$_5$ solid electrolytes such as an increase in the contact area between them would realize highly repetitive electrochemical deposition and dissolution in bulk-type solid-state batteries.

On the other hand, understanding the structural and morphological changes both at the interface between electrodes and solid electrolytes and within electrodes (active materials) is extremely important in developing the all-solid-state batteries with high performance. For example, Sakuda et al. investigated the interface between the LiCoO$_2$ electrodes and Li$_2$S-P$_2$S$_5$ solid electrolytes after charge reaction by TEM observation, indicating that the interfacial resistance layer were formed by mutual diffusion of Co, P and S elements at the interface [120]. By coating oxide solid electrolytes on LiCoO$_2$ particles to suppress the diffusion, the electrochemical performance was greatly enhanced [121]. In this way, the structural characterization after charge-discharge tests mentioned above gives us useful information to develop all-solid-state batteries with high performance. The previous characterization of bulk-type solid-state batteries has been restricted to ex-situ analysis techniques. The ex-situ measurement requires the post treatment such as the dismantlement of a battery and the wash of an electrolyte. This process has a risk of damage to the sample. To obtain more detailed information about the structure and morphology at the electrode-electrolyte interface and within electrodes (active materials), their characterization during operation of a battery is needed. Kuwabata et al. reported that ionic liquids can be observed by scanning electron microscope (SEM) without accumulation of electron charges.
and developed in-situ electrochemical SEM observation system [123]. Use of this system revealed the changes in polypyrrole film thickness during its redox reaction and electrochemical silver deposition and dissolution [123]. In the field of lithium-ion batteries, in-situ SEM experiments have been pursued by several groups [124,125]. They used a polymeric electrolyte [124] and a room temperature ionic liquid [125]. Although in-situ studies of the bulk-type solid-state batteries have never been reported, they are useful approaches to guide the design of superior composite electrode in all-solid-state batteries with high capacity.

The objectives of the present study focus on the improvement of battery performance and the understanding of structural and morphological changes in electrodes toward the realization of innovative rechargeable batteries. There are two key points to improve the battery performance. One is the choice of high-capacity electrode materials suitable for all-solid-state batteries and the other one is the construction of a favorable solid-solid interface between electrode and electrolyte using several approaches such as mechanical milling and vacuum evaporation. The all-solid-state cells using a variety of high-capacity electrode materials to meet the above requirement were fabricated, and their electrochemical performances such as long cyclability, rate capability and wide temperature operation were investigated. The structural and morphological changes in electrodes were explored by X-ray diffraction, Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy. In-situ techniques using Raman spectroscopy and SEM were developed in bulk-type batteries.

This doctoral thesis consists of five chapters indicated below:

Chapter 1

This chapter describes the background, the objectives and the contents of this thesis.

Chapter 2

This chapter describes the characterization of sulfur-based positive electrodes in
all-solid-state cells using Li$_2$S-P$_2$S$_5$ solid electrolytes. In the section 2-3-1, Cu$_x$Mo$_6$S$_{8-y}$ Chevrel-phase compound was selected as a model active material of sulfur-based electrodes. Their electrochemical performance was investigated in the wide temperature range where the conventional batteries using liquid electrolytes are difficult to be charged and discharged. The interfacial analyses between the active materials and the Li$_2$S-P$_2$S$_5$ electrolytes were carried out by the impedance measurements and transmission electron microscopy (TEM). Based on the information obtained from the above characterization, the design of Cu$_x$Mo$_6$S$_{8-y}$ composite electrodes to achieve long cyclability and high rate performance was proposed as follows: the chemical removal of copper and the addition of nanocarbon. In the section 2-3-2, sulfur and Li$_2$S with extremely high theoretical capacity were applied to the all-solid-state cells. To improve the charge-discharge performance of all-solid-state Li/S cells, several approaches were performed. The first is that mechanical milling was applied to the pulverization of active materials and the construction of nanointerface among electrode components. The second is that liquid-solid interface using molten sulfur was formed to obtain larger contact area between sulfur and conductive additives. The third is the new approach to increase energy density of the batteries; Li$_2$S-P$_2$S$_5$ glass materials were used as an active material. Typical bulk-type solid-state cells consist of active materials, solid electrolytes and conductive additives, while in the new type cells the addition of active materials is not required. This is because Li$_2$S-P$_2$S$_5$ materials with a large amount of Li$_2$S components are composed of Li$_2$S crystal and Li$_2$S-P$_2$S$_5$ glass and are expected to play a role as not only a lithium ion conducting path but also an active material. Moreover, the detailed reaction mechanism and the morphology on a nano-scale in sulfur-based electrodes were explored by using high-resolution TEM.

**Chapter 3**

In this chapter, the electrochemical performance and the morphological observation in high-capacity negative electrodes in all-solid-state cells using Li$_2$S-P$_2$S$_5$ solid electrolytes were investigated. Lithium alloys such as Li-Si and Li-Sn, metal phosphide such as Sn$_4$P$_3$, 
phosphorus and lithium metal were used. Metal phosphide reacts with lithium ion, resulting in the formation of lithium phosphide (Li$_3$P). Li$_3$P with high lithium ion conductivity can act as a matrix stabilizer. The effects of the presence of matrix on electrochemical performance and morphological change with cycling were discussed. Phosphorus has several allotropes, and among them black phosphorus has superior properties of relatively high electronic conductivity and a layered structure. Additionally, phosphorus is one of the constituent elements of Li$_2$S-P$_2$S$_5$ solid electrolytes. Black phosphorus is expected to be a promising negative electrode in all-solid-state cells with high capacity. In the case of using lithium metal as a negative electrode, the dendritic growth of lithium is a major problem, resulting in the deterioration of the safety and the cyclability of the batteries. To suppress the dendritic growth, the construction of a favorable interface between lithium electrodes and Li$_2$S-P$_2$S$_5$ solid electrolytes and the decrease in the grain boundaries in the solid electrolytes are required. The formation of favorable electrode-electrolyte interface by vacuum evaporation and the decrease in the grain boundaries in the solid electrolytes by their softening adhesion were carried out.

Chapter 4

This chapter reports the investigation of structural and morphological change in the all-solid-state cells during their operation by in-situ techniques using Raman and SEM. In-situ Raman spectroscopy was applied to the LiCoO$_2$ electrodes in the all-solid-state cells with Li$_2$S-P$_2$S$_5$ solid electrolytes. The electrochemical reaction mechanism of LiCoO$_2$ electrodes in all-solid-state cells was compared to that in conventional liquid-type cells. The lithium deposition and dissolution reaction on solid electrolytes greatly affects the performance of the bulk-type lithium metal batteries. Thus, a fundamental understanding of the morphological change at the interface between the lithium electrodes and the solid electrolytes is essential. Lithium deposition and dissolution mechanism in the bulk-type cells using Li$_2$S-P$_2$S$_5$ solid electrolytes was investigated by in-situ SEM observation at different current densities. The cell configuration was Li / 80Li$_2$S·20P$_2$S$_5$ glass-ceramic /
stainless-steel, and morphological changes at the interface, where lithium was electrochemically deposited, were observed. The influences of current density on morphological change during lithium deposition and dissolution reaction were examined.

Chapter 5

This chapter summarizes all the conclusions in this thesis.
References


2. Development of positive electrode materials for all-solid-state rechargeable Li/S batteries with high capacity

2.1. Introduction

An all-solid-state rechargeable battery using inorganic solid electrolytes is one of the promising candidates for power sources for large-scale applications such as eco cars and smart grids because of their high safety and reliability. Furthermore, the batteries In/LiCoO$_2$ with Li$_2$S-P$_2$S$_5$ glass-ceramics having high lithium ion conductivities of over $10^{-3}$ S cm$^{-1}$ were charged and discharged for several hundred cycles with a capacity of about 100 mAh g$^{-1}$ [1]. There is an increasing need for improvement of energy density of rechargeable batteries to build large-scale batteries. For example, about 5 times higher energy density is required to meet battery performance of next-generation electric vehicles [2]. It would be difficult to achieve this goal by using the current electrode materials. The construction of innovative rechargeable batteries with extremely high capacity is one of the urgent works. Lithium-sulfur batteries have been attracting much attention because sulfur has 10 times higher theoretical capacity than that of LiCoO$_2$ [3,4]. However, sulfur electrodes have poor cycle performance in these batteries with organic liquid electrolytes due to the high solubility of polysulfide ions formed during electrochemical reaction. The recent approaches focus on confining sulfur active materials in porous nanostructures to capture the polysulfide ions [5-9]. On the other hand, the all-solid-state Li/S batteries are anticipated to show a long cycle life because there would be no or less dissolution of lithium polysulfides into sulfide-based solid electrolytes. Several attempts have been made to enhance utilization of sulfur-based electrodes in all-solid-state Li/S cells with inorganic solid electrolytes [10-14]. It was reported that the formation of favorable electron conducting paths to the active materials contributes to enhancement of reversible capacity at a limited current density. There are some challenges to be overcome in electrochemical performance of all-solid-state Li/S cells. The first is the enhancement of rate capability, the second is improvement of energy density normalized by the weight of electrodes and the third is cycle life for more than 100 cycles.
Additionally, detailed reaction mechanism and morphology in submicron and nano-scale of sulfur-based electrodes has not been understood.

In the present chapter, the electrochemical performance and the morphological and structural change in sulfur-based positive electrodes in all-solid-state rechargeable batteries using Li$_2$S-P$_2$S$_5$ solid electrolytes were investigated. First, Cu$_x$Mo$_{0.6}$S$_{8-y}$ Chevrel-phase compound was used as a model active material of sulfur-based electrode in all-solid-state batteries using Li$_2$S-P$_2$S$_5$ solid electrolytes (SEs). Their electrochemical performance was investigated and interfacial analyses between the active material and the Li$_2$S-P$_2$S$_5$ SEs were carried out by impedance measurements and transmission electron microscopy (TEM). Based on information obtained from the above characterization, the batteries with long cyclability and high rate performance in wide temperature range, where the conventional batteries are difficult to operate, were fabricated. Next, sulfur and Li$_2$S active materials with high theoretical capacity were applied to the all-solid-state Li/S cells. Several approaches were carried out to improve the cell performance of all-solid-state Li/S cells. The first approach is the construction of favorable lithium ion paths as well as electron conducting paths to active material by mechanical milling of electrode components. The second approach is the formation of liquid-solid interface between molten sulfur and acetylene black (AB): the mixture of sulfur and AB was milled at 155 °C, where molten sulfur has the lowest viscosity. The third approach is the pulverization of Li$_2$S active materials on dry or wet milling conditions using toluene solvent prior to the preparation of the composite electrodes. The fourth approach is the use of Li$_2$S-P$_2$S$_5$ SEs as an active material; Li$_2$S-P$_2$S$_5$ materials with high Li$_2$S content were used as an active material. Moreover, the detailed reaction mechanism and the morphology in nano-scale of sulfur-based electrodes were explored by using high-resolution TEM.

2.2. Experimental

2.2.1. Cell construction

The xLi$_2$S-(100-x)P$_2$S$_5$ (mol%, x = 70, 75, 80 and 87.5) glass [15] and glass-ceramic [16]
electrolytes were prepared by the mechanochemical reaction process. Reagent-grade Li$_2$S (Idemitsu Kosan Co.) and P$_2$S$_5$ (Aldrich Chem., 99%) crystalline powders were used as starting materials. The mixture of these materials was mechanically milled at room temperature by a planetary ball mill apparatus (Pulverisette 7, Fritsch) using an zirconia pot (volume of 45 mL) with 500 zirconia balls (4 mm in diameter); the milling time was 8-24 h at a rotating speed of 510 rpm to obtain the glass electrolytes. All the processes were performed in a dry Ar-filled glove box. The xLi$_2$S-(100-x)P$_2$S$_5$ were prepared by heating the obtained glasses over crystallization temperatures under a dry Ar atmosphere.

Most of active materials for composite electrodes were obtained from companies; Cu$_x$Mo$_6$S$_{8-y}$ (Nippon Inorganic Colour & Chemical Co., Ltd), sulfur (Aldrich) and lithium sulfide (Idemitsu Kosan Co.). Mo$_6$S$_{8-y}$ powders were prepared by removing Cu from Cu$_x$Mo$_6$S$_{8-y}$; Cu$_x$Mo$_6$S$_{8-y}$ after stirring in 6 M HCl solution for 1 week, filtering in the air atmosphere and drying at 150°C under vacuum overnight [17].

The composite electrodes for all-solid-state lithium secondary batteries were prepared as follows. Cu$_x$Mo$_6$S$_{8-y}$ or Mo$_6$S$_{8-y}$ electrodes with the weight ratio of active materials : Li$_2$S-P$_2$S$_5$ glass-ceramic SE : acetylene black (AB, Denki Kagaku Kogyo) = z : (100-z) : 0 or 5 (z = 40, 60, 70 and 80) were prepared by grinding with an agate mortar.

The sulfur and Li$_2$S nanocomposite electrodes of sulfur or Li$_2$S active material, AB and SE with the weight ratio of 25 : 25 : 50 were prepared by grinding with a mortar or ball-milling with the planetary ball mill apparatus in a dry Ar-filled glove box. The composite materials are divided into the following three types: (S or Li$_2$S + AB + SE) electrode, (S-AB or Li$_2$S-AB + SE) electrode and S-AB-SE or Li$_2$S-AB-SE electrode. The (S or Li$_2$S + AB + SE) electrode was obtained by hand grinding of S or Li$_2$S active material, AB and SE. The (S-AB or Li$_2$S-AB + SE) electrode was obtained by milling the mixture of sulfur or Li$_2$S and AB and then hand grinding the mixture of S-AB or Li$_2$S-AB composites and SE. S-AB-SE or Li$_2$S-AB-SE electrode is obtained by milling the mixture of S-AB or Li$_2$S-AB composite and SE. Mechanical milling conditions are as follows. A ZrO$_2$ pot (45 ml) with 100 ZrO$_2$ balls (5 mm in diameter) was used and the rotation speed was fixed with
Laboratory-scaled solid-state lithium cells were constructed as follows. The above composite electrodes were used as a working electrode. An indium foil (Furuuchi Chem., 100 or 300 µm in thickness, 99.999%) and a lithium foil (Furuuchi Chem., 250 µm in thickness, 99.9%) were used as a counter electrode and the surface of both foils was roughly polished before use. The composite electrode and the SE powder were set in a polycarbonate tube and were then pressed under 360 MPa. Then In foil or Li-In foil was put on the SE layer as a counter and a reference electrode; a pressure of 120 or 240 MPa was applied to the three-layered pellet and was then relieved. Finally, two-electrode cells sandwiched by two stainless steel rods as current collectors were obtained.

2.2.2. Characterization

X-ray diffraction (XRD) measurements (CuKα) were performed using a diffractometer (M18XHF22-SRA, Mac Science or Ultima IV, Rigaku) to identify crystalline phases. The morphologies of active materials and composite electrodes were examined using a scanning electron microscope (SEM, JSM-5300 or JSM-6610A, JEOL) equipped with an energy-dispersive X-ray spectroscopy (EDX) system. Specific surface area was determined using the Brunauer-Emmett-Teller (BET) method and pore volume was calculated by the Barrett-Joyner-Halenda (BJH) method with a surface area measuring instrument (Tristar 3000, Micrometritics). Before this analysis, the samples were preheated for three hours at 50°C under vacuum. Local structures of the composites were analyzed using Raman spectroscopy with a spectrometer (LabRAM HR-800, HORIBA).

The bulk-type solid-state cells were charged and discharged using a charge-discharge measuring device (BTS-2004, Nagano Co.). Cycle performances of the cells were evaluated under various constant current densities at wide temperature range from -30°C to 160°C in an Ar atmosphere. Electrochemical impedance measurements were performed for the electrochemical cells, which were charged or discharged to different depths at the constant current or constant voltage conditions and then aged for several hours. An impedance
analyzer (Solartron 1287 coupled with Solartron 1260) was used and a small perturbation voltage of 50 mV in the frequency range of 10 mHz-1 MHz was applied for the measurements.

The morphology and elemental analysis of the composite electrode layer were analyzed by scanning transmission electron microscope and electron energy loss spectroscopy (STEM-EELS). Samples of the cross-section of the working electrode for TEM observations were obtained by using focused ion beam (FIB). STEM-EELS studies were conducted on JEM-2100F (JEOL) at 200 kV equipped with electron energy loss spectrometer (GATAN GIF Tridiem). All processes described above were carried out in a dry Ar-filled glove box. Elemental point analysis for the cross-section of the composite electrode layer was carried out using energy dispersive X-ray spectroscopy (EDX, JED-2300T, JEOL). In order to explore the structure and morphology at nanoscale of Li$_2$S electrode, high-resolution TEM (HRTEM) observation of the electrodes was carried out before and after charge-discharge tests of the cells. Prior to TEM observation, the cell was disassembled, Li$_2$S composite electrode was scratched, and then the obtained powders were placed on a grid for TEM observation without any damages for the samples. These samples were packed in a folder to maintain the inert atmosphere, and then were transferred to TEM apparatus (JEM-2100F, JEOL).

2.3. Results and discussion

2.3.1. Chevrel-phase compound electrodes

A so-called Chevrel-phase compound, Cu$_x$Mo$_6$S$_{8-y}$, as one example of M$_x$Mo$_6$S$_8$ (M=Cu, Ni, Fe etc), has been studied as positive electrode materials in lithium batteries using conventional liquid electrolytes [18-20]. Cu$_x$Mo$_6$S$_{8-y}$ exhibits high electronic conductivity and high Li diffusion coefficient, and thus lithium ions are intercalated into Cu$_x$Mo$_6$S$_{8-y}$ at high current densities. Kanno et al. reported that Mo$_6$S$_8$ obtained by leaching copper from Cu$_2$Mo$_6$S$_8$ with concentrated HCl solution was applied to the electrode of the all-solid-state cells and the cells of Li-Al/thio-LISICON/Mo$_6$S$_8$ showed a good cycle performance at 1.3 mA
cm$^{-2}$ [21]. Then, Cu$_x$Mo$_6$S$_{8-y}$ Chevrel-phase compound was used as a model active material of sulfur-based electrode in all-solid-state batteries using Li$_2$S-P$_2$S$_5$ SEs. In this section, their electrochemical performance was investigated and interfacial analyses between the active material and the Li$_2$S-P$_2$S$_5$ SE were carried out by impedance measurements and transmission electron microscopy (TEM). Based on information obtained from the above characterization, the batteries with long cyclability and high rate performance in wide temperature range, where the conventional batteries are difficult to operate, were fabricated.

