Title: Phase- and morphology-controlled synthesis of M_mX_n (M=Sn, Ni; X=P, S) active materials by a hot soap technique and formation of solid-solid interfaces in all-solid-state batteries

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Phase- and morphology-controlled synthesis of $M_mX_n$ ($M = \text{Sn, Ni}; X = \text{P, S}$) active materials by a hot soap technique and formation of solid-solid interfaces in all-solid-state batteries

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Phase- and morphology-controlled synthesis of $M_mX_n$ ($M = \text{Sn, Ni}; X = \text{P, S}$) active materials by a hot soap technique and formation of solid-solid interfaces in all-solid-state batteries

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1. General introduction

Lithium-ion batteries are used as power sources for a wide range of portable devices because of their high operating voltage, high energy density, light weight, and longer cycle life [1]. Large-sized lithium-ion batteries with safe characteristics are presently in demand for application as power sources for plug-in hybrid vehicle (PHV) and battery electric vehicles (BHV). In commercialized lithium-ion batteries, there are fundamental safety concerns which are the risk of ignition and explosion because of using a flammable organic liquid electrolyte. Therefore, next generation lithium-ion batteries using solid electrolytes such as organic polymers and inorganic materials have been studied because these batteries are extremely safe, reliable, and free from electrolyte leakage [2-4]. Especially, all-solid-state lithium secondary batteries using inorganic solid electrolytes with high lithium-ion conductivities have been attracting much attention [3,4].

In inorganic solid electrolytes, there are two types of oxide-based and sulfide-based solid electrolytes. Much effort has been directed to develop the solid electrolytes with high lithium-ion conductivity [5-14]. It was reported that oxide-based solid electrolytes such as Perovskite-type Li_{0.34}La_{0.51}TiO_{2.94}, NASICON-type Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3, and Garnet-type Li_3La_3Zr_2O_{12} showed high lithium-ion conductivity of over 10^{-4} S cm^{-1} at room temperature [5-7]. The use of oxide-based solid electrolytes requires sintering process at high temperature (around 1000 °C) in order to reduce the resistance at grain boundaries. On the other hand, sulfide-based solid electrolytes such as glasses, crystals, and glass-ceramics are promising because of high lithium-ion conductivities at room temperature without the sintering process. Sulfide glasses in the systems Li_2S-SiS_2 and Li_2S-P_2S_5 prepared by the melt-quenching method are known as lithium-ion conductors with high conductivities of over 10^{-4} S cm^{-1} at room temperature [8-11]. Kanno et al. have found that the sulfide crystalline lithium superionic conductor, thio-LISICON (such as solid solutions in the system Li_4GeS_4-Li_3PS_4), exhibited high lithium-ion conductivities of 10^{-7} to 10^{-3} S cm^{-1} at room temperature [12]. Recently, they reported the preparation of Li_{10}GeP_2S_{12} solid electrolyte, which exhibited a quite high lithium-ion conductivity of over 10^{-2} S cm^{-1} at room temperature.
On the other hand, we have reported that the crystallization of Li$_2$S-P$_2$S$_5$ glasses prepared by a mechanical milling technique improved their conductivities [14]. Li$_2$S-P$_2$S$_5$ glass-ceramic electrolytes showed a high lithium-ion conductivity of $5 \times 10^{-3}$ S cm$^{-1}$ at room temperature [15].

We have reported the electrochemical performance of all-solid-state cells using the Li$_2$S-P$_2$S$_5$ glass-ceramic solid electrolytes [16-20]. For example, the all-solid-state cells using LiCoO$_2$ and Li$_4$Ti$_5$O$_{12}$ as an active material exhibited high capacities and excellent cycle performance during 500 and 700 cycles under the current density of 0.064 mA cm$^{-2}$ at room temperature [16]. For the commercialization of all-solid-state batteries, further improvement of the battery performance such as high energy density and high rate capability is required. In our research group, active materials with high capacity have been investigated for development of all-solid-state batteries [17-20].

Metal sulfides and phosphides have been tried to apply as active materials to lithium batteries using organic liquid electrolytes [21]. In our research group, it was reported that the all-solid-state cells using tin- and nickel-based active materials (SnS, Sn$_4$P$_3$, NiS, and NiP$_2$) exhibited the large capacity of about 600-1100 mAh g$^{-1}$ and good cycle performance [19,20,22-24]. The effective utilization of tin- and nickel-based active materials will contribute to the development of the all-solid-state cells with high capacity and high rate capability. We reported that the all-solid-state cell using SnS active materials showed the higher electrochemical performance than the cell using SnO active materials [22]. It was reported that the charge-discharge mechanism of the Li/SnS cell using a liquid electrolyte is the formation of metallic Sn at the first discharge process and subsequent generation of Li-Sn alloy [25].

$$\text{SnS} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Sn} + \text{Li}_2\text{S}$$
$$\text{Sn} + 4.4\text{Li}^+ + 4.4\text{e}^- \rightarrow \text{Li}_{4.4}\text{Sn}$$

In addition, Kim et al. reported that tin phosphide SnP$_{0.94}$ had good cycle performance and high reversible capacity in liquid electrolyte cells [26]. The SnP$_{0.94}$ electrode in the cells using a liquid electrolyte undergoes the lithium intercalation/deintercalation mechanism.

$$\text{SnP}_{0.94} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{SnP}_{0.94}$$
On the other hand, nickel-based materials such as NiS and NiP$_2$ have been studied as an active material with high capacity. NiS has a large theoretical capacity of 590 mAh g$^{-1}$. It was reported that the mechanism of the Li/NiS cell using a liquid electrolyte at the discharge process is the formation of Ni$_3$S$_2$ and Li$_2$S, and subsequent generation of metallic Ni and Li$_2$S [27].

$$3\text{NiS} + 2\text{Li}^+ + 2\text{e}^- \rightleftharpoons \text{Ni}_3\text{S}_2 + \text{Li}_2\text{S}$$

$$\text{Ni}_3\text{S}_2 + 4\text{Li}^+ + 4\text{e}^- \rightleftharpoons 3\text{Ni} + 2\text{Li}_2\text{S}$$

It was reported that NiP$_2$ had a relatively high capacity (1000-1300 mAh g$^{-1}$) and good cycle performance in a cell using a liquid electrolyte. Gillot et al. reported that the cell using NiP$_2$ underwent a conversion process which involves the change of NiP$_2$ to Ni and Li$_3$P after lithiation [28]. Lithium phosphide (Li$_3$P) shows high lithium-ion conductivity of over $10^{-4}$ S cm$^{-1}$ [29].

$$\text{NiP}_2 + 6\text{Li}^+ + 6\text{e}^- \rightleftharpoons \text{Ni} + 2\text{Li}_3\text{P}$$

Several papers reported that the morphology and size of the particles as an active material affected the electrochemical performance of the cells using an organic liquid electrolyte [30-35]. The morphology and size of active materials are important in order to form the favorable “solid-solid interfaces” in all-solid-state batteries.

In bulk-type all-solid-state batteries, a composite positive or negative electrode consisting of three components of active materials, solid electrolytes (lithium-ion conduction path), and conductive additives (electron conduction path) is commonly used (Figure 1-1). Electrochemical reactions proceed at the solid-solid interfaces and are affected by the states of the interfaces in the composite electrode. In our research group, several papers about the construction of solid-solid interfaces in the composite electrodes have been reported, and are listed here:

(a) Use of carbon fibers as a conductive additive [36]
(b) Preparation of composite electrodes by various mechanical milling techniques [19,20,37]
(c) Preparation of composite electrodes by using the softening behavior of Li$_2$S-P$_2$S$_5$ glass electrolytes [38]
(d) Deposition of Li$_2$S-P$_2$S$_5$ solid electrolyte thin films on electrode particles by pulsed laser
Fig. 1-1 Schematic illustration of all-solid-state batteries.
deposition (PLD) method [39,40]

In addition, we reported that monodispersed $\alpha$-Fe$_2$O$_3$ particles of various sizes were synthesized by a solution process using a NaOH aqueous solution [41]. The all-solid-state cell with a submicron $\alpha$-Fe$_2$O$_3$ electrode exhibited higher capacity than that of the cell using a micron-size $\alpha$-Fe$_2$O$_3$ electrode. In order to fabricate the all-solid-state batteries with both high capacity and high rate capability, development of nano-sized active materials with high capacity is also very important. It is expected that the solid-solid interfaces in an electrode layer will increase with decreasing the particle size of monodispersed active materials. In general, nano-sized active materials can decrease the diffusion length of lithium ions in insertion/extraction process which remarkably improves rate performance of electrode materials. However, there are also several disadvantages for use of nano-sized active materials, for example, synthetic routes for nanoparticles are more complex compared to conventional solid state reactions.

There are two different approaches to synthesize nanoparticles: the “top-down” approach, which utilizes physical methods, and the “bottom-up” approach, which employs solution-phase colloidal chemistry. The synthesis of uniform-sized nanoparticles and their size control is very difficult to achieve by using the physical synthetic methods such as mechanical milling. In contrast, colloidal chemical synthetic methods such as the sol-gel method, hydrothermal method, and solvothermal method can be used to synthesize uniform nanoparticles with controlled particle size. Furthermore, various-shaped nanoparticles including nanoplates, nanorods, and nanowires can be synthesized by varying reaction conditions.

Nanomaterials prepared by a solution process using high-boiling solvents as a surfactant have been attracting attention [42-44]; it is called “hot soap technique”. Figure 1-2 shows the schematic illustration of hot soap technique. High-boiling solvents such as long-chain organic molecules are often used as reaction media. Long-chain organic molecules as a surfactant are important in this technique. To protect the nanoparticles from growth or agglomeration, the particle surfaces must be saturated immediately after nucleation by steric stabilization such as an adsorption of long-chain organic molecules. Particle nucleation and
Fig. 1-2 Schematic illustration of a hot soap technique for the synthesis of nanoparticles [44].
growth are controlled by the long-chain organic molecules as a surfactant. Many studies on the size- or morphology-controlled synthesis of various compounds have been reported (Table 1-1 and Figure 1-3) [45-59]. For example, it was reported that various metal phosphides such as MnP, Co₃P, FeP, and Ni₂P, and sulfides such as Cu₂S, ZnS, MnS, and PbS were synthesized using this process [50,51], which is a facile route to prepare nanoparticles having uniform size with various morphologies by varying reaction conditions [60-63]. In addition, Lee et al. reported that copper sulfide nanoparticles were grown on carbon nanotubes using a high-boiling solvent such as oleylamine [64], which is widely used as a coordinating solvent with a high boiling point. Pang et al. also reported that composites including metal oxide and graphene were prepared by using oleylamine as a surfactant [65]. The hot soap technique is effective in both morphology-controlled synthesis of active materials and construction of favorable solid-solid interfaces between active materials and conductive additives.

In addition to the synthesis of the morphology-controlled active materials with high capacity, formation of intimate electrode-electrolyte solid-solid interfaces in the bulk-type all-solid-state batteries is very important to realize high performance of all-solid-state batteries. In order to form intimate electrode-electrolyte interfaces, we have reported the coating of Li₂S-P₂S₅ solid electrolyte on LiCoO₂ particles (SE-coated LiCoO₂) by the pulsed laser deposition method [40]. Charge-discharge capacities of all-solid-state cells using the SE-coated LiCoO₂ particles were higher than those of the cells with uncoated LiCoO₂. Preparation of solid electrolytes via liquid phase instead of gas phase must be a very facile and cost-effective process to form good electrode-electrolyte interfaces. Recently, preparation of a Li₃.₃₅Ge₀.₂₅P₀.₇₅S₄ (LGPS) thin film by a solution process using a hydrazine-based solvent has been reported [66]. LGPS crystals synthesized by a solid state reaction were dissolved in the hydrazine-based solvent, and a solution-processed LGPS film was obtained after removing the solvent by heat treatment of the solution. However, hydrazine has some toxicity. In our research group, it was observed that Li₂S-P₂S₅ glass solid electrolyte powders were not dissolved by using several organic solvents such as acetonitrile, pyridine, tetrahydrofuran, and N,N-dimethylformamide. N-methylformamide
<table>
<thead>
<tr>
<th>Materials</th>
<th>Precursors</th>
<th>Surfactants</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal (Fe)</td>
<td>Fe(CO)$_5$</td>
<td>Trioctylphosphine</td>
<td>[45]</td>
</tr>
<tr>
<td>Alloy (FePt)</td>
<td>Fe(OCH$_2$CH$_3$)$_3$</td>
<td>Oleylamine</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>Pt(C$_2$H$_2$O$_2$)$_2$</td>
<td>Oleic acid</td>
<td></td>
</tr>
<tr>
<td>Metal nitride (Ta$_2$N$_4$)</td>
<td>TaCl$_5$</td>
<td>Trioctylphosphine</td>
<td>[47]</td>
</tr>
<tr>
<td>Metal oxide</td>
<td>$M$(NO$_3$)$_x$</td>
<td>Octadecylamine</td>
<td>[48]</td>
</tr>
<tr>
<td>(Mn$_3$O$_4$, NiO, ZnO, CeO$_2$, CoO)</td>
<td>($M = Mn$, Ni, Zn, Ce, Co)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkaline earth metal fluoride</td>
<td>M(CF$_3$COO)$_2$</td>
<td>Oleylamine</td>
<td>[49]</td>
</tr>
<tr>
<td>(MgF$_2$, CaF$_2$, SrF$_2$)</td>
<td>($M = Mg$, Ca, Sr)</td>
<td>Oleic acid</td>
<td></td>
</tr>
<tr>
<td>Metal phosphide</td>
<td>M(CO)$_3$ ($M = Mn$, Fe)</td>
<td>Trioctylphosphine oxide</td>
<td>[50]</td>
</tr>
<tr>
<td>(MnP, Co$_2$P, FeP, Ni$_3$P)</td>
<td>M(C$_2$H$_2$O$_2$)$_2$ ($M = Co$, Ni)</td>
<td>Hexadecylamine</td>
<td></td>
</tr>
<tr>
<td>Metal sulfide</td>
<td>MCl$_x$nH$_2$O ($M = Cu$, Cd, Zn, Mn)</td>
<td>Oleylamine</td>
<td>[51]</td>
</tr>
<tr>
<td>(Cu$_2$S, CdS, ZnS, MnS, PbS)</td>
<td>Pb(NO$_3$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxysulfide (Eu$_2$O$_2$S)</td>
<td>Eu(C$_2$H$_2$N$_2$)$_3$ (S$_2$CN(CH$_2$CH$_3$)$_2$)$_3$</td>
<td>Oleylamine</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Trisilane (Si$_3$H$_6$)</td>
<td>Oleic acid</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td>Trioctylphosphine</td>
<td>[53]</td>
</tr>
<tr>
<td>LiMnPO$_4$</td>
<td>LiOH·H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn(NO$_3$)$_2$·6H$_2$O</td>
<td>Oleylamine</td>
<td>[54]</td>
</tr>
<tr>
<td>NaFeF$_3$</td>
<td>NaOCOCOF$_3$</td>
<td></td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>Fe powder</td>
<td>Oleylamine</td>
<td></td>
</tr>
<tr>
<td>Yb$^{3+}$, Er$^{3+}$-doped NaYF$_4$</td>
<td>Na$_2$CO$_3$, Y$_2$(CO$_3$)$_3$</td>
<td></td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>Yb$_2$(CO$_3$)$_3$, Er$_2$(CO$_3$)$_3$</td>
<td></td>
<td></td>
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</tbody>
</table>
Fig. 1-3 TEM images of (a) Ag nanocubes [57], (b) ZnO triangular nanoplates [48], (c) SnS$_2$ hexagonal nanoplates [58], and (d) CoP nanowires [59] prepared by a hot soap technique.
(NMF) is known to dissolve some materials containing $\text{PS}_4^{3-}$ groups or $\text{P}_2\text{S}_6^{4-}$ groups [67,68], and it has lower toxicity than hydrazine. On the other hand, Liu et al. reported the synthesis of crystalline $\text{Li}_3\text{PS}_4$ solid electrolyte by heat treatment (at 140 °C under vacuum) of $\text{Li}_3\text{PS}_4\cdot3\text{THF}$ (THF: tetrahydrofuran) which was prepared by the reaction of $\text{Li}_2\text{S}$ and $\text{P}_2\text{S}_5$ in THF at room temperature [69]. Conventionally, $\text{Li}_3\text{PS}_4$ is synthesized by the solid state reaction of $\text{Li}_2\text{S}$ and $\text{P}_2\text{S}_5$ at 500 °C [70]. The Use of NMF may contribute to the low-temperature synthesis of $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid electrolyte powders via precursor solution including $\text{Li}_2\text{S}$, $\text{P}_2\text{S}_5$, and NMF, whereas $\text{Li}_3\text{PS}_4$ solid electrolyte powders are synthesized via thermal decomposition of powders of $\text{Li}_3\text{PS}_4\cdot3\text{THF}$ complex by using THF. Homogeneous solid-liquid interfaces are formed among active materials, conductive additives, and precursor solutions of solid electrolytes. Simple preparation of composite electrodes including active materials, conductive additives, and solid electrolytes can be achieved by removing solvents. Nanocomposites, in which nano-sized active materials with less suppression of aggregation have contacts with solid electrolytes and conductive additives, are preferable as composite electrodes for high-performance all-solid-state batteries to form favorable lithium-ion and electron conduction paths.