**Figure 2-1** shows SEM images of (a) Cu$_x$Mo$_6$S$_{8-y}$ and (b) Mo$_6$S$_{8-y}$ particles. The Cu$_x$Mo$_6$S$_{8-y}$ particles were agglomerates with size in the range 10-30 µm. Mo$_6$S$_{8-y}$ particles were prepared by removing Cu from Cu$_x$Mo$_6$S$_{8-y}$ chemically. The obtained particles were identified with Mo$_6$S$_{8-y}$ phase from XRD analysis, but the diffraction peaks due to Cu$_x$Mo$_6$S$_{8-y}$ of the starting material were slightly observed. The Mo$_6$S$_{8-y}$ particles were finer (below 3 µm) and well dispersed. **Figure 2-2** shows the charge-discharge curves (a) and the cycle performance (b) of an all-solid-state cell of Li-In / 80Li$_2$S・20P$_2$S$_5$ glass-ceramic / Cu$_x$Mo$_6$S$_{8-y}$. The cell was discharged and then charged between 0 and 3.0 V (vs. Li-In) at the current density of 1.3 mA cm$^{-2}$. In this figure, the axis of ordinate on the left side represents the cell potential vs Li-In electrode (counter electrode), and that on the right side represents the potential vs Li electrode which was calculated on the basis of potential difference between Li-In and Li electrode (0.62 V) [22]. Although an irreversible capacity was observed during an initial few cycles in the cell, subsequently the cell showed the charge-discharge efficiency of about 100% up to the 2000th cycle. One plateau at about 1.9 V (vs. Li) was observed during discharge process in the cell and the plateau voltage was almost the same as that reported in a conventional liquid electrolyte cell [19]. The Li-In/Cu$_x$Mo$_6$S$_{8-y}$ cell using the Li$_2$S-P$_2$S$_5$ SEs exhibited an excellent cycle performance with capacities of about 100 mAh g$^{-1}$ for 2000 cycles. **Figure 2-3** shows the change of XRD patterns for the Cu$_x$Mo$_6$S$_{8-y}$ electrodes before and after the charge-discharge tests. The diffraction peaks before cycling (a) were attributed to Cu$_x$Mo$_6$S$_{8-y}$ [23]. The peak positions in XRD patterns for the electrode after the first charge (b) and the 100th charge (c) were almost the same as those before cycling.
It was found that a Chevrel phase, which has a stable three dimensional framework based on $\text{Mo}_6\text{S}_8$ cluster, is retained after 100 cycles, suggesting that retaining the crystal structure during cycling lead to a good cyclability. The all-solid-state cells are expected to be charged and discharged in the wide temperature range where the operation of conventional batteries is difficult, and then the electrochemical performance in the wide temperature range from -30°C to 120°C of Li-In/Cu$_x$Mo$_6$S$_{8-y}$ cells using Li$_2$S-P$_2$S$_5$ SEs was investigated. Figure 2-4 depicts (A) the discharge curves and (B) the cycling performance of the all-solid-state cells (a) under 0.13 mA cm$^{-2}$ at -30°C, (b) under 1.3 mA cm$^{-2}$ at 25°C and (c) under 12.8 mA cm$^{-2}$ at 120°C. The cells were discharged even at -30°C and 120°C. The discharge capacity at -30°C (a) was 80 mAh g$^{-1}$, which was lower compared with that at 25°C. On the other hand, the all-solid-state cell had the discharge capacity of 200 mAh g$^{-1}$ higher than the theoretical capacity of 110 mAh g$^{-1}$ even at the high current density of 12.8 mA cm$^{-2}$ at 120°C. The cells were charged and discharged without capacity loss for 50 cycles in the wide temperature range between -30°C and 120°C. Especially, the cell retained the reversible capacity higher than 200 mAh g$^{-1}$ under 12.8 mA cm$^{-2}$ at 120°C. The reaction mechanism of Cu$_x$Mo$_6$S$_{8-y}$ electrodes was reported to be the conversion from Cu$_x$Mo$_6$S$_{8-y}$ to Mo$_6$S$_{8-y}$ and Cu metal after several cycles in conventional batteries using liquid electrolytes [24]. It is thus presumed that Cu metal formed during electrochemical reaction chemically reacted with Li$_2$S-P$_2$S$_5$ SEs and the reaction product contributed to the large capacity of the cells with Cu$_x$Mo$_6$S$_{8-y}$ electrodes. Therefore, we compared the electrochemical performance of the all-solid-state cells with Mo$_6$S$_{8-y}$ and Cu$_x$Mo$_6$S$_{8-y}$ electrodes at high temperatures. In order to study the cause for the additional capacity in the cells from the viewpoint of the presence or absence of Cu metal in Chevrel phase, the configuration of the working electrodes was simplified; the electrodes consisted of the Cu$_x$Mo$_6$S$_{8-y}$ or Mo$_6$S$_{8-y}$ active material and the Li$_2$S-P$_2$S$_5$ SEs without adding conductive additives like AB. Figure 2-5 shows the cycle performance of the all-solid-state cells using (a) the Cu$_x$Mo$_6$S$_{8-y}$ and (b) the Mo$_6$S$_{8-y}$ active material at 12.8 mA cm$^{-2}$ at 100°C. The cell using Cu$_x$Mo$_6$S$_{8-y}$ showed the first discharge capacity of about 180 mAh g$^{-1}$, which was higher than its theoretical capacity and the remarkable capacity loss
through the 200th cycle. On the other hand, the cell using Mo$_6$S$_{8-y}$ exhibited the initial capacity of 135 mAh g$^{-1}$ and the good cyclability with the capacity of about 100 mAh g$^{-1}$ for 1000 cycles. The result revealed that the first discharge capacity and the cyclability were greatly different in the cells using Cu$_x$Mo$_6$S$_{8-y}$ and Mo$_6$S$_{8-y}$. In order to understand how the formed Cu existed in the composite electrodes, we carried out STEM observations of the Cu$_x$Mo$_6$S$_{8-y}$ electrode (Fig. 2-6) and the Mo$_6$S$_{8-y}$ electrode (Fig. 2-7) after the cells were charged and discharged at 12.8 mA cm$^{-2}$ at 100$^\circ$C for 100 cycles. Figure 2-6 shows (a) a high angle annular dark field (HAADF) STEM image and (b-e) EDX maps for (c) sulfur, (d) copper and (e) molybdenum and (b) a superposition of these maps of a cross-section of the Cu$_x$Mo$_6$S$_{8-y}$ electrode. The HAADF-STEM image showed that particles represented in white color have the size of 1-6 µm and small particles with the size less than hundreds of nanometer existed around the white colored particles. Sulfur (in Cu$_x$Mo$_6$S$_{8-y}$ particles or Li$_2$S-P$_2$S$_5$ particles), copper (in Cu$_x$Mo$_6$S$_{8-y}$ particles or Cu) and molybdenum (in Cu$_x$Mo$_6$S$_{8-y}$ particles) are shown in red, green and blue, respectively. The signals of molybdenum and sulfur were observed in the particles represented in white color in the STEM image, indicating that these particles correspond to the active materials. The presence of Cu was confirmed in the small particles existing around the active materials. Figure 2-6 suggests that Cu diffused from the active materials to the Li$_2$S-P$_2$S$_5$ SE matrix during the long cycle test at high operating temperatures. On the other hand, the Mo$_6$S$_{8-y}$ electrode (Fig. 2-7) had the particles represented in white color have the size of 0.5-2 µm without the presence of the submicrometer-sized particles. EDX analysis of the Mo$_6$S$_{8-y}$ electrode shows that the diffusion of Mo into the SEs was not observed. The signals of copper were slightly observed in the active materials and the SEs, because Cu was not completely removed from Cu$_x$Mo$_6$S$_{8-y}$ for the preparation of Mo$_6$S$_{8-y}$ particles. Figure 2-8 shows impedance profiles of the all-solid-state cells using (a) the Cu$_x$Mo$_6$S$_{8-y}$ electrode and (b) the Mo$_6$S$_{8-y}$ electrode after 1000 cycles at 100$^\circ$C. A resistance component in a middle frequency region (at around 1000 Hz) was observed in the impedance profile of the cells with the Cu$_x$Mo$_6$S$_{8-y}$ electrode, but the resistance was significantly small in the Mo$_6$S$_{8-y}$ electrode. In our previous reports, the
all-solid-state cells using LiCoO$_2$ electrode and Li$_2$S-P$_2$S$_5$ SE showed the resistance at the frequency region (the peak top frequency of 500 Hz) after the first charge process, and this resistance would result from the interface between the electrode and the SE [25]. The resistance component observed at the middle-frequency region in the cells with Cu$_x$Mo$_6$S$_{8-y}$ electrodes was considered to correspond to the interfacial resistance ($R_{\text{interface}}$) between the Cu$_x$Mo$_6$S$_{8-y}$ electrode and the Li$_2$S-P$_2$S$_5$ SE. The combination of TEM observation of the electrode and impedance measurement of the cells after the cycle test at high operating temperatures demonstrates that a resistance layer between the electrode and the electrolyte was formed by diffusion of Cu into the solid electrolyte. These results suggest that the diffusion of Cu into the solid electrolytes is mainly responsible for both the excess capacity over the theoretical capacity and the remarkable capacity fading of the cells with the Cu$_x$Mo$_6$S$_{8-y}$ electrode. It was found that chemical removal of Cu from Chevrel phase contributed strongly to the improvement of a long cyclability in the cells at extremely high temperatures. In order to enhance the electrochemical performance of the all-solid-state cells using the Cu$_x$Mo$_6$S$_{8-y}$ electrode at high temperatures, a coating on Cu$_x$Mo$_6$S$_{8-y}$ particles is required to suppress the diffusion of Cu into the SEs. In fact, the all-solid-state cells with the Cu$_x$Mo$_6$S$_{8-y}$ electrodes including acetylene black (AB) of a conductive additive exhibited the excellent cycle performance at high temperatures as shown in **Fig. 2-4**. This is because AB properly would act as the materials to trap the diffusion of Cu. The effects of the addition of AB on electrochemical performance of the Cu$_x$Mo$_6$S$_{8-y}$ electrode were examined. We applied the Cu$_x$Mo$_6$S$_{8-y}$ electrodes with or without AB to the all-solid-state cells, and the cells were charged and discharged on more severe conditions of 40 mA cm$^{-2}$ (60 C rate) at 160$^\circ$C. **Figure 2-9** shows the cycle performance of the all-solid-state cells using the Cu$_x$Mo$_6$S$_{8-y}$ electrodes (a) without AB and (b) with AB. The Cu$_x$Mo$_6$S$_{8-y}$ electrodes with AB exhibited better cyclability than that of the electrodes without AB, and the cells using the electrodes with AB retained the reversible capacity of about 190 mAh g$^{-1}$ for 100 cycles at 60 C rate at 160$^\circ$C. This result indicated that addition of AB was valid in enhancement of cycle performance of the cells using Cu$_x$Mo$_6$S$_{8-y}$ electrodes at high temperatures. The design of
Chevrel phase electrodes in all-solid-state cells with Li$_2$S-P$_2$S$_5$ solid electrolytes resulted in the outstanding electrochemical performance under the severe charge-discharge conditions such as very high operating temperatures, high current densities and prolonged cycle tests.

2.3.2. Sulfur-based electrodes in all-solid-state Li/S cells

2.3.2.1. Sulfur electrodes

Sulfur has an extremely high theoretical capacity of 1672 mAh g$^{-1}$ which is 10 times higher than that of conventional electrode materials. However, sulfur electrodes in liquid-type cells were reported to show capacity degradation during cycling because of the high solubility of polysulfide ions into liquid electrolytes. For fundamental improvement in inhibiting the dissolution of lithium polysulfides, the use of inorganic solid electrolytes instead of organic liquid electrolyte is an effective approach. Several attempts have been made to enhance the utilization of sulfur-based electrodes in all-solid-state Li/S cells [10-14].

In this section, several approaches to improve performance in all-solid-state Li/S cells using Li$_2$S-P$_2$S$_5$ solid electrolytes such as rate capability, energy density per weight of the electrodes and long cycle life for more than 100 cycles were carried out.

Three different composite electrode materials were prepared as follows: (a) (S + AB + SE), (b) (S-AB + SE), and (c) S-AB-SE. The (S + AB + SE) electrode was obtained by grinding sulfur, AB and SE with a mortar. The (S-AB + SE) electrode was obtained by milling the mixture of sulfur and AB using a planetary ball-mill apparatus and then grinding a mixture of the S-AB composite and SE using a mortar. The S-AB-SE electrode was obtained by milling the mixture of S-AB composite and SE. The morphologies of these S-based composite electrodes were investigated by SEM. Figure 2-10 shows SEM images of the (a) (S-AB + SE) and (b) S-AB-SE electrodes. Two different particle sizes of 1-5 µm and 20-50 µm were observed in the prepared (S-AB + SE) electrodes. The particle sizes of the S-AB composites obtained by milling were 20-50 µm, which suggests that the 20-50 µm particles were the S-AB composite and the 1-5 µm particles were the SE. The S-AB-SE electrodes formed agglomerates less than 10 µm. Therefore, mechanical milling of the
S-AB composite with the SE particles resulted in a decrease in the particle size and a change in surface morphology in the sulfur-based electrodes. From XRD analysis, a halo pattern was observed for the S-AB-SE electrode material, which indicates that the sulfur in S-AB-SE became amorphous. Figure 2-11 shows room temperature charge-discharge curves of the all-solid-state cells with the three types of sulfur-based electrodes at 0.064 mA cm$^{-2}$. The obtained capacity was normalized by the weight of sulfur in the electrode. The cells with the (S + AB + SE) electrodes (a) had poor performance with a capacity of less than 100 mAh g$^{-1}$, due to the insulative nature of sulfur. In the (S-AB + SE) electrodes (b), mechanical milling of S and AB increased a first discharge capacity (approximately 300 mAh g$^{-1}$), but the consecutive charge capacity of the cell was still low (100 mAh g$^{-1}$), which implied there were insufficient lithium ion conducting paths to sulfur. Therefore, the S-AB composite and the SE were mechanically milled, which resulted in a significant increase of the reversible capacity of the cell. The cell with the S-AB-SE electrodes (c) exhibited the discharge capacity of 1220 mAh g$^{-1}$ and the charge capacity of 1550 mAh g$^{-1}$ at the first cycle. The cell retained a reversible capacity of approximately 1400 mAh g$^{-1}$ for 10 cycles. The discharge plateau of the all-solid-state cell with the S-AB-SE electrode was $ca.$ 2 V vs Li/Li$^+$. This plateau was identical to that observed in Li/S cells using conventional liquid electrolytes and polymer electrolytes [26,27]. The first charge capacity was larger than the first discharge capacity by 330 mAh g$^{-1}$. We assume that the difference in capacity between charge and discharge process was due to Li$_2$S in SE of the S-AB-SE electrode; a part of Li$_2$S in SE would be activated during the first discharge process and mainly contributed to the additional capacity in the first charge process. This hypothesis is supported by our preliminary experimental results that the milled AB-SE electrode gave a charge capacity larger than a discharge capacity at the initial cycle. When the additional capacity was eliminated from the overall capacity of the S-AB-SE electrode, the capacity normalized by the weight of sulfur was calculated to be about 1050 mAh g$^{-1}$ after 10 cycles. In order to clarify the reasons for the improvement in the reversible capacity of the cells, the total conductivity of the (S-AB + SE) and S-AB-SE electrodes was measured using the a.c. impedance method.
The electrical conductivities of the (S-AB + SE) and S-AB-SE electrodes were $1.1 \times 10^{-3} \text{ S cm}^{-2}$ and $1.6 \times 10^{-3} \text{ S cm}^{-2}$, respectively. The conductivities were almost the same; therefore, it is difficult to discuss the difference in cell performance with regard to the conductivity of the working electrode. Zhang et al. [28] and Ji et al. [3,5] have reported that the capacity of Li/S cells was increased by heating a mixture of sulfur and carbon materials to amorphize sulfur in the composite electrode material. We also believe that the transformation of crystalline sulfur to amorphous sulfur is a key factor for improvement of the cell performance. Another key factor is the particle size of the composite electrode material. The decrease of particle size in the S-AB-SE electrodes (Fig. 2-10) would imply the formation of closer contacts among sulfur, AB and SE compared with the (S-AB + SE) electrode. It is thus considered that those two factors, amorphization of sulfur and particle size, contribute to the enhancement of the reversible capacity in an all-solid-state Li/S cell. Figure 2-12 shows the cycling performance of an all-solid-state cell with the S-AB-SE electrodes under several current densities from 0.38 to 1.3 mA cm$^{-2}$ at room temperature. The current density of 1.3 mA cm$^{-2}$ corresponds to 333 mA g$^{-1}$ (0.3 C). The coulombic efficiency of approximately 100% was maintained after the second cycle at each current density. The all-solid-state cells using the sulfur-based electrode are charged and discharged reversibly even at higher than 1 mA cm$^{-2}$. The cells exhibited an excellent cycling performance with a reversible capacity of 853 mAh g$^{-1}$ at 1.3 mA cm$^{-2}$ and a capacity of 996 mAh g$^{-1}$ at 0.64 mA cm$^{-2}$ for 200 cycles. Li/S cells with conventional liquid electrolytes have been reported to exhibit rapid capacity degradation upon cycling, due to dissolution of polysulfides into the electrolyte. However, the use of an inorganic SE is effective to suppress the dissolution of polysulfides, so that an all-solid-state Li/S cell with a solid electrolyte is expected to exhibit good cyclability and be effective for improvement of capacity retention. Figure 2-13 shows charge-discharge curves of the all-solid-state cell using the S-AB-SE electrodes at 80°C. The tests were carried out at current densities higher than 10 mA cm$^{-2}$. The cell exhibited reversible capacities of 960 mAh g$^{-1}$ at 12.8 mA cm$^{-2}$ and 520 mAh g$^{-1}$ at 19.2 mA cm$^{-2}$. Enhancement of the rate performance of the cells was achieved by elevating the operation temperature. Furthermore,
the S-AB-SE electrodes retained the high reversible capacity of 1100 mAh g\(^{-1}\) even at a low temperature of -20°C at 0.064 mA cm\(^{-2}\), and no capacity fading was observed for 10 cycles. It is concluded that the formation of intimate contact among the electrode components achieved by the milling treatment was effective for enhancement of the capacity of an all-solid-state Li/S cell.

As described above, it was found that the construction of favorable solid-solid interface among electrode components is important for improvement of cell performance of all-solid-state Li/S cells. Construction of favorable interface between sulfur and smaller amounts of conductive additives is desired to further improve energy density of the cells (for example, an increase in sulfur ratio in the electrodes). To increase the sulfur content from 25 wt.% to 50 wt.% the mixture of sulfur and nanocarbon was mechanically milled at high temperatures where molten sulfur has very low viscosity. It is expected that the contact area between sulfur and nanocarbon achieved by mechanical milling at temperatures over melting points becomes larger than that achieved by mechanical milling at room temperature because a liquid-solid (molten sulfur and nanocarbon) interface would be formed during milling in the former case.

XRD patterns of sulfur-acetylene black (S-AB) composites prepared by mechanical milling at (a) 25°C and (b) 155°C are shown in Fig. 2-14. The peaks attributable to \(\alpha\)-S (JCPDS #078-1888) were observed in the composites prepared by mechanical milling at 25°C. On the other hand, no trace of crystalline sulfur was detected by increasing mechanical milling temperatures from 25°C to 155°C, suggesting that crystalline sulfur changed into amorphous sulfur. Figure 2-15 shows SEM images of composites with sulfur and AB prepared by mechanical milling at different temperatures. Aggregates of particles with 100 nm existed in the S-AB composite prepared by milling at 25°C. By milling at 155°C, sulfur melted and grain boundaries between sulfur and AB were not clearly observed, revealing that contact area between them became larger. The Brunauer-Emmett-Teller (BET) surface area of the AB particles (39.6 m\(^2\) g\(^{-1}\)) and the S-AB composites prepared by milling at 25°C (4.14 m\(^2\) g\(^{-1}\)) and 155°C (0.23 m\(^2\) g\(^{-1}\)) was confirmed. These results obtained from BET
measurements support that the S-AB composites prepared by milling at 155°C had larger contact area, and close contacts between sulfur and AB were formed in the composites. **Figure 2-16** shows (a, b) DTA and (c, d) TG curves of S-AB composites prepared by mechanical milling at (a, c) 25°C and (b, d) 155°C. DTA curves show that the endothermic peaks due to melting of sulfur at temperatures between 100°C and 120°C disappeared in the S-AB composite prepared by milling at 155°C. This represents amorphization of crystalline sulfur, which was consistent with the XRD analysis (**Fig. 2-14**). The weight of the composite prepared by milling at 25°C decreased drastically in the temperature range from 200°C to 300°C. On the other hand, the weight of the composite prepared at 155°C decreased at temperatures from 200°C to 400°C in two steps. These temperature ranges where sulfur evaporates would be ascribable to the difference of their morphology such as adhesion between sulfur and AB. The evaporation of sulfur at temperatures from 300°C to 400°C was caused because their contact area and adhesion were increased. In other words, AB was fully and strongly coated with sulfur, and this idea is supported by the SEM observation (**Fig. 2-15**). **Figure 2-17** shows the Raman spectra of the S-AB composites prepared by mechanical milling at (a) 25°C and (b) 155°C in the wavenumbers (A) from 200 cm\(^{-1}\) to 600 cm\(^{-1}\) and (B) from 1200 cm\(^{-1}\) to 1800 cm\(^{-1}\). The Raman spectra revealed that the S-AB composites prepared at 25°C had the bands at 218 cm\(^{-1}\) and 472 cm\(^{-1}\), which are attributable to \(\alpha\)-S [29]. The intensity of these bands decreased for the composite prepared at 155°C (**Fig. 2-17** (A-b)), implying that amorphous sulfur was obtained. In **Fig. 2-17** (B), the D band and G band [30] derived from AB with graphite structure, were also observed in both the composites at 1350 cm\(^{-1}\) and 1580 cm\(^{-1}\), respectively. The new bands at about 400 cm\(^{-1}\) and 1430 cm\(^{-1}\) along with the bands originating in sulfur and nanocarbon were observed by mechanical milling at 155°C. It was reported that the band at 404 cm\(^{-1}\) is assigned to the C-S stretching in thiophenol having the bonds between carbon of benzene ring and sulfur [31,32]. This means that the opening of \(S_8\) ring to form \(S_8\) chain would occur and a part of \(S_8\) chains would form a covalent bond (C-S bond) with graphite by mechanical milling of sulfur and AB at 155°C. When disorder is introduced into graphite structure, D band is
observed at about 1350 cm\(^{-1}\) [30]. In the high wavenumber region (Fig. 2-17 (B-b)), the shoulder at 1430 cm\(^{-1}\) observed in the region of the D band would be associated with the formation of bonds between amorphous sulfur and partially-disordered graphite in AB. The characterization by XRD, SEM, DTA-TG and Raman spectroscopy revealed that high temperature mechanical milling of the mixture of sulfur and AB brought about amorphization of sulfur with smaller particle size and increase in contact area between sulfur and AB.

**Figure 2-18** (A) shows the first charge-discharge voltage profiles of the all-solid-state cells Li-In/S at a constant current density of 0.064 mA cm\(^{-2}\) at 25°C. The all-solid-state cell with the S-AB composite prepared by mechanical milling at 25°C (a) showed the discharge capacity of 1180 mAh g\(^{-1}\) and the charge capacity of 520 mAh g\(^{-1}\) in voltage range from 0.3 V to 2.7 V vs. Li-In. The large irreversible capacity was observed, but its reason has not been clarified yet. We assume that electron conducting paths to sulfur were not sufficiently maintained because of large volume contraction during charging process. On the other hand, the cells using the S-AB composite prepared by mechanical milling at 155°C showed the first discharge capacity of 1087 mAh g\(^{-1}\) and the coulombic efficiency of 97 % in voltage range from 0.7 V to 2.7 V vs. Li-In. The S-AB composite prepared by milling at 155°C had contacts between sulfur and AB more strongly. This intimate contact accommodated the volumetric change in sulfur and then electron and lithium ion conducting paths to sulfur were kept. Thus, the cell resulted in high coulombic efficiency at the 1st cycle. Mechanical milling of sulfur and AB at 155°C increased reversible capacity and decreases overpotential between charge and discharge reaction. Cycling performance of the cells with the composite electrode using the S-AB composite prepared by mechanical milling at 155°C is also shown in Fig. 2-18 (B). The current densities were 0.064 mA cm\(^{-2}\) from the 1st to 20th cycle and from the 41st to 50th cycle, and 0.64 mA cm\(^{-2}\) (0.2 C with respect to sulfur electrode) from the 21st to 40th cycle. The cell worked as a secondary battery at a relatively high current density of 0.64 mA cm\(^{-2}\) and showed the capacity of 450 mAh g\(^{-1}\). Furthermore, the cell had an excellent cycle performance with a high capacity of 1050 mAh g\(^{-1}\) at 0.064 mA cm\(^{-2}\) for 50 cycles. The sulfur-based electrodes using the S-AB composite prepared by mechanical
milling at high temperature exhibited an outstanding cell performance regarding reversible capacity (utilization of sulfur), cyclability, coulombic efficiency in all-solid-state Li/S batteries. To clarify the origin of this large capacity and good capacity retention, we carried out STEM observations of the electrodes using S-AB composite prepared by mechanical milling at 155°C. Figure 2-19 shows (a) a high-annular dark field (HAADF) STEM image and (b-f) electron energy loss spectroscopy (EELS) maps of a cross-section of the composite electrode after 50 cycles. HAADF-STEM image showed that the size of the particles having black diffraction contrast was smaller than 200 nm and the intimate contacts among electrode components (sulfur, AB, Li$_2$S-P$_2$S$_5$ SE) were formed. Figures 2-19 (b-e) show EELS maps for lithium, carbon, phosphorus and sulfur, respectively. Figure 2-19 (f) shows a superposition of these EELS maps. Carbon (in AB particles), phosphorus (in Li$_2$S-P$_2$S$_5$ SE particles) and sulfur (S or Li$_2$S-P$_2$S$_5$ SE particles) were shown in blue, green and red, respectively. The intensity of sulfur signals (red) was high in the region where the black diffraction contrast was observed in the STEM image, implying that these signals corresponded to sulfur active materials; the sulfur particles were uniformly dispersed in the field of view. The phosphorus signals with high intensity were observed around sulfur active materials, meaning that Li$_2$S-P$_2$S$_5$ SE was present in the region. These results revealed that sulfur particles with the size less than 200 nm are homogeneously dispersed in the Li$_2$S-P$_2$S$_5$ SE matrix. However, carbon signals (blue) were not definitely observed in the composite electrodes. There are two possibilities that carbon signals were not detected in the region; one is that very fine AB particles would be distributed throughout the sulfur-based composite electrodes, and the other is that AB would be fully coated with sulfur. The morphology of S-AB composite in the latter case would be consistent with the SEM observation (Fig.2-15), leading to the formation of sufficient electron conducting paths to sulfur active materials. By investigating the microstructure morphology of sulfur-based composite electrodes from TEM observation, it was revealed that the presence of submicron-sized sulfur particles and the retention of intimate contacts among sulfur, AB and Li$_2$S-P$_2$S$_5$ SE during cycles resulted in excellent cyclability with a high capacity and rate capability. In order to see whether
mechanical milling of sulfur and AB at 155 °C was effective in improving the reversible capacity, the cells using the composites prepared by only heating the mixture of sulfur and AB at 155°C were fabricated. Figure 2-20 shows the initial charge-discharge curves of the all-solid-state Li/S cells using the two types of composites prepared by (a) only heating and (b) mechanical milling of the mixture of sulfur and AB at 155°C. The all-solid-state cell using the composite prepared by heating at 155°C showed the reversible capacity of 550 mAh g\(^{-1}\) (normalized by the weight of sulfur), which was about half as high as that of the cells using the composite prepared by mechanical milling at 155°C. Smaller particle size of sulfur and intimate contact between sulfur and AB achieved by mechanical milling at high temperature were mainly responsible for large utilization of the sulfur active material. The gravimetric energy density of the cells is calculated by multiplying the obtained capacity of the total weight of the electrodes by the operating potential. The capacity based on the total weight of sulfur-based composite electrodes was 530 mAh g\(^{-1}\) and the average discharge operating potential of ca. 1.9 V vs. Li, and then the gravimetric energy density of the cells was 1007 Wh kg\(^{-1}\). This energy density was much higher than that calculated based on multiplying the theoretical capacity of a typical cathode active material (without consideration of the weight of any additives) by the theoretical operating potential in conventional lithium-ion batteries, such as Li/LiFePO\(_4\) [33] (595 Wh kg\(^{-1}\) calculated based on 170 mAh g\(^{-1}\) and 3.5 V) and Li/LiMn\(_2\)O\(_4\) [34] (592 Wh kg\(^{-1}\) calculated based on 148 mAh g\(^{-1}\) and 4 V). Preparation of sulfur composite electrode by mechanical milling at high temperature is very effective in increasing practical sulfur content in the electrode and gravimetric energy density of the Li/S cells.