The objectives of the present study focus on morphology-controlled synthesis of high-capacity active materials suitable for all-solid-state batteries and design of composite electrode’s morphology for development of high-performance all-solid-state batteries. Tin- and nickel-based active materials were synthesized by a hot soap technique, and electrochemical performance of the all-solid-state cells using the morphology-controlled active materials was investigated. Figure 1-4 shows the schematic illustration of our proposed composite electrode. The use of carbon fiber would make it possible to form a continuous electron conducting paths in the composite electrodes, and active material with uniform size would contact intimately with both carbon fiber and solid electrolyte. Nickel sulfide (NiS) nanoparticles and vapor grown carbon fiber (VGCF, Showa Denko) were respectively selected as active materials and conductive additives. NiS-VGCF composites were prepared by hot soap technique to form favorable electron conduction paths to an active material. In addition, $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid electrolyte powders were prepared via a liquid-phase
Fig. 1-4 Schematic illustration of our proposed composite electrode.
such as $N$-methylformamide. The composite electrodes with favorable solid-solid interfaces among NiS nanoparticles, VGCF, and solid electrolytes were prepared by removing the $N$-methylformamide from the mixture of NiS-VGCF composites and precursor solutions of solid electrolytes. All-solid-state cells using the obtained composite electrodes were fabricated, and the effects of electrode-electrolyte solid-solid interfaces in the composite electrode on the electrochemical properties were investigated in order to develop the all-solid-state batteries with high capacity and high rate capability.

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**

In this chapter, morphology-controlled metal phosphides and sulfides as an active material were synthesized by a hot soap technique. $\text{SnP}_{0.94}, \text{NiP}_2$, SnS, and NiS are selected as active materials with high capacity. $\text{SnP}_{0.94}$ and $\text{NiP}_2$ were synthesized by thermal decomposition of metal salts and trioctylphosphine as a phosphorus source. On the other hand, SnS and NiS were synthesized by thermal decomposition of metal salts and 1-dodecanethiol as a sulfur source. In the hot soap technique, it is known that understanding of formation mechanism is very important for morphology-controlled synthesis of metal phosphides and sulfides. The formation mechanism and morphology control of these materials were also investigated by changing reaction conditions. The effects of the crystal phase and morphology on the electrochemical performance of all-solid-state cells were discussed.

**Chapter 3**

The purpose of this chapter is to prepare newly designed nanocomposites (Figure 1-4) for use of composite electrodes by combination of hot soap technique and pulsed laser deposition method. NiS nanoparticles and vapor grown carbon fiber (VGCF, Showa Denko) were respectively selected as active materials and conductive additives. Firstly, in order to form
electron conduction paths for NiS active materials, NiS-VGCF composites were synthesized by a hot soap technique. Next, composite materials including NiS-VGCF composites and sulfide-based solid electrolytes were prepared by deposition of the Li$_2$S-$P_2$S$_5$ solid electrolyte thin films onto NiS-VGCF composites using pulsed laser deposition in order to form favorable lithium-ion conduction paths to the NiS active materials. All-solid-state cells using the obtained nanocomposites were fabricated, and then the effects on the electrochemical performance by forming intimate electron and lithium-ion conduction paths to the NiS nanoparticles were investigated.

**Chapter 4**

This chapter describes the preparation of sulfide-based solid electrolytes and composite electrodes via liquid phase. The sulfide-based solid electrolyte powders were reprecipitated via liquid phase. Powders of Li$_2$S-$P_2$S$_5$ glass solid electrolytes originally prepared by mechanical milling were dissolved into N-methylformamide (NMF) and a homogeneous solution was obtained. As another approach, precursor solution of sulfide-based solid electrolytes was prepared by the reaction of Li$_2$S powders, $P_2$S$_5$ powders, and NMF. The NMF was removed under vacuum to obtain the precipitates, and ionic conductivity of the powders obtained from the NMF solution was measured by the AC impedance measurement. In addition, sulfide-based solid electrolyte was coated on LiCoO$_2$ particles and NiS-VGCF composites by using the NMF solution including precursor of sulfide-based solid electrolytes to form favorable solid-solid interfaces in composite electrodes. The obtained materials were applied to all-solid-state cells.

**Chapter 5**

This chapter summarizes all the conclusions in this thesis.
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196, 6735-6741.


4269-4273.


2. Synthesis of active materials by a hot soap technique for application to all-solid-state batteries

2.1. Introduction

Nanomaterials have received much attention as an active material in lithium ion batteries [1]. In general, nano-sized active materials can decrease the diffusion length of lithium ion in the insertion/extraction process, which improves the rate performance in the lithium ion batteries. Nanomaterials prepared by a solution process using high-boiling solvents as a surfactant have been attracting attention [2,3]; it is called “hot soap technique”. High-boiling solvents such as long-chain organic molecules are often used as reaction media. Long-chain organic molecules as a surfactant are important in this technique. Particle nucleation and growth are controlled by the long-chain organic molecules as a surfactant. It was reported that various metal phosphides such as MnP, Co$_2$P, FeP, and Ni$_2$P, and sulfides such as Cu$_2$S, ZnS, MnS, and PbS were synthesized using high-boiling solvents [4,5]. A hot soap technique makes it possible to synthesize nanoparticles with uniform size and various morphologies by varying reaction conditions. On the other hand, metal phosphides and sulfides have been applied as active materials with high capacity to lithium-ion batteries using organic liquid electrolytes or inorganic solid electrolytes [6-10]. In our research group, it was reported that the all-solid-state cells using tin- and nickel-based active materials (SnS, Sn$_4$P$_3$, NiS, and NiP$_2$) exhibited the large capacity of about 600-1100 mAh g$^{-1}$ and good cycle performance [7,11-14].

In bulk-type all-solid-state batteries, a composite electrode consisting of three components of active materials, solid electrolytes (lithium ion conduction path), and conductive additives (electron conduction path) is commonly used as a positive or negative electrode. Electrochemical reactions proceed at the solid-solid interfaces, and are affected by the states of the interfaces in the composite electrode. It is expected that the solid-solid interface in the composite electrode will increase with decreasing the particle size of monodispersed active materials. We reported that monodispersed α-Fe$_2$O$_3$ particles of various sizes were synthesized by a solution process using a NaOH aqueous solution [15]. The all-solid-state
cell with a submicron $\alpha$-Fe$_2$O$_3$ electrode exhibited higher capacity than that of the cell using a micron-size $\alpha$-Fe$_2$O$_3$ electrode. The synthesis of tin- and nickel-based active materials with uniform size and various morphologies will contribute to the development of the all-solid-state cells with high capacity and high rate capability.

In this chapter, metal phosphides and sulfides as an active material were synthesized by a hot soap technique. Table 2-1 shows the high-boiling solvents used in this chapter. SnP$_{0.94}$, NiP$_2$, SnS, and NiS are selected as active materials with high capacity. SnP$_{0.94}$ and NiP$_2$ were synthesized by thermal decomposition of metal salts and trioctylphosphine as a phosphorus source. On the other hand, SnS and NiS were synthesized by thermal decomposition of metal salts and 1-dodecanethiol as a sulfur source. In the hot soap technique, understanding of formation mechanism is very important for morphology-controlled synthesis. The formation mechanism and morphology control of these materials were also investigated by changing reaction conditions. The effects of the crystal phase and morphology on the electrochemical performance of all-solid-state cells were discussed.

2.2. Experimental

2.2.1. Synthesis of SnP$_{0.94}$ active materials by a hot soap technique

Kim et al. reported the synthesis of tin phosphide (SnP$_{0.94}$) by using trioctylphosphine as a phosphorus source and trioctylphosphine oxide as a coordinating solvent [16]. Tin acetate (0.36 g, 1.5×10$^{-3}$ mol) was mixed with trioctylphosphine (TOP; 10 ml, 2.2×10$^{-2}$ mol) and trioctylphosphine oxide (TOPO; 2.5 g, 6.5×10$^{-3}$ mol) in a 200 mL four-necked flask. In order to investigate the formation mechanism of tin phosphide, the mixture in the flask was heated to 360 °C and refluxed for 3 min or 1 h in an Ar atmosphere. After heating, the mixture was cooled to room temperature and was subsequently washed with hexane and ethanol. The resultant particles were isolated by centrifuging the mixture and then removing the supernatants.
Table 2-1. High-boiling solvents used in this chapter.

<table>
<thead>
<tr>
<th>High-boiling solvent</th>
<th>Boiling point</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{CH}_3\text{(CH}_2\text{)}_7\text{]}_3\text{P}) ((\text{Trioctylphosphine, TOP}))</td>
<td>284-291 °C / 50 mmHg</td>
<td>Phosphorus source Coordinating solvent</td>
</tr>
<tr>
<td>(\text{CH}_3\text{(CH}<em>2\text{)}</em>{11}\text{SH}) ((\text{1-Dodecanethiol, DT}))</td>
<td>266-283 °C</td>
<td>Sulfur source Coordinating solvent</td>
</tr>
<tr>
<td>([\text{CH}_3\text{(CH}_2\text{)}_7\text{]}_3\text{PO}) ((\text{Trioctylphosphine oxide, TOPO}))</td>
<td>201-202 °C / 2 mmHg</td>
<td>Coordinating solvent</td>
</tr>
<tr>
<td>(\text{CH}_3\text{(CH}_2\text{)}_7\text{CH}=\text{CH(CH}_2\text{)}_7\text{CH}_2\text{NH}_2) ((\text{Oleylamine, OAm}))</td>
<td>348-350 °C</td>
<td>Coordinating solvent</td>
</tr>
<tr>
<td>([\text{CH}_3\text{(CH}_2\text{)}_7\text{]}_3\text{N}) ((\text{Trioctylamine, TOA}))</td>
<td>365-367 °C</td>
<td>Coordinating solvent</td>
</tr>
<tr>
<td>(\text{CH}_3\text{(CH}<em>2\text{)}</em>{15}\text{CH}=\text{CH}_2) ((\text{1-Octadecene, ODE}))</td>
<td>179 °C / 15 mmHg</td>
<td>Noncoordinating solvent</td>
</tr>
<tr>
<td>(\text{CH}_3\text{(CH}<em>2\text{)}</em>{20}\text{CH}_3) ((\text{Docosane, DCS}))</td>
<td>369 °C</td>
<td>Noncoordinating solvent</td>
</tr>
</tbody>
</table>
2.2.2. Synthesis of NiP\textsubscript{2} active materials by a hot soap technique

Nickel(II) acetylacetonate (Ni(acac)\textsubscript{2}; 0.385 g, 1.5×10\textsuperscript{-3} mol) was mixed with trioctylphosphine (TOP; 10 ml, 2.2×10\textsuperscript{-2} mol) as a phosphorus source and trioctylphosphine oxide (TOPO; 2.5 g, 6.5×10\textsuperscript{-3} mol) as a coordinating solvent in a 200 mL four-necked flask. The mixture in the flask was heated to 360 °C and refluxed for 1 h in an Ar atmosphere. This is referred to as the “original condition for nickel phosphide” throughout. After heating, the mixture was cooled to room temperature and was subsequently washed with hexane and ethanol. The resultant particles were isolated by centrifuging the mixture and then removing the supernatants. The obtained powder was dried in a vacuum oven at 120 °C for 6 h. The following four parameters were investigated for control of crystal phases of nickel phosphide particles: the use of docosane (DCS; CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{20}CH\textsubscript{3}, 2.5 g) as a noncoordinating solvent, the amount of TOP, the reaction temperature, and the type of nickel precursor used, such as nickel acetylacetonate dihydrate (Ni(acac)\textsubscript{2}-2H\textsubscript{2}O) and nickel acetate tetrahydrate (Ni(Ac)\textsubscript{2}-4H\textsubscript{2}O).

2.2.3. Synthesis of SnS active materials by a hot soap technique

Tin acetate (0.36 g, 1.5×10\textsuperscript{-3} mol) was mixed with 1-dodecanethiol (DT; 2 mL, 8.3×10\textsuperscript{-3} mol) as a sulfur source, trioctylphosphine (TOP; 10 ml, 2.2×10\textsuperscript{-2} mol) as a coordinating solvent, and 1-octadecene (ODE; 10 mL, 3.0×10\textsuperscript{-2} mol) as a noncoordinating solvent in a 200 mL four-necked flask. This condition is called “original condition for tin sulfide”. The mixture in the flask was heated at 280 °C for 2 h in an Ar atmosphere. After heating, the mixture was cooled to room temperature and was subsequently washed with hexane and ethanol. The resultant particles were isolated by centrifuging the mixture and then removing the supernatants. In order to control morphology of the obtained tin sulfide particles, we investigated the kind of coordinating solvents, the concentration of tin acetate, reaction temperatures, and the amounts of trioctylphosphine (TOP) or 1-dodecanethiol (DT). We chose not only trioctylphosphine (TOP) but also oleylamine (OAm, 10mL, 3.0×10\textsuperscript{-2} mol) as a coordinating solvent.
2.2.4. Synthesis of NiS active materials by a hot soap technique

Nickel(II) acetylacetonate (Ni(acac)$_2$; 0.385 g, 1.5×10$^{-3}$ mol) was mixed with 1-dodecanethiol (DT; 2 ml, 8.3×10$^{-3}$ mol) as a sulfur source in oleylamine (OAm; 10 ml, 3.0×10$^{-2}$ mol) or 1-octadecene (ODE; 10 ml, 3.0×10$^{-2}$ mol) in a 200 mL four-necked flask. OAm was used as a coordinating solvent, whereas ODE was used as a noncoordinating solvent. In order to investigate the formation mechanism of nickel sulfide, the mixture was heated in a flask to several temperatures (180, 240, or 280 °C), and was subsequently kept for 0, 5, or 24 h under stirring in an Ar atmosphere. After heating, the mixture was cooled to room temperature and was subsequently washed with hexane and ethanol. The resultant particles were isolated by centrifuging the mixture and then removing the supernatants.

2.2.5. Cell construction

Laboratory-scale solid-state cells were fabricated as follows. The 80Li$_2$S·19P$_2$S$_5$·1P$_2$O$_5$ (mol %) or 80Li$_2$S·20P$_2$S$_5$ (mol %) glass-ceramic solid electrolyte powders were prepared by mechanical milling and subsequent heat treatment. The prepared electrolyte exhibited a wide electrochemical window and high ionic conductivity at room temperature [17,18]. A composite electrode as a working electrode was prepared by hand-grinding of a mixture of the obtained active material (5.7 mg), the glass-ceramic electrolyte (8.5 mg), and vapor grown carbon fiber (VGCF) as a conductive additive (0.8 mg).

Two-electrode cells were fabricated using the composite electrode, the glass-ceramic electrolyte, and a Li-In alloy as a counter electrode. The composite electrode and solid electrolyte were placed in a polycarbonate tube (10 mm diameter) and pressed together under 360 MPa at room temperature. The Li-In alloy was placed on the surface of the solid electrolyte side of the bilayer pellet. Then pressure of 120 MPa was applied to obtain a three-layered pellet. The three-layered pellet was finally sandwiched with two stainless-steel disks as current collectors. All preparation processes of the cells were conducted in a dry Ar-filled glove box.
2.2.6. Characterization

X-ray diffraction (XRD; UltimaIV; Rigaku) measurements were performed using Cu Kα radiation to identify the crystalline phases. The morphology of the obtained particles was investigated using transmission electron microscopy (TEM; JEM-2000FX; JEOL). The thermal decomposition of the obtained intermediates for synthesis of nickel sulfide was characterized by differential thermal analysis and thermogravimetry (DTA-TG; Thermo Plus 2 TG-8110; Rigaku). Nuclear magnetic resonance (NMR) and fourier transform infrared (FT-IR) spectra of the obtained intermediates for synthesis of nickel sulfide were measured with a NMR apparatus (JNM-ECX 400; JEOL) and FT-IR spectrophotometer (Spectrum GX; Perkin Elmer). The morphology of the surface of a pelletized composite electrode prepared using the obtained tin sulfide particles was observed using scanning electron microscopy (SEM; JSM-6610A; JEOL) coupled with an energy dispersive X-ray spectrometer (EDX; JED-2300; JEOL). Electrochemical tests were conducted under a constant current density of 0.13 and 1.3 mA cm\(^{-2}\) at 25 °C in an Ar atmosphere using a charge-discharge measurement device (BTS-2004; Nagano Co.).

2.3. Results and discussion

2.3.1. Synthesis of SnP\(_{0.94}\) active materials by a hot soap technique and their application to all-solid-state batteries

Figure 2-1and Figure 2-2 respectively show the XRD patterns and TEM images of the samples prepared by refluxing at 360 °C for 3 min and 1 h. The mixture of Sn and SnP\(_{0.94}\) was obtained by refluxing for 3 min (Figure 2-1 (a)), whereas SnP\(_{0.94}\) is prepared by refluxing for 1 h (Figure 2-1 (b)). In addition, the morphology of the obtained particles changed from spherical particles (Figure 2-2 (a)) to teardrop-shaped particles with the size of 500 nm (Figure 2-2 (b)). These results suggest that spherical Sn particles is formed first by thermal decomposition of tin acetate in a mixed solvent of TOP and TOPO, and then teardrop-shaped SnP\(_{0.94}\) particles are prepared by diffusion of phosphorus derived from TOP into Sn.

The teardrop-shaped SnP\(_{0.94}\) particles with the size of 500 nm were applied to the all-solid-state cell. SnP\(_{0.94}\) active materials have not been investigated in all-solid-state
Figure 2-1 XRD patterns of the samples prepared by refluxing at 360 °C for (a) 3 min and (b) 1 h.
Figure 2-2 TEM images of the samples prepared by refluxing at 360 °C for (a) 3 min and (b) 1 h.
Figure 2-3 (a) Charge-discharge curves and (b) cycle performance of the all-solid-state cell Li-In/\(80\text{Li}_2\text{S} \cdot 19\text{P}_2\text{S}_5 \cdot 1\text{P}_2\text{O}_5/\text{SnP}_{0.84}\) under a constant current density of 0.13 mA cm\(^{-2}\) at 25 °C.
batteries. Figure 2-3 (a) and (b) respectively show the initial charge-discharge curve and cycle performance of the all-solid-state cell Li-In/80Li$_2$S·19P$_2$S$_5$·1P$_2$O$_5$/SnP$_{0.94}$ under a constant current density of 0.13 mA cm$^{-2}$ at 25 °C. The cutoff voltages were -0.6 and 1.9 V (vs. Li-In). Li-In alloy was used as a counter electrode because Li-In alloy exhibits a stable potential plateau at 0.62 V vs. Li$^+$/Li, as observed in all-solid-state cells with sulfide electrolytes. In Figure 2-3 (a), the right-side ordinate axis shows the electrode potential vs. Li, as calculated based on the potential difference between Li-In and Li electrodes (0.62 V). In addition, the obtained capacity was normalized by the weight of SnP$_{0.94}$ in the composite electrode. The cell showed the initial discharge capacity of about 1000 mAh g$^{-1}$ at 1.3 mA cm$^{-2}$ (corresponding to ca. 177 mA g$^{-1}$), and retained a discharge capacity of 620 mAh g$^{-1}$ after 10 cycles. It was reported that the cell using an organic liquid electrolyte exhibited the initial discharge capacity of 850 mAh g$^{-1}$ at the current density of 120 mA g$^{-1}$ [16]. The all-solid-state cell using submicron SnP$_{0.94}$ particles exhibits higher capacity than the cell with an organic liquid electrolyte even at a higher current density. These results suggest that the all-solid-state cell using metal phosphide particles prepared by a hot soap technique show the good electrochemical performance.

2.3.2. Synthesis of NiP$_2$ active materials by a hot soap technique and their application to all-solid-state batteries

Figure 2-4 shows the XRD patterns of the samples prepared using various parameters. Figure 2-4 (a) shows the XRD pattern of the sample prepared under the “original condition for nickel phosphide”. The sample was identified as Ni$_3$P$_4$ (JCPDS #018-0883). The effect of the reaction conditions on the crystal phase of the obtained nickel phosphide particles was investigated. DCS was used as a noncoordinating solvent, which has no effect on the diffusion of phosphorus derived from TOP to nickel atoms in Ni(acac)$_2$. Wang et al. reported that the phase control of cobalt phosphide was achieved by changing the ratio of metal to TOP (phosphorus source) and the reaction time [19]. In the present study, the amount of TOP was increased from 10 (2.2×10$^{-2}$ mol) to 20 mL (4.4×10$^{-2}$ mol) and the reaction time was increased from 1 to 5 h. Figure 2-4 (b) and (c) respectively shows the
Figure 2-4 XRD patterns of the samples prepared using (a) the “original condition for nickel phosphide” (reflux with TOPO at 360 °C for 1 h), (b) DCS instead of TOPO, (c) changing the amount of TOP or (d) refluxing at 360 °C for 5 h.
XRD patterns of the samples prepared using DCS as a noncoordinating solvent and with an increased amount of TOP. The crystal phase of both samples was still Ni$_5$P$_4$. The sample obtained by heating for 5 h (Figure 2-4 (d)) was a mixture of Ni$_5$P$_4$ and NiP$_2$ (JCPDS #021-0590), which suggests that Ni$_5$P$_4$ particles are generated first by thermal decomposition of Ni(acac)$_2$ in TOP, and then NiP$_2$ particles are formed by further diffusion of phosphorus derived from TOP into Ni$_5$P$_4$.

Figure 2-4 shows the XRD patterns of the samples prepared by changing the nickel precursors. Figure 2-4 (a) and (b) respectively shows the XRD patterns of samples prepared by refluxing Ni(acac)$_2$ and Ni(acac)$_2$·2H$_2$O in TOPO at 360 °C for 5 h. Both samples were a mixture of Ni$_5$P$_4$ and NiP$_2$. The relative peak intensity of NiP$_2$ in the sample prepared using Ni(acac)$_2$·2H$_2$O was stronger than that prepared using Ni(acac)$_2$. In contrast, NiP$_2$ was obtained as a single phase using Ni(Ac)$_2$·4H$_2$O, as shown in Figure 2-4 (c). In the crystal structure of Ni(Ac)$_2$·4H$_2$O, nickel atoms are surrounded by four water molecules and two oxygen atoms which belong to two different acetate groups [20,21]. Silva et al. reported that cobalt nanoparticles were synthesized using acetylene-bridged dicobalt hexacarbonyl (starting material) and TOP (surfactant); the lone pair of the phosphorus atom in TOP could easily coordinate to cobalt atoms in acetylene-bridged dicobalt hexacarbonyl [22]. In our case, TOP molecules as a phosphorus source could possibly substitute for water molecules in the structure of Ni(Ac)$_2$·4H$_2$O, and thus Ni(Ac)$_2$·4H$_2$O could promote diffusion of phosphorus derived from TOP to nickel atoms (Figure 2-6).

Figure 2-7 shows the TEM images of the sample prepared by the “original condition for nickel phosphide” and by changing the nickel precursor. The crystal phases of the prepared samples were identified by XRD measurements as shown in Figure 2-4 and Figure 2-5. Spherical Ni$_5$P$_4$ particles with diameters of 500 nm were obtained under the “original condition for nickel phosphide” (Figure 2-4 (a) and Figure 2-7 (a)). The particle size of the mixture of Ni$_5$P$_4$ and NiP$_2$ prepared using Ni(acac)$_2$ and heating for 5 h (Figure 2-5 (a) and Figure 2-7 (b)) was not different from that prepared under the “original condition for nickel phosphide”. However, the morphologies of the mixture of Ni$_5$P$_4$ and NiP$_2$ prepared using Ni(acac)$_2$·2H$_2$O (Figure 2-5 (b) and Figure 2-7 (c)) and the NiP$_2$ particles prepared using
Figure 2-5 XRD patterns of the samples prepared by refluxing (a) Ni(acac)$_2$, (b) Ni(acac)$_2$·2H$_2$O, or (c) Ni(Ac)$_2$·4H$_2$O in TOPO at 360 °C for 5 h.
Figure 2-6 Schematic illustration of our proposed formation mechanism of NiP$_2$ prepared by using Ni(Ac)$_2$·4H$_2$O and TOP.
Figure 2-7 TEM images of the samples prepared by refluxing (a, b) Ni(acac)$_2$, (c) Ni(acac)$_2$·2H$_2$O, or (d) Ni(Ac)$_2$·4H$_2$O in TOPO at 360 °C. The reaction time was 1 h for (a) and 5 h for (b, c, and d).
Ni(Ac)$_2$·4H$_2$O (Figure 2-5 (c) and Figure 2-7 (d)) were not uniform, and their particle sizes were in the range of 200-500 nm.

The 200-500 nm NiP$_2$ particles prepared using Ni(Ac)$_2$·4H$_2$O were used to prepare the composite electrode for the all-solid-state cell. Figure 2-8 (a) shows charge-discharge curves of the all-solid-state cell Li-In/80Li$_2$S·20P$_2$S$_5$/NiP$_2$. The cutoff voltages were -0.6 and 0.9 V (vs. Li-In). The obtained capacity was normalized by the weight of NiP$_2$ in the composite electrode. The cell showed an initial discharge capacity of 1100 mAh g$^{-1}$ in the voltage range from 0 to 1.5 V (vs Li) under a constant current density of 0.13 mA cm$^{-2}$ at 25 °C. We reported that the all-solid-state cell using NiP$_2$ prepared by a mechanical milling technique underwent a conversion process, as also reported in the cells using liquid electrolytes [7]. This conversion process involves the change of NiP$_2$ to Ni and Li$_3$P after lithiation [23]:

$$\text{NiP}_2 + 6\text{Li}^+ + 6e^- \leftrightarrow \text{Ni} + 2\text{Li}_3\text{P}$$

The charge-discharge profiles of the all-solid-state cell shown in Figure 2-8 (a) are similar to those for NiP$_2$ prepared by mechanical milling. Therefore, 200-500 nm NiP$_2$ particles prepared by the solution process would also undergo the conversion process. Figure 2-8 (b) shows the cycle performance for all-solid-state cells using NiP$_2$ or Ni$_5$P$_4$ particles under a constant current density of 0.13 mA cm$^{-2}$ at 25 °C. Ni$_5$P$_4$ particles prepared under the “original condition for nickel phosphide” were used as the active material. The cell using NiP$_2$ particles exhibited a larger capacity than the cell using Ni$_5$P$_4$ particles over 10 cycles. It was reported that an all-solid-state cell using micrometer-size NiP$_2$ particles exhibited an initial discharge capacity of 1100 mAh g$^{-1}$ at a current density of 0.064 mA cm$^{-2}$ [7]. In this study, the all-solid-state cell with 200-500 nm NiP$_2$ particles exhibited a capacity of 1100 mAh g$^{-1}$, even at a higher current density of 0.13 mA cm$^{-2}$. The high capacity for the all-solid-state cell using submicrometer-size NiP$_2$ particles is attributable to the decrease in particle size. The cell using submicrometer-size NiP$_2$ particles retained a discharge capacity of 750 mAh g$^{-1}$ and a charge-discharge efficiency of approximately 100% after 10 cycles, which suggests that submicrometer-size NiP$_2$ particles prepared by a hot soap technique are preferable as an active material for all-solid-state batteries.
Figure 2-8 (a) Charge–discharge curves of the all-solid-state cell Li-In/80Li$_2$S-20P$_2$S$_5$/NiP$_2$. (b) Cycle performance for all-solid-state cells using NiP$_2$ or Ni$_5$P$_4$ particles.
2.3.3. Synthesis of SnS active materials by a hot soap technique and their application to all-solid-state batteries

Figure 2-9 (a) shows the XRD pattern of the sample prepared under “original condition for tin sulfide”. Figure 2-9 (b) shows the XRD pattern of the sample prepared by using OAm instead of TOP, while Figure 2-9 (c) and (d) shows the XRD patterns of the samples prepared by changing the concentration of tin acetate (increased from 0.07 to 0.13 mol L\(^{-1}\)) and reaction temperature (decreased from 280 to 250 °C). The concentration of tin acetate was increased from 0.07 to 0.13 mol L\(^{-1}\) by removing noncoordinating solvents and using only TOP (10 mL) as a solvent. All the samples prepared were identified as SnS (JCPDS #071-3679). The XRD pattern and its intensity ratio for the obtained SnS particles were almost the same as those of the JCPDS. The TEM images of the obtained particles as shown in Figure 2-9 are displayed in Figure 2-10. Needlelike SnS particles with the average length and width of about 2.5 μm and 250 nm (estimated from TEM image of Figure 2-10 (a)) were obtained under the “original condition for tin sulfide”, while the platelike SnS particles with the size of about 2.5 μm (Figure 2-10 (b)) were obtained in OAm as a coordinating solvent. SnS particles with different morphology were synthesized by changing coordinating solvents. It was reported that platelike SnS particles were prepared by liquid-phase synthesis such as solvothermal or polyol process [24,25]. On the other hand, Park et al. proposed that nanorods were formed by the effect of the large difference of capping ability between two surfactants [26]. In our case, needlelike SnS particles would be formed by the different capping ability of TOP and DT. Duan et al. reported that the concentration of metal precursor affected the size of the obtained particles [27]. Figure 2-10 (c) shows the TEM image of the obtained particles prepared by changing the concentration of tin acetate from 0.07 mol L\(^{-1}\) (“original condition for tin sulfide”, Figure 2-10 (a)) to 0.13 mol L\(^{-1}\) [removing noncoordinating solvents from the condition of Figure 2-10 (a) and using only TOP (10 mL)]. The aspect ratio of the sample prepared in only TOP at 280 °C (Figure 2-10 (c)) was slightly larger than that of the sample prepared in ODE and TOP at 280 °C (Figure 2-10 (a)). In addition, Shen et al. reported that the morphology of the obtained Cu\(_2\)S nanoparticles changed by reaction temperature; Cu\(_2\)S nanorods were obtained at lower temperature, while Cu\(_2\)S
Figure 2-9 XRD patterns of the samples prepared by using (a) the mixed solvent of octadecene (ODE) and trioctylphosphine (TOP) at 280 °C for 2 h, (b) the mixed solution of ODE and oleylamine (OAm) at 280 °C for 2 h, (c) only TOP at 280 °C for 2 h, and (d) only TOP at 250 °C for 2 h.
Figure 2-10 TEM images of the samples prepared by using (a) the mixed solvent of ODE and TOP at 280 °C for 2 h, (b) the mixed solvent of ODE and OAm at 280 °C for 2 h, (c) only TOP at 280 °C for 2 h and (d) only TOP at 250 °C for 2 h.
nanodisks were obtained at higher temperature [28]. Figure 2-10 (d) shows the TEM image of the obtained particles prepared by changing reaction temperature from 280 to 250 °C [using only TOP (10 mL)]. The aspect ratio of the sample prepared in only TOP at 250 °C (Figure 2-10 (d)) was larger than that of the sample prepared in only TOP at 280 °C (Figure 2-10 (c)). In our study, by increasing tin concentration and decreasing reaction temperature, the aspect ratio of the needlelike particles was larger than that of the particles prepared under “original condition for tin sulfide”.