2.3.2.2. Li\(_2\)S electrodes

Lithium sulfide, Li\(_2\)S, which is a discharge reaction product in the lithium/sulfur battery, has advantages of its high theoretical capacity (ca. 1170 mAh g\(^{-1}\)) and the diversification of selecting negative electrodes without lithium sources. In this section, the electrochemical performance, the structural analysis and morphological observation for nano-scaled Li\(_2\)S
composite electrodes in all-solid-state Li/S cells were characterized.

The Li$_2$S-based composite composites were divided into the following three types: Li$_2$S + AB + SE electrode, Li$_2$S-AB + SE electrode and Li$_2$S-AB-SE electrode. The Li$_2$S + AB + SE electrode was obtained by hand grinding of Li$_2$S, AB and SE. The Li$_2$S-AB + SE electrode was obtained by milling the mixture of Li$_2$S and AB and then hand grinding the mixture of the Li$_2$S-AB composite and SE. The Li$_2$S-AB-SE electrode was obtained by milling the mixture of the Li$_2$S-AB composite and SE. **Figure 2-21** shows XRD patterns of (a) (Li$_2$S + AB + SE), (b) (Li$_2$S-AB + SE) and (c) Li$_2$S-AB-SE electrodes. All the peaks observed in each composite electrode were indexed by the cubic unit cell (Fm3m) of Li$_2$S. Mechanical milling of the mixture of Li$_2$S and AB resulted in the broadening of the peaks, which indicated that the crystallite size of the (Li$_2$S-AB + SE) and the Li$_2$S-AB-SE electrodes was smaller than that of the (Li$_2$S + AB + SE) electrode. Furthermore, no new peaks were observed and the peaks became slightly broader in the Li$_2$S-AB-SE electrode. **Figure 2-22** shows the SEM images of (a) (Li$_2$S + AB + SE), (b) (Li$_2$S-AB + SE) and (c) Li$_2$S-AB-SE electrodes and the EDX mappings for (d) carbon, (e) phosphorus and (f) sulfur of the Li$_2$S-AB-SE electrode. The (Li$_2$S + AB + SE) electrode was composed of large Li$_2$S particles of above 100 µm in size, SE particles with several ten micrometers and agglomerated AB particles. The large Li$_2$S particles had smooth surface, which suggested that Li$_2$S was not covered with AB or SE particles. On the other hand, mechanical milling of the mixture of Li$_2$S and AB brought about a decrease in particle size of Li$_2$S-based composite electrodes. The (Li$_2$S-AB + SE) electrode formed an agglomeration with the size of 10-30 µm without large Li$_2$S particles of above 100 µm. The particles had rough surface and were covered with submicrometer-sized AB. However, isolated SE particles were also observed in the (Li$_2$S-AB + SE) electrode. The particles in the Li$_2$S-AB-SE electrode became finer and the particle size was below 10 µm. EDX mappings revealed that carbon element of AB particles, phosphorus element of SE particles and sulfur element of Li$_2$S or SE particles were entirely detected in the Li$_2$S-AB-SE electrode. This result indicates that both electron and lithium ion conducting paths to Li$_2$S active materials were formed. It was found that the
mechanical milling of the Li$_2$S-AB composite added with SE was effective in decreasing the particle size of Li$_2$S-based composite electrodes and forming favorable contacts among Li$_2$S, AB and SE. Figure 2-23 shows the charge-discharge curves of the all-solid-state cells using Li$_2$S composite electrodes at 0.064 mA cm$^{-2}$ (0.03 C) at 25°C. The obtained capacity is normalized by the weight of Li$_2$S. In all charge-discharge tests, the all-solid-state cells were initially charged and then discharged. The cell with the (Li$_2$S + AB + SE) electrode (a) was difficult to operate because of insulative nature of Li$_2$S. On the other hand, the capacity was increased by mechanical milling for the mixture of Li$_2$S and AB; the (Li$_2$S-AB + SE) electrode (b) showed the first reversible capacity of 170 mAh g$^{-1}$ because of enhancing electronic conductivity of Li$_2$S composite electrodes. However, the reversible capacity was much lower than the theoretical capacity of Li$_2$S (1170 mAh g$^{-1}$), implying that lithium ion conducting paths to Li$_2$S were insufficient. Mechanical milling of the Li$_2$S-AB composite and SE increased reversible capacity drastically. The cell using the Li$_2$S-AB-SE electrode (c) exhibited the first charge capacity of 830 mAh g$^{-1}$ and the coulombic efficiency of 81%. The cell retained the capacity of about 700 mAh g$^{-1}$ for 10 cycles with a little capacity fading. SEM images of the surface of Li$_2$S-AB-SE electrodes (a) before cycling, (b) after 1st charge and (c) after 1st discharge are shown in Fig. 2-24. Before cycling, Li$_2$S-AB-SE electrodes had a few pores in the surface, but remarkable change in the surface was not observed during charge-discharge reaction. SEM images provide information about the morphology and interface in micrometer-size. In order to investigate the causes for this large reversible capacity and good cycle performance in more detail, TEM observation of the Li$_2$S-AB-SE electrode layer of the all-solid-state cells before and after cycle tests is very useful. Figure 2-25 exhibits a HAADF-STEM image and EELS maps for cross-section of the Li$_2$S-AB-SE composite electrodes after charge-discharge reaction for 10 cycles. HAADF-STEM image (a) shows that there were the particles with the size of about 100 nm and 500 nm and intimate contacts among these particles were formed. The EELS maps for Li (b), C (c), P (d) and S (e) elements are shown. Figure 2-25 (f) shows the mapping image summarizing these mappings (Fig. 2-25 (b)-(e)). It was revealed that nanocomposites in which AB particles of
100 nm, Li$_2$S particles of 500 nm and SE particles were homogeneously dispersed were achieved. **Figure 2-26** compares a HAADF-STEM image and an EELS map for a cross-sectional Li$_2$S composite electrode before charge-discharge tests (a,b) with the image and the mapping after 10 cycles (c,d). The STEM image and EELS mapping of the cross-sectional Li$_2$S electrode before the charge-discharge test show that nanocomposites having intimate contacts among particles in the electrode were obtained by mechanical milling of Li$_2$S, AB and SE particles. This intimate contact among Li$_2$S, AB and SE particles mainly contributes to large utilization of Li$_2$S active material. The particle sizes of Li$_2$S, AB and SE and the particles’ dispersion in the electrode were hardly changed before and after 10 cycles. Retaining favorable contacts among Li$_2$S, AB and SE during cycles would bring about a good cyclability with a high capacity of the cell with the Li$_2$S-AB-SE electrode.

Reaction mechanism during charge-discharge processes in all-solid-state Li/S cells was examined. The characterization of structural and morphological change at nanoscale by high-resolution TEM observation is important and will give new insights for developing high-performance all-solid-state cells including Li/S cells. Li$_2$S composite electrodes consisting of Li$_2$S active materials, acetylene black (AB) and 75Li$_2$S-25P$_2$S$_5$ (mol%) glass SEs were prepared by mechanical milling, and cold pressing method at room temperature were applied to fabricate three-layered pellet of indium (counter and reference electrodes) / 75Li$_2$S-25P$_2$S$_5$ glass SE / Li$_2$S (working electrode).

In order to observe the morphology of the electrode layer and the electrode-electrolyte interface clearly, cross-section of a bi-layer of the Li$_2$S electrode and the SE was prepared by an ion-milling technique. **Figure 2-27**(a) shows the cross-sectional SEM image of the bi-layer. The brightest (white) grains were SEs, darkest (black) grains were AB and the intermediate gray contrast was the region where Li$_2$S, AB and the SE were well mixed by mechanical milling. The gray contrast was observed in large areas of the electrodes, meaning that enough conducting paths of electrons and lithium ions to Li$_2$S active materials were formed in the electrode. **Figure 2-27**(b) shows the magnifying image of the rectangle region of (a). The smooth and adhesive contacts between the Li$_2$S electrode layer and the SE
layer were constructed by cold pressing as shown in Fig. 2-27 (b).

The electrochemical properties of the all-solid-state cells using the Li$_2$S electrode were examined. The charge-discharge curves (a) and cycle performance (b) of the cells In/Li$_2$S were also shown in Fig.2-28. The cell was initially charged (extraction of lithium ion from Li$_2$S active material) and subsequently discharged (insertion of lithium ion into Li$_2$S active material) at 25°C. The cell had the initial charge capacity of 900 mAh g$^{-1}$ and the discharge capacity of 620 mAh g$^{-1}$ with the average operating potential of about 2 V vs. Li, as displayed in Fig. 2-28 (a). The cell exhibited a good cyclability with high capacity of 450 mAh g$^{-1}$ for 20 cycles at 0.064 mA cm$^{-2}$ and 0.13 mA cm$^{-2}$. The cell capacity was significantly three times higher than that of current layered metal oxide and phosphate cathodes. To explore the reaction mechanism of the all-solid-state In/Li$_2$S cells, ex-situ X-ray diffraction measurements on the Li$_2$S electrode were performed in the pristine electrode and subsequently in the electrodes after the first charge and discharge, and the 20th discharge. Figure 2-29 (a) clearly shows changes of the crystal structures from the crystalline Li$_2$S active materials to the amorphous Li$_2$S during the cycling performance. Note that in the X-ray diffraction profile of the pristine electrode, all the diffraction peaks were indexed by the cubic structure (space group : $Fm\bar{3}m$), which should stem from the crystalline Li$_2$S active material. In addition, a halo pattern derived from 75Li$_2$S·25P$_2$S$_5$ glass SE can be detected. After the first charge, the peak intensities due to the cubic structure of Li$_2$S drastically decreased and, on the other hand, a new broad profile appeared at around $\theta = 22^\circ$ as displayed in Fig. 2-29 (b), implying that crystalline Li$_2$S active material changed into amorphous sulfur. After the initial discharge, Fig. 2-29 (c) shows that the broad profile due to amorphous sulfur disappears and there was no significant change in the peaks due to the crystalline Li$_2$S active material. From these results, it is suggested that amorphous sulfur should react with lithium ion to form amorphous lithium polysulfide (Li$_2$S$_x$, 1$\leq x \leq 8$), although the existence of Li$_2$S$_x$ has not been confirmed by XRD. The peaks due to the crystalline Li$_2$S active material disappeared completely after 20 cycles, as understood in Fig. 2-29 (d). The intensity profiles due to the crystalline Li$_2$S active material after 20 cycles coincided with those after the 1st discharge, implying that the
following electrochemical reaction proceeded reversibly after the 2nd cycle: amorphous Li$_2$S$_x$ $\leftrightarrow$ amorphous sulfur.

In order to clarify morphology in Li$_2$S electrode at the nanoscale and its reaction mechanism, we carried out high-resolution TEM observation on the electrode in the cells. Before cycling, both HRTEM images (Fig. 2-30 (a)) and electron diffraction (ED) patterns (Fig. 2-30 (b)) revealed that nano-particles with different crystal orientations distributed randomly in the matrix consisting of amorphous SE and AB. Their average size of the nano-particles can be estimated to be approximately 5 nm, which is consistent with the size calculated based on Scherrer’s equation from XRD pattern in Fig. 2-29 (a). To identify the nano-particles found in the high-resolution TEM image, lattice parameters were calculated from the intensity peaks labeled by the asterisks in Fig. 2-30 (c); the lattice parameters coincided with those of the crystalline Li$_2$S. These results imply that, since 75Li$_2$S·25P$_2$S$_5$ glass SE consists of Li$^+$ and PS$_4^{3-}$, crystalline Li$_2$S can be regarded as only Li$_2$S active material. On the other hand, dark-field image (not shown here) obtained using the diffraction spot due to the crystalline Li$_2$S electrode clearly revealed that the crystalline Li$_2$S active material with the size of about 5 nm was well dispersed, in addition to a scatter of the particles with the size larger than 50 nm. This morphology comprising the Li$_2$S nano-particles, SE and AB should play a crucial role in the high capacity of the all-solid-state Li/S cells.

Another striking phenomena found in this work was the reversible structural changes between the crystalline nano-particles and the amorphous structure during cycles. To elucidate changes of the microstructures during the charge process, high-resolution TEM images, ED patterns were examined in the Li$_2$S electrode after the 1st charge. As shown in Fig. 2-30 (d) no lattice fringes due to the crystalline Li$_2$S can be seen and there exists the characteristic contrast due to amorphous structure in the whole region. In the ED pattern and the intensity profile of Figs 2-30 (e) and 2-30 (f), only halo pattern can be seen. Considering the X-ray diffraction profiles in Fig. 2-29 (b), the amorphous sulfur should result in the halo pattern. On the other hand, significant phenomena in the understanding of the good capacity
retention with high capacity were found in the samples after the 1st and the 20th discharge performance. As shown in Figs. 2-30 (g) and 2-30 (j), lattice fringes clearly seen in high-resolution TEM images at the 1st and 20th discharge stage, suggesting that amorphous sulfur was converted into crystalline active nanoparticles during discharge reaction. Both the crystalline sizes were about 5 nm, which is almost consistent with that in the pristine electrode of Fig. 2-30 (a). On the other hand, significant features in ED patterns of Figs. 2-30 (h) and 2-30 (k) were found. One of the features is the appearance of the Debye-Scherrer rings due to the nano-particles with randomly distributed crystal orientations and the other is the presence of the diffraction spots originating from the crystalline particles. The Debye-Scherrer rings resulted from the crystalline Li$_2$S active nanoparticles. On the other hand, the diffraction spots indicated by arrows in Figs. 2-30 (h) and 2-30 (k) should stem from the crystal structure of lithium polysulfide (~200 nm). It should be noticed that conventional X-ray diffraction experiment could not detect the reflection peaks due to the Li$_2$S crystallines with the size less than 5 nm while high-resolution TEM experiments revealed the existence of crystalline Li$_2$S active nanoparticles. From careful analysis of the ED patterns in Figs. 2-30 (h) and 2-30 (k), lattice parameters calculated from the reflection spots indicated by arrows were estimated to be about 3.89 Å, which correspond to those of Na$_2$S$_2$ with the hexagonal unit cell (P63/mmc) or Na$_2$S$_4$ (I4-2D). Unfortunately, to the best of our knowledge, the crystal structure and lattice constants of lithium polysulfide such as Li$_2$S$_2$ or Li$_2$S$_4$ have never been reported so far. If sodium sites in a sodium polysulfide would be replaced for lithium ions, discharge reaction product could be identified as lithium polysulfide. These results suggest that the reversible reaction of Li$_2$S ↔ S + 2Li$^+$ + 2e$^-$ proceeded in Li$_2$S particles with the smaller size (less than 10 nm), and irreversible reaction occurred in the particles with larger size (ca. 200 nm): charge reaction of Li$_2$S → S and discharge reaction of S → Li$_2$S$_2$ or Li$_2$S$_4$ took place.

Figures 2-31 (a) and 2-31 (b) respectively show high-resolution TEM image and EDX line profile of Li$_2$S electrode after the 1st charge. EDX analysis was carried out on the line (25 nm in length) in the high-resolution TEM image. Here the two particles were focused on,
which are labeled as ① and ②, respectively. The EDX intensity due to sulfur element in the particle ② is much stronger than that in the particle ① and, on the other hand, the EDX intensity due to carbon element in the particle ② is much weaker. These indicate that the particle ① corresponded to AB particle, and the particle ② can be identified as compound consisting of Li$_2$S active material and AB. The EDX intensity due to phosphorus element remains intact in the two particles ① and ②. Li$_2$S-P$_2$S$_5$ SE is distributed homogeneously in the electrode because the volume of the SE is larger than that of Li$_2$S active material. EDX analysis of individual particles revealed that intimate contact among Li$_2$S active material, AB and Li$_2$S-P$_2$S$_5$ SE is retained on the nanometer scale. Based on these ex-situ XRD and high-resolution TEM experiments of Li$_2$S electrode in all-solid-state In/Li$_2$S cells, its reaction mechanism could be proposed as follows,

<1st charge>

\[ \text{Li}_2\text{S (crystalline)} \rightarrow \text{S (amorphous)} + 2\text{Li}^+ + 2\text{e}^- \]

<1st discharge & subsequent cycles from 2nd cycle>

\[ \text{S (amorphous)} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{crystalline Li}_2\text{S (size: ~ 10 nm)} \]

\[ x\text{S (amorphous)} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{crystalline Li}_2\text{S}_x \ (x=2 \text{ or } 4) \ (\text{size: 50 ~ 200 nm}) \]

Let us discuss their origin of high-capacity and cycling stability in all-solid-state lithium batteries consisting of In / Li$_2$S-P$_2$S$_5$ SE / Li$_2$S. It is well-known that Li$_2$S has the low lithium ion diffusion coefficient [35], in addition to low electronic conductivity and Li$_2$S undergoes the large volumetric expansion and contraction during cycling. It is recognized that capacity and cycling stability are insufficient in conventional liquid-type cells using Li$_2$S electrode [36]. We demonstrate here the unprecedented good cell performance in all-solid-state Li/S cells, as shown in Figs. 2-28 (a) and 2-28 (b). In the case of all-solid-state Li/S cells, highly adhesive electrode/electrolyte interface should play a crucial role in the cell performance. Because Li$_2$S active materials with the size less than 10 nm were surrounded by the AB and SE particles in the pristine electrode, electron and lithium ion conduction paths to the Li$_2$S active material are realized and diffusion distance of lithium ion is shorten within the Li$_2$S nanoparticles. These morphologies of the electrolyte/electrode lead
to the achievement of high utilization of Li$_2$S at the initial charge process.

Focused on the initial discharge process, two distinct reaction processes were found depending on the Li$_2$S particle sizes. One is an irreversible reaction characterized by the conversion to the lithium polysulfide (Li$_2$S$_2$ or Li$_2$S$_4$) in active materials with the size larger than 50 nm and the other is a reversible reaction by the conversion between nanosized crystalline Li$_2$S and amorphous sulfur proceeded in the Li$_2$S particles less than 10 nm as shown in Figs. 2-30 (d) and 2-30 (e). It is suggested that the former process results in the irreversible capacity at the initial cycle. To enhance the reversible capacity in the all-solid-state Li/S cells at the initial cycle, it should be indispensable that the Li$_2$S nanoparticles less than ~10 nm in size are well dispersed in the matrix consisting of AB and SE particles.

The excellent cycling stability during 20 cycles is due to the fact that there were little changes of the morphologies of the Li$_2$S electrodes at the initial discharge (Fig. 2-30 (g)) and at the 20th discharge states (Fig. 2-30 (j)). The significant point to be considered is that the uniform dispersion of the Li$_2$S nanoparticles in the AB and SE matrix remains intact during cycling without their agglomeration. This is because the Li$_2$S-P$_2$S$_5$ SE would play a key role in suppressing the volumetric change of Li$_2$S active materials. As shown in Figs. 2-27 (a) and (b), the SE was significantly densified by applying the cold pressing method at room temperature. Therefore, it is considered that Li$_2$S-P$_2$S$_5$ SE which is flexible and has favorable elastic properties and works effectively as an inhibition of the volume change of the electrodes.

HRTEM observation revealed the reaction mechanism of all-solid-state Li/S cells and the morphology (the crystalline size of an active material and the dispersion and adhesion of particles in the electrode) on a nanoscale. In order to demonstrate the rate-limiting process, open circuit voltage (OCV) measurements and a.c. impedance measurements at open circuit voltage at each charge state were conducted in all-solid-state In/Li$_2$S cells. Figure 2-32 shows (a) the OCV profile and (b) a.c. impedance profile before cycling and after each charge state (50, 500, 1000 mAh g$^{-1}$) in the cells using the Li$_2$S composite electrodes. As the charge
capacity became higher, a difference between the voltages of each charged state and the OCV became larger and the resistance in low frequency regions increased. These results suggest that lithium ion diffusion process in the Li$_2$S particles or in the electrodes rather than charge-transfer process would be the rate-limiting process. High resolution TEM observation and impedance measurement suggests that a decrease in the size of Li$_2$S particles without their inhomogeneous distribution would lead to achieving higher utilization of Li$_2$S active material. Then, Li$_2$S particles were milled on dry condition and wet condition using toluene prior to preparation of the Li$_2$S-AB-SE electrode. **Fig. 2-33** shows SEM images of Li$_2$S particles prepared by dry milling for 2 h (a), 20 h (b) and 50 h (c) and wet milling for 10 h (d). Li$_2$S particles without milling had the size above 100 µm as shown in **Fig. 2-22** (a). On dry milling condition, the Li$_2$S particles were pulverized and the particle size and the agglomeration decreased as milling time was longer. However, the dry milling of Li$_2$S was difficult to eliminate the agglomeration completely. On the other hand, the wet-milled Li$_2$S particles were well dispersed and the particle size was below 3 µm. **Figure 2-34** shows the SEM images of Li$_2$S-AB-SE electrodes using (a) non-milled Li$_2$S and (b) dry-milled Li$_2$S particles. These images revealed that the particle size of the Li$_2$S-AB-SE electrode prepared by using the milled Li$_2$S particles was smaller than that of the Li$_2$S-AB-SE electrode using the non-milled Li$_2$S particles. The effects of the particle size of the Li$_2$S active materials in the composite electrodes on utilization of Li$_2$S, reversible capacity, and rate performance of all-solid-state cells were investigated. **Figure 2-35** shows the charge-discharge curves at the 1st cycle of the all-solid-state cells with Li$_2$S-AB-SE electrodes using (a) non-milled, (b) dry-milled and (c) wet milled Li$_2$S particles under 0.064 mA cm$^{-2}$. The discharge plateau potential of the cells using the Li$_2$S-AB-SE electrodes with the non-milled Li$_2$S and the milled Li$_2$S particles was almost the same. In addition, the use of the milled Li$_2$S particles enhanced a reversible capacity of the all-solid-state cells. Composite electrodes with the dry-milled Li$_2$S and wet-milled Li$_2$S particles exhibited reversible capacities of about 800 and 860 mAh g$^{-1}$, respectively. **Figure 2-36** shows rate performance of the all-solid-state cells with the Li$_2$S-AB-SE electrode prepared by using the non-milled and wet-milled Li$_2$S
particles. The charge-discharge measurements were carried out by changing the discharge current densities of 0.13, 1.3 and 6.4 mA cm$^{-2}$ (0.07, 0.7 and 3.5 C) and the charge current density was kept constant at 0.064 mA cm$^{-2}$ (0.03 C). Even at 0.7 C current rate, the cells using Li$_2$S-AB-SE electrode with the non-milled Li$_2$S particles exhibited the reversible capacity of 487 mAh g$^{-1}$. Moreover, the use of Li$_2$S particles with wet milling in advance improved rate performance, and the electrodes showed the reversible capacity of 580 mAh g$^{-1}$ at 0.7 C rate and 271 mAh g$^{-1}$ at 3.5 C rate, which is higher than the rates in previous reports.[37-41] This result suggests that the formation of favorable contacts among electrode components and the decrease in particle size of Li$_2$S active materials are important for improving reversible capacity and rate performance in all-solid-state cells using Li$_2$S-based electrodes.