In order to investigate the formation mechanism of needlelike SnS particles (Figure 2-10 (d)), the crystal phase and morphology of the obtained samples prepared by changing reaction temperatures were investigated, and the XRD patterns and TEM images of the samples are shown in Figure 2-11 and Figure 2-12, respectively. The product obtained by heating at 210 °C without holding time was the mixture of Sn and SnS (Figure 2-11 (a)), while SnS was prepared by heating at 250 °C for 2 h (Figure 2-11 (b)). In addition, the morphology of the particles changed from spherical particles (Figure 2-12 (a)) to needlelike particles (Figure 2-12 (b)). It is suggested that spherical Sn particles were formed first by thermal decomposition of tin acetate in a mixture of TOP and DT, and then needlelike SnS particles were formed by diffusion of sulfur derived from DT into Sn (Figure 2-13). In general, reactions with TOP require higher temperatures more than 300 °C in order to liberate active phosphorus from TOP [29]. In this study, TOP acted as not a phosphorus source but a coordinating solvent. In the previous section of 2.3.1., we also reported that SnP_{0.94} particles were prepared by diffusion of phosphorus derived from TOP as a phosphorus source into Sn. The formation mechanism of SnS is similar to that of SnP_{0.94}.

Table 2-2 and Figure 2-14 respectively show the reaction conditions and TEM images of the samples prepared by changing the amount of TOP in the range from 1 to 10 mL. The amount of DT (2 ml, 8.3×10^{-3} mol) was fixed, whereas the amount of TOP was changed to investigate the effect of the amount of TOP on morphology of the obtained SnS particles. ODE was used as a noncoordinating solvent, and the total volume of TOP, DT, and ODE in Table 2-2 was 12 mL in order to fix the concentration of tin acetate. The morphology of the obtained SnS particles was not changed by the amount of TOP. Table 2-3, Figure 2-15, and
Figure 2-11 XRD patterns of the samples prepared by heating at (a) 210 °C without holding time or (b) 250 °C for 2 h in only TOP.
Figure 2-12 TEM images of the samples prepared by heating at (a) 210 °C without holding time or (b) 250 °C for 2 h in only TOP.
Collision of spherical Sn particles
Diffusion of sulfur derived from $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$

$[\text{CH}_3(\text{CH}_2)_{12}]_3\text{P}$ (---): Coordinating solvent
$\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ (••••): Sulfur source and coordinating solvent

Figure 2-13 Schematic illustration of our proposed formation mechanism of needle-like SnS particles prepared by using $[\text{CH}_3(\text{CH}_2)_{12}]_3\text{P}$ (TOP) and $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ (DT).
Table 2-2. Reaction conditions for the samples prepared by changing the amount of triocytlyphosphine (TOP). The amount of 1-dodecanethiol (DT) was fixed. Octadecene (ODE) was used as a noncoordinating solvent in order to fix the concentration of tin acetate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of TOP</th>
<th>Amount of DT</th>
<th>Amount of ODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>1 mL</td>
<td>2 mL</td>
<td>9 mL</td>
</tr>
<tr>
<td></td>
<td>(2.2 \times 10^{-3}) mol</td>
<td>(8.3 \times 10^{-3}) mol</td>
<td>(2.8 \times 10^{-2}) mol</td>
</tr>
<tr>
<td>(b)</td>
<td>3 mL</td>
<td>2 mL</td>
<td>7 mL</td>
</tr>
<tr>
<td></td>
<td>(6.7 \times 10^{-3}) mol</td>
<td>(8.3 \times 10^{-3}) mol</td>
<td>(2.2 \times 10^{-2}) mol</td>
</tr>
<tr>
<td>(c)</td>
<td>10 mL</td>
<td>2 mL</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>(2.2 \times 10^{-2}) mol</td>
<td>(8.3 \times 10^{-3}) mol</td>
<td>—</td>
</tr>
</tbody>
</table>
Figure 2-14 TEM images of the samples prepared by changing the amount of trioctyolphosphine (TOP) by heating at 250 °C for 2 h.
Figure 2-16 respectively show the reaction conditions, XRD patterns, and TEM images of the samples prepared by changing the amount of DT. The amount of DT was changed to investigate the effect of the amount of DT on morphology of the obtained SnS particles. The total volume of TOP, DT, and ODE in Table 2-3 was 12 mL in order to fix the concentration of tin acetate. The crystal phase of the obtained particles was not changed from SnS. On the other hand, the amount of DT affected the aspect ratio of the obtained needlelike SnS particles. The aspect ratio of the obtained needlelike SnS particles decreased with an increase in the amount of DT. This is because the fraction of DT that coordinates at the surface of Sn particle relatively increased compared to the fraction of TOP in the formation mechanism of needlelike SnS particles as shown in Figure 2-13.

The obtained SnS particles with different morphology were applied to all-solid-state cells. Figure 2-17 (a) and (b) respectively show the initial charge-discharge curves and cycle performance for the all-solid-state cells Li-In/80Li$_2$S·20P$_2$S$_5$/SnS with short needle (Figure 2-10 (a)), plate (Figure 2-10 (b)), or long needle (Figure 2-10 (d)) under the current density of 0.13 mA cm$^{-2}$ at 25 °C. The cutoff voltages were -0.6 and 1.4 V (vs. Li-In). The obtained capacity was normalized by the weight of SnS in the composite electrode. It was reported that the mechanism of the Li/SnS cell using an organic liquid electrolyte is the formation of metallic Sn at the first discharge process and subsequent generation of Li-Sn alloy [30].

$$\text{SnS} + 2\text{Li}^+ + 2e^- \rightarrow \text{Sn} + \text{Li}_2\text{S}$$

$$\text{Sn} + 4.4\text{Li}^+ + 4.4e^- \leftrightarrow \text{Li}_{4.4}\text{Sn}$$

As shown in Figure 2-17 (a), two plateaus at around 1.3 and 0.3 V (vs. Li) were observed on the first discharge curve of all-solid-state cells Li-In/80Li$_2$S·20P$_2$S$_5$/SnS as well as the cell using an organic liquid electrolyte. It is considered that the all-solid-state cell Li-In/80Li$_2$S·20P$_2$S$_5$/SnS undergoes the same reaction mechanism as the cell using an organic liquid electrolyte.

The cells using SnS particles with short needle, long needle, and plate respectively showed the initial discharge capacities of 1090, 1000, and 880 mAh g$^{-1}$ (theoretical capacity is ca. 1140 mAh g$^{-1}$). All the cells exhibited the higher initial discharge capacity than the cell with mechanically milled SnS particles with micrometer-size (720 mAh g$^{-1}$) [13]. The
Table 2-3. Reaction conditions for the samples prepared by changing the amount of 1-dodecanethiol (DT). Octadecene (ODE) was used as a noncoordinating solvent in order to fix the concentration of tin acetate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of TOP</th>
<th>Amount of DT</th>
<th>Amount of ODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>10 mL</td>
<td>1 mL</td>
<td>1 mL</td>
</tr>
<tr>
<td></td>
<td>(2.2 × 10^{-2} mol)</td>
<td>(4.2 × 10^{-3} mol)</td>
<td>(3.1 × 10^{-3} mol)</td>
</tr>
<tr>
<td>(b)</td>
<td>10 mL</td>
<td>2 mL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(2.2 × 10^{-2} mol)</td>
<td>(8.3 × 10^{-3} mol)</td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>8 mL</td>
<td>4 mL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(1.8 × 10^{-2} mol)</td>
<td>(1.7 × 10^{-2} mol)</td>
<td></td>
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</tbody>
</table>
Figure 2-15 XRD patterns of the samples prepared by changing the amount of dodecanethiol (DT) at 250 °C for 2 h.
Figure 2-16 TEM images of the samples prepared by changing the amount of dodecanethiol (DT) at 250 °C for 2 h.
Figure 2-17 (a) Initial charge-discharge curves and (b) cycle performance of the all-solid-state cells Li-In/80Li$_2$S·20P$_2$S$_5$/SnS with different morphologies.
Figure 2-18 SEM images and EDX mapping for tin element of the surface of the pelletized composite electrodes prepared using (a-d) platelike and (e-h) needlelike SnS particles before and after 15 cycles.
increase of the initial discharge capacity with the all-solid-state cells using prepared SnS particles is attributable to decreasing the particle size. On the other hand, after 15 cycles, the discharge capacity of the three cells is almost the same (Figure 2-17 (b)). Figure 2-18 shows the SEM images and EDX mapping for tin element of the surface of the pelletized composite electrodes prepared using platelike and needlelike (long needle) SnS particles before and after 15 cycles. The morphology of SnS particles after 15 cycles was changed from that of platelike and needlelike SnS particles before cycling. It is known that the charge-discharge mechanism of the cell using SnS is the formation of metallic Sn at the first discharge process and subsequent generation of Li-Sn alloy accompanied by large volume change. These results suggest that a similar capacity fading of the cells using platelike and needlelike SnS particles is attributed to a large volume change and contact loss with solid electrolyte particles during charge-discharge cycles. However, the initial discharge capacity of the all-solid-state cell using needlelike SnS particles as an active material was larger than that of the cell with platelike SnS particles. This result suggests that the use of needlelike particles as an active material increases contact area among three components (SnS particles, solid electrolytes, and conductive additives), and then forms a continuous lithium-ion conducting paths in composite electrodes at first cycle. The one-dimensional structure of needlelike particles as an active material is probably favorable in all-solid-state batteries.

2.3.4. Synthesis of NiS active materials by a hot soap technique and their application to all-solid-state batteries

Figure 2-19 shows the XRD patterns of the sample prepared in OAm as a coordinating solvent at several temperatures. An intermediate was obtained by heating at 180 ℃ (without holding time), and then Ni₉S₈ (JCPDS #078-1886) particles were prepared at 240 ℃ (without holding time) and at 280 ℃ for 24 h. Figure 2-20 shows the XRD patterns of the sample prepared in ODE as a noncoordinating solvent at several temperatures. An intermediate was obtained by heating at 180 ℃ (without holding time) similar to the case using OAm, and then NiS (JCPDS #012-0041) particles were prepared via Ni₉S₈ at 280 ℃ for 5 h. Figure 2-21 shows the TEM images of the Ni₉S₈ or NiS particles prepared by heating at 280 ℃ for 5 h in
Figure 2-19 XRD patterns of the samples prepared by heating at (a) 180 °C, (b) 240 °C, (c) 280 °C for 5 h, and (d) 280 °C for 24 h in oleylamine (OAm).
Figure 2-20 XRD patterns of the samples prepared by heating at (a) 180 °C, (b) 240 °C, and (c) 280 °C for 5 h in octadecene (ODE).
Figure 2-21 TEM images of (a) Ni$_9$S$_8$ or (b) NiS particles prepared by heating at 280 °C for 5 h in OAm or ODE.
Ni$_9$S$_8$ nanorods with the size of about 100 nm were obtained, whereas NiS nanoparticles with the size of about 50 nm were prepared. Nickel sulfide (Ni$_9$S$_8$ or NiS) crystals with different phases and morphologies were obtained by selecting the high-boiling solvent as reaction media. This will be because OAm has a stronger capping ability than ODE. On the other hand, several studies on metal thiolates as the intermediate for synthesis of metal sulfides have been reported [31-33]. It is predicted that the obtained intermediate is nickel dodecanethiolate; nickel sulfides (Ni$_9$S$_8$ and NiS) are formed by thermal decomposition of nickel dodecanethiolate.

Scheme 2-1 shows the three synthetic routes (Routes 1, 2, and 3) for investigation of reaction mechanism of nickel sulfide. Firstly, the obtained intermediate was examined by “Route 1” shown in Scheme 2-1. Figure 2-22 (a) shows the XRD pattern of the sample prepared by heating the intermediate in 10 mL of ODE at 280 ºC for 5 h. The obtained sample was identified as NiS. In addition, the thermal decomposition behavior of the obtained intermediate was characterized by DTA-TG measurements. Figure 2-22 (b) shows the DTA-TG curves of the intermediate under N$_2$ flow. The sharp endothermic peak observed about 70 ºC is due to melting of the intermediate, whereas the endothermic peak around 260 ºC accompanied with weight loss is attributed to decomposition of the intermediate. The weight change with the decomposition is 79%, which closely corresponds to the theoretical weight change of 80% from the metal thiolate of Ni and dodecanethiol (molar ratio of 1:2) to NiS.

In order to further investigate the structure of the intermediate, $^{13}$C NMR and FT-IR spectra were measured. Figure 2-23 shows the $^{13}$C NMR spectra of 1-dodecanethiol and the intermediate prepared by heating at 180 ºC in OAm or ODE. 1-dodecanethiol and the intermediate were dissolved in CDCl$_3$. The peaks of the intermediate are almost attributed to that of 1-dodecanethiol [34]. Figure 2-24 (a), (b), and (c) respectively show the FT-IR spectra of 1-dodecanethiol, the intermediate prepared in OAm at 180 ºC, and the intermediate prepared in ODE at 180 ºC. Figure 2-24 (d), (e), and (f) respectively show the enlarged spectra between 2650 and 2450 cm$^{-1}$ for 1-dodecanethiol, the intermediate prepared in OAm, and the intermediate prepared in ODE. In Figure 2-24 (a), pure 1-dodecanethiol exhibits
Scheme 2-1. Synthetic routes for investigation of reaction mechanism of nickel sulfide.
Figure 2-22 (a) XRD pattern of the sample prepared by heating the intermediate in ODE at 280 °C for 5 h ("Route 1" shown in Scheme 2-1). (b) DTA-TG curves of the intermediate under N₂ flow.
Figure 2-23 $^{13}$C NMR spectra of (a) 1-dodecanethiol and (b,c) intermediate prepared by heating at 180 °C in (b) OAm or (c) ODE.
Figure 2-24 (a-c) FT-IR spectra of (a) 1-dodecanethiol and (b,c) intermediate prepared by heating at 180 °C in (b) OAm or (c) ODE. (d-f) show the enlarged spectra between 2650 and 2450 cm⁻¹ for the (a-c) samples.
sharp bands at 2921 cm\(^{-1}\) and 2850 cm\(^{-1}\) attributed to asymmetric methyl stretching vibration, and the asymmetric and symmetric methylene stretching vibration [32]. Two bands at 2921 cm\(^{-1}\) and 2850 cm\(^{-1}\) were clearly present in the spectra of the intermediate (Figure 2-24 (b) and (c)), whereas the band at 2579 cm\(^{-1}\) attributed to the S-H vibrations of 1-dodecanethiol (Figure 2-24 (d)) was not observed in the spectra of Figure 2-24 (e) and (f). These results suggest that the obtained intermediate is nickel(II) dodecanethiolate, and nickel sulfides (Ni\(_9\)S\(_8\) and NiS) are formed by thermal decomposition of nickel(II) dodecanethiolate. In addition, it was reported that the structure of nickel(II) thiolates was cyclic architecture (Figure 2-25 (a)) [35,36]. We believe that the structure of the obtained nickel(II) dodecanethiolate is also cyclic ring-system (Figure 2-25 (b)).