As described above, bulk-type solid-state cells are usually fabricated using composite electrodes consisting of three kinds of powder materials: an active material, a SE and a conductive additive (such as acetylene black). The design of the composite electrodes is very important to secure favorable solid-solid contacts with continuous conducting paths of lithium ion and electron [42,43]. In order to improve energy density of solid-state batteries, it is useful that lithium ion can be electrochemically extracted from not only active materials but also Li$_2$S-P$_2$S$_5$ SEs in the composite electrode. This is because Li$_2$S components in the Li$_2$S-P$_2$S$_5$ SEs are expected to act as an active material. A possibility of using the Li$_2$S-P$_2$S$_5$ SEs as an active material in the composite electrodes was investigated. It was found that the cells operated by using the composite electrodes with copper metal and the Li$_2$S-P$_2$S$_5$ SEs. A Cu-added Li$_2$S-P$_2$S$_5$ material was prepared by grinding in an agate mortar of copper, the 80Li$_2$S·20P$_2$S$_5$ solid electrolyte and acetylene black with the weight ratio of 38/57/5, which is a typical ratio of the composite electrode in all-solid-state cell. The weight ratio corresponds to the molar ratio of Li$_2$S/Cu = 48/52. For comparison, the composites at the different molar ratio of Li$_2$S/Cu = 75/25, 86/14, and 100/0 were also obtained. Figure 2-37 shows the initial charge-discharge curves of the all-solid-state cells of In / 80Li$_2$S·20P$_2$S$_5$-Cu at the current density of 0.064 mA cm$^{-2}$; the molar ratios of Li$_2$S/Cu in the 80Li$_2$S·20P$_2$S$_5$-Cu composite
electrodes are (a) 100/0, (b) 86/14, (c) 75/25 and (d) 48/52. The cell capacity was described as the normalized capacity by the weight of 80Li$_2$S·20P$_2$S$_5$-Cu. It was difficult for the cell (a) using the 80Li$_2$S·20P$_2$S$_5$ electrolyte without Cu as a working electrode to be charged and discharged, indicating that the 80Li$_2$S·20P$_2$S$_5$ electrolyte itself is electrochemically inactive. On the other hand, the cells using the composite electrodes by mixing Cu and 80Li$_2$S·20P$_2$S$_5$ electrolyte were initially charged and then discharged. It is noteworthy that the 80Li$_2$S·20P$_2$S$_5$ electrolyte was partially used as an active material by the addition of Cu. The cells had one plateau during a charge process and two plateaus during a discharge process. The increase of Cu content in the composites enhanced the charge-discharge capacity of the cells. The composite electrode with Li$_2$S/Cu = 48/52 (d) showed the largest initial capacity; the charge and discharge capacities were about 150 and 110 mAh g$^{-1}$, respectively. The charge-discharge mechanism of the 80Li$_2$S·20P$_2$S$_5$–Cu composite electrodes was examined by ex situ XRD measurements. Figure 2-38 shows the XRD patterns of the 80Li$_2$S·20P$_2$S$_5$–Cu composite electrode with Li$_2$S/Cu = 48/52 before (a) and after the charge to 3.0 V (b), after the discharge from 3.0 to 1.2 V (c), and after the discharge from 3.0 to 0 V (d). Before charge, the XRD peaks attributable to Cu and the 80Li$_2$S·20P$_2$S$_5$ glass–ceramic electrolyte, consisting of Li$_2$S and thio-LISICON analog crystals, were observed. The intensity of the peaks due to Cu decreased and the peaks due to Li$_2$S in the electrolyte disappeared after charge to 3.0 V. The peaks due to Cu$_{1.8}$S newly appeared at this stage. After discharge from 3.0 to 1.2 V, the XRD pattern was almost the same as that before discharge. The peaks due to Cu$_{1.8}$S disappeared and then the peaks due to Li$_2$S and Cu$_{1.96}$S appeared after discharge to 0 V. The XRD results suggest the following reaction mechanism of the 80Li$_2$S·20P$_2$S$_5$–Cu composite electrode. At the initial charge process, Li$_x$Cu$_y$S domains would be formed by reaction between Cu and Li$_2$S and then lithium ions are deintercalated from the Li$_x$Cu$_y$S domains to finally form Cu$_{1.8}$S. Lithium insertion to Cu$_{1.8}$S to form Li$_x$Cu$_{1.8}$S is a possible process at the first discharge plateau. A similar discharge mechanism was reported in a cell using the CuS electrode [44], in which the first discharge plateau corresponded to the formation of Li$_x$Cu$_y$S by lithium insertion to CuS; the XRD
patterns of Li$_x$Cu$_y$S are almost the same as those of CuS. Further lithium insertion to Li$_x$Cu$_{1.8}$S produced Cu$_{1.96}$S and Li$_2$S at the end of the second discharge plateau. Copper sulfide Cu$_{1.8}$S was formed during the initial charge process and then Cu$_{1.8}$S worked as active materials during a consecutive discharge process. The increase of the Cu content in the 80Li$_2$S·20P$_2$S$_5$–Cu composite electrode would lead to the formation of large Cu$_{1.8}$S active domains and thus the increase of initial cell capacity as shown in Fig. 2-37. The thio-LISICON analog in the solid electrolyte was possibly used in electrochemical reaction. However, structural change of the thio-LISICON analog was not clearly observed by ex situ XRD measurements as shown in Fig. 2-38; structural analyses by several spectroscopic techniques are needed to clarify the role of thio-LISICON analog in electrochemical reaction. 

Figure 2-39 shows cycle performance of the all-solid-state cells In / 80Li$_2$S·20P$_2$S$_5$ electrolyte / 80Li$_2$S·20P$_2$S$_5$–Cu with molar ratio of Li$_2$S/Cu = 48/52 and 75/25. A constant current density of 0.064 mA cm$^{-2}$ was used. Although larger initial capacity is obtained in the cell using the 80Li$_2$S·20P$_2$S$_5$–Cu electrode with Li$_2$S/Cu = 48/52 as shown in Fig. 2-37, the cell with Li$_2$S/Cu = 75/25 exhibited better cycle performance and retained the capacity of about 60 mAh g$^{-1}$ after 50 cycles. The capacity of the cell with Li$_2$S/Cu = 48/52 drastically decreased during charge–discharge cycling, and the cell showed about 30 mAh g$^{-1}$ after 50 cycles. To elucidate a potential reason of capacity fading, structure of the composite electrode before and after charge–discharge cycles was analyzed by XRD and Raman techniques. Figure 2-40 shows XRD patterns (a) and Raman spectra (b) of the 80Li$_2$S·20P$_2$S$_5$–Cu composite electrode with Li$_2$S/Cu = 48/52 before cycling and after the 1st and 50th cycles. The XRD peaks due to Cu$_{1.96}$S were observed after the 1st cycle, while the peaks due to Cu$_{1.8}$S, which is the product after the 1st charge, were observed after the 50th cycle. The intensity of the peaks due to Cu was considerably decreased and the peaks due to Li$_2$S disappeared after the 50th cycle. The Raman peak at 420 cm$^{-1}$, which is attributable to PS$_4^{3-}$ ions in the thio-LISICON analog (in the electrolyte) [45], was observed in the Raman spectra of the composite electrode before and after the 1st cycle. After the 50th cycle, the peak at 470 cm$^{-1}$ was newly observed in addition to the PS$_4^{3-}$ peak. The peak at 470 cm$^{-1}$ is
attributable to several copper sulfides \( \text{Cu}_x \text{S} \) (\( x = 1.0, 1.8, \) and \( 2.0 \)) \[46,47\]. Structural analyses suggest that gradual reaction of \( \text{Li}_2\text{S} \) in the electrolyte and \( \text{Cu} \) during charge–discharge for 50 cycles formed large copper sulfide domains, which play a role in preventing lithium ion conduction path supplied by the electrolyte. Lack of lithium ion conduction in the composite electrode is a possible reason of capacity fading of the electrode with \( \text{Li}_2\text{S}/\text{Cu} = 48/52 \) as shown in Fig. 2-39. On the other hand, the electrode with \( \text{Li}_2\text{S}/\text{Cu} = 75/25 \) exhibited better cycling performance in an all-solid-state cell. Figure 2-41 shows Raman spectra of the \( 80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5-\text{Cu} \) composite electrodes with \( \text{Li}_2\text{S}/\text{Cu} = 75/25 \) and \( 48/52 \) after charge–discharge for 50 cycles. In the cell using the electrode with \( \text{Li}_2\text{S}/\text{Cu} = 75/25 \), the Raman peak due to copper sulfides at 470 cm\(^{-1}\) was also observed, but the peak intensity was considerably lower than that in the cell with \( \text{Li}_2\text{S}/\text{Cu} = 48/52 \). The decrease of Cu content in the electrode is useful for preventing excess formation of copper sulfide domains during cycling and it would bring about good cyclability of the cell using the electrode with \( \text{Li}_2\text{S}/\text{Cu} = 75/25 \).

The addition of copper metal enables the \( \text{Li}_2\text{S}-\text{P}_2\text{S}_5 \) SE to act as an active material. However, the copper addition lowers the capacity based on the total weight of the electrode in the all-solid-state cells. To activate the \( \text{Li}_2\text{S}-\text{P}_2\text{S}_5 \) SE as an electrode without adding the copper metal, the sufficient formation of favorable electron conducting paths to \( \text{Li}_2\text{S}-\text{P}_2\text{S}_5 \) material is achieved by mechanically milling the mixture of the \( \text{Li}_2\text{S}-\text{P}_2\text{S}_5 \) material and AB. The \( 80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5 \) and \( 87.5\text{Li}_2\text{S}-12.5\text{P}_2\text{S}_5 \) glass materials were used as SEs because they have large \( \text{Li}_2\text{S} \) contents. The composite electrodes are composed of SEs and conductive additives and thus the improvement of the energy density of the solid-state batteries is anticipated. Figure 2-42 and Figure 2-43 shows charge-discharge curves of the all-solid-state cells using (a) \( 80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5-\text{AB} \) and (b) \( 87.5\text{Li}_2\text{S}-12.5\text{P}_2\text{S}_5-\text{AB} \) composite electrode under 0.064 mA cm\(^{-2}\) at 25°C. The weight ratio of the SE : AB is 2 : 1. Both the cells were initially charged and then discharged. The \( 80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5-\text{AB} \) composite electrodes show the initial charge capacity of 50 mAh g\(^{-1}\) and discharge capacity of 42 mAh g\(^{-1}\), while the \( 87.5\text{Li}_2\text{S}-12.5\text{P}_2\text{S}_5-\text{AB} \) electrodes exhibit the reversible capacity of over 280
mAh g\(^{-1}\). The Li\(_2\)S-P\(_2\)S\(_5\)-AB composite electrodes using the Li\(_2\)S-P\(_2\)S\(_5\) SEs with a larger amount of Li\(_2\)S component exhibited a higher capacity. Therefore, it is considered that lithium ions can be mainly extracted from remaining crystalline Li\(_2\)S in the Li\(_2\)S-P\(_2\)S\(_5\) SEs. Furthermore, both the Li\(_2\)S-P\(_2\)S\(_5\) glass-AB composite electrodes have a good cyclability and high coulombic efficiency, and 87.5Li\(_2\)S·12.5P\(_2\)S\(_5\)-AB electrodes retained the reversible capacity of about 300 mAh g\(^{-1}\) for 10 cycles. Figure 2-44 shows XRD patterns of 87.5Li\(_2\)S·12.5P\(_2\)S\(_5\)-AB composite electrodes (a) before cycling, (b) after 1st charge and (c) after 10th discharge. The diffraction peaks attributable to Li\(_2\)S and Si as an internal standard are observed before and after cycling. After the 1st charge, the intensity of Li\(_2\)S peaks decrease, meaning that Li\(_2\)S component in the Li\(_2\)S-P\(_2\)S\(_5\) glass-AB composites works as an active material and lithium ion is extracted from the Li\(_2\)S component. After 10 cycles, Li\(_2\)S peaks remain and a new reaction product is not observed and less structural change is responsible for a good cyclability. It is revealed that a Li\(_2\)S-P\(_2\)S\(_5\) glass material with a large Li\(_2\)S contents acts as an electrode including two components of Li\(_2\)S active material with high capacity and Li\(_2\)S-P\(_2\)S\(_5\) electrolyte with high conductivity. These two components have an intimate contact and thus the cell with the glass electrolyte exhibited a high capacity and a good cyclability.

2.4. Summary

The electrochemical performance and the morphology of sulfur-based positive electrodes in all-solid-state rechargeable Li/S batteries using Li\(_2\)S-P\(_2\)S\(_5\) solid electrolytes were investigated. The cells using Cu\(_x\)Mo\(_6\)S\(_{8-y}\) electrodes were repeatedly charged and discharged at 1.3 mA cm\(^{-2}\) over 2000 cycles at 25\(^\circ\)C, and showed good cyclability in the wide temperature range from -30\(^\circ\)C to 120\(^\circ\)C. The cells had the reversible capacity of 200 mAh g\(^{-1}\) higher than the theoretical capacity under 12.8 mA cm\(^{-2}\) at 120\(^\circ\)C. The diffusion of copper elements was detected by the TEM observations with EDX analyses and the interfacial resistance between the electrodes and the solid electrolyte was observed in the impedance measurements after the cells were charged and discharged for 1000 cycles at 100\(^\circ\)C. It was
clarified that the interfacial resistance was attributed to the formation of a resistance layer between the electrode and electrolyte by diffusion of Cu into the electrolyte. It was found that the chemical removal of Cu from Cu$_x$Mo$_6$S$_{8-y}$ and the physical trap such as addition of conductive additives to the electrodes contributed strongly to the improvement of a long cyclability in the cells at temperatures higher than 100°C.

Mechanical milling of the mixture of sulfur-based active materials, Li$_2$S-P$_2$S$_5$ solid electrolytes and electron conducting additives drastically increased the reversible capacity and rate capability in the all-solid-state Li/S cells. The cells using sulfur active materials exhibited the extremely high capacity of about 1450 mAh g$^{-1}$ at 0.064 mA cm$^{-2}$ at 25°C, and the capacity is 5 times higher than that of conventional positive electrode materials. The cells had a good rate capability and a long cycle life, and retained the capacity of about 1000 mAh g$^{-1}$ at 0.64 mA cm$^{-2}$ for 200 cycles. The formation of liquid-solid interface between molten sulfur and AB by milling at 155°C led to enhancement of a gravimetric energy density per weight of electrode, and the energy density rose to 1007 Wh kg$^{-1}$. This energy density was much higher than the theoretical energy density of a typical positive electrode such as LiFePO$_4$ (595 Wh kg$^{-1}$). STEM-EELS observation of microstructure in the composite electrodes revealed that the presence of submicron-sized sulfur particles and the retention of intimate contacts among sulfur, AB and Li$_2$S-P$_2$S$_5$ solid electrolyte during cycles resulted in excellent cyclability with a high capacity and rate capability. Pulverization of Li$_2$S active materials on dry or wet milling conditions using toluene solvent prior to the preparation of the composite electrodes enhanced reversible capacity and rate capability. Composite electrodes with dry-milled Li$_2$S and wet-milled Li$_2$S particles exhibited reversible capacities of about 800 and 860 mAh g$^{-1}$, respectively. Especially, the cells with wet-milled Li$_2$S particles showed the reversible capacity of 580 mAh g$^{-1}$ at 0.7 C rate and 271 mAh g$^{-1}$ at 3.5 C rate. It was revealed that a Li$_2$S-P$_2$S$_5$ glass material with a large amount of Li$_2$S component functioned as an electrode having the favorable interface between Li$_2$S active material and Li$_2$S-P$_2$S$_5$ solid electrolyte and exhibited a good cyclability with a high capacity. It was also clarified that the control of morphology in the sulfur-based composite electrodes such as
decrease in particle size and construction of favorable electron and lithium ion conducting paths to the active materials largely affected on the electrochemical performance in the all-solid-state Li/S cells.

High-resolution TEM and EDX experiments revealed that the crystalline Li$_2$S active nanoparticles having the intimate contact with AB were well dispersed in the Li$_2$S-P$_2$S$_5$ solid electrolyte, and there were little changes of the morphologies of the Li$_2$S electrodes at the initial discharge and at the 20th discharge states. The crystalline Li$_2$S nanoparticles were decomposed into the amorphous sulfur by the delithiation and, on the other hand, subsequent lithiation induced the crystallization of sulfur-based active materials such as Li$_2$S$_x$. These morphological and structural reversibilities during cycles resulted in an excellent cycling stability with a high capacity of the all-solid-state Li/S cells with Li$_2$S-P$_2$S$_5$ solid electrolytes.
2.5. References


Figure 2-1  SEM images of (a) $\text{Cu}_x\text{Mo}_6\text{S}_{8-y}$ and (b) $\text{Mo}_6\text{S}_{8-y}$. 
Figure 2-2 (a) Charge-discharge curves and (b) cycle performance of the all-solid-state cells of Li-In / $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass-ceramic / $\text{Cu}_x\text{Mo}_6\text{S}_{8-y}$ at 25°C. The cutoff voltage is between 0 and 3 V (vs. Li-In).
Figure 2-3  XRD patterns for the working electrode using $\text{Cu}_x\text{Mo}_6\text{S}_{8-y}$ (a) before cycling, (b) after the 1st charge and (c) after the 100th charge.
Figure 2-4  (A) Discharge capacity and (B) cycle performance of all-solid-state cells Li-In / 70Li₂S·30P₂S₅ glass-ceramic / Cu₉Mo₆S₈-y (a) under 0.13 mA cm⁻² (0.2 C) at -30°C, (b) under 1.3 mA cm⁻² (2 C) at 25°C and (a) under 12.8 mA cm⁻² (20 C) at 120°C.
Figure 2-5  Cycle performance of all-solid-state cells using (a) Cu$_x$Mo$_6$S$_{8-y}$ active material and (b) Mo$_6$S$_{8-y}$ active material at 12.8 mA cm$^{-2}$ (20 C) at 100°C.
Figure 2-6  (a) HAADF-STEM image and EDX maps of a cross-section of the 
Cu$_x$Mo$_y$S$_8$ electrode after charge-discharge at 12.8 mA cm$^{-2}$ (20 C) at 100°C for 100 
cycles; (a) HAADF-STEM image and corresponding EDX maps of (c) sulfur, (d) 
copper and (e) molybdenum and (b) superposition of the maps in the figures (c-e).
Figure 2-7 HAADF-STEM image and EDX maps of a cross-section of the Mo$_6$S$_{8-y}$ electrode after charge-discharge at 12.8 mA cm$^{-2}$ (20 C) at 100°C for 100 cycles; (a) HAADF-STEM image and corresponding EDX maps of (c) sulfur, (d) copper and (e) molybdenum and (b) superposition of the maps in the figures (c-e).
Figure 2-8  Impedance profiles of all-solid-state cells using (a) Cu$_x$Mo$_y$S$_{8-y}$ and (b) Mo$_y$S$_{8-y}$ electrode after the cells were charged and discharged at 12.8 mA cm$^{-2}$ (20 C) at 100°C for 1000 cycles.
Figure 2-9  Cycle performance of all-solid-state cells using $\text{Cu}_x\text{Mo}_6\text{S}_{8-y}$ electrodes (a) without AB and (b) with AB at 40 mA cm$^{-2}$ (60 C) at 160°C.
Figure 2-10  SEM images of (a) (S-AB + SE) and (b) S-AB-SE electrodes. The particles with the size of 20-50 µm are the S-AB composites (dotted circles) and the 1-5 µm particles are the SE in Fig. (a). The intimate contacts among S, AB and SE are formed and the size of the agglomerates is less than 10 µm.
Figure 2-11 Charge-discharge curves of all-solid-state cells of Li-In / 80Li$_2$S·20P$_2$S$_5$ glass-ceramic / S using (a) (S + AB + SE), (b) (S-AB + SE), and (c) S-AB-SE electrodes as the working electrode.
Figure 2-12 Cycling performance of an all-solid-state cell using the S-AB-SE electrode under various current densities from 0.38 to 1.3 mA cm$^{-2}$ at 25°C. The cut-off voltage was between 0.7 and 2.7 V (vs Li-In).
Figure 2-13 Charge-discharge curves of an all-solid-state cell using the S-AB-SE electrode at 80°C and high current densities of 12.8 and 19.2 mA cm$^{-2}$. 
Figure 2-14  XRD patterns of S-AB composites prepared by mechanical milling at (a) 25°C and (b) 155°C.
Figure 2-15  SEM images of S-AB composites prepared by mechanical milling at (a) 25°C and (b) 155°C.
Figure 2-16  (a,b) DTA and (c,d) TG curves of S-AB composites prepared by mechanical milling at (a,c) 25°C and (b,d) 155°C.
Figure 2-17  Raman spectra of the S-AB composites prepared by mechanical milling at (a) 25°C and (b) 155°C in the wavenumbers (A) from 200 cm\(^{-1}\) to 600 cm\(^{-1}\) and (B) from 1200 cm\(^{-1}\) to 1800 cm\(^{-1}\).
Figure 2-18  (A) Room temperature charge-discharge curves of the all-solid-state cells Li-In/S using S-AB composites prepared by mechanical milling at (a) 25°C and (b) 155°C at 0.064 mA cm\(^{-2}\) at the initial cycle.  (B) Cycling performance of the cells with the composite electrodes using the S-AB composites prepared by milling at 155°C at 0.064 mA cm\(^{-2}\) (1st to 20th cycle and 41st to 20th cycle) and 0.64 mA cm\(^{-2}\) (21st to 40th cycle) at 25°C.
Figure 2-19  HAADF scanning TEM image and EELS maps of a cross-section of the sulfur electrode using the S-AB composite prepared by mechanical milling at 155°C after 50 cycles; (a) HAADF-STEM image and corresponding EELS maps of (b) lithium, (c) carbon, (d) phosphorus and (e) sulfur and (f) superposition of the maps in the figures (b-e). Carbon (in AB particles), phosphorus (in Li$_2$S-P$_2$S$_5$ SE particles) and sulfur (in S or Li$_2$S-P$_2$S$_5$ SE particles) are shown in blue, yellow and red, respectively in the figure (f).
Figure 2-20 The initial charge-discharge curves of the all-solid-state Li/S cells using the two types of composites: a mixture of sulfur and AB was only heated at 155°C (a) and mechanically milled at 155°C (b).
Figure 2-21  XRD patterns of the (a) (Li$_2$S + AB + SE), (b) (Li$_2$S-AB + SE), and (c) Li$_2$S-AB-SE electrodes. Detailed explanation for the abbreviation is in the text.
Fig. 2-22 SEM images of (a) (Li$_2$S + AB + SE), (b) (Li$_2$S-AB + SE), (c) Li$_2$S-AB-SE electrodes and EDX maps for (d) carbon, (e) phosphorus and (f) sulfur for the Li$_2$S-AB-SE electrode.
Fig. 2-23  Charge-discharge curves of all-solid-state cells of In / 80Li$_2$S·20P$_2$S$_5$ glass-ceramic / Li$_2$S using (a) (Li$_2$S + AB + SE), (b) (Li$_2$S-AB + SE), and (c) Li$_2$S-AB-SE electrodes as the working electrode under 0.064 mA cm$^{-2}$ (0.03 C) at 25°C.
Fig. 2-24 SEM images of the surface of Li$_2$S-AB-SE electrodes in all-solid-state cells (a) before cycling, (b) after 1st charge, and (c) after 1st discharge under 0.064 mA cm$^{-2}$ (0.03 C) at 25°C.
Figure 2-25  Cross-sectional high-angle annular dark field (HAADF) scanning TEM image (a) and the corresponding electron energy loss spectroscopy (EELS) mappings of (b) lithium, (c) carbon, (d) phosphorus and (e) sulfur for the Li$_2$S-AB-SE electrodes in all-solid-state cells after 10 cycles. The mapping image summarizing (b)-(e) is also shown in (f).
Figure 2-26  Cross-sectional HAADF-STEM image (a) and the corresponding EELS mapping (b) for Li$_2$S composite electrodes before a charge-discharge test. Cross-sectional HAADF-STEM image (c) and EELS mapping (d) of the electrodes after 10 cycles, which were already shown in figures 4(a) and 4(f), are also shown for comparison.
Figure 2-27 (a) SEM image showing the interface between SE and the composites of Li$_2$S, AB and SE glass. (b) Magnifying image of the rectangle region of (a).
Figure 2-28  (a) The first charge-discharge curves of the all-solid-state cells of In / 75Li₂S·25P₂S₅ glass / Li₂S using composite electrodes prepared by mechanical milling under 0.064 mA cm⁻² at 25°C.  (b) Cycling performance of the cells at the current densities of 0.064 mA cm⁻² (1st to 10th cycle) and 0.13 mA cm⁻² (11st to 20th cycle) at 25°C.
Figure 2-29  XRD patterns of the Li$_2$S composite electrodes in the all-solid-state cells of In / 75Li$_2$S·25P$_2$S$_5$ glass / Li$_2$S (a) before cycling, (b) after 1st charge, (c) after 1st discharge, and (d) after 20th discharge at 25°C.
Figure 2-30 High-resolution TEM images, electron diffraction patterns and their intensity profiles of Li$_2$S electrode. (a)-(c) before cycling, (d)-(f) after 1st charge, (g)-(i) after 1st discharge and (j)-(l) after 20 times cycles.
Figure 2-31 (a) HRTEM image in the Li₂S composite electrodes after 1st charge and (b) EDX line profiles on the line in the TEM image of carbon, phosphorus and sulfur. (c) Schematic description of proposing the reaction mechanism of Li₂S-based electrode in next generation all-solid-state Li/S batteries.
Figure 2-32  (a) Open circuit voltage of the all-solid-state cells of In/80Li$_2$S·20P$_2$S$_5$ glass/Li$_2$S using Li$_2$S composites prepared by mechanical milling. The measure condition is twenty times of charging process (50 mAh g$^{-1}$) under 0.064 mA cm$^{-2}$ and a rest for 10 h. (b) AC impedance profiles of the cells before cycling and after each charge state.
Figure 2-33  SEM images of Li$_2$S particles prepared by dry milling for (a) 2 h, (b) 20 h, (c) 50 h and (d) wet milling for 10 h.
Figure 2-34  SEM images of Li$_2$S-AB-SE electrodes using (a) non-milled Li$_2$S and (b) dry-milled Li$_2$S particles.
Figure 2-35  Charge-discharge curves of room temperature charge-discharge curves at the first cycle of the all-solid-state cells with Li$_2$S-AB-SE electrode prepared by using (a) non-milled, (b) dry-milled and (c) wet-milled Li$_2$S particles under 0.064 mA cm$^{-2}$ (0.03 C) at 25°C.
Figure 2-36 Discharge curves of all-solid-state cells using $\text{Li}_2\text{S}$-AB-SE electrode with wet-milled $\text{Li}_2\text{S}$ (solid line) and non-milled $\text{Li}_2\text{S}$ (dashed line) at current densities of 0.13, 1.3 and 6.4 mA cm$^{-2}$ (0.07, 0.7 and 3.5 C). The cells were charged at constant current densities of 0.064 mA cm$^{-2}$ (0.03 C). The inset shows plots for the discharge capacity of the cells operating at various current rates. Solid circles and triangles denote the capacities of the composite electrodes with milled-$\text{Li}_2\text{S}$ and reagent $\text{Li}_2\text{S}$, respectively.
Figure 2-37 Initial charge-discharge curves of the all-solid-state cells of In / $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5 \cdot \text{Cu}$ at the current density of 0.064 mA cm$^{-2}$; the molar ratios of Li$_2$S/Cu in the $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5 \cdot \text{Cu}$ composite electrodes are (a) 100/0, (b) 86/14, (c) 75/25 and (d) 48/52.
Figure 2-38 XRD patterns of the 80Li$_2$S·20P$_2$S$_5$–Cu composite electrode with Li$_2$S/Cu = 48/52 before (a) and after the charge to 3.0 V (b), after the discharge from 3.0 to 1.2 V (c), and after the discharge from 3.0 to 0 V (d)
Figure 2-39  Cycle performance of the all-solid-state cells In / 80Li$_2$S·20P$_2$S$_5$–Cu with molar ratio of Li$_2$S/Cu = 48/52 and 75/25. A constant current density of 0.064 mA cm$^{-2}$ was used.
Figure 2-40  XRD patterns (a) and Raman spectra (b) of the 80Li$_2$S·20P$_2$S$_5$–Cu composite electrode with Li2S/Cu = 48/52 before cycling and after the 1st and 50th cycles
Figure 2-41  Raman spectra of the 80Li$_2$S·20P$_2$S$_5$–Cu composite electrodes with Li$_2$S/Cu = 75/25 and 48/52 after charge–discharge for 50 cycles. The spectrum of CuS is also shown for comparison.
Figure 2-42 Charge-discharge curves of all-solid-state cells using (a) $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass-AB composite and (b) $87.5\text{Li}_2\text{S} \cdot 12.5\text{P}_2\text{S}_3$ glass-AB composite prepared by mechanical milling under 0.064 mA cm$^{-2}$ at 25°C.
Figure 2-43 Cycle performance of all-solid-state cells using (a) $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass-AB composite and (b) $87.5\text{Li}_2\text{S} \cdot 12.5\text{P}_2\text{S}_5$ glass-AB composite prepared by mechanical milling under $0.064$ mA cm$^{-2}$ at $25^\circ$C.
Figure 2-44  XRD patterns of the 87.5Li$_2$S·12.5P$_2$S$_5$ glass-AB composite electrodes in the all-solid-state cells (a) before cycling, (b) after 1st charge, and (c) after 10th discharge.
3. Development of negative electrode materials for all-solid-state rechargeable Li/S batteries with high capacity

3.1. Introduction

Improvement of energy density of rechargeable batteries in various fields of applications is increasingly needed. To achieve higher energy density of the present all-solid-state cells, researching high-capacity negative electrode materials is very important. Graphite has been used as a negative electrode because of excellent cycle performance and rate capability. Additionally, the cells using graphite electrodes exhibited the reversible capacity of about 370 mAh g\(^{-1}\) which is equivalent to its theoretical capacity \([1,2]\). Thus, further upgrade of performance of graphite electrodes is very difficult, and development of new negative electrode materials with higher capacity than graphite is desired to enhance the energy density of the cells. Negative electrode materials are divided into the three types according to the charge-discharge reaction mechanism: alloying reaction materials, intercalation reaction materials and deposition and dissolution reaction materials.

First, typical active materials with alloying reaction such as Si and Sn have extremely high theoretical capacities. However, they undergo large volumetric change during charge-discharge reaction. This leads to a pulverization of the active materials, a progressive decohesion and a capacity loss \([3,4]\). In order to solve these problems, various approaches have been carried out. Especially, lithium-alloy materials which form inactive matrix during cycling have been studied intensively. Among these materials, metal phosphides showed a lower working potential compared to metal oxides and a large specific capacity. Lithium phosphide (Li\(_3\)P), which is formed by lithium insertion to metal phosphides, shows high lithium ion conductivity \([5]\); Li\(_3\)P can act as a matrix stabilizer like Li\(_2\)O in tin oxide materials. Thus, phosphide materials are considered to be suitable for a negative electrode of all-solid-state cells because of self-formation of a good lithium conduction matrix by lithium insertion process. Tin phosphide Sn\(_4\)P\(_3\) has been reported to show high capacity and good cyclability in liquid-type cells \([6,7]\). Sn\(_4\)P\(_3\) has a high electron conductivity and Sn has a
high diffusion coefficient of lithium ions [8] and Li$_3$P has high a lithium ion conductivity as mentioned above. Therefore, Sn$_4$P$_3$ is also expected to be attractive materials for the negative electrode with high capacity of all-solid-state cells. Thus, the charge-discharge properties, structural analyses and morphological changes of alloying reaction materials such as Si, Sn and Sn$_4$P$_3$ in all-solid-state cells using Li$_2$S-P$_2$S$_5$ solid electrolytes (SEs) were investigated. The comparison of cell performance and reaction mechanism between all-solid-state cells and liquid-type cells was discussed.

Secondly, active materials with intercalation reaction, where lithium ion can be inserted with retaining crystalline structure have advantages of good capacity retention and high rate capability. Graphite is well known as an intercalation reaction material. Like carbon, phosphorus has a number of allotropes. Black phosphorus is the most stable form and has a relatively high electronic conductivity among them. Black phosphorus has a similar layered structure to graphite with larger interlayer spacing, so a similar lithium storage mechanism to graphite was reported [9]. Furthermore, black phosphorus shows the large theoretical capacity of 2596 mAh g$^{-1}$ in the case of the reaction from black phosphorus to Li$_3$P. Recently, Park et al. reported that lithium batteries using a black phosphorus electrode and an organic liquid electrolyte showed the 1st reversible capacity of over 1800 mAh g$^{-1}$ [10]. However, its capacity decreased drastically in the wide potential range from 0 to 2 V (vs. Li). Thus, black phosphorus was firstly applied to the negative electrode of all-solid-state cells with Li$_2$S-P$_2$S$_5$ SEs. Phosphorus is one of the constituent elements of the electrolytes, and the favorable interface between black phosphorus electrodes and the SEs would be formed. In order to improve cyclability with high capacity and rate capability of the cells, the composites with black phosphorus and nanocarbon were obtained by using several ball mill apparatuses. The cell performance and the reaction mechanism of the composite electrodes were investigated.

Thirdly, a typical active materials with deposition and dissolution reaction is lithium metal. Lithium is ultimate negative electrode material having the highest theoretical capacity and the lowest reaction potential. However, the rechargeable lithium metal batteries
have some concerns about safety and cyclability because of the dendritic growth of lithium in liquid electrolytes [11, 12]. Meanwhile, suppression of the dendritic growth is anticipated by the use of inorganic SEs as a separator in bulk-type solid-state batteries. However, charge-discharge properties in rechargeable bulk-type solid-state batteries with lithium metal electrode and sulfide-based SEs have been hardly studied. Morphological observations of lithium deposition and dissolution of all-solid-state lithium metal batteries as well as their electrochemical properties were explored. By understanding how lithium is deposited in all-solid-state cells, the strategies to improve the reversibility of electrochemical deposition and dissolution and the rate performance of the cells were obtained.

3.2. Experimental

3.2.1. Cell construction

The preparation procedure of the 80Li$_2$S-20P$_2$S$_5$ (mol%) glass-ceramic SEs was described in the chapter 2. The laboratory-scaled solid-state cells were constructed as described in the chapter 2. In this chapter, alloying reaction materials such as Si, Sn and Sn$_4$P$_3$, a lithium intercalation material such as black phosphorus and a deposition-dissolution material such as lithium metal were used as an active material. In order to examine the performance of bulk-type cells using lithium metal electrodes, Li$_4$Ti$_5$O$_{12}$ and sulfur electrodes were also used as a counter electrode. A composite electrode was prepared by mixing of Sn or Sn$_4$P$_3$, the SE, and AB powders with the weight ratio of 40 : 60 : 6. Other composite electrode was prepared by mixing of Si, black phosphorus or Li$_4$Ti$_5$O$_{12}$, the SE and AB powders with the weight ratio of 40 : 60 : 10. Sulfur composite electrode was prepared by mechanical milling of sulfur, the SE and AB with the weight ratio of 35 : 35 : 30.

3.2.2. Sample preparation

Sn$_4$P$_3$ particles were prepared by the mechanochemical method. Sn (Aldrich, 99.9%) and red phosphorus (Kojundo chemical, 99.9%) were used as a starting material. Stoichiometric amounts of starting materials were put into a ZrO$_2$ vessel (45 ml) with 10 ZrO$_2$
balls (10 mm diameter) and reacted in a planetary ball mill apparatus (Fritsch Pulverisette 7) with a fixed rotation speed of 370 rpm for 2 h under an Ar atmosphere.

Black phosphorus was prepared by ball-milling. Red phosphorus powder was used as a starting material and put into stainless steel (SS) pot with 10 SS balls (10 mm or 12.7 mm in diameter), and mechanical milling process was carried out in an Ar atmosphere for 1 h using a planetary ball-mill and a mixer mill (SPEX, 8000M Mixer/Mill). Composites with black phosphorus and acetylene black (AB) were prepared by the same milling technique for 1 h. The composition of the composite was 80 wt.% black phosphorus and 20 wt.% AB.

3.2.3. Characterization

The morphologies of the active materials, the SE layer and the electrode-electrolyte interface after a charge-discharge test were examined by using a scanning electron microscope (SEM, JSM-5300, JEOL) and Nano Search Microscope (OLS3500, OLYMPUS and SFT-3500, Shimadzu). The structures of the electrodes after an electrochemical test were analyzed using XRD with a diffractometer (M18XHF22-SRA, Mac Science or Ultima IV, Rigaku) and Raman spectroscopy with a spectrometer (LabRAM HR-800, HORIBA).

D.C. polarization measurements of the Sn₄P₃ active material pellets were carried out using a Potentiostat / Galvanostat device (Solartron 1287 coupled with Solartron 1260) at room temperature. A pair of SS plates as non-blocking electrodes was attached to both faces of the pellet. The D.C. conductivities were calculated from the current values obtained by applying a constant D.C. voltage to the pellets at room temperature.

Galvanostatic tests of the cells were conducted at current densities from 0.013 and 3.8 mA cm⁻² at 25°C in an Ar atmosphere using a charge-discharge measuring device (BTS-2004, Nagano Co.).

3.3. Results and discussion

3.3.1. Alloying reaction materials

The possibility of using alloying reaction materials as a negative electrode in
all-solid-state cells was investigated. First, the charge-discharge properties and structural analysis of Si electrodes in the all-solid-state cells were examined. Figure 3-1 shows (a) the initial charge-discharge curves at 0.064 mA cm$^{-2}$ and (b) the cycle performance of all-solid-state cells of Li-In / 80Li$_2$S·20P$_2$S$_5$ glass-ceramic / Si. The inset of Fig. 3-1 (a) is the SEM image of Si particles. The Si particles used as an active material in the cell had the particle size larger than 5 µm. The cells using the Si particles showed the discharge capacity of 2887 mAh g$^{-1}$ and the coulombic efficiency of 88% at the 1st cycle. The cells retained high reversible capacity of 1865 mAh g$^{-1}$ for 50 cycles as shown in Fig. 3-1 (b). The cells using micrometer-sized Si particles and liquid electrolytes were reported to show the initial coulombic efficiency of 38% and the cell capacity remarkably decreased to 200 mAh g$^{-1}$ after 10 cycles [13]. The all-solid-state cells using micrometer-sized Si particles exhibited superior cell performance to liquid-type cells. Figure 3-2 shows XRD patterns of Si electrodes (a) before cycling and after (b) the 1st discharge and (c) the 10th charge. The alloying reaction proceeds in Si electrodes by reacting with lithium ion, and Li$_{15}$Si$_4$ was formed. The Si electrodes have the theoretical capacity of 3580 mAh g$^{-1}$ in the case of conversion from Si to Li$_{15}$Si$_4$. XRD patterns after the 1st discharge showed that the peaks due to Si remained slightly, meaning that only a small amount of Si particles which did not contribute to the electrochemical reaction were present. After 10 cycles, the peaks attributable to Si and Li$_{15}$Si$_4$ almost disappeared, and the reaction products in the electrode were amorphous. The electrochemical reaction was reported to occur with retaining amorphous structure in the liquid-type cells using Si electrodes [13]. It was found that the reaction mechanism of Si electrodes in all-solid-state cells was similar to that in the liquid-type cells.

Next, Sn foil (thickness: 7 µm) was applied to an electrode in all-solid-state cells, and the electrochemical performance and morphological change of Sn electrodes were investigated. Figure 3-3 shows the charge-discharge curves of all-solid-state cells of Li-In / 80Li$_2$S·20P$_2$S$_5$ glass-ceramic / Sn at 0.064 mA cm$^{-2}$ at 25°C. The cells showed the 1st discharge capacity of 600 mAh g$^{-1}$ with an irreversible capacity. However, the capacity of
the cells was almost steady from the 2nd cycle to the 10th cycle. The three plateaus at 0.7, 0.6 and 0.45 V (vs. Li⁺/Li) and the slope voltage from 0.45 to 0 V were observed in the all-solid-state cells, and the cells have almost the same charge-discharge profiles as those reported in the liquid-type cells [14]. Compared with the cycle performance of the liquid-type cells with Sn electrodes, the all-solid-state cells using Li₂S-P₂S₅ SEs showed better performance. To investigate the cause for their good cyclability, morphological observation of change in the Sn electrodes before and after cycling was performed by SEM. Figure 3-4 show the SEM images of (left) the surface and (right) the cross-section (a) before cycling, after (b) the 1st discharge and (c) the 1st charge, (d) the 2nd discharge and (e) the 10th charge. SEM observation revealed the large volumetric change of the Sn electrodes in the all-solid-state cells by alloying and dealloying reaction, which was similar to that in the liquid-type cells. The thickness of the electrodes increased from 6.8 µm to 22.6 µm during the 1st discharge (alloying reaction). XRD analysis of the electrodes after the 1st discharge confirmed the formation of Li₁₃Sn₅. Although, the volume of Li₁₃Sn₅ is 2.4 times as high as that of the Sn, the volume change in this paper was higher than the theoretical value. During the 1st charge, the thickness of the electrodes decreased from 22.6 µm to 10.5 µm and large cracks generated. The thickness of the electrodes after the 1st charge did not entirely get back to that before cycling and this would correspond to the irreversible capacity at the 1st cycle. From the 2nd cycle, volumetric change of the electrodes took place reversibly, and the intimate contacts between electrode and electrolytes were retained, which supports the good capacity retention of the cells with Sn electrodes. Additionally, XRD analysis of the electrodes demonstrated that the reversible reaction of Sn ↔ Li₁₃Sn₅ proceeded. It was found that alloying reaction materials such as Si and Sn are promising negative electrodes in bulk-type solid-state cells with high capacity.

In order to further improve cyclability with high capacity in all-solid-state cells, a metal phosphide, Sn₄P₃ was used as a working electrode in all-solid-state cells. Figure 3-5 shows (a) XRD pattern (b) SEM image of the sample synthesized by mechanical milling for the mixture of Sn and phosphorus. All peaks were attributable to Sn₄P₃ (JCPDS#071-2221),
indicating that Sn₄P₃ was prepared by mechanical milling. The Sn₄P₃ consisted of agglomerated particles of about 1-10 µm in size. The prepared Sn₄P₃ showed the electronic conductivity of 0.83 S cm⁻¹ at 25°C. Figure 3-6 shows the discharge-charge curves of the all-solid-state cell with Sn₄P₃ negative electrode at 0.064 mA cm⁻². The composite electrode with Sn₄P₃, SE and AB was used as a working electrode. The obtained capacity was normalized by the weight of Sn₄P₃ in the electrode. In this study, “discharge” is defined as lithium insertion process to Sn₄P₃. The potential profiles of all-solid-state cell with Sn₄P₃ are similar to those of a liquid-type cell [15,16]. The discharge-charge mechanisms of Sn₄P₃ reported in a liquid-type cell are shown as follows:

\[
\text{Sn}_4\text{P}_3 + 3 \text{Li}^+ + 3 e^- \rightarrow 4 \text{Sn} + 3 \text{LiP} \quad (1)
\]

\[
3 \text{LiP} + 6 \text{Li}^+ + 6 e^- \rightarrow 3 \text{Li}_3\text{P} \quad (2)
\]

\[
4 \text{Sn} + 4x \text{Li}^+ + 4x e^- \rightarrow 4 \text{Li}_x\text{Sn} \quad (0 \leq x \leq 4.4) \quad (3)
\]

Some plateaus were observed in discharge process; the first and second plateaus centered at ca. 0.9 V and 0.6 V (vs. Li⁺/Li) are considered to be the conversion reactions of (1) and (2), respectively. Theoretical capacity of the conversion reactions is calculated to be ca.450 mAh g⁻¹. The third plateau centered at ca. 0.35 V (vs. Li⁺/Li) was observed and then the potential fell down to 0 V (vs. Li⁺/Li). In this potential range, alloying reaction of (3) proceeded. The cell showed the first discharge and charge capacity of 1080 mAh g⁻¹ and 950 mAh g⁻¹, and the first coulombic efficiency of 88% at 0.064 mA cm⁻². The first coulombic efficiency of the all-solid-state cell was higher than that of the liquid-type cells (below 80%) [15,16]. The cell kept the discharge capacity of 890 mAh g⁻¹ for 5 cycles and it is calculated to be 83 % of the first discharge capacity. The cycle performance of the cell will be discussed later. In order to explore the reaction mechanism of Sn₄P₃ in detail, the working electrode was analyzed by XRD and Raman after the initial discharge and charge processes. The XRD patterns of the working electrode at the current collector side are shown in Fig. 3-7 (A). Silicon was used as an internal standard for XRD measurements. Li₂S which remained in the SE was partially observed in the working electrodes. The diffraction peaks of Sn₄P₃ were observed before discharge-charge process. After the first discharge process,
the diffraction peaks of Sn₄P₃ disappeared and a broad peak attributable to Li₁₃Sn₅ alloy (JCPDS#071-9518) appeared. Although the formation of lithium phosphide, LiP and Li₃P, was not confirmed by XRD, Sn ions in Sn₄P₃ were reduced and metallic tin and lithium phosphides would be formed by lithium insertion, and then Li–Sn alloy was formed. Raman spectroscopy of the Li₃P powders and the Sn₄P₃ electrodes after the 1st discharge and charge reaction was carried out to confirm the presence of Li₃P. Figure 3-7 (B) shows that the Raman band at 945 cm⁻¹ was observed in (a) the Li₃P powders and (b) the Sn₄P₃ electrode after the 1st discharge. The Raman spectra suggest that Li₃P would be formed after lithium insertion to Sn₄P₃. However, Li₃PO₄ powders also have the bands at around 950 cm⁻¹, and thus the detailed characterization using ³¹P NMR is needed to clarify the existence of lithium phosphides. After the initial charge process, the XRD peaks of Li₁₃Sn₅ alloy disappeared and those of Sn and Sn₄P₃ appeared. Raman spectra also show that the bands at 945 cm⁻¹ disappeared, implying that lithium ion was extracted from Li₃P. It is noted that re-formation of Sn₄P₃ was observed. In the liquid-type cell [17], the electrochemical reactions were reported to proceed in order of the equations (1), (2), (3) as mentioned above, and the first two reactions (Sn₄P₃ to give Sn + LiP, and LiP to Li₃P) were not reversible. However, Sn₄P₃ was partially formed again in the all-solid-state cell. The re-formation of Sn₄P₃ resulted in the higher coulombic efficiency of the all-solid-state cell than that of the liquid-type cell. Further detailed analyses are required to clarify the origin of the difference in the reaction mechanism.

In general, the electrode of all-solid-state cell consists of active material, SE and AB for ease conduction of lithium ion and electron to the active material. The results mentioned above suggest that Sn₄P₃ showed high electronic conductivity and Li₃P with lithium ion conductivity formed in the 1st discharge process. Thus, Sn₄P₃ itself is expected to work as a negative electrode without SE and AB. The use of only Sn₄P₃ active material leads to the improvement of energy density of the cell per weight of the working electrode. Thus, Sn₄P₃ was applied to the negative electrode without SE and AB. Figures 3-8 shows (a) discharge-charge curves and (b) cycle performance of the cell with only Sn₄P₃. The cell of Sn₄P₃ was initially discharged and then charged. The potential profiles of the cell without SE
and AB was similar to that of the cell with SE and AB as shown in Fig. 3-6. The cell of Sn₄P₃ without SE and AB showed the first discharge capacity of 800 mAh g⁻¹ and the first coulombic efficiency of 81% (a). The cells showed a good capacity retention with the capacity of 450 mAh g⁻¹ for 5 cycles (b). Although the irreversible capacity of the Sn₄P₃ electrode without SE and AB was somewhat larger than that of the cell of the Sn₄P₃ electrode with SE and AB, the first discharge capacity in terms of the total weight of the working electrode of the former cell was about two times larger than that of the latter cell.

The effects of the self-formation of Li₃P as a matrix on the cell performance were investigated. Figure 3-9 shows the charge-discharge curves of the cells using Sn (a), SnO (b) and Sn₄P₃ (c) active materials without conducting additives and SE at 0.064 mA cm⁻² at 25°C. Figure 3-9 (c) and Fig. 3-8 (a) are the same charge-discharge profiles. To compare the cell performance of Sn (a) and Sn₄P₃ (c) electrodes in terms of the presence or absence of matrix, the cells using the electrodes with almost the same thickness were fabricated. The capacity of the cells with only Sn₄P₃ was higher than that with Sn (58 µm), suggesting that self-formation of lithium ion conducting path was effective in improving cell performance.