Additional experiments (“Route 2” and “Route 3” shown in Scheme 2-1) were performed in order to investigate the effects of OAm on crystal phase of nickel sulfide. As shown in Figure 2-20 (c), NiS was ordinarily obtained by heating at 280 °C for 5 h in ODE as reaction media. Figure 2-26 shows the XRD pattern for the sample prepared by injection of OAm (5 mL) into ODE (5 mL) at 180 °C (“Route 2”). Ni\(_9\)S\(_8\) was obtained by injection of OAm at 180 °C. Considering that both nickel(II) dodecanethiolate and free DT act as a sulfur source in “Route 2”, the fact of the formation of Ni\(_9\)S\(_8\) suggests that the sulfur diffusion to nickel ions in nickel(II) dodecanethiolate is prevented by OAm molecules with their strong capping ability (Figure 2-27). As another approach, Table 2-4 and Figure 2-28 respectively show the reaction conditions and XRD patterns of the samples prepared by changing the amount of OAm in the range from 10 to 2 mL (“Route 3”). The amount of DT (2 ml, 8.3×10\(^{-3}\) mol) was fixed, whereas the amount of OAm was changed to investigate the effect of the amount of OAm on crystal phase of nickel sulfide. ODE was used as a noncoordinating solvent, and the total volume of OAm, DT, and ODE in Table 2-4 was 12 mL in order to fix the concentration of nickel(II) acetylacetonate. The crystal phase of the obtained particles was changed from Ni\(_9\)S\(_8\) to NiS by decreasing the amount of OAm against the fixed amount of DT. This is because the fraction of free DT that is not related to the formation of nickel(II) dodecanethiolate relatively increased compared to the fraction of OAm (Figure 2-29). The results of these additional experiments (“Route 2” and “Route 3”) suggest that the excessive
Figure 2-25 Schematic illustration of (a) proposed reaction pathways and (b) the structure of nickel thiolates \([\text{Ni(SR)}_2]_n\) ring [35,36].
Figure 2-26 XRD pattern of the sample prepared by injection of OAm at 180 °C ("Route 2" shown in Scheme 2-1).
Figure 2-27 Schematic illustration of the structure of nickel(II) dodecanethiolate coordinated by OAm and DT in the case of injection of OAm at 180 °C ("Route 2" shown in Scheme 2-1).
Table 2-4. Reaction conditions for the samples prepared by changing the amount of oleylamine (OAm). The amount of 1-dodecanethiol (DT) was fixed. Octadecene (ODE) was used as a noncoordinating solvent in order to fix the concentration of nickel(II) acetylacetone.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of OAm</th>
<th>Amount of DT</th>
<th>OAm/DT (molar ratio)</th>
<th>Amount of ODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>10 mL (3.0 × 10⁻² mol)</td>
<td>2 mL (8.3 × 10⁻³ mol)</td>
<td>3.6</td>
<td>—</td>
</tr>
<tr>
<td>(b)</td>
<td>5 mL (1.5 × 10⁻² mol)</td>
<td>2 mL (8.3 × 10⁻³ mol)</td>
<td>1.8</td>
<td>5 mL (1.5 × 10⁻² mol)</td>
</tr>
<tr>
<td>(c)</td>
<td>2 mL (6.0 × 10⁻³ mol)</td>
<td>2 mL (8.3 × 10⁻³ mol)</td>
<td>0.72</td>
<td>8 mL (2.4 × 10⁻² mol)</td>
</tr>
</tbody>
</table>
Figure 2-28 XRD patterns of the samples prepared by changing the amount of OAm (“Route 3” shown in Scheme 2-1).
Figure 2-29 Schematic illustration of the structure of nickel(II) dodecanethiolate coordinated by OAm and DT with the molar ratio of (a) OAm/DT=3.6 and (b) OAm/DT=0.72 (“Route 3” shown in Scheme 2-1).
amount of OAm molecules has a strong capping ability to nickel ions in nickel(II) dodecanethiolate, and thus the OAm molecules prevent the diffusion of sulfur derived from nickel(II) dodecanethiolate and free DT.

Figure 2-30 shows the TEM images of the samples prepared by changing the amount of OAm. The morphology of the Ni$_9$S$_8$ particles prepared by the condition of excessive amount of OAm [OAm/DT = 3.6 (molar ratio)] is nanorod with the size of 100 nm, whereas that of the NiS particles prepared by the condition of small amount of OAm [OAm/DT = 0.72 (molar ratio)] was aggregated and not uniform. This is because the amount of OAm as a surfactant is too small to control the morphology of NiS particles. In order to synthesize the NiS nanoparticles with various morphologies by the condition of excessive amount of surfactant, trioctylamine (TOA, [CH$_3$(CH$_2$)$_7$]$_3$N) was used as a coordinating solvent [TOA/DT = 4.1 (molar ratio)]. Figure 2-31 shows the XRD patterns of the samples prepared by heating at 280 ºC for 5 h using 10 mL of OAm or TOA. The obtained particles were the mixture of NiS (major phase) and Ni$_9$S$_8$ (minor phase) by using TOA as a coordinating solvent. This is because the excessive amount of TOA molecules has a weaker capping ability to nickel ions in nickel(II) dodecanethiolate than that of OAm, and thus TOA accelerates the diffusion of sulfur derived from nickel(II) dodecanethiolate and free DT (Figure 2-32). On the other hand, Figure 2-33 shows the TEM images of the samples prepared by heating at 280 ºC for 5 h using 10 mL of OAm or TOA. Ni$_9$S$_8$ nanorods with the size of 100 nm are obtained by using OAm, whereas the obtained NiS particles prepared by using TOA are not uniform. It is thus difficult to synthesize one-dimensional NiS active material by a hot soap technique.

The obtained NiS or Ni$_9$S$_8$ nanoparticles prepared by using ODE (Figure 2-21 (b)) or OAm (Figure 2-21 (a)) were applied to the all-solid-state cell. Figure 2-34 (a) shows the charge-discharge curves for the all-solid-state cell Li-In/80Li$_2$S·20P$_2$S$_5$/NiS. The cutoff voltages were -0.6 and 3.4 V (vs. Li-In). The obtained capacity was normalized according to the weight of NiS in the composite electrode. The all-solid-state cell exhibited the initial discharge capacity of 780 mAh g$^{-1}$ in the voltage range from 0 to 4.0 V (vs. Li) under a constant current density of 0.13 mA cm$^{-2}$. It has been reported that the mechanism of the Li/NiS cell using an organic liquid electrolyte at the discharge process was the formation of
Figure 2-30 TEM images of the samples prepared by changing the amount of OAm ("Route 3" shown in Scheme 2-1).
Figure 2-31 XRD patterns of the samples prepared by heating at 280 °C for 5 h using (a) OAm or (b) TOA.
Figure 2-32 Schematic illustration of the structure of nickel(II) dodecanethiolate coordinated by (a) OAm or (b) TOA.
Figure 2-33 TEM images of the samples prepared by heating at 280 °C for 5 h using (a) OAm or (b) TOA.
Figure 2-34 (a) Charge-discharge curves of the all-solid-state cell Li-In/80Li₂S·20P₂S₅/NiS. (b) Cycle performance for the all-solid-state cells using NiS or Ni₉S₈ nanoparticles. NiS or Ni₉S₈ nanoparticles were synthesized at 280 °C for 5 h by using ODE or OAm.
Ni$_3$S$_2$ and Li$_2$S, and subsequent generation of metallic Ni and Li$_2$S [37].

$$3\text{NiS} + 2\text{Li}^+ + 2e^- \leftrightarrow \text{Ni}_3\text{S}_2 + \text{Li}_2\text{S}$$
$$\text{Ni}_3\text{S}_2 + 4\text{Li}^+ + 4e^- \leftrightarrow 3\text{Ni} + 2\text{Li}_2\text{S}$$

As shown in Figure 2-34 (a), four plateaus at 1.8 and 1.3 V (discharge process), and 1.9 and 2.2 V (charge process) (vs. Li) are observed on the first charge-discharge curve of the all-solid-state cell as well as the cell using an organic liquid electrolyte [37]. It is considered that the all-solid-state cell Li-In/80Li$_2$S·20P$_2$S$_5$/NiS undergoes the same reaction mechanism as the cell using an organic liquid electrolyte. Figure 2-34 (b) shows the cycle performance for the all-solid-state cells using NiS or Ni$_9$S$_8$ nanoparticles under a constant current density of 0.13 mA cm$^{-2}$ at 25 ºC. The cell using NiS nanoparticles exhibited a larger capacity than that of the cell using Ni$_9$S$_8$ nanorods during 20 cycles. This is because the theoretical capacity of NiS active material (590 mAh g$^{-1}$) is larger than that of Ni$_9$S$_8$ active material (550 mAh g$^{-1}$). It was reported that the capacity fading occurred during cycling in the cell using an organic liquid electrolyte [38]. This is because soluble lithium polysulfides, which are formed during a discharge process, are dissolved in the liquid electrolytes. On the other hand, the all-solid-state cells using NiS or Ni$_9$S$_8$ showed the excellent cycle performance during 20 cycles. The cell using NiS nanoparticles retained the discharge capacity of 680 mA h g$^{-1}$ and the charge-discharge efficiency of about 100% from 2 to 20 cycles. This result suggests that NiS nanoparticles are preferable as an active material for all-solid-state batteries.

2.4. Summary

Tin phosphide (SnP$_{0.94}$) particles were synthesized by a hot soap technique. Teardrop-shaped SnP$_{0.94}$ particles with the size of 500 nm were obtained by using TOPO as a coordinating solvent. Spherical Sn particles were obtained by refluxing for 3 min, whereas teardrop-shaped SnP$_{0.94}$ particles were prepared by refluxing for 1 h. Teardrop-shaped SnP$_{0.94}$ particles were prepared by diffusion of phosphorus derived from TOP into spherical Sn particles. The teardrop-shaped SnP$_{0.94}$ particles with the size of 500 nm were applied to the all-solid-state cell. The cell Li-In/80Li$_2$S·19P$_2$S$_5$·1P$_2$O$_5$/SnP$_{0.94}$ exhibited the discharge capacity of about 1000 mAh g$^{-1}$ at the current density of 1.3mA cm$^{-2}$ at the 1st cycle. The
all-solid-state cell exhibited higher capacity than the cell using an organic liquid electrolyte.

Nickel phosphide particles were synthesized by a hot soap technique. Ni$_5$P$_4$ particles (500 nm) were obtained by thermal decomposition of Ni(acac)$_2$ as a nickel precursor in a mixed solvent of TOP and TOPO at 360 °C for 1 h. The crystal phase of the obtained particles changed from Ni$_5$P$_4$ to NiP$_2$ by increasing the reaction time and using hydrate nickel precursors such as Ni(acac)$_2$·2H$_2$O and Ni(Ac)$_2$·4H$_2$O. NiP$_2$ particles with diameters of 200-500 nm were obtained by thermal decomposition of Ni(Ac)$_2$·4H$_2$O as a nickel precursor in a mixed solvent of TOP and TOPO at 360 °C for 5 h. An all-solid-state cell was fabricated using NiP$_2$ particles (200-500 nm) as an active material. The cell Li-In/80Li$_2$S·20P$_2$S$_5$/NiP$_2$ exhibited an initial discharge capacity of 1100 mAh g$^{-1}$ at 0.13 mA cm$^{-2}$ and retained a discharge capacity of 750 mAh g$^{-1}$ after 10 cycles.

Tin sulfide (SnS) particles were synthesized from tin acetate and DT by a hot soap technique. Needlelike SnS particles were obtained by using TOP as a coordinating solvent, whereas platelike SnS particles were obtained by using OAm as a coordinating solvent. Needlelike SnS particles were formed by the diffusion of sulfur derived from DT into spherical Sn particles. In addition, the aspect ratio of needlelike SnS particles was affected by the amount of DT as a sulfur source. The obtained needlelike and platelike SnS particles were applied to the all-solid-state cells. The initial discharge capacity of the all-solid-state cells using needlelike SnS particles as an active material was ca. 1000 mAh g$^{-1}$, which was larger than that of the cell with platelike SnS particles under the current density of 0.13 mA cm$^{-2}$.

Nickel sulfide particles were synthesized from nickel(II) acetylacetonate and DT in OAm or ODE. Ni$_9$S$_8$ was obtained by using OAm as a coordinating solvent, whereas NiS was prepared by using ODE as a noncoordinating solvent. Both Ni$_9$S$_8$ and NiS were formed via thermal decomposition of nickel(II) dodecanethiolate. Nickel sulfide crystals with different phases were obtained by selecting the solvent (OAm or ODE) as reaction media. This is because the excessive amount of OAm molecules has a strong capping ability to nickel ions in nickel(II) dodecanethiolate, and the OAm molecules prevent the diffusion of sulfur derived from nickel(II) dodecanethiolate and free DT. The all-solid-state cells using NiS
nanoparticles with the size of about 50 nm as an active material were fabricated. The cell Li-In/80Li$_2$S·20P$_2$S$_5$/NiS exhibited the initial discharge capacity of 780 mA h g$^{-1}$ at 0.13 mA cm$^{-2}$ and a good cycle performance during 20 cycles.

A hot soap technique contributed to morphology-controlled synthesis of SnS particles and phase-selective synthesis of nickel phosphides and sulfides. The all-solid-state cells using the obtained particles (SnP$_{0.94}$, NiP$_2$, SnS, and NiS) synthesized by a hot soap technique exhibited the good electrochemical performance. The initial discharge capacity of the all-solid-state cell using needlelike SnS particles as an active material was larger than that of the cell using platelike SnS particles. However, after 15 cycles, the discharge capacity of the cells is almost the same because of a large volume change and contact loss with solid electrolyte particles during charge-discharge cycles. On the other hand, the cell using NiS nanoparticles with the size of 50 nm exhibited high capacity retention during 20 cycles, and shows the excellent cycle performance. It was difficult to synthesize one-dimensional NiS active material by a hot soap technique. Therefore, in order to form one-dimensional lithium-ion and electron conduction paths in a composite electrode, morphology-design of the composite electrode is needed as an alternative to synthesis of one-dimensional NiS active material.
2.5. References


[17] Ohtomo, T.; Mizuno, F.; Hayashi, A.; Tadanaga, K.; Tatsumisago, M. *J. Power Sources*


3. Design of composite electrodes using nano-sized NiS active materials for development of all-solid-state batteries

3.1. Introduction

In bulk-type all-solid-state batteries, a composite positive or negative electrode consisting of three components of active materials, solid electrolytes (lithium-ion conduction path), and conductive additives (electron conduction path) is commonly used. Electrochemical reactions proceed at the solid-solid interfaces and are affected by the states of the interfaces in the composite electrode. In the chapter 2, we focused on the morphology-controlled synthesis of tin- and nickel-based active materials by a hot soap technique, for example the synthesis of one-dimensional active materials. From the result of the initial charge-discharge curves of the all-solid-state cells using the platelike and needlelike SnS particles, it was obvious that the use of the needlelike SnS active materials with one-dimensional structure increased contact area among three components (SnS particles, solid electrolytes, and conductive additive), and formed a continuous lithium-ion and electron conducting paths in composite electrodes. However, it was found that utilization of one-dimensional SnS active material for all-solid-state batteries was not effective because of a large volume change during charge-discharge cycles. It is known that the charge-discharge mechanism of the cell using SnS is the formation of metallic Sn at the first discharge process and subsequent generation of Li-Sn alloy accompanied by large volume change. On the other hand, synthesis of one-dimensional NiS active material, which undergoes a conversion process including the change of NiS to Ni and Li$_2$S after lithiation, was difficult. Therefore, in order to form one-dimensional lithium-ion and electron conduction paths in the composite electrode, the use of nanocomposites (Figure 3-1) as composite electrodes is selected as an alternative to one-dimensional NiS active material in the present chapter. We believe that the use of carbon fiber would make it possible to form a continuous electron conducting paths in the composite electrodes, and active material with uniform size would contact intimately with both carbon fiber and solid electrolyte. Lee et al. reported that copper sulfide nanoparticles were grown on carbon nanotubes using a high-boiling solvent such as oleylamine [1]. Pang
Figure 3-1 Schematic illustration of the SE-coated NiS-VGCF composite. SE denotes the 80Li$_2$S·20P$_2$S$_5$ (mol %) solid electrolyte.
et al. also reported that composites including metal oxide and graphene were prepared by using oleylamine [2]. A hot soap technique is effective in construction of favorable solid-solid interfaces between active materials and conductive additives. On the other hand, we reported that a highly conductive Li$_2$S-P$_2$S$_5$ solid electrolyte was coated on LiCoO$_2$ particles using pulsed laser deposition (PLD) to form intimate solid-solid contacts between LiCoO$_2$ and solid electrolyte [3,4].

In this chapter, nanocomposites (Figure 3-1) for application to composite electrodes were prepared by combination of hot soap technique and pulsed laser deposition (Figure 3-2) in order to improve the rate performance of all-solid-state batteries. Nanocomposites shown in Figure 3-1 will contribute to the formation of favorable lithium-ion and electron conduction paths to NiS active materials. NiS nanoparticles and vapor grown carbon fiber (VGCF, Showa Denko) were respectively selected as active materials and conductive additives. In the previous chapter 2, NiS nanoparticles with the size of 50 nm were synthesized by a hot soap technique. Firstly, in order to form electron conduction paths for NiS active materials, NiS-VGCF composites were synthesized by a hot soap technique. Next, composite materials including NiS-VGCF composites and sulfide-based solid electrolytes were prepared by deposition of the Li$_2$S-P$_2$S$_5$ solid electrolyte thin films onto NiS-VGCF composites using pulsed laser deposition (PLD) in order to form favorable lithium-ion conduction paths to the NiS active materials. Finally, as shown in Figure 3-2, different composite electrodes using NiS as an active material were prepared for comparison; all the composite electrodes included the sulfide solid electrolyte particles in order to form sufficient lithium-ion conduction paths for composite electrode. These composite electrodes were applied to all-solid-state batteries. The effects on the electrochemical performance by forming intimate electron and lithium-ion conduction paths were investigated.

3.2. Experimental

3.2.1. Synthesis of NiS-VGCF composites by a hot soap technique

In the previous chapter 2, NiS nanoparticles of 50 nm diameter were synthesized in a mixed solvent of 1-dodecanethiol and 1-octadecene. For synthesis of NiS-VGCF composite,
Figure 3-2 Schematic illustration of different composite electrodes prepared in the present chapter.
nickel(II) acetylacetonate (0.385 g, 1.5×10⁻³ mol) and vapor grown carbon fiber (VGCF, Showa Denko, 5 and 10 mg) were mixed with 1-dodecanethiol (2 ml, 8.3×10⁻³ mol) as a sulfur source in 1-octadecene (10 ml). The mixture was heated in a 200 mL four-necked flask to 280 °C and was subsequently kept at 280 °C for 5 h under stirring in an Ar atmosphere. After heating, the mixture was cooled to room temperature and was subsequently washed with hexane and ethanol. The resultant particles were isolated by centrifuging the mixture and then removing the supernatants. The weight ratio of NiS and VGCF in the NiS-VGCF composite was 9:1, as calculated from the weight of the added VGCF (10 mg) and the obtained NiS-VGCF composite (100 mg).

3.2.2. Preparation of NiS-VGCF composites with Li₂S·P₂S₅ solid electrolytes by pulsed laser deposition

An 80Li₂S·20P₂S₅ (mol %) solid electrolyte (SE) was coated on the NiS-VGCF composites using pulsed laser deposition (PLD). SE thin films of 80Li₂S·20P₂S₅ were fabricated using PLD with a KrF excimer laser (λ = 248 nm, LPXPro, Lambda Physik) [5]. A pelletized mixture of Li₂S and P₂S₅ powder with a molar ratio of 80:20 was used as a target. The 80Li₂S·20P₂S₅ films deposited on Si substrates were amorphous and showed the lithium-ion conductivity of 7.9×10⁻⁵ S cm⁻¹ at 25 °C [5]. Target holders were attached to the upper side of a PLD vacuum chamber, and a vibrating sample holder was equipped at the bottom side. This PLD system allowed the formation of an SE layer on the electrode particles. During deposition of the SE, the NiS-VGCF composite powders were fluidized by a vibration system (VIB-FB, Nara Machinery Co., Ltd.) to form a uniform SE layer on the NiS-VGCF composites. The frequency of the square pulse used to fluidize the particles was 500 Hz and the deposition time was 120 min.

3.2.3. Cell construction

Laboratory-scale solid-state cells were fabricated as follows. The 80Li₂S·20P₂S₅ (mol %) glass-ceramic solid electrolyte powder was prepared by mechanical milling of a mixture of Li₂S and P₂S₅ and subsequent heat treatment. The prepared electrolyte exhibited a wide electrochemical window and high ionic conductivity at room temperature [6].
A composite electrode was prepared by hand-grinding of a mixture of NiS-VGCF composite (5.5 mg) and the glass-ceramic electrolyte (8.5 mg) in a mortar. For comparison, a mixture electrode was prepared by hand-grinding of a mixture of NiS active material (5.7 mg), the glass-ceramic electrolyte (8.5 mg), and VGCF (0.8 mg) in a mortar.

Nanocomposite (100 wt.% SE-coated NiS-VGCF composite) was used as a composite electrode of all-solid-state cell, and electrochemical properties were investigated. In order to investigate the effect of lithium-ion conduction paths on the electrochemical performance, three composite electrodes which consisted of the SE-coated NiS-VGCF composites (100, 80, and 40 wt.%) and the glass-ceramic electrolytes (0, 20, and 60 wt.%) were also prepared by hand-grinding of the mixtures in a mortar. For comparison, a composite electrode which consisted of the uncoated NiS-VGCF composite (40 wt.%) and the glass-ceramic electrolyte (60 wt.%) was prepared by hand-grinding of the mixture in a mortar.

Two-electrode cells were fabricated using the composite electrode, the glass-ceramic electrolyte, and a Li-In alloy as a counter electrode. The composite electrode and solid electrolyte were placed in a polycarbonate tube (10 mm diameter) and pressed together under 360 MPa at room temperature. The Li-In alloy was placed on the surface of the solid electrolyte side of the bilayer pellet. Then pressure of 120 MPa was applied to obtain a three-layered pellet. The three-layered pellet was finally sandwiched with two stainless-steel disks as current collectors. All preparation processes of the cells were conducted in a dry Ar-filled glove box.

3.2.4. Characterization

X-ray diffraction (XRD; Ultima IV; Rigaku) measurements were performed using Cu Kα radiation to identify crystalline phases. The morphology of the obtained particles was investigated using scanning electron microscopy (SEM; JSM-6610A; JEOL) coupled with an energy dispersive X-ray spectrometer (EDX; JED-2300; JEOL), and transmission electron microscopy (TEM; JEM-2100F; JEOL). Electrochemical tests were conducted under a constant current density of 0.13, 0.64, 1.3, 2.5, and 3.8 mA cm⁻² at 25 °C in an Ar atmosphere using a charge-discharge measurement device (BTS-2004; Nagano Co.).
3.3. Results and discussion

3.3.1. NiS-VGCF composite

Figure 3-3 shows the charge-discharge curves of all-solid-state cell using the mixture electrode prepared by hand-grinding of a mixture of NiS, solid electrolyte, and VGCF under the current density of 0.13 mA cm\(^{-2}\). The cutoff voltages were -0.6 and 3.4 V (vs. Li-In). Li-In alloy was used as a counter electrode because Li-In alloy exhibits a stable potential plateau at 0.62 V vs. Li\(^+\)/Li, as observed in all-solid-state cells with sulfide electrolytes. In Figure 3-3, the right-side ordinate axis shows the electrode potential vs. Li, as calculated based on the potential difference between Li-In and Li electrodes (0.62 V). In addition, the obtained capacity was normalized by the weight of NiS in the mixture electrode. The all-solid-state cell exhibits the initial discharge capacity of 780 mAh g\(^{-1}\) in the voltage range from 0 to 4.0 V (vs. Li) under a constant current density of 0.13 mA cm\(^{-2}\), and shows the charge-discharge efficiency of about 100% from 2 to 20 cycles.

Figure 3-4 (a) shows the rate performance of the all-solid-state cell with the mixture electrode prepared by hand-grinding of a mixture of NiS of 50 nm diameter, solid electrolyte, and VGCF. At a low current density such as 0.13 mA cm\(^{-2}\) (corresponding to \(ca. 1/30\) C), the cell exhibited a high discharge capacity of 680 mAh g\(^{-1}\) after 20 cycles. However, at a relative high current density such as 1.3 mA cm\(^{-2}\) (\(ca. 1/3\) C), the cell showed a small discharge capacity of 140 mAh g\(^{-1}\). In addition, after cycling at 2.5 mA cm\(^{-2}\) (\(ca. 2/3\) C), the discharge capacity recovered to their initial capacities at 0.13 mA cm\(^{-2}\). Figures 3-4 (b) and (c) respectively show the SEM image and EDX mapping for nickel element of the surface of the pelletized mixture electrode prepared by hand-grinding of the three components. The NiS nanoparticles were aggregated in the mixture electrode (bright part: NiS nanoparticles; dark part: solid electrolytes). These results suggest that a small capacity at high current density is attributed to a small contact area among NiS nanoparticles, the solid electrolyte, and VGCF. Therefore, we synthesized the NiS-VGCF composite by a hot soap technique in order to construct solid-solid interfaces between active materials (NiS) and conductive additives (VGCF).

Figure 3-5 presents XRD patterns of the prepared NiS, VGCF (Showa Denko), and the
Figure 3-3 Charge-discharge curves of the all-solid-state cell using a mixture electrode prepared by hand-grinding of a mixture of NiS, solid electrolyte, and VGCF under the current density of 0.13 mA cm\(^{-2}\).
Figure 3-4 (a) Rate performance of the all-solid-state cell with the mixture electrode prepared by hand-grinding of a mixture of NiS, solid electrolyte, and VGCF. (b) SEM image and (c) EDX mapping for nickel element of the mixture electrode prepared by hand-grinding of three constituents (NiS, solid electrolyte, and VGCF).
prepared NiS-VGCF composite. The pattern of the NiS-VGCF composite (Figure 3-5 (c)) was almost identical to the pattern of NiS (Figure 3-5 (a)). The XRD pattern of the obtained particles is attributable to NiS (JCPDS #012-0041). In addition, a peak at $2\theta = 26.2^\circ$ was attributed to VGCF (Figure 3-5 (b)). The crystal phase of nickel sulfide prepared was not changed from NiS by adding VGCF to the precursor used for synthesis of NiS nanoparticles. Figures 3-6 (a) and (b) respectively show the SEM images of VGCF and the NiS-VGCF composite synthesized by adding VGCF (10 mg). The composites including NiS nanoparticles and VGCF were synthesized by a hot soap technique. Figure 3-6 (c) shows a TEM image of the NiS-VGCF composite synthesized by adding VGCF (5 mg). Figures 3-6 (d) and (e) present TEM images of the NiS-VGCF composite synthesized by adding VGCF (10 mg). Figure 3-6 (e) is a magnified image of Figure 3-6 (d). In Figure 3-6 (c), NiS nanoparticles were aggregated in the NiS-VGCF composite synthesized using 5 mg of VGCF. On the other hand, NiS nanoparticles of 50 nm were formed on the VGCF surface in the NiS-VGCF composite synthesized using 10 mg of VGCF, as shown in Figure 3-6 (d) and (e).

A composite electrode was prepared by hand-grinding of a mixture of NiS-VGCF composite (synthesized using 10 mg of VGCF) and the 80Li$_2$S·20P$_2$S$_5$ solid electrolyte. It is expected that the NiS-VGCF composites are on the surface and inside of the pelletized composite electrode. Figures 3-7 (a) and (b) respectively show an SEM image and EDX mapping for Ni element of the surface of the pelletized composite electrode prepared by hand-grinding of a mixture of NiS-VGCF composite and the solid electrolyte. NiS nanoparticles were on a rod-shaped VGCF surface in the composite electrode (Figure 3-7 (b)); then the NiS-VGCF composite (bright part of Figure 3-7 (a)) contacted with the solid electrolyte (dark part of Figure 3-7 (a)). This result shows suppression of the aggregation of NiS nanoparticles. Figure 3-7 (c) shows the charge-discharge curves of all-solid-state cell using the NiS-VGCF composite at the 10th, 20th, and 30th cycles under the current density of 1.3 mA cm$^{-2}$ (ca. 1/3 C). The cutoff voltages were -0.6 and 3.4 V (vs. Li-In). The obtained capacity was normalized by the weight of NiS in the composite electrode. The all-solid-state cell using NiS-VGCF composite retained a discharge capacity of 520 mAh g$^{-1}$ and a charge-discharge efficiency of approximately 100% after 30 cycles in the voltages of 0-4.0 V.
Figure 3-5 XRD patterns of (a) the NiS particles, (b) VGCF (Showa Denko), and (c) the prepared NiS-VGCF composite.
Figure 3-6 SEM images of (a) VGCF and (b) the prepared NiS-VGCF composite. TEM images of the NiS-VGCF composite synthesized by changing the amount of VGCF [(c) 5 and (d, e) 10 mg]. (e) is a magnified image of (d).
Figure 3-7 (a) SEM image and (b) EDX mapping for Ni element of a composite electrode prepared by hand-grinding of a mixture of NiS-VGCF composite and solid electrolyte. (c) Charge-discharge curves of the all-solid-state cells using the composite electrode under the current density of 1.3 mA cm\(^{-2}\).
Figure 3-8 Cycle performance of the all-solid-state cells using the NiS-VGCF composite and a mixture of three components (NiS, solid electrolyte, and VGCF) as an electrode at 1.3 mA cm$^{-2}$. 
(vs. Li) under a constant current density of 1.3 mA cm\(^{-2}\) at 25 °C. Figure 3-8 shows the cycle performance of the all-solid-state cells using the NiS-VGCF composite and a mixture of three components (NiS, solid electrolyte, and VGCF) as an electrode. The cell using the NiS-VGCF composite exhibited better cycle performance than the cell using the mixture electrode prepared by hand-grinding of NiS, solid electrolyte, and VGCF. This result suggests that the formation of intimate NiS-VGCF interfaces gives favorable electron conduction paths to NiS nanoparticles, and the contact area among three components in composite electrodes was increased by formation of favorable interfaces between NiS nanoparticles and VGCF in advance of having the interfaces with the solid electrolytes. As described herein, NiS-VGCF composites were synthesized as the first step toward constructing nanocomposites composed of active materials, solid electrolytes, and conductive additives. The use of NiS-VGCF composites was effective in developing the electrochemical performance of all-solid-state batteries.

3.3.2. NiS-VGCF composite coated with Li\(_2\)S-P\(_2\)S\(_5\) solid electrolyte by pulsed laser deposition

Figures 3-9 (a) and (b) respectively show the SEM image and EDX mapping for Ni element of the NiS-VGCF composite coated with the 80Li\(_2\)S-20P\(_2\)S\(_5\) (mol %) solid electrolyte (SE) by pulsed laser deposition (PLD). The signals of EDX mapping for Ni element were uniformly distributed as shown in Figure 3-9 (b). Figure 3-9 (c) is a magnified image of Figure 3-9 (a). Figure 3-9 (d) shows the SEM image of the uncoated NiS-VGCF composite for comparison. NiS nanoparticles with the size of 50 nm were formed on VGCF surface in the uncoated NiS-VGCF composites. NiS nanoparticles were on VGCF surface after SE-coating by using PLD, and morphology of the SE-coated NiS-VGCF composite was not largely changed from the uncoated NiS-VGCF composite. Figures 3-10 (a) and (b) respectively show the TEM and high-resolution TEM (HRTEM) images of the SE-coated NiS-VGCF composite. In Figure 3-10 (b), an amorphous SE thin film with the thickness of ca. 5 nm was observed on NiS nanoparticles with lattice fringes (the amorphous SE thin film was denoted with an arrow).