As understood by the comparison of Fig. 3-3 and Fig. 3-9 (a), an increase in the thickness of the Sn electrodes (7 µm → 58 µm) resulted in the decrease in the cell capacity. It is considered that the Sn electrodes near the current collector did not contribute to an electrochemical reaction because of the formation of insufficient lithium ion conducting paths. Next, the affects of lithium ion conductivity of matrix on cell performance were investigated. The SnO electrodes, which form Li₂O as a matrix by lithium insertion, were used in the all-solid-state cells. Although the cells with the SnO electrodes (b) exhibited higher capacity than those with Sn₄P₃ electrodes (c), the coulombic efficiency of the cells using Sn₄P₃ electrodes was much higher. This result suggests that lithium ion conductivity of Li₃P is higher than that of Li₂O, which largely affected the cell performance. It was revealed that the self-formation of matrix with high lithium ion conductivity was essential for enhancing the reversible capacity of the all-solid-state cells using only active materials without SE and conductive additives. The use of only active material for the electrode is effective in
achieving higher energy density of all-solid-state cell, and Sn₄P₃ is an appropriate negative electrode for all-solid-state cells.

3.3.2. Black phosphorus – Lithium intercalation reaction material

Figure 3-10 shows XRD patterns of (a) red phosphorus powders and (b,c) black phosphorus powders prepared by mechanical milling process for 1 h with (b) the planetary ball-mill apparatus and (c) the mixer mill apparatus. Red phosphorus used as a starting material was amorphous. Black phosphorus was prepared by milling for 1 h. The peaks of black phosphorus prepared by milling with the mixer mill apparatus were sharper than those of black phosphorus with the planetary ball-mill apparatus. This suggests that black phosphorus with higher crystallinity was prepared by using the mixer mill apparatus. The difference in crystallinity of black phosphorus as shown in Fig. 3-10 (b) and (c) would be based on the difference of impact for mechanochemical reaction in two types of ball mill apparatuses. Oumellal et al. reported that the reaction between magnesium hydride and lithium metal were conducted by using the two ball mill apparatuses, and a higher yield of reaction was achieved by using the mixer mill apparatus [18]. Because the mixer mill apparatus gave more efficient impact interaction for reaction from red phosphorus to black phosphorus than the planetary ball-mill apparatus, black phosphorus was effectively prepared in the former case. The black phosphorus prepared by the mixer mill apparatus was used for electrochemical measurements. Electronic conductivity of the obtained black phosphorus was 8.1×10⁻⁴ S cm⁻¹ at room temperature.

Figure 3-11 shows SEM images of (a) black phosphorus powder and (b) the composites with black phosphorus and AB prepared by milling with the mixer mill apparatus. The prepared black phosphorus (a) was agglomerated to form secondary particles and their size was about 30 µm. On the other hand, the composites (b) showed less agglomeration and included smaller secondary particles with the size of 1-5 µm. The mechanical milling of black phosphorus and AB brought about a decrease in size of secondary particles of black phosphorus.
Figure 3-12 shows the initial charge-discharge curves of all-solid-state cells of Li-In / 80Li2S·20P2S5 glass-ceramic / phosphorus under the current density of 0.064 mA cm\(^{-2}\) (24 mA g\(^{-1}\)) at 25\(^{\circ}\)C. The all-solid-state lithium cell using red phosphorus (a) as an active material showed the first discharge capacity of 1345 mAh g\(^{-1}\). However, the charge-discharge coulombic efficiency was only 12% and the large irreversible capacity was observed. On the other hand, the cell using black phosphorus (b) as an active material exhibited the discharge capacity of 1777 mAh g\(^{-1}\) and the coulombic efficiency of 61%. In addition, in order to enhance the electrochemical performance of the cells, black phosphorus and AB were milled and the obtained composites were applied to the electrodes of all-solid-state cells. The all-solid-state cell using the composites (c) exhibited superior electrochemical performance than the cell using the mixture of black phosphorus and AB, and the discharge capacity of 1962 mAh g\(^{-1}\) and the coulombic efficiency of 89% were obtained in the former cell. One long plateau at about 0.7 V (vs. Li) during discharge process and the discharge capacity were in agreement with those reported in the cells with liquid electrolytes under a current density of 100 mA g\(^{-1}\) [10]. In order to understand the difference in the specific capacity of the cells between (b) and (c), we measured the total conductivity of the pellets of these working electrodes sandwiched with two SS plates (current collectors) by the A.C. impedance method. Both the working electrodes were composed of black phosphorus, AB and the SE components. The electronic conductivity at room temperature of the electrode (b) was 4.0×10\(^{-2}\) S cm\(^{-1}\) and that of the electrode (c) was 4.3×10\(^{-2}\) S cm\(^{-1}\); it was hard to clarify the cause of the difference in the specific capacity in terms of the conductivity of the working electrodes. It is thus considered that a smaller particle size of the black phosphorus/AB composite in the electrode (c) as shown in Fig. 3-11 contributed to the enhancement of the capacity and the coulombic efficiency of the cells.

The discharge-charge reaction mechanism of the black phosphorus electrode was investigated by ex-situ XRD measurements. XRD patterns of black phosphorus electrodes before cycling (a), after discharge to 0 V (vs. Li) (b) and after charge to 2.5 V (vs. Li) (c) are shown in Fig. 3-13. Silicon was used as an internal standard in XRD measurements.
Before cycling, the peaks due to black phosphorus and thio-LISICON analog in the electrolyte were observed. The peaks of black phosphorus disappeared and the peaks attributable to Li$_3$P newly appeared after the cell was discharged to 0 V. After charge from 0 V to 2.5 V, no obvious peaks derived from black phosphorus electrode were observed. Because the cells using the composite exhibited the high coulombic efficiency for the first cycle, the reversible electrochemical reaction between black phosphorus and Li$_3$P would occur and the reaction products in charge process were probably amorphized black phosphorus. A similar reaction mechanism of the black phosphorus active material (P $\leftrightarrow$ Li$_3$P) has already been reported in an electrochemical cell with an organic liquid electrolyte [10]. Although the formation of Li$_3$P was confirmed by XRD measurement, the obtained capacity was equivalent to two-thirds of the theoretical capacity of black phosphorus; this suggests that a part of black phosphorus in the working electrode did not contribute to the electrochemical reaction. Further research about preparation conditions such as weight ratio and milling condition of composites is important to enhance the utilization of black phosphorus.

Cycle performance and high-rate performance of all-solid-state cells using the composites with black phosphorus and AB were examined. Figure 3-14 shows the cycle performance of the all-solid-state cell at the current density of 0.064 mA cm$^{-2}$. The cutoff potential was between 0 V and 2.5 V (vs. Li). The all-solid-state cells retained the reversible capacity of 1350 mAh g$^{-1}$ for 30 cycles with little capacity fading with increasing the cycle number. Although the coulombic efficiency of the cell was 89% at the first cycle, the cell subsequently exhibited the coulombic efficiency of about 100% for 30 cycles. Capacity fading was observed in the cell with a black phosphorus electrode and an organic liquid electrolyte in the potential range from 0 to 2 V (vs. Li) [10]. On the other hand, all-solid-state cell exhibited good cycle performance in the wide potential range from 0 to 2.5 V (vs. Li). Figure 3-15 shows the performance of the cell at 25°C in the potential range from 0 to 2.5 V (vs. Li) at the current density of 3.8 mA cm$^{-2}$ (1.47 A g$^{-1}$), which is much higher than the current density (0.1 A g$^{-1}$) reported in the cell using a liquid electrolyte [10].
The discharge-charge profiles at the 2nd cycle and the 150th cycle were almost the same, although the profile at the 1st cycle was slightly different and two plateaus were observed for the discharge process. The cell exhibited an excellent cycle performance with the capacity of over 500 mAh g$^{-1}$ for 150 cycles at 3.8 mA cm$^{-2}$ (1.47 A g$^{-1}$). The cell with a liquid electrolyte demonstrated the reversible capacity of 600 mAh g$^{-1}$ at the current density of 0.1 A g$^{-1}$ [10]. The all-solid-state cells exhibited the similar capacity of over 500 mAh g$^{-1}$ even at the current density of 1.47 A g$^{-1}$ which is about 15 times larger than that for the cell with a liquid electrolyte. It is noteworthy that the rate performance of the all-solid-state cells was superior to that of the cell with a liquid electrolyte. High capacity and high rate performance were achieved in the all-solid-state cells using black phosphorus-AB composite and Li$_2$S-P$_2$S$_5$ SEs. Black phosphorus is one of the most attractive negative electrodes for all-solid-state cells with high capacity.

3.3.3. Lithium metal – Deposition and dissolution reaction material

The initial charge-discharge curves for a bulk-type solid-state Li / 80Li$_2$S·20P$_2$S$_5$ / Li$_4$Ti$_5$O$_{12}$ cell at 0.064 mA cm$^{-2}$ are shown in Fig. 3-16. The cells were galvanostatically discharged to 1.1 V and then charged to 2 V at 25°C. The cell showed the discharge capacity of about 120 mAh g$^{-1}$ and the discharge plateau of 1.55 V vs. Li, which was the same as that of the cell using conventional liquid electrolyte [19]. However, an abrupt potential change was observed at the end of charge process. It was reported that this behavior was due to internal short-circuit in lithium metal batteries using a polymer electrolyte [20]. A resistance of this cell by the A.C. impedance method was measured before and after this charge-discharge test as shown in Fig. 3-16. The resistance was 150 Ω before the test and drastically decreased to less than 10 Ω after the test. This would imply that the solid-state cell resulted in internal short circuit as observed in the polymer lithium batteries. To explore the cause for the decrease in the cell resistance, ex-situ SEM observation of the surface and the cross-section of the SE layer was performed after lithium was electrochemically deposited on the SE layer at different current densities. The bulk-type cells with simple configuration
of Li / Li₂S-P₂S₅ / SS were fabricated.  **Figure 3-17** (a) shows SEM images of the SE surface before the test.  A fully-dense pellet having intimate contacts among Li₂S-P₂S₅ particles was formed by only cold pressing at room temperature.  **Figures 3-17** (b) and (c) show the morphology of the SE surface after lithium was deposited on the surface at a low current density of 0.064 mA cm⁻² for 10 h and 72 h, respectively.  After the lithium deposition for 10 h, the areas reflected in black color were observed.  EDX showed that the intensity of signals of phosphorus and sulfur elements in these areas was much lower than that in the other areas, meaning that lithium was deposited on the SE particles and in the pores.  After the further electrochemical deposition, lithium was uniformly deposited at almost all the SE surface.  **Figures 3-17** (d) and (e) show the morphologies of the lithium deposition at a relatively high current density of 0.64 mA cm⁻² for 1 h.  After the electrochemical test, the cell resistance drastically decreased.  **Figures 3-17** (d) and (e) show the SEM images of the SE surface.  **Figure 3-17** (d) shows that lithium deposited on the SE particles grew toward the current collector.  The amount of lithium deposition in **Fig. 3-17** (d) is the same as that in **Fig. 3-17** (b).  However, the sites of deposited lithium in electrochemical test at a high current density was smaller than those in electrochemical test at a low current density, suggesting that large current distribution generated in bulk-type solid-state cells at a high current density.  Furthermore, **Fig. 3-17** (e) represents that lithium existed in the pores rather than on the SE particles.  In order to investigate how lithium grew in the SE layer, cross-sectional SEM observation of the SE layer was carried out as shown in **Fig. 3-17** (f).  **Figure 3-17** (f) reveals that lithium existed in the SE layer as shown in the dotted circles.  This indicates that lithium grew in the pores and along the grain boundaries.  It is considered that growth of lithium in the SE layer is one of the causes for the short circuit of the all-solid-state cells at high current density.

Further enhancement of the reversibility of lithium dissolution and deposition is required.  Kotobuki *et al.* reported that the increment in the contact area between SE and lithium metal electrode would be a solution for improvement of a reversible capacity in bulk-type cells with oxide SEs such as Li₇La₃Zr₂O₁₂ [21].  To obtain favorable contacts
between a Li$_2$S-P$_2$S$_3$ SE and a lithium metal electrode, a lithium thin film was formed on the SE by vacuum evaporation. **Fig. 3-18** shows the SEM image for cross-section of the interface between the Li$_2$S-P$_2$S$_3$ SE and the lithium thin film. The electrode/electrolyte interface having intimate contact was obtained, and the thickness of lithium thin film was about 1 µm. The galvanostatic cycling performances for symmetric cells with Li / 80Li$_2$S·20P$_2$S$_5$ SE / Li using a lithium foil (a) without and (b) with the lithium thin film are depicted in **Fig. 3-19**. The total current flow time in both the cells is shown in the x-axis in **Fig. 3-19**, and the lithium deposition and dissolution were switched every 3 hours at a constant current density of 0.064 mA cm$^{-2}$. The resistance of the cells was measured by the A.C. impedance method after each lithium deposition and dissolution reaction. In **Fig. 3-19** (a), the cell voltage dropped significantly with an increase in the current flow time. Decrease in the resistance was also observed, and the resistance became about 3Ω after lithium dissolution and deposition for 5 cycles (about 30 hours). On the other hand, by inserting the lithium thin film between the SE and the lithium foil, the cell exhibits stable voltage of +20 mV or -20 mV during repetitive lithium dissolution or deposition for 5 cycles as shown in **Fig. 3-19** (b). There was little change in the cell resistance and the resistance remained about 400 Ω for 5 cycles. In the cells using the lithium thin film, lithium dissolution and deposition take place reversibly for more than 30 hours. It was revealed that the formation of the lithium thin film by evaporation onto the SE layer leads to improving reversibility of lithium dissolution and deposition in bulk-type cells. This is because an increase in contact area between the electrode and the electrolyte brings about homogeneous dissolution and deposition of lithium through the interface. Sulfur has the highest theoretical capacity among positive electrodes in lithium-ion batteries. Therefore, the rechargeable bulk-type solid-state Li/S cells are expected to become extremely high energy density. **Fig. 3-20** shows the charge-discharge curves for the Li/S cell. In previous chapter, the ball-milled composite electrodes consisting of sulfur, the Li$_2$S-P$_2$S$_3$ SE and AB showed a good cyclability with a high capacity in all-solid-state cells; Li-In alloy was used as a negative electrode. A lithium negative electrode instead of Li-In alloy to assemble all-solid-state Li/S
cells was used. The lithium thin film was placed at the interface between the lithium foil and the SE. The cells were galvanostatically discharged to 1.3 V and then charged to 2.6 V at 25°C. The current densities were 0.013 mA cm⁻² at the 1st and 2nd cycle and 0.064 mA cm⁻² (0.03 C with respect to sulfur electrode) from the 3rd to 20th cycle. The obtained capacities are normalized by the weight of the sulfur active material. The reversible capacity of the cell was about 1350 mAh g⁻¹ at 0.013 mA cm⁻². The cell exhibited the reversible capacity of 945 mAh g⁻¹ at the 3rd cycle at 0.064 mA cm⁻². The cell retained the reversible capacity of 920 mAh g⁻¹, which was about 97% of the reversible capacity at the 3rd cycle after 20 cycles. The discharge plateau was ca. 2 V, which was coincident with the potential in Li/S cells using a liquid electrolyte [22], suggesting that lithium metal worked successfully as a negative electrode in bulk-type solid-state Li/S cells. The use of the lithium thin film contributed to the achievement of the bulk-type cells with high energy density and good cycle performance because of forming an intimate contact between the lithium thin film and the SE. To the best of our knowledge, the operation of the bulk-type solid-state Li/S cells using lithium metal electrode as shown here is the first report. The use of a lithium thin film prepared by vacuum evaporation contributes to developing the fabrication of bulk-type solid-state lithium metal batteries. However, the cell performance was investigated only at a low current rate (0.03 C).

Further improvement of rate performance in bulk-type solid-state batteries with a lithium metal electrode is required and has not been studied yet. Then, indium metal which forms alloys with lithium was inserted to the interface between a lithium metal electrode and a Li₂S·P₂S₅ SE to reduce the overvoltage for charge-discharge reaction in bulk-type lithium metal batteries. Lithium-indium alloy has a high lithium ion diffusion coefficient [23] and is known to be used as a stable electrode for charge-discharge cycles in bulk-type solid-state cells using sulfide-based SEs [24,25]. The effects of the insertion of an indium film prepared by vacuum-evaporation on the rate performance of all-solid-state lithium metal batteries were investigated. Indium was evaporated on the 80Li₂S·20P₂S₅ SE layer, and the morphologies of the SE layer with an indium thin film were investigated. Figure 3-21
shows the cross-sectional SEM image of the SE layer with the indium metal evaporated. The thickness of the indium thin film was about 500 nm and intimate contacts between the indium thin film and the SE layer were formed. An indium thin film was formed on the surface of lithium metal foil as well as the SE layer. The effects of the position of the indium film on the cell performance were examined. The bulk-type Li/Li$_4$Ti$_5$O$_{12}$ cells were fabricated by evaporating indium on the surface of the 80Li$_2$S-20P$_2$S$_5$ SE layer (Fig. 3-22 (B)) and on the surface of lithium foil (Fig. 3-22 (C)); electrochemical properties of these cells were compared. Figure 3-22 (A) shows the charge-discharge curves of the Li/Li$_4$Ti$_5$O$_{12}$ cells using indium thin films at the 10th cycle. The capacity based on the weight of Li$_4$Ti$_5$O$_{12}$ is shown on the lower horizontal-axis and that based on lithium is shown on the upper horizontal-axis in the figure. These cells operated at the current density of 0.13 mA cm$^{-2}$ at 25°C. Both the cells using lithium electrode exhibited an average discharge potential of about 1.55 V, which coincided with the theoretical operating potential of Li$_4$Ti$_5$O$_{12}$ versus lithium metal [26]. It was confirmed that the insertion of the indium thin film at the interface between the lithium electrode and the SE layer did not change the operating potential of lithium metal cells. Figure 3-23 shows the XRD pattern of the lithium electrode after charge-discharge tests. The peaks attributable to Li$_{13}$In$_3$ alloy and lithium were observed. Li$_{13}$In$_3$ alloy would have almost the same potential as lithium [24], and thus the cells shown in Fig. 3-22 (A) had the operating potential of about 1.55 V. The cells prepared by evaporating indium on the SE layer (Fig. 3-22 (A-a)) exhibited a higher capacity and a lower overpotential than those of the cells using indium evaporated on the lithium foil (Fig. 3-22 (A-b)). This result suggests that the construction of a favorable interface between the indium thin film and the SE layer contributes to the enhancement of reversible capacity. To study rate performance of the cells prepared by evaporating indium on the SE layer, the charge-discharge measurements were conducted at current densities from 0.13 mA cm$^{-2}$ to 1.3 mA cm$^{-2}$ at 25°C. Figures 3-24 (a) and (b) respectively show the charge-discharge curves and cycle performance of the Li/Li$_4$Ti$_5$O$_{12}$ cell with the indium thin film. Both the capacities based on the weight of lithium as well as Li$_4$Ti$_5$O$_{12}$ are shown in the figures. The current
density was increased from 0.13 mA cm\(^{-2}\) to 1.3 mA cm\(^{-2}\) by every 20 cycles. The slope in the voltage of 1.6-2.0 V appeared in the first discharge curve and the irreversible capacity in the first cycle was observed; the electrochemical reaction mechanism at the slope has not been understood. In the subsequent cycles, the bulk-type lithium metal cells showed a flat discharge plateau without the slope. The cells maintained the reversible capacity of 105 mAh g\(^{-1}\) based on the weight of Li\(_4\)Ti\(_5\)O\(_{12}\), which corresponded to 27 mAh g\(^{-1}\) of lithium metal, at 0.13 mA cm\(^{-2}\) for 20 cycles and exhibited an excellent cycle performance at every current density. The all-solid-state cell, in which indium was evaporated on the lithium electrode, also showed a good cycling performance at 0.13 mA cm\(^{-2}\) for 10 cycles. On the other hand, bulk-type solid-state cells using lithium foil without the indium thin film were not charged and discharged at a low current density of 0.13 mA cm\(^{-2}\) (the data are not shown here.). The bulk-type lithium metal cells with the indium thin film worked successfully at 1.3 mA cm\(^{-2}\), which is a high current density for all-solid-state system, indicating that insertion of indium thin film at the interface between the lithium electrode and the SE layer is effective in improving the rate performance of the cells. However, the reversible capacities decrease and the larger overpotential was observed at higher current densities. A low lithium diffusion coefficient of Li\(_4\)Ti\(_5\)O\(_{12}\) would be responsible for the lower capacity at a high current density.

It is expected that the use of the positive electrode materials achieving high rate performance in all-solid-state cells [27, 28] leads to further improvement of rate performance of the lithium metal cells. **Figure 3-25** shows the SEM images of the surface of the SE layer with the indium thin-film (a) before and (b) after the cells were charged and discharged for 120 cycles as shown in **Fig. 3-24**. After the cycle tests, the cells were disassembled and lithium foil was removed from the SE layer, and the morphology of the SE surface was observed by SEM. The surface morphology showed little change before and after cycles, and perceptible cracks and dendritic areas were not observed. Retaining morphology with a smooth surface during cycles resulted in a good cyclability and a high rate capability for the all-solid-state lithium metal cells, as shown in **Fig. 3-24**.

It was found that the growth of lithium along the grain boundaries or pores inside the SE
layer would trigger the short circuit and the formation of intimate contacts between the lithium electrode and the SE layer by vacuum evaporation. Additionally, the elimination of the grain boundaries or pores is also anticipated to improve the performance of lithium deposition and dissolution. The softening adhesion of glass electrolytes [29] was carried out to prepare the pellet with few grain boundaries. Figure 3-26 shows the nano search microscopy images of (a,c) surface and (b,d) cross-section of 80Li₂S·20P₂S₅ glass pellets prepared by (a,b) cold press and (c,d) hot press at 210°C for 4 h. Compared with the images (a) and (c), the pellet prepared by cold press (a,b) had rougher surface than that prepared by hot press (c,d). This difference affected the contact area of the interface between lithium electrodes and SEs, and the pellets prepared by hot press would have more intimate contacts between them. SEM images in Fig. 3-27 reveal that softening adhesion of the electrolytes prepared by hot press (b) resulted in the disappearance of pores and grain boundaries compared with the electrolytes by cold press (a). Here, only lithium foil was used as a counter electrode without a lithium or indium thin film to investigate the effect of the disappearance of grain boundaries on the cell performance. Fig. 3-28 shows the lithium deposition and dissolution profiles in the bulk-type symmetric cells of Li / 80Li₂S·20P₂S₅ / Li using the SE pellets prepared by hot press. This electrochemical test was conducted at 25°C at the current densities of 0.7 mA cm⁻² and 1.4 mA cm⁻² for 3 h and 1.5 h, respectively. The utilization of lithium was 10%. The cell exhibited the relatively stable voltage at each current density, indicating that reversible lithium deposition and dissolution reaction occurred even at 0.7 mA cm⁻² and 1.4 mA cm⁻². At the end of each process overpotential was observed because the contacts between lithium foil and SE pellets would become insufficient due to lithium deposition and dissolution. However, the use of the SE pellets prepared by hot press suppressed the short circuit of the cells. The removal of pores and grain boundaries by hot press contributed to enhancing the rate capability of the bulk-type solid-state cells with lithium metal electrodes. It is revealed that two approaches such as increase in contact area and disappearance of grain boundaries are effective in improving the performance of bulk-type lithium metal batteries.
3.4. Summary

Structural analysis and morphological observation of the alloying reaction materials such as Si and Sn active materials in all-solid-state batteries were investigated by XRD and SEM. As well as the cells using liquid electrolytes, the reaction mechanism of both alloying and dealloying reactions and large volumetric change of the electrodes were clarified. However, all-solid-state cells using micrometer-sized active materials exhibited much better cycle performance with higher capacity and higher coulombic efficiency than those of the liquid cells. This is because the intimate contacts between the electrodes and Li$_2$S-P$_2$S$_5$ SEs were retained during cycling and the electrodes were not exfoliated from the current collector by applying a pressure to the cells. Furthermore, XRD analysis and Raman spectroscopy of Sn$_4$P$_3$ electrodes revealed that Li$_3$P and Li$_{13}$Sn$_5$ were formed during discharge process and Sn$_4$P$_3$ was partially formed again in charge process. To achieve the large energy density of the cells, Sn$_4$P$_3$ was applied to the electrode of all-solid-state cell without SE and AB. The cell with only Sn$_4$P$_3$ was discharged and charged at room temperature. It was revealed that the self-formation of the matrix with high lithium ion conductivity was effective in upgrading the reversible capacity of the cells using only active materials without SE and conducting additives.

Black phosphorus was prepared by using a mixer mill apparatus. The mechanical milling of black phosphorus and AB brought about a decrease in size of secondary particles of the composite material. The all-solid-state cells with the composites and Li$_2$S-P$_2$S$_5$ glass-ceramic SEs exhibited the initial discharge capacity of 1962 mAh g$^{-1}$ and the coulombic efficiency of 89%. The all-solid-state cells worked at the current density of 3.8 mA cm$^{-2}$ at 25°C and showed the excellent cycle performance with a high capacity of over 500 mAh g$^{-1}$ for 150 cycles.

Bulk-type solid-state lithium metal batteries showed an abrupt potential profile during lithium deposition process. SEM observation revealed that the surface area of the deposition of lithium on the SE surface was small and lithium grew inside the SE layer in the case of short circuit of the batteries. To improve the performance of lithium deposition and
dissolution in the all-solid-state cells, two approaches such as the formation of favorable electrode-electrolyte interface by vacuum evaporation and the decrease in the pores and grain boundaries in the SE layer by its softening adhesion were carried out. Inserting a lithium thin film layer between the interfaces improved the reversibility of deposition and dissolution, and the Li/S cells retained the reversible capacity of 900 mAh g\(^{-1}\) for 20 cycles. The softening adhesion of the Li\(_2\)S-P\(_2\)S\(_5\) glass electrolytes enhanced remarkably the rate performance of the bulk-type solid-state cells, and the cells worked even at over 1 mA cm\(^{-2}\).
3.5. References


Figure 3-1  Charge-discharge curves (a) and cycle performance (b) of the all-solid-state cells of Li-In / 80Li₂S·20P₂S₅ glass-ceramic / Si under various current densities at 25°C.
Figure 3-2 XRD patterns of Si electrode before cycling, after 1st discharge and after 10th charge.
Figure 3-3 Charge-discharge curves of the all-solid-state cells of Li-In / 80Li$_2$S·20P$_2$S$_5$ glass-ceramic / Sn under 0.064 mA cm$^{-2}$ at 25°C.
Figure 3-4  SEM images of (left) the surface and (right) the cross-section of Sn electrodes (a) before cycling, (b) the 1st discharge and (c) charge, (d) the 2nd discharge and (e) the 10th charge. Charge-discharge tests of the all-solid-state cells of Li-In / 80Li2S·20P2S5 glass-ceramic / Sn under 0.064 mA cm⁻² at 25°C were carried out.
Figure 3-5  XRD pattern and SEM image of Sn₄P₃ prepared by mechanical milling.
Figure 3-6 Charge-discharge curves of the all-solid-state cells of Li-In / 80Li$_2$S·20P$_2$S$_5$ glass-ceramic / Sn$_4$P$_3$ under 0.064 mA cm$^{-2}$ at 25$^\circ$C.
Figure 3-7  (A) XRD patterns and (B) Raman spectra of the Sn₄P₃ composites before cycling or Li₃P powder (a), after 1st charge (b) and after 1st discharge (c).
Figure 3-8  (a) Initial charge-discharge curves and (b) cycle performance of the all-solid-state cell with (a) only Sn₄P₃ active materials.
Figure 3-9 Charge-discharge curves of all-solid-state cells using the three types of active materials without AB and Li$_2$S-P$_2$S$_5$ SE. (a) Sn (58 µm) active material, (b) SnO active material and (c) Sn$_4$P$_3$ active material.
Figure 3-10  XRD patterns of red phosphorus (a) and black phosphorus prepared by mechanical milling with a planetary ball-mill (b) and a mixer mill (c).
Figure 3-11  SEM images of black phosphorus powders (a) and the composites with black phosphorus and AB (b).
Figure 3-12  The first charge-discharge curves of all-solid-state cells of Li-In / 80Li₂S·20P₂S₅ glass-ceramic / phosphorus. (a) Red phosphorus, (b) black phosphorus and (c) the composites with black phosphorus and AB were used as an active material.
Figure 3-13  XRD patterns for the working electrode using black phosphorus before cycling (a), after discharge to 0 V (vs. Li) (b) and after charge to 2.5 V (vs. Li) (c).
Figure 3-14 Cycle performance of the all-solid-state cells using the composites with black phosphorus and AB at 25°C. The cutoff voltage is between 0 V and 2.5 V (vs. Li).
Figure 3-15 High rate performance of the all-solid-state cells using the composites with black phosphorus and AB at 3.8 mA cm\(^{-2}\) at 25°C.
Figure 3-16 Charge-discharge curves of an all-solid-state Li / Li$_2$S-P$_2$S$_5$ solid electrolyte / Li$_4$Ti$_5$O$_{12}$ cell using a lithium foil at 0.064 mA cm$^{-2}$ at 25°C.
Figure 3-17  SEM images of the surface of SE layer (a-d) and the cross-section of SE layer (e,f) after the all-solid-state cells Li / 80Li2S·20P2S5 glass-ceramic / SUS were discharged (lithium were electrochemically deposited at the surface between SE layer and SUS current collector) on various conditions of current densities and deposition time. (a) 0.1 mA cm$^{-2}$ for 10 h, (b) 0.1 mA cm$^{-2}$ for 100 h, (c,d) 1 mA cm$^{-2}$ for 1 h and (e,f) 1 mA cm$^{-2}$ for 72 h
Figure 3-18 SEM image of cross-section of a solid electrolyte (SE) layer with a lithium thin film.
Figure 3-19  Lithium dissolution and deposition curves in the all-solid-state cells (a) Li foil / SE / Li foil and (b) Li foil / Li thin film / SE / Li thin film / Li foil at 0.064 mA cm$^{-2}$. 
Figure 3-20 Charge-discharge curves of all-solid-state Li / Li thin film / Li$_2$S-P$_2$S$_5$ SE / S cell at 25°C at 0.013 mA cm$^{-2}$ (1st, 2nd) and 0.064 mA cm$^{-2}$ (0.03 C, 3rd-20th).
Figure 3-21  Cross-sectional SEM image of a Li$_2$S-P$_2$S$_5$ solid electrolyte (SE) pellet on which indium metal was vacuum-evaporated.
Figure 3-22 (A) Charge-discharge curves of all-solid-state cells Li / indium thin film / 80Li$_2$S·20P$_2$S$_5$ / Li$_4$Ti$_5$O$_{12}$, in which indium was evaporated on the SE layer (a) or on the lithium foil (b). Schematics of the interface between lithium and 80Li$_2$S·20P$_2$S$_5$ SE are shown in (B) and (C); (B) indium was evaporated on the SE layer and then lithium foil was attached to the indium thin film and (C) indium was evaporated on lithium foil and the side of indium thin film was attached on the SE layer.
Figure 3-23 XRD pattern of lithium metal electrode after charge-discharge tests.
Figure 3-24  (a) Charge-discharge curves and (b) cycle performance of all-solid-state cells Li / indium thin film / 80Li$_2$S·20P$_2$S$_5$ / Li$_4$Ti$_5$O$_{12}$ at current densities from 0.13 to 1.3mA cm$^{-2}$ at 25°C.
Figure 3-25  SEM images of the surface of the SE layer with indium thin films (a) before and (b) after the cells were charged and discharged for 120 cycles as shown in Fig. 3-23.
Figure 3-26  Nano search microscopy images of (a,c) surface and (b,d) cross-section of 80Li$_2$S·20P$_2$S$_5$ glass pellets prepared by cold press (a,b) and hot press (c,d).
Figure 3-27  SEM images of the surface of the 80Li$_2$S·20P$_2$S$_5$ glass pellets prepared by (a) cold press and (b) hot press.
Figure 3-28 Lithium dissolution and deposition curves in the all-solid-state cells of Li / $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ / Li using SE pellets prepared by hot press.
4. In-situ measurements of structure and morphology at the interface between electrode and electrolyte for improving electrochemical properties of all-solid-state cells

4.1. Introduction

In the previous chapters 2 and 3, the electrochemical properties, the structural analysis and the microstructural observation of the electrodes with high capacity in all-solid-state cells were studied. It is revealed that the understanding of the structural changes of electrodes accompanied by charge-discharge reactions and the morphology of electrodes such as particle size, interfacial contacts between electrode and electrolytes and dispersion of active materials in the solid electrolyte (SE) matrix is essential for developing the all-solid-state cells with high performance. In-situ analyses provide some useful information about the structural evolution of the electrode materials and the electrode-electrolyte interface during operation of a battery. Therefore, in-situ structural characterization by XRD [1,2] and spectroscopy [3-5] techniques has eagerly been performed in conventional liquid-type cells. Furthermore, Kuwabata et al reported that ionic liquids with negligible vapor pressure enable us to observe the morphology of the electrode by scanning electron microscope (SEM) [6], and electrochemical reactions in ionic liquids can be directly observed by SEM [7-13] and transmission electron microscope (TEM) [14-18]. However, the previous characterization of bulk-type solid-state cells with inorganic SEs has been limited to ex-situ analysis techniques.

The ion transport in SEs is entirely different from those in liquid electrolytes. Both lithium ions and anions migrate in liquid electrolytes, and desolvation process for lithium ions is required to insert lithium ions into active materials. Meanwhile, transference number of Li$_2$S-P$_2$S$_5$ SEs is close to one, which means that only lithium ions move in the SEs, and a reaction such as the desolvation process does not occur. The reaction mechanism in all-solid-state cells is not necessarily the same as that in the conventional liquid-type cells. Additionally, since an electrochemical reaction proceed at the solid-solid interface between
electrode and electrolyte in all-solid-state cells, ensuring the conducting paths to active materials has significant influence on the cell performance. As mentioned in the previous chapter 3, the performance of the all-solid-state cells using lithium metal, which is an ultimate negative electrode in terms of theoretical capacity and operating potential, was drastically improved by forming a favorable electrode-electrolyte interface. An ex-situ morphological observation of a lithium metal electrode is very difficult because lithium has a very high reactivity to moisture and gas such as nitrogen, oxygen and carbon dioxide. Therefore, the more complete investigation of the structure and the morphology of the solid-solid interface is required by the means of in-situ microscopic observation.

In this chapter, the structural and morphological changes in all-solid-state cells with Li$_2$S-P$_2$S$_5$ SEs during their operation were investigated by in-situ techniques. In-situ XRD measurement and Raman spectroscopy were applied to the typical LiCoO$_2$ electrodes. The reaction mechanism of the electrodes in the all-solid-state cells was compared to that in liquid-type cells. The effects of the addition of electron conducting additives on reaction mechanism in the cells were also investigated. Lithium deposition and dissolution mechanism in the all-solid-state cells was explored by in-situ SEM observation. The cell configuration was Li / Li$_2$S-P$_2$S$_5$ SEs / stainless steel (SS), and morphological changes at the interface, where lithium was electrochemically deposited, were observed. The influences of operating current densities on morphological changes during the deposition and dissolution reaction were examined. Finally, these in-situ techniques suggest the possible strategies to improve the performance of the all-solid-state cells.

4.2. Experimental

LiCoO$_2$, a typical active material, was used for in-situ Raman spectroscopy (LabRAM HR-800, HORIBA) and X-ray diffraction with a diffractometer (Ultima IV, Rigaku). The bulk-type solid-state cells of In / 80Li$_2$S·20P$_2$S$_5$ glass-ceramic SE / LiCoO$_2$ were fabricated. LiCoO$_2$ composite electrodes consisting of LiCoO$_2$ : SE = 70 : 30 were prepared by grinding with an agate mortar. The pellets of a cuboid of LiCoO$_2$ composite electrode and the SE
layer were prepared by pressing under 360 MPa. In the case of the cells for in-situ XRD, In foil was put on the SE layer as a counter and a reference electrode and subsequently SS powders were added; a pressure of 120 MPa was applied to the four-layered pellet. In the case of the cells for in-situ Raman, In foil was only attached to the SE layer and the three-layered pellet was obtained. Finally, both the cells sandwiched by two SS rods as current collectors were obtained. In Raman spectroscopy measurement, the cell was put in a container, which allows the electrochemical test with Ar flow, in a dry Ar-filled glove box. In XRD measurement, a charge-discharge test of a cell was stopped at each state, XRD analysis of the cell was conducted, and after the analysis a subsequent charge-discharge test was carried out. Since the above processes are repeated, XRD measurements can be performed in the same cell at all the states of the charge-discharge tests.

The lithium deposition and dissolution mechanism was investigated by in-situ SEM observation. The bulk-type solid-state cells of Li / 80Li₂S·20P₂S₅ glass-ceramic SE / SS were fabricated. The SE pellet of a cuboid was prepared by pressing under 360 MPa and the lithium foil was attached on the pellet and then the bilayer pellet was sandwiched with two SS disks as a current collector. The batteries were transferred to a SEM apparatus (VE-9800, Keyence) in an inert atmosphere. A conceptual illustration of in-situ SEM system is shown in the previous papers [7-12]. The actual system consisted of the SEM apparatus and a potentiostat/galvanostat with an insulating transformer (Ivium, CompactStat). The interface between the SS current collector and the SE layer was mainly observed by SEM during lithium deposition and dissolution reaction. The edges of the SS current collector were curved to make it easier to observe the morphology of lithium deposition and dissolution.

4.3. Results and discussion

4.3.1. In-situ Raman spectroscopy and X-ray diffraction

In-situ Raman spectroscopy and XRD analysis were applied to the LiCoO₂ electrode in the all-solid-state cells with Li₂S·P₂S₅ SEs. The electrochemical reaction mechanism of LiCoO₂ electrode in all-solid-state cells was compared to that in liquid-type cells.
structural change at the electrode-electrolyte interface was investigated by using laser Raman microscope; the minimum spot size of the laser is 3 μm at the surface of samples. This microscope allows the observation of the electrode and the interface within 3 μm. First, the reaction mechanism of LiCoO$_2$ electrode in a cell with liquid electrolyte is described as follows [3]. **Figure 4-1** (a) shows the traces of the LiCoO$_2$ electrode potential during extraction of lithium ion to different x values and the crystallographic phase assignment. **Figures 4-1** (b) and (c) show the variation of the Raman spectra at different x values; A-J corresponds to those in **Fig. 4-1** (a). The cell potential rose rapidly at the initial stage and then a potential plateau at 3.92 V up to 70 mAh g$^{-1}$ (F) is observed. The plateau is attributable to two-phase region consisting of the two types of hexagonal phase with a slightly different lattice parameter. In the two-phase region (spectra B-F), the intensity Raman bands decreased and a shoulder peak appeared and grew in intensity at lower wavenumber side of the original bands as the capacity increased. In the region 0.25 < x < 0.47 (spectra F-H, 70 ~ 130 mAh g$^{-1}$), the potential changed monotonically with increase in x, which corresponds to a single-phase reaction of the second hexagonal phase. In this region, the peak wavenumber of each band shifted gradually in the lower direction, according to the increase in the c-axis length with the removal of lithium ions. **Figure 4-2** (a) shows the photograph of setup for in-situ Raman spectroscopy. An all-solid-state cell was in a container which enables the electrochemical test with Ar flow. Structural change of the LiCoO$_2$ electrode during operation of a cell can be investigated from the window by the microscope. **Figure 4-2** (b) shows the top view of the cells in the container as shown in **Fig. 4-2** (a). The cell configuration is In / 80Li$_2$S·20P$_2$S$_5$ SE / LiCoO$_2$. The interface between the LiCoO$_2$ electrode and the SE layer was observed as shown in the dotted circle in **Fig. 4-2** (b). **Figure 4-2** (c) presented the charge curve of the all-solid-state cell for in-situ Raman spectroscopy at 25°C. The cell was charged up to 3.6 V (vs. Li-In) at the current density of 0.064 mA cm$^{-2}$. The current flow time is shown on the lower horizontal-axis and the capacity of the cell is shown on the upper horizontal-axis in the **Fig. 4-2** (c). The cell showed the charge capacity of 110 mAh g$^{-1}$ and the plateau potential of about 4 V (vs. Li).
Figure 4-3 shows optical micrograph of the interface between LiCoO$_2$ electrode and Li$_2$S-P$_2$S$_5$ SEs of the all-solid-state cell. The white contrast represents LiCoO$_2$ active material and the dark (green) contrast represents the SE. Before cycling (a), the favorable interface was observed. As the capacity increased, the morphology at the interface changed gradually, showing the deterioration of the interface. The use of untreated LiCoO$_2$ particles or the volumetric change in the LiCoO$_2$ active materials is considered to affect the interfacial morphology. To probe the interfacial reaction between electrodes and electrolytes, in-situ Raman spectroscopy was performed at two different positions of 1 and 2. Raman spectra of LiCoO$_2$ electrodes in Fig. 4-4 show a clear difference between the positions 1 and 2. At the position 1, the intensity of each original band decreased and a shoulder grew in intensity at lower wavenumber at each band with increase in capacity of the cells as shown in the cells using liquid electrolytes in Fig. 4-1. On the other hand, at the position 2, the new band at about 675 cm$^{-1}$ was observed at the capacity of 70 mAh g$^{-1}$. The new band would be assigned to cobalt sulfides such as CoS (683 cm$^{-1}$) or Co$_3$O$_4$ (690 cm$^{-1}$). Sakuda et al reported that the interfacial TEM observation revealed the formation of the interfacial layer between LiCoO$_2$ electrode and Li$_2$S-P$_2$S$_5$ SEs after charging the all-solid-state cells. Moreover, Co, P and S elements mutually diffused between them. By combining the results obtaining from the TEM and in-situ Raman, CoS would be locally formed at the interface during charge process, which would cause degradation of the interface. Next, in-situ XRD analysis of the LiCoO$_2$ electrode was applied to the all-solid-state cells. The electrochemical reaction mechanism of LiCoO$_2$ electrode in all-solid-state cells was compared to that in conventional liquid-type cells. Laser Raman microscope provides information about local structure within a few µm, and on the other hand, X-ray diffraction measurement gives information about average structure over a large area of the electrode near the current collector. Figure 4-5 (a) displays XRD patterns of LiCoO$_2$ electrode in the cells with a liquid electrolyte (1M LiAsF$_6$ in PC/EC) at the various stages during the charge process [1]. The most obvious effect of the lithium extraction is the steady decrease of the (003) Bragg angle and hence an increase in c-axis length. This steady decrease seems to stop at about 0.5
Li$^+$, i.e., in the middle of the ordered phase. The (003) peak also reveals the gradual disappearance of the original peak near 0.2 Li$^+$ and the appearance of a new peak at a lower angle. This is a clear indication of a first-order phase transition with the coexistence region signified by the simultaneous presence of the peaks. Figure 4-5 (b) shows the XRD patterns of the LiCoO$_2$ electrodes consisting of LiCoO$_2$ and Li$_2$S-P$_2$S$_5$ SE (70 : 30, wt.%) in the all-solid-state cells at the various states during lithium extraction. At 40 mAh g$^{-1}$ (0.15 Li$^+$), the intensity of the original peak remained almost unchanged and a slight shoulder at lower angle side at the original peak appeared. As the capacity increased up to 110 mAh g$^{-1}$, the intensity of the original peak decrease and the new peak attributable to the second hexagonal phase shifted to a lower angle with increase in its intensity. Although the structural change in the LiCoO$_2$ electrodes in the all-solid-state cells is similar to that in the liquid-type cell, there is one significantly different point between them. The original peak due to the first hexagonal phase remained at 110 mAh g$^{-1}$ in the all-solid-state cells suggesting that there are some active materials which cannot contribute to an electrochemical reaction. It was reported that the addition of vapor growth carbon fiber (VGCF) improved the rate performance of the all-solid-state cells, meaning that the formation of favorable conducting paths to the active materials [19]. The effects of the addition of VGCF to the electrodes on the reaction mechanism of the all-solid-state cells were investigated. Figure 4-5 (c) shows the XRD patterns of the LiCoO$_2$ electrodes consisting of LiCoO$_2$, Li$_2$S-P$_2$S$_5$ SE and VGCF with the weight ratio of 40 : 60 : 4. Compared with Fig. 4-5 (b), it was found that the intensity of the original peak in the cells with VGCF is lower than that in the cells without VGCF at 110 mAh g$^{-1}$. It is considered that the ratio of LiCoO$_2$ active materials, where lithium ions can be extracted, increases by adding VGCF to the electrode. As capacity increased from 110 mAh g$^{-1}$ to 140 mAh g$^{-1}$, although the peak shift of the second hexagonal phase to a lower angle are clearly confirmed, the intensity of the original peak seem mostly unchanged. These results demonstrated that a small amount of “dead” LiCoO$_2$ particles, which do not work as an active material, in the electrode are present. After the 1st discharge, the peak of the second hexagonal phase shifted to a higher angle and the intensity of the
original peak grew, meaning that lithium ions were intercalated into LiCoO$_2$ active materials. The peak of the second hexagonal phase did not return to the peak position of the first hexagonal phase completely, which is responsible for the appearance of an irreversible capacity at the 1st cycle. The XRD pattern after the 2nd charge is almost the same as that after the 1st charge. Based on the information obtained from in-situ analysis, the suppression of a side reaction and the formation of both electronic and ionic conducting paths to the active materials are expected to achieve an excellent cell performance of all-solid-state cells.

4.3.2. In-situ scanning electron microscopy observation

In order to clarify the mechanism of lithium deposition and dissolution, an in-situ optical microscope technique was applied to bulk-type solid-state cells. The photograph of setup for the in-situ microscopical observation is shown in Fig. 4-2 (a). Morphological changes of the cell during lithium deposition can be observed from the window by the microscope. Figure 4-6 (a) shows the schematic of the cells in the container. The cell configuration is Li / 80Li$_2$S·20P$_2$S$_5$ SE / SS. The interface between the SE layer and the SS current collector is observed as shown in the dotted circle in Fig. 4-6 (a). Figure 4-6 (b) shows the schematic from the front of the cell as shown in Figure 4-6 (a). There is a space at the interface of the top of the cell because of using the SS with chamfered corners. Figures 4 (c-e) show the optical microscope images of the interface (c) before lithium deposition and after lithium deposition (d) at 2 mA cm$^{-2}$ for 730 sec and (e) at 20 mA cm$^{-2}$ for 2 h. Before lithium deposition, the relatively flat SE layer with the space at the left side as shown in Fig. 4-6 (b) was observed. Compared with the morphology before lithium deposition, several cracks were formed near the interface immediately after the short circuit that occurred at 730 sec. When a very high current density of 20 mA cm$^{-2}$ was continuously applied to the cells after the short circuit, new cracks were hardly observed, but the existing cracks became larger and larger. Although dendritic growth of lithium was not observed on top of the cell, its growth would proceed in the SE layer. The formation of cracks may be caused by the stress
involved with dendritic growth of lithium. The observation of dynamic process during battery operation revealed that occurrence of cracks triggered the short circuit of the bulk-type solid-state cells.