Figures 3-11 (a) and (b) respectively show the charge-discharge curves of the
Figure 3-9 (a) SEM image and (b) EDX mapping for nickel element of the SE-coated NiS-VGCF composite. (c) is a magnified image of (a). (d) SEM image of the uncoated NiS-VGCF composite. SE denotes the 80Li$_2$S-20P$_2$S$_6$ (mol %) solid electrolyte.
Figure 3-10 (a) TEM and (b) HRTEM images of the SE-coated NiS-VGCF composite. An amorphous SE thin film was denoted with an arrow in (b).
all-solid-state cells with the composite electrodes using 100 wt % SE-coated NiS-VGCF composites and those using a mixture of 80 wt.% SE-coated NiS-VGCF composites and 20 wt.% solid electrolyte (SE) particles, at a current density of 0.64 mA cm$^{-2}$. The obtained capacity was normalized by the weight of the SE-coated NiS-VGCF composite. The initial charge-discharge capacity and efficiency of the cell with the composite electrode using 100 wt.% SE-coated NiS-VGCF composite was low; the initial discharge capacity (175 mAh g$^{-1}$) of the cell with the composite electrode using 100 wt.% SE-coated NiS-VGCF composite was lower during 50 cycles than the initial capacity (220 mAh g$^{-1}$) of the cell with the composite electrode using a mixture of 80 wt.% SE-coated NiS-VGCF composites and 20 wt.% SE particles. This result suggests that the formation of lithium-ion conduction paths is not sufficient in the composite electrode with 100 wt.% SE-coated NiS-VGCF composites, and the addition of SE particles is effective in forming lithium-ion conduction paths. Figure 3-12 shows the charge-discharge curves of the all-solid-state cell with the composite electrode using a mixture of 40 wt.% SE-coated NiS-VGCF composites and 60 wt.% SE particles under the current density of 1.3 mA cm$^{-2}$. Even at a higher current density of 1.3 mA cm$^{-2}$, the cell exhibited the charge-discharge efficiency of approximately 100% and a large capacity of 430 mAh g$^{-1}$ at the 50th cycle. This is because the addition of SE particles gives the favorable lithium-ion conduction paths in the composite electrode.

Figures 3-13 (a) and (b) respectively show the charge-discharge curves of all-solid-state cell using the uncoated or SE-coated NiS-VGCF composite at the first, second, and 50th cycles under the current density of 3.8 mA cm$^{-2}$ (corresponding to ca. 1 C). The two composite electrodes consisted of the 40 wt.% uncoated or SE-coated NiS-VGCF composites, and 60 wt.% SE particles. The obtained capacity of the cell using the uncoated or SE-coated NiS-VGCF composite was normalized by the weight of the uncoated or SE-coated NiS-VGCF composite in the composite electrode. At the first cycle, the charge-discharge efficiency of the cell with the SE-coated NiS-VGCF composite is higher than that of the cell with the uncoated NiS-VGCF composite. As a result, the discharge capacity (240 mAh g$^{-1}$) of the cell with the SE-coated NiS-VGCF composite is larger at the second cycle than the capacity (100 mAh g$^{-1}$) of the cell with the uncoated NiS-VGCF composite. The increase of
Figure 3-11 Charge-discharge curves of the all-solid-state cells with the composite electrodes using (a) 100 wt.% SE-coated NiS-VGCF composite, or (b) a mixture of 80 wt.% SE-coated NiS-VGCF composite and 20 wt.% solid electrolyte (SE) particles, at a current density of 0.64 mA cm$^{-2}$. 
Figure 3-12 Charge-discharge curves of the all-solid-state cell with the composite electrode using a mixture of 40 wt.% SE-coated NiS-VGCF composite and 60 wt.% SE particles at a current density of 1.3 mA cm$^2$. 

$25 \, ^\circ C$, $1.3 \, mA \, cm^2$
Figure 3-13 Charge-discharge curves of the all-solid-state cells using the uncoated or SE-coated NiS-VGCF composite at the 1st, 2nd, and 50th cycles under the current density of 3.8 mA cm$^{-2}$. (corresponding to ca. 1 C).
Figure 3-14 Cycle performance of all-solid-state cells using the different composite electrodes at the current density of 3.8 mA cm$^{-2}$ (ca. 1 C).

Mixture electrode(1) : NiS + VGCF + solid electrolyte
Composite electrode(2) : Uncoated NiS-VGCF composite + solid electrolyte
Composite electrode(3) : SE-coated NiS-VGCF composite + solid electrolyte
capacity during cycling is attributed to formation and increase of contact area between NiS active materials and solid electrolyte powders.

Figure 3-14 shows the cycle performance of all-solid-state cells using three different composite electrodes (see Figure 3-2) at the current density of 3.8 mA cm\(^{-2}\) (ca. 1 C). At a high current density of 3.8 mA cm\(^{-2}\), the all-solid-state cell using the SE-coated NiS-VGCF composite (composite electrode (3)) showed the initial discharge capacity of 300 mAh g\(^{-1}\), and exhibited the best cycle performance in the three different composite electrodes. This result suggests that the formation of intimate interfaces among NiS, VGCF, and SE gives favorable electron and lithium-ion conduction paths to NiS nanoparticles (see Figure 3-1). At the present stage, the formation of lithium-ion conduction paths was not sufficient in the composite electrode with 100 wt.% SE-coated NiS-VGCF composites, and the addition of SE particles in the composite electrode was necessary to fabricate the all-solid-state cells with high capacity. However, the use of the SE-coated NiS-VGCF composite was more effective in improving the electrochemical performance at a high current density of 3.8 mA cm\(^{-2}\) (ca. 1 C) than that of the uncoated NiS-VGCF composite.

3.4. Summary

Composites of NiS nanoparticles and VGCF were prepared by a hot soap technique to form electron conduction paths for NiS active materials. The NiS-VGCF composites were synthesized using thermal decomposition of nickel acetylacetonate and 1-dodecanethiol in a mixture of VGCF and 1-octadecene. NiS nanoparticles with 50 nm in diameter were formed on the VGCF surface. An electrode prepared by mixing the NiS-VGCF composite and solid electrolyte was applied to all-solid-state cells. NiS nanoparticles were on the VGCF surface in the electrode, which suppressed aggregation of NiS nanoparticles. The all-solid-state cell using the NiS-VGCF composite exhibited better cycle performance than the cell with the electrode prepared by hand-grinding of a mixture of NiS nanoparticles, solid electrolyte, and VGCF at a current density of 1.3 mA cm\(^{-2}\) (ca. 1/3 C). The electrochemical performance in all-solid-state batteries was improved by formation of favorable NiS-VGCF interfaces.

Composite materials with NiS active materials, solid electrolytes (SE), and conductive
additives were prepared by coating Li$_2$S-P$_2$S$_5$ SE onto the NiS-VGCF composite using PLD to form favorable lithium-ion and electron conduction paths for the NiS active materials. NiS nanoparticles were on the VGCF surface after the deposition of SE thin films. At a high current density of 3.8 mA cm$^{-2}$ (ca. 1 C), an all-solid-state cell using the SE-coated NiS-VGCF composite showed the initial discharge capacity of 300 mAh g$^{-1}$, and exhibited better cycle performance than the cell using the uncoated NiS-VGCF composite. Electrochemical performance in all-solid-state cells was improved by forming favorable NiS-VGCF-SE interfaces.
3.5. References


4. Synthesis of sulfide solid electrolyte via liquid phase for all-solid-state batteries

4.1. Introduction

In bulk-type all-solid-state batteries, a composite positive or negative electrode consisting of three components of active materials, solid electrolytes (lithium-ion conduction path), and conductive additives (electron conduction path) is commonly used. Electrochemical reactions proceed at the solid-solid interfaces and are affected by the states of the interfaces in the composite electrode. In order to realize high performance of all-solid-state batteries, formation of intimate solid-solid interfaces between active materials and solid electrolytes is very important as well as the synthesis of the morphology-controlled active materials with high capacity. We have reported the coating of Li$_2$S-P$_2$S$_5$ solid electrolyte on LiCoO$_2$ particles (SE-coated LiCoO$_2$) by the pulsed laser deposition (PLD) method [1,2]. Charge-discharge capacities of all-solid-state cells using the SE-coated LiCoO$_2$ particles were higher than those of the cells with uncoated LiCoO$_2$. Preparation of solid electrolytes via liquid-phase method instead of gas-phase method such as PLD must be a very facile and cost-effective process to form good electrode-electrolyte interfaces.

Recently, preparation of a Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ (LGPS) thin film by a solution process using a hydrazine-based solvent has been reported [3]. LGPS crystals synthesized by a solid state reaction were dissolved in the hydrazine-based solvent, and a solution-processed LGPS film was obtained after removing the solvent by heat treatment of the solution. However, hydrazine has some toxicity. In our research group, it was observed that Li$_2$S-P$_2$S$_5$ glass solid electrolyte powders prepared by the mechanical milling method were not dissolved by using several organic solvents such as acetonitrile, pyridine, tetrahydrofuran, and N,N-dimethylformamide. N-methylformamide (NMF) is known to dissolve some materials containing PS$_4^{3-}$ groups or P$_2$S$_6^{4-}$ groups [4,5], and it has lower toxicity than hydrazine. The use of NMF would make it possible to dissolve the Li$_2$S-P$_2$S$_5$ glass solid electrolyte powders and form favorable electrode-electrolyte interfaces in the all-solid-state batteries. However, this process needs the preparation of solid electrolytes in advance by solid-state reaction or the mechanical milling method to obtain solutions of solid electrolytes. A new process of
direct synthesis of solid electrolytes via precursor solution including starting materials of Li₂S and P₂S₅ will be more effective in forming the composite electrodes with large contact area between electrode and electrolyte.

Liu et al. reported the synthesis of Li₃PS₄ by heat treatment (at 140 °C under vacuum) of Li₃PS₄·3THF (THF: tetrahydrofuran) which was prepared by the reaction of Li₂S and P₂S₅ in THF at room temperature [6]. The Li₃PS₄·3THF was obtained as a precipitation in THF and subsequent heat treatments of the Li₃PS₄·3THF gave the Li₃PS₄ crystal. Conventionally, Li₃PS₄ crystal is synthesized by the solid state reaction of Li₂S and P₂S₅ at 500 °C [7]. The use of NMF, which is known to dissolve some materials containing PS₄³⁻ groups, may contribute to the direct synthesis of Li₃PS₄ crystal via precursor solution including Li₂S, P₂S₅, and NMF. If homogeneous solid-liquid interfaces are formed among active materials, conductive additives, and the precursor solutions of solid electrolytes, simple preparation of composite electrodes can be achieved by removing solvents.

In this chapter, sulfide solid electrolytes and composite electrodes were prepared via liquid phase. Firstly, the sulfide solid electrolyte powders were reprecipitated from liquid phase. Powders of Li₂S-P₂S₅ glass solid electrolytes originally prepared by mechanical milling were dissolved in N-methylformamide (NMF) and a homogeneous solution was obtained. Moreover, the sulfide solid electrolyte was directly synthesized from the Li₂S and P₂S₅ by a liquid-phase reaction using NMF and n-hexane as reaction media. In this process, the precursor solution of sulfide solid electrolytes was directly prepared from Li₂S, P₂S₅, and NMF; the preparation of solid electrolytes in advance by the mechanical milling method is unnecessary. The NMF was removed under vacuum to obtain the precipitates, and ionic conductivity of the powders prepared via liquid phase was measured by the AC impedance measurement. In addition, sulfide solid electrolyte was deposited on LiCoO₂ particles and NiS-VGCF composites (see the previous chapter 3) by using the precursor solution of sulfide solid electrolytes. The obtained materials were applied to all-solid-state cells, and the effects of electrode-electrolyte solid-solid interfaces in the composite electrodes on the electrochemical properties were investigated in order to develop the all-solid-state batteries with high capacity and high rate capability.
4.2. Experimental

4.2.1. Formation of sulfide solid electrolyte from $N$-methylformamide solution of glass solid electrolyte

Powders of $80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$ (mol %) glass solid electrolyte were prepared by the mechanical milling method [8]. Reagent-grade $\text{Li}_2\text{S}$ (Idemitsu Kosan, 99.9%) and $\text{P}_2\text{S}_5$ (Aldrich, 99%) crystalline powders were used as starting materials. A mixture of these materials was mechanically milled at room temperature by a planetary ball mill apparatus (Fritsch, Pulverisette 7) using a zirconia pot (volume 45 mL) with 500 pieces of zirconia balls (4 mm in diameter). A rotating speed was 510 rpm and a milling time was 8 h.

The powders of $80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$ glass solid electrolyte were dissolved in anhydrous $N$-methylformamide (NMF), and a homogeneous transparent yellow solution was obtained. The concentration of the glass solid electrolyte in the solution was 18.5 wt.%. The NMF solution was dried at 150 °C for 3 h under vacuum to remove NMF, and pale yellow powders were obtained. All processes including the mechanical milling were performed in a dry Ar-filled glove box.

4.2.2. Synthesis of sulfide solid electrolyte from $\text{Li}_2\text{S}$ and $\text{P}_2\text{S}_5$ by a liquid-phase reaction using $N$-methylformamide and $n$-hexane

The $\text{Li}_3\text{PS}_4$ solid electrolyte was directly synthesized from crystalline powders of $\text{Li}_2\text{S}$ (Idemitsu Kosan, 99.9%) and $\text{P}_2\text{S}_5$ (Aldrich, 99%) by liquid-phase reaction using $N$-methylformamide (NMF) and $n$-hexane as reaction media. $\text{Li}_2\text{S}$ and $\text{P}_2\text{S}_5$ were mixed in a mortar, and the mixture was dispersed into 1.5 mL of $n$-hexane in a flask (volume 50 mL). The molar ratio of $\text{Li}_2\text{S}$ to $\text{P}_2\text{S}_5$ was 75 : 25 and the total weight of the mixture ($\text{Li}_2\text{S}$ and $\text{P}_2\text{S}_5$) was 300 mg. 1.5 mL of NMF was added dropwise to the suspension of $n$-hexane with stirring and cooling in an ice bath. After adding NMF, $n$-hexane phase (an upper phase) and NMF phase (a lower phase) were separated. The solution was stirred for 1 h with cooling, and the solution was stirred for 5 h under room temperature. A precursor solution was obtained after stirring and removing the $n$-hexane phase. The precursor solution was heated under vacuum at 180 °C for 3 h to remove NMF and obtained powder.
Sulfide solid electrolytes were deposited on LiCoO$_2$ particles (D-10, Toda Kogyo Corp.) and NiS-VGCF composites (see the previous chapter 3) by using the precursor solution. The precursor solution was mixed with LiCoO$_2$ particles or NiS-VGCF composites using a mortar and dried at 180 °C for 3 h under vacuum to remove NMF. The weight ratio of LiCoO$_2$ (or NiS-VGCF) to dissolved solid electrolyte was LiCoO$_2$ (or NiS-VGCF) : solid electrolyte = 92.5 : 7.5. LiCoO$_2$ particles used in this study were coated with LiNbO$_3$ layer in advance because all-solid-state cells using LiCoO$_2$ particles coated with oxides such as Li$_4$Ti$_5$O$_{12}$, LiNbO$_3$, or Li$_2$SiO$_3$ showed a high power density [9-11]. All processes were performed in a dry Ar-filled glove box.

4.2.3. Cell construction

All-solid-state cells using LiCoO$_2$ particles or NiS-VGCF composites coated with solid electrolyte (SE-coated LiCoO$_2$ particles or SE-coated NiS-VGCF composites) were constructed to investigate their electrochemical performance as follows.

SE-coated LiCoO$_2$ particles were used as a positive electrode. Neither solid electrolytes nor conductive additives were added to the positive electrode. The 80Li$_2$S·20P$_2$S$_5$ (mol%) glass-ceramic electrolyte was used as a separator. The 80Li$_2$S·20P$_2$S$_5$ glass-ceramic electrolyte was prepared by the mechanical milling method and subsequent heat treatment [8]. Indium foils were used as a negative electrode. Bilayer pellets (10 mm in diameter) consisting of the SE-coated LiCoO$_2$ as a positive electrode and the glass-ceramic electrolyte as a separator were prepared by pressing under 360 MPa, and then the indium foils were attached to the pellet by pressing under 240 MPa.