As indicated above, in-situ optical microscope technique is an effective way to visually know what reaction occurs in the bulk-type solid-state cells. However, it is not enough to observe the micro- or nano-scale reaction. SEM has a better spatial resolution than optical microscope, and is expected to provide useful information on microstructural evolution. Based on the fact that SE does not show charging behavior, we conceived to apply in-situ SEM observation system for electrochemical reactions in ionic liquid to the bulk-type solid-state cell [7-12]. Here, in-situ SEM observation with the tilt of the stage at a 30 degrees angle was carried out as shown in Fig. 4-7 (a) in order to observe the interface between the SE and the electrode. Figure 4-7 (b) shows lithium deposition curves of the all-solid-state cells Li / 80Li2S·20P2S5 SE / SS at 2 mA cm⁻². Inset is the magnification of the curve in the voltage range from -0.02 V to 0 V. The time range was 600 to 2000 sec. The polarization of the cells increased significantly with an increase in the current flow time, and afterward the voltage became about 2 mV, meaning the short circuit of the cells. SEM images of the interface between the SS and the SE layer at different positions of the same cell before (c) and after lithium deposition for 600 sec (d) and 1920 sec (e) are shown in Fig. 4-7 (c-e). The SE layer had very flat surface without any cracks as shown in Fig. 4-7 (c). Several cracks appeared in the dotted circles in locally generated just before short circuit of the cells (d), and the lithium growing from the SE layer toward the SS was observed after the short circuit (e). The growth of lithium proceeded at only the positions where cracks have already occurred, and new cracks and deposits were hardly observed at the other positions, viz. lithium deposition was initiated at the positions which had a contact between the SE layer and the SS, and the deposited lithium grew along grain boundaries under this condition as shown in Fig. 3-17 (f). Figure 4-7 (d) and (e) are in-situ SEM images that some lithium deposits push the SE layer aside. Further investigation was conducted by using one of such lithium deposits.
Figure 4-8 shows the SEM images of the morphology of the interface between the SE layer and the SS at the same position in the same cell (a) just after the short circuit of the cells, (b) lithium deposition at 5 mA cm$^{-2}$ for 10 min after the short circuit and (c) lithium dissolution at 20 mA cm$^{-2}$ for 20 min after (b). These figures show the morphological change when the electrochemical tests were forcibly carried out at very high current density after short circuit of the cells, which means that only limited lithium deposition and dissolution occurs. Figure 4-8 (a) shows that a pillared deposit was observed from the large cracks in the surface of the SE layer. The pillared deposit was different from the morphology of the SE layer and thus the deposit was considered to be lithium. Figure 4-8 (b) shows that lithium slightly grew during lithium deposition reaction compared with Fig. 4-8 (a). The length of the dotted line in the figures (a) and (b) is 6.6 µm and 12.8 µm, respectively. A new large crack on the right side of the pillared deposition was observed; the crack was considered to occur with the elongation of the lithium deposition. This result suggests that lithium extends from the inside of the SE layer. On the other hand, Fig. 4-8 (c) shows that the pillared deposit shrunk after the lithium dissolution reaction. The length of the dotted line in Fig. 4-8 (c) was 10.9 µm, which was somewhat shorter than that in Fig. 4-8 (b), suggesting that contraction of lithium was confirmed. Surprisingly, the deposition and dissolution of lithium proceeded with retention of the pillared structure of lithium and the contact interface between lithium and the SE. It is considered that Li$_2$S-P$_2$S$_5$ SE would have flexibility to accommodate the expansion of lithium during the lithium deposition.

In order to investigate the mechanism for the lithium deposition and dissolution at low current densities, in situ SEM observation of the interface between the SE and the SS was carried out to investigate the mechanism for the lithium deposition and dissolution at low current densities. Figure 4-9 (a) shows schematics for the cells of Li / SE / SS before cycling and the magnification of the interface between the SE and SS during charge and discharge reaction. As lithium was deposited on the SS during charge reaction, the space between the SE and the SS expanded because of the increase in thickness of the deposited lithium. Meanwhile, as lithium ion was dissolved into the SE during discharge reaction, the
space became narrower. **Figure 4-9** (b) shows the lithium deposition and dissolution voltage curves of the all-solid-state cells of Li / SE / SS at 0.01 mA cm\(^{-2}\) at the 1st and 2nd cycles and at 0.05 mA cm\(^{-2}\) at the 3rd and 4th cycles. The cell exhibited relatively stable voltage of +40 mV or -40 mV for only 2 cycles at 0.01 mA. Before cycling the resistance obtained from the impedance measurements was about 4000 Ω, and the resistance was almost corresponding to that estimated from the electrochemical tests. The cell resistance was much larger than that in the previous chapter because the cells were designed for in-situ SEM observation and enough pressure was not applied to the cells. **Figure 4-10** show the morphological evolution of the interface between the SE and the current collector after the 1st cycle and 2nd cycle. SEM images of the interface (a) after 1st charge, (b) after 1st discharge, (c) after 2nd charge and (d) after 2nd discharge are shown in **Fig. 4-10**. Unlike morphology observed in the electrochemical tests at high current density, new cracks and pillared deposits were not observed over a wide range of the SE surface during the charge-discharge reaction at a low current density of 0.01 mA cm\(^{-2}\). Deposited lithium was not also observed because uniform lithium layer would be preferentially deposited on the SS current collector under this condition. However, these SEM images revealed that deposition and dissolution of lithium on the SE brought about a slight change in the space between them. As shown in **Fig. 4-10** (a), the distance between them became longer during the lithium deposition (charge) reaction and the distance became shorter during the lithium dissolution (discharge) reaction. In-situ morphological observation of bulk-type solid-state cells demonstrates that current densities largely affect lithium deposition and dissolution behavior.

At current densities higher than 1 mA cm\(^{-2}\), lithium was locally deposited, which triggered large cracks because the SEs cannot accommodate volumetric change by the deposited lithium. The generated cracks lead to the short circuit of the cells. On the other hand, lithium was homogeneously deposited on the SE surface as low current densities less than 0.05 mA cm\(^{-2}\), and thus few cracks occurred and lithium did not not grow inside the SE layer, which enabled the reversible deposition and dissolution. These results suggest that the formation of the interface which allows homogeneous deposition and dissolution of lithium
on the SE is a key to achieve the highly repetitive deposition and dissolution reaction. In the previous chapter, construction of intimate contacts between the lithium electrode and the SEs by inserting a lithium or indium thin film improved the reversibility of the cells. Furthermore, it was found that lithium would grow along the pores and boundaries inside of the SE layer. The softening of glass electrolyte is an effective way for suppression of the growth of dendritic lithium because a dense SE layer without obvious grain boundaries or any pores is obtained [20]. This in-situ SEM observation reveals the morphological change of metal electrodes during charge-discharge processes at different current densities and guides the design to improve the performance of the next generation bulk-type solid-state cells using not only using sulfide and oxide SEs with high Li\(^+\) and Na\(^+\) ion conductivity [21-25].

4.4. Summary

The structure of LiCoO\(_2\) electrodes in all-solid-state Li\(_2\)S-P\(_2\)S\(_5\) SEs was investigated using in-situ Raman and XRD. These techniques showed that reaction mechanism of LiCoO\(_2\) electrodes in the all-solid-state cells is similar to that in a conventional liquid-type cell. However, in-situ Raman revealed that CoS or Co\(_3\)O\(_4\) was locally formed at the interface between LiCoO\(_2\) electrodes and Li\(_2\)S-P\(_2\)S\(_5\) SEs. As presented in the previous reports [26], this result reflects a side reaction at the electrode-electrolyte interface, which induces the degradation of the interface. Unlike a liquid-type cell, it was found that a small amount of LiCoO\(_2\) active materials with the first hexagonal phase (starting materials) was still present in the all-solid-state cells after the extraction of lithium ion from a LiCoO\(_2\) electrode without conductive additives. This suggests that all the LiCoO\(_2\) active materials can not contribute to electrochemical reaction homogeneously. It is found that a ratio of LiCoO\(_2\), whose electrochemical reaction can proceed, significantly increased by adding an electronic conducting additive such as VGCF. This is due to the formation of favorable conducting paths to LiCoO\(_2\) active materials.

The morphology of lithium deposition and dissolution in the all-solid-state cells Li / Li\(_2\)S-P\(_2\)S\(_5\) SE / SS was examined by in-situ SEM observation. This technique revealed that
the current densities largely affected the morphology during lithium deposition and dissolution. At high current densities, lithium was locally deposited and grew along the grain boundaries in the Li$_2$S-P$_2$S$_5$ SEs, and cracks generated in those positions. This is because the cells cannot accommodate the volume change by lithium deposition. The generated cracks would bring about the short circuit of the cells. On the other hand, at low current densities, homogeneous lithium deposition and dissolution took place over large areas of the SE. Based on these results, it is suggested that the formation of the interface which enables the homogeneous lithium deposition and dissolution and the disappearance of the grain boundaries in the SEs are effective in improving the performance of the all-solid-state cells with lithium metal electrodes.
4.5. References


Fig. 4-1  (a) Variations of electrode potential with specific capacity during electrochemical lithium deintercalation (top) and (b) Raman spectra of $\text{Li}_{1-x}\text{CoO}_2$ at different $x$ values in the region $0.18 < x < 0.60$. [5]
Fig. 4-2  (a) Photograph and (b) schematic diagram of cell for in-situ Raman spectroscopy.  
(c) Charge curve of the In/LiCoO$_2$ cell of for in-situ Raman spectroscopy.
Fig. 4-3  Optical micrograph of interface between LiCoO$_2$ electrode and Li$_2$S-P$_2$S$_3$ solid electrolyte in the cell for in-situ Raman spectroscopy (a) before cycling and (b-d) after charge capacity of (b) 10 mAh g$^{-1}$, (c) 50 mAh g$^{-1}$ and (d) 110 mAh g$^{-1}$. 

LiCoO$_2$ electrode  SE layer
Fig. 4-4  Raman spectra of LiCoO$_2$ at various stages during charge process at (a) position 1 and (b) position 2 as shown in Fig. 4-3.
Fig. 4-5  XRD patterns of the LiCoO$_2$ electrode in the all-solid-state cells of In / LiCoO$_2$ (a) without or (b) without VGCF and (c) the liquid-type cells Li/LiCoO$_2$ at various states during charge and discharge process.
Fig. 4-6  (a) Schematic of the all-solid-state cell for the in-situ measurements. Observation of morphological changes at the position of dotted circle. (b) Schematic of the cells observed from the direction vertical to that of SEM observation. Interspace at the interface between stainless steel and Li$_2$S-P$_2$S$_5$ SE at the edge of the current collector on top of the cells is shown by an arrow. (c-e) Optical microscope images of the SE layer and the interface between SE and stainless steel (c) before the test, (d,e) after lithium deposition at the interface of (d) 2 mA cm$^{-2}$ for 730 sec. and (e) 100 mA cm$^{-2}$ for 2 h.
Fig. 4-7  (a) Schematic of the all-solid-state cell for the in-situ SEM observation with the tip of the stage at a 30 degree angle.  (b) Lithium deposition curve of the all-solid-state cells Li / 80Li$_2$S·20P$_2$S$_5$ / stainless steel at 2 mA cm$^{-2}$. Inset is the magnification of the curve in the voltage range from -0.02 V to 0 V.  (c-e) SEM images of the interface between the current collector and the SE layer at different positions of the same cell (c) before and (d,e) after lithium deposition for (d) 600 sec and (e) 1920 sec.
Fig. 4-8  SEM images of the morphology of the interface between the SE and stainless steel at the same position in the same cell (a) just after the short circuit of the cells, (b) lithium deposition at 5 mA cm$^{-2}$ for 10 min after the short circuit, and (c) lithium dissolution at 20 mA cm$^{-2}$ for 20 min soon after the (b).
Fig. 4-9  (a) Schematics for the cells of Li / SE / stainless steel before cycling and the magnification of the interface between the SE and stainless steel during charge and discharge reaction.  (b) Lithium deposition and dissolution curves of the all-solid-state cells of Li / SE / stainless steel at 0.01 mA cm\(^{-2}\) at the 1st and 2nd cycle and at 0.05 mA cm\(^{-2}\) at the 3rd and 4th cycle.
Fig. 4-10 SEM images of the interface (a) after 1st charge, (b) after 1st discharge, (c) after 2nd charge and (d) after 2nd discharge.
5. General conclusions

In this thesis, the electrochemical properties of various high-capacity electrode materials in rechargeable all-solid-state Li/S batteries using Li$_2$S-P$_2$S$_5$ solid electrolytes were examined. The structural analysis and microstructural observation at the electrode-electrolyte interface were performed by X-ray diffraction (XRD), electron diffraction (ED), Raman spectroscopy, scanning electron microscope (SEM), transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDX). The obtained experimental findings were fed back to the design of composite electrodes to achieve the enhancement of the capacity of the all-solid-state cells. Furthermore, in-situ techniques of the bulk-type solid-state cells were established to investigate the structure and morphology at the electrode-electrolyte interface during operation of a battery. The following results and considerations were obtained.

1. The all-solid-state cells using Cu$_x$Mo$_6$S$_{8-y}$ electrodes exhibited the excellent cycle performance with the capacity of 100 mAh g$^{-1}$ at 1.3 mA cm$^{-2}$ over 2000 cycles. The cells had the reversible capacity higher than its theoretical capacity at 40 mA cm$^{-2}$ at temperatures above 100°C. However, TEM-EDX observation revealed the diffusion of copper elements into the Li$_2$S-P$_2$S$_5$ solid electrolytes and impedance measurements indicated the increase in the interfacial resistance between Cu$_x$Mo$_6$S$_{8-y}$ and the electrolyte. These results suggested that the interfacial resistance was attributed to the formation of a resistance layer at the interface. It was found that the chemical removal of copper from Cu$_x$Mo$_6$S$_{8-y}$ and the physical trap such as addition of conductive additives to the electrodes were effective in improving a long cyclability over 1000 cycles at extremely high temperatures.

2. The electrochemical properties and the microstructural morphologies of the sulfur-based composite electrodes in the all-solid-state Li/S cells were carried out. First, it is revealed that a decrease in particle size and an increase in contact area among electrode
components achieved by mechanical milling of sulfur or Li$_2$S active material, Li$_2$S-P$_2$S$_5$ solid electrolytes and electron conducting additives drastically increased the reversible capacity and rate capability of the cells. Especially, the cells using the sulfur active material retained the capacity of about 1000 mAh g$^{-1}$ at 0.64 mA cm$^{-2}$ for 200 cycles, and the capacity is 5 times higher than that of conventional positive electrode materials. Secondly, liquid-solid interface using molten sulfur was formed to further increase contact area between sulfur and AB. The formation of the liquid-solid interface by milling of sulfur and AB at 155 °C contributed to enhancement of gravimetric energy density per the weight of electrode. Microstructural observation of the composite electrodes by STEM-EELS demonstrated that the presence of submicron-sized sulfur particles and the retention of intimate contacts among electrode components during cycling resulted in excellent cyclability with high capacity and rate capability. Thirdly, Li$_2$S active materials were pulverized on dry or wet milling conditions to lower the lithium-ion diffusion distance in Li$_2$S particles. Their pulverization prior to the preparation of the composite electrodes upgraded the cell performance using Li$_2$S composite electrodes. Especially, the cells with wet-milled Li$_2$S particles had the reversible capacity of 580 mAh g$^{-1}$ at 0.7 C rate and 271 mAh g$^{-1}$ at 3.5 C rate because Li$_2$S particles were well dispersed without forming an agglomeration and their size was smaller than that of dry-milled Li$_2$S. Finally, electrochemical performance of a Li$_2$S-P$_2$S$_5$ glass material with a large amount of Li$_2$S component as an electrode was investigated. The addition of copper metal and the formation of sufficient electron conduction paths by milling with AB activated electrochemically the Li$_2$S-P$_2$S$_5$ materials. It was revealed that a Li$_2$S-P$_2$S$_5$ glass material with a large amount of Li$_2$S component acts as an electrode having the favorable contact between Li$_2$S active material and Li$_2$S-P$_2$S$_5$ solid electrolyte and exhibits a good cycling stability with a high capacity.

3. High-resolution TEM and EDX experiments clarified the morphology of Li$_2$S composite electrodes at nanoscale and their reaction mechanism during cycling. These results
indicated that the crystalline Li$_2$S nanoparticles having the intimate contact with AB were well dispersed in the Li$_2$S-P$_2$S$_5$ solid electrolyte, and there were little changes of their morphologies at the initial discharge and at the 20th discharge states. The crystalline Li$_2$S nanoparticles were decomposed into the amorphous sulfur by the delithiation process. On the other hand, subsequent lithiation induced two distinct reaction processes depending on the Li$_2$S particle sizes at the initial cycle. One is an irreversible reaction characterized by the conversion to the lithium polysulfides in Li$_2$S particles larger than 50 nm and the other is a reversible reaction by the conversion between nanosized crystalline Li$_2$S and amorphous sulfur proceeded in the particles less than 10 nm. These results revealed the origin of high-capacity, excellent cycle performance and irreversible capacity at the initial cycle in all-solid-state In/Li$_2$S cells.

4. High-capacity negative electrodes suitable for all-solid-state cells were developed. First, alloying reaction materials such as Si and Sn were used. SEM observation of these electrodes showed large volumetric change of the electrodes during cycling. On the other hand, the all-solid-state cells using alloying materials exhibited much better cycle performance than the liquid-type cells. This is because the flexible and elastic properties of the solid electrolyte resulted in retaining intimate contacts between the electrodes and the solid electrolytes during cycling. Furthermore, XRD and Raman spectroscopy of Sn$_4$P$_3$ electrodes revealed that Li$_{13}$Sn$_5$ and Li$_3$P were formed by lithium insertion into Sn$_4$P$_3$. Since self-formation of favorable lithium conduction matrix is achieved in the electrode by lithium insertion, it is newly found that the cell of only Sn$_4$P$_3$ active materials without SE and AB showed the large reversible capacity of 650 mAh g$^{-1}$.

5. Black phosphorus was prepared by mechanical milling of red phosphorus with a mixer mill apparatus. Although the all-solid-state cells using red phosphorus showed charge-discharge coulombic efficiency of 12%, the cells using the composite with black phosphorus and nanocarbon exhibited the coulombic efficiency of about 90% and the
reversible capacity of 1700 mAh g\(^{-1}\). XRD analysis of black phosphorus electrode indicated that the electrochemical reaction between Li\(_3\)P and amorphized black phosphorus would proceed.

6. Bulk-type solid-state lithium metal batteries occasionally showed an abrupt potential profile during lithium deposition process. In such a case, cell resistance drastically decreased, suggesting that the short circuit of the cells occurred. Cross-sectional SEM observation revealed that deposited lithium existed in the grain boundaries of the solid electrolytes. The cause for the short circuit is that the contacts between lithium metal and the solid electrolyte was insufficient and then high current locally flew during lithium deposition. A vacuum evaporation of metals such as lithium and indium was applied to construct the favorable electrode-electrolyte interface in the all-solid-state cells. The intimate contacts between lithium metal electrode and Li\(_2\)S-P\(_2\)S\(_5\) solid electrolyte by inserting a lithium or indium thin film successfully contributed to reproducible lithium dissolution and deposition. The disappearance of the grain boundaries in the Li\(_2\)S-P\(_2\)S\(_5\) glass electrolyte by its softening adhesion enhanced remarkably the rate performance of the all-solid-state lithium metal batteries, and the batteries were charged and discharged reversibly even at a high current density of over 1 mA cm\(^{-2}\).

7. In-situ XRD and Raman spectroscopy of LiCoO\(_2\) electrodes in bulk-type solid-state batteries with Li\(_2\)S-P\(_2\)S\(_5\) solid electrolytes were first carried out to directly investigate the structure of the LiCoO\(_2\) electrode during operation of a battery. It was found that their reaction mechanism was similar to that in a conventional liquid-type cell, but an interfacial layer with CoS or Co\(_3\)O\(_4\) was partially formed. The effects of adding conducting additives such as VGCF to the LiCoO\(_2\) electrode on electrochemical reaction were investigated. In the case of the composite electrodes without VGCF, a part of LiCoO\(_2\) active materials did not contribute to the electrochemical reaction. The proportion of LiCoO\(_2\) particles whose electrochemical reaction can proceed, significantly
increased by adding VGCF to the electrode. These results indicated that favorable conducting paths to LiCoO\textsubscript{2} active materials were formed by adding VGCF and a homogeneous electrochemical reaction proceeded.

8. The lithium deposition and dissolution mechanism in the bulk-type solid-state cells Li / Li\textsubscript{2}S-P\textsubscript{2}S\textsubscript{5} solid electrolyte / stainless-steel was directly examined by in-situ SEM observation. This technique revealed that the current densities largely affected the morphology during lithium deposition and dissolution. At current densities higher than 1 mA cm\textsuperscript{-2}, lithium was locally deposited and grew along grain boundaries of the solid electrolyte, and cracks generated in those positions. This is because the cells cannot accommodate the volume change by lithium deposition. The generated cracks would bring about the short circuit of the cells. On the other hand, at current densities lower than 0.05 mA cm\textsuperscript{-2}, homogeneous lithium deposition and dissolution took place over large areas of the solid electrolytes. It is thus suggested that the short circuit of the cells is due to occurrence of cracks of the solid electrolytes by the growth of dendritic lithium along the grain boundaries. In-situ analysis regarding morphological change during operation of a bulk-type solid-state battery was successfully established for the first time.
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List of Publications

Original articles regarding this study are as follows:

1. “Characterization of all-solid-state lithium secondary batteries using Cu$_x$Mo$_6$S$_{8-y}$ electrode and L$_2$S-P$_2$S$_5$ solid electrolyte”
   M. Nagao, H. Kitaura, A. Hayashi, and M. Tatsumisago,

2. “High rate performance, wide temperature operation and long cyclability of all-solid-state rechargeable lithium batteries using chevrel-phase compound”
   M. Nagao, H. Kitaura, A. Hayashi, and M. Tatsumisago,

3. “Sulfur-carbon composite electrode for all-solid-state Li/S battery with Li$_2$S-P$_2$S$_5$ solid electrolyte”
   M. Nagao, A. Hayashi, and M. Tatsumisago,

4. “Electrochemical performance of all-solid-state Li/S batteries with sulfur-based composite electrodes prepared by mechanical milling at high temperature”
   M. Nagao, A. Hayashi, and M. Tatsumisago,
   *Energy Technology*, accepted for publication.

5. “Characterization of Li$_2$S-P$_2$S$_5$-Cu composite electrode for all-solid-state lithium secondary batteries”
   A. Hayashi, R. Ohtsubo, M. Nagao and M. Tatsumisago,
6. “High-capacity Li$_2$S-nanocarbon composite electrode for all-solid-state rechargeable lithium batteries”
   M. Nagao, A. Hayashi, and M. Tatsumisago,

(Chapter 2)

7. “Origin of high-capacity and cycling stability in all-solid-state lithium-sulfur batteries”
   M. Nagao, A. Hayashi, M. Tatsumisago, T. Ichinose, T. Ozaki, Y. Togawa, and S. Mori,

(Chapter 2)

8. “Electrochemical performance of all-solid-state lithium batteries with Sn$_4$P$_3$ negative electrode”
   A. Ueda, M. Nagao, A. Inoue, A. Hayashi, Y. Seino, T. Ota, and M. Tatsumisago,
   *J. Power Sources*, accepted for publication.

(Chapter 3)

9. “All-solid-state lithium secondary batteries with high capacity using black phosphorus negative electrode”
   M. Nagao, A. Hayashi, and M. Tatsumisago,
   *J. Power Sources*, **196** (2011) 6902-6905.

(Chapter 3)

10. “Bulk-type lithium metal secondary battery with indium thin layer at interface between Li electrode and Li$_2$S-P$_2$S$_5$ solid electrolyte”
    M. Nagao, A. Hayashi, and M. Tatsumisago,

(Chapter 3)

11. “Fabrication of favorable interface between sulfide solid electrolyte and Li metal electrode for bulk-type solid-state Li/S battery”
    M. Nagao, A. Hayashi, and M. Tatsumisago,
12. “In-situ SEM study of Li deposition and dissolution mechanism in bulk-type solid-state cell with Li$_2$S-P$_2$S$_5$ solid electrolyte”