SE-coated NiS-VGCF composites and the glass-ceramic electrolyte were mixed in a mortar to prepare the composite electrode; the weight ratio of SE-coated NiS-VGCF composites : the glass-ceramic electrolyte is 40 : 60. For comparison, the composite electrode which consisted of the SE-coated NiS-VGCF composites prepared by pulsed laser deposition (40 wt.%) and the glass-ceramic electrolyte (60 wt.%) was prepared by mixing in a mortar. Two-electrode cells were fabricated using the composite electrode as a working electrode, the glass-ceramic electrolyte as a separator, and a Li-In alloy as a counter electrode.
The composite electrode and solid electrolyte were placed in a polycarbonate tube (10 mm diameter) and pressed together under 360 MPa at room temperature. The Li-In alloy was placed on the surface of the solid electrolyte side of the bilayer pellet. Then pressure of 120 MPa was applied to obtain a three-layered pellet. The three-layered pellet was finally sandwiched with two stainless-steel disks as current collectors. All preparation processes of the cells were conducted in a dry Ar-filled glove box.

4.2.4. Characterization

X-ray diffraction (XRD; Ultima IV; Rigaku) measurements were performed using Cu K\(\alpha\) radiation to identify the crystalline phases of the powder obtained via liquid phase. Raman spectroscopy was performed using a Raman spectrophotometer (LabRam HR-800; HORIBA Jobin Yvon) to identify structural units of the powder obtained via liquid phase after drying and the NMF solution of the solid electrolyte. The morphologies of SE-coated LiCoO\(_2\) particles and SE-coated NiS-VGCF composites were investigated using scanning electron microscopy (SEM; JSM-6610A; JEOL) coupled with an energy dispersive X-ray spectrometer (EDX; JED-2300; JEOL). Ionic conductivity of the powders obtained via liquid phase was measured by the AC impedance measurement at room temperature using an impedance analyzer (Solartron 1260) in the frequency range of 1 Hz to 1 MHz. The measurement was carried out for a pelletized sample with 10 mm in diameter and about 0.7 mm in thickness. A temperature dependence of ionic conductivity of the powders prepared via liquid phase was measured by the AC impedance using an impedance analyzer (Solartron 1260) in the frequency range of 1 Hz to 1 MHz. A pelletized sample with 10 mm in diameter and about 1 mm in thickness was used for the measurements. Carbon paste was applied to both faces of the pellet as a current collector. Electrochemical tests of the all-solid-state cells using SE-coated LiCoO\(_2\) particles and SE-coated NiS-VGCF composites were conducted under a constant current density of 0.13 and 3.8 mA cm\(^{-2}\) at 25 °C in an Ar atmosphere using a charge-discharge measurement device (BTS-2004; Nagano Co.).
4.3. Results and discussion

4.3.1. Formation of sulfide solid electrolyte from \(N\)-methylformamide solution of glass solid electrolyte

The powders of \(80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5\) (mol %) glass solid electrolyte were dissolved in anhydrous \(N\)-methylformamide (NMF), and a homogeneous transparent yellow solution was obtained (Figure 4-1). Figure 4-2 shows Raman spectra of (a) the original \(80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5\) glass solid electrolyte prepared by the mechanical milling method, (b) the NMF solution of the glass solid electrolyte, and (c) the obtained powder from the NMF solution after dried at 150 °C for 3 h. Raman band at 420 cm\(^{-1}\) is observed in all Raman spectra. Tachez et al. has reported that the band at 420 cm\(^{-1}\) is attributed to \(\text{PS}_4^{3-}\) ions [12]. This result suggests that the main structural unit in the obtained powder from the NMF solution is \(\text{PS}_4^{3-}\), which is the same as that of the original \(80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5\) glass.

Figure 4-3 shows the XRD patterns of the original \(80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5\) glass and the powder obtained from the NMF solution of the glass solid electrolyte after dried under vacuum. The original \(80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5\) glass prepared by the mechanical milling method was amorphous with a partial Li\(_2\)S crystal (Figure 4-3 (a)), whereas the powder obtained from the NMF solution after dried at 130 °C for 3 h was a mixture of Li\(_2\)S and unknown crystal (Figure 4-3 (b)). On the other hand, the diffraction pattern of the powder obtained from the NMF solution after dried at 150 °C for 3 h was attributed to the Li\(_3\)PS\(_4\) and Li\(_2\)S crystal (Figure 4-3 (c)). From these results, it is predicted that the unknown crystal obtained after dried at 130 °C for 3 h (Figure 4-3 (b)) is an intermediate for preparation of Li\(_3\)PS\(_4\) crystal; the Li\(_3\)PS\(_4\) crystal was formed by further heating of the intermediate at 150 °C. However, the thio-LISICON analogue (Li\(_{3+5x}\)P\(_{1-x}\)S\(_4\)) with high lithium-ion conductivity was not obtained.

Figure 4-4 shows the impedance spectra of the original \(80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5\) glass and the obtained powders from the NMF solution at room temperature. Total ionic conductivity of the original \(80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5\) glass was \(2.3\times10^{-4}\) S cm\(^{-1}\). The impedance spectrum of the obtained powder from the NMF solution showed a semicircle corresponding to the grain boundary resistance and the total ionic conductivity was \(2.6\times10^{-6}\) S cm\(^{-1}\). From the XRD patterns (Figure 4-3), it was confirmed that the original \(80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5\) glass was crystallized.
A number of lithium ion conducting glasses of oxides [4,5], sulfides [6,7], oxyhalides [8], thiohalides [9], and oxysulfides [10–13] with high performance as solid electrolytes have been fabricated using a melt-quenching technique. We have prepared series of glassy solid electrolytes of oxides and oxysulfides [14] with extremely high conductivity of lithium ions using a twin-roller quenching technique [16]. However, when these glasses are used as solid electrolyte for lithium secondary batteries, the glasses should be ground into fine powders in order to make good contact with the electrode materials [17]. Mechanochemical preparation of sulfide-based glasses and glass-ceramics has also been developed from the idea that they are

Figure 4-1 The photograph of $N$-methylformamide (NMF) solution of the 80Li$_2$S·20P$_2$S$_5$ (mol %) glass electrolyte.
Figure 4-2 (a) Raman spectra of the original 80Li$_2$S·20P$_2$S$_5$ (mol %) glass solid electrolyte, (b) the NMF solution of the glass electrolyte, and (c) the obtained powder from the NMF solution of the glass electrolyte after dried at 150 °C for 3 h under vacuum.
Figure 4-3 XRD patterns of (a) the original 80Li$_2$S·20P$_2$S$_5$ (mol %) glass and the powder obtained from the NMF solution of the glass electrolyte after dried at (b) 130 °C or (c) 150 °C for 3 h under vacuum.
Figure 4-4 Nyquist plots of (a) the original 80Li₂S·20P₂S₅ (mol %) glass solid electrolyte and (b) the solid electrolyte obtained from the NMF solution of the glass electrolyte.
Figure 4-5 Temperature dependence of ionic conductivity of the solid electrolyte obtained from the NMF solution of the glass electrolyte.
through dissolving in NMF and reprecipitation. Crystallized materials often have lower ionic conductivity than glassy ones, and crystallization of amorphous solid electrolyte should cause increasing grain boundary resistance. Rather low ionic conductivity of the obtained powder in this study must be caused by the crystallization of solid electrolyte and increasing of grain boundary resistance.

Figure 4-5 shows the temperature dependence of ionic conductivity of a pelletized solid electrolyte obtained from the NMF solution. The ionic conductivity obeyed the Arrhenius law; the activation energy for the ionic conduction calculated from the slope of the plots was 42 kJ mol\(^{-1}\). The ionic conductivity of the solid electrolyte obtained from the NMF solution was lower than that of the original 80Li\(_2\)S·20P\(_2\)S\(_5\) glass [8], and the activation energy was higher than that of original 80Li\(_2\)S·20P\(_2\)S\(_5\) glass (37 kJ mol\(^{-1}\)) [13]. Although ionic conductivity of the solid electrolyte prepared from the NMF solution was lower than that of original 80Li\(_2\)S·20P\(_2\)S\(_5\) glass, the conductivity was higher than that of the Li\(_3\)PS\(_4\) crystal (10\(^{-7}\) S cm\(^{-1}\)) [7]. This suggests that a glass phase with higher conductivity partially exists in the prepared electrolyte. Although the obtained powders from the NMF solution showed lower ionic conductivity than the original 80Li\(_2\)S·20P\(_2\)S\(_5\) glass prepared by mechanical milling, the sulfide solid electrolytes powders were reprecipitated via NMF solution.

### 4.3.2. Synthesis of sulfide solid electrolyte from Li\(_2\)S and P\(_2\)S\(_5\) by a liquid-phase reaction using N-methylformamide and \(n\)-hexane

It was observed that P\(_2\)S\(_5\) can be dissolved in \(N\)-methylformamide (NMF), and then Li\(_2\)S can be dissolved in the NMF solution of P\(_2\)S\(_5\). After removing NMF from the solution under vacuum, the starting material of Li\(_2\)S was reprecipitated. It is important that NMF is mixed with the suspension of both Li\(_2\)S and P\(_2\)S\(_5\) in \(n\)-hexane to prepare Li\(_2\)S-P\(_2\)S\(_5\) electrolytes as shown in Figure 4-6. A precursor solution (Figure 4-7) was obtained after stirring and removing the \(n\)-hexane phase. Figure 4-8 shows the Raman spectra of (a) the powder obtained from the precursor solution using NMF and \(n\)-hexane as reaction media after drying at 180 °C for 3 h under vacuum and (b) the precursor solution after stirring and removing \(n\)-hexane. For comparison, the spectra for (c) NMF and (d) P\(_2\)S\(_5\) used as the starting material
Figure 4-6 Schematic illustration of the experimental setup for liquid-phase synthesis of Li$_3$PS$_4$ solid electrolyte.
solid electrolytes with high electronic conductivity are found to be the most important task in recent years. One of the most promising candidates is lithium ion (Li$^{+}$) with a high ion mobility at elevated temperatures. The photograph (Figure 4-7) shows a reaction mixture of Li$_2$S and P$_2$S$_5$ after stirring and removing n-hexane.
Figure 4-8 Raman spectra of (a) the powder obtained from the NMF precursor solution after dried at 180 °C for 3 h under vacuum, (b) the NMF precursor solution after stirring and removing n-hexane, (c) NMF, and (d) P$_2$S$_5$ used as the starting material.
were also shown in Figure 4-8. Raman bands at 420 cm$^{-1}$ were observed in the spectrum for the powder obtained from the precursor solution after drying at 180 °C for 3 h under vacuum (Figure 4-8 (a)) and that of the precursor solution (Figure 4-8 (b)) were attributed to PS$_4^{3-}$ ions. Raman bands due to P$_2$S$_5$ (Figure 4-8 (d)) were not observed in the spectrum of the precursor solution (Figure 4-8 (b)). From these results, it was suggested that P$_2$S$_5$ used as the starting material reacted with Li$_2$S in NMF, and the presence of PS$_4^{3-}$ ions was detected by Raman spectroscopy in the precursor solution. After drying at 180 °C for 3 h under vacuum, the powder (consisting of PS$_4^{3-}$) was obtained by removal of NMF and its main structural units were not changed from that of the precursor solution.

Figure 4-9 (a) and (b) respectively show the XRD patterns of the powder obtained from the precursor solution after dried at 150 °C or 180 °C for 3 h under vacuum. The pattern of Li$_2$S crystal used as a starting material is also shown. The powder obtained from the precursor solution after dried at 150 °C for 3 h was a mixture of Li$_3$PS$_4$ and unknown crystal (Figure 4-9 (a)). The pattern of the unknown crystal was the same as that of the intermediate for preparation of Li$_3$PS$_4$ crystal as shown in Figure 4-3 (b). From this result, Li$_3$PS$_4$ crystal must be formed as a single phase by heating at more than 150 °C. As shown in Figure 4-9 (b), the observed peaks in the diffraction pattern of the obtained powder from the precursor solution after dried at 180 °C for 3 h were attributed to that of Li$_3$PS$_4$ crystal, and the diffraction peaks of Li$_2$S used as the starting material were not observed in the XRD pattern. From these results, Li$_2$S completely reacted with P$_2$S$_5$ and the Li$_3$PS$_4$ crystal was prepared after drying the precursor solution at 180 °C for 3 h under vacuum. The obtained Li$_3$PS$_4$ crystal has the composition corresponding to a nominal composition of starting materials (Li$_2$S : P$_2$S$_5$ = 3 : 1).

Figure 4-10 shows the temperature dependence of ionic conductivity of a pelletized Li$_3$PS$_4$ obtained from the precursor solution. Ionic conductivity of the Li$_3$PS$_4$ was 2.3×10$^{-6}$ S cm$^{-1}$ at room temperature, which was almost the same as that of the solid electrolyte reprecipitated from the NMF solution of 80Li$_2$S·20P$_2$S$_5$ (mol %) glass. The ionic conductivity obeyed the Arrhenius law; the activation energy for ionic conduction calculated from the slope of the plots was 45 kJ mol$^{-1}$. 

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Figure 4-9 XRD patterns of the powder obtained from the NMF precursor solution after dried at (a) 150 °C or (b) 180 °C for 3 h under vacuum. The pattern of Li$_2$S crystal used as a starting material is also shown.
Figure 4-10 Temperature dependence of ionic conductivity of the Li$_3$PS$_4$ solid electrolyte obtained from the NMF precursor solution.
Figure 4-11 (a) shows the SEM image of uncoated LiCoO$_2$ particles, whereas Figure 4-11 (b-f) shows the SEM and EDX mapping (Co, Nb, P, and S) of the Li$_3$PS$_4$ solid electrolyte-coated LiCoO$_2$ (SE-coated LiCoO$_2$) particles. The SEM image showed that the size of the LiCoO$_2$ particles was about 10 µm; the coating materials were observed on the LiCoO$_2$ particles. The particle size of LiCoO$_2$ was not changed by the coating. Niobium element of LiNbO$_3$ coating layer was detected on LiCoO$_2$ particles. Phosphorus and sulfur elements of Li$_3$PS$_4$ solid electrolyte layer were also detected on LiCoO$_2$ particles, indicating that the LiCoO$_2$ particles were covered with Li$_3$PS$_4$ solid electrolyte layer. The thickness of the solid electrolyte on the LiCoO$_2$ was calculated from the surface area of LiCoO$_2$ (0.12 m$^2$ g$^{-1}$) and the density of Li$_3$PS$_4$ crystals (1.872 g cm$^{-3}$) [14]. The estimated thickness of the solid electrolyte layers was about 360 nm.

All-solid-state cells using the prepared SE-coated LiCoO$_2$ (LiCoO$_2$ : SE layer = 92.5 : 7.5, wt.%) and uncoated LiCoO$_2$ as a positive electrode were fabricated. Figure 4-12 shows initial charge-discharge curves of these all-solid-state In / LiCoO$_2$ cells with SE-coated LiCoO$_2$ or uncoated LiCoO$_2$. Neither solid electrolyte particles nor conductive additive particles such as acetylene black were added to the positive electrode in this study. These cells were charged up to 3.6 V (vs. Li-In) and then discharged to 2 V (vs. Li-In) at a current density of 0.13 mA cm$^{-2}$. The cell using uncoated LiCoO$_2$ particles did not discharge. On the other hand, the cell using SE-coated LiCoO$_2$ worked as a rechargeable battery without the addition of solid electrolyte and conductive additive particles to the positive electrode, and showed an initial discharge capacity of 32 mAh g$^{-1}$. Although the ionic conductivity of the Li$_3$PS$_4$ solid electrolyte obtained from the NMF solution was relatively low at the present stage, the all-solid-state cell was charged and discharged by coating LiCoO$_2$ with solid electrolyte layer using the NMF solution. These results suggest that the favorable electrode-electrolyte interfaces with large contact area were formed by using of the precursor solution of the solid electrolyte.

A composite electrode consisting of NiS active materials, sulfide solid electrolytes, and conductive additives was prepared via liquid phase by using NiS-VGCF composites (see the previous chapter 3) and the precursor solution. Figure 4-13 shows the SEM and EDX
Figure 4-11 (a) SEM image of uncoated LiCoO$_2$ particles. (b) SEM and (c-f) EDX mapping (Co, Nb, P, and S) of SE-coated LiCoO$_2$ particles prepared by using the NMF precursor solution. SE denotes the solid electrolyte.
Figure 4-12 Initial charge-discharge curves of all-solid-state cells using SE-coated LiCoO$_2$ particles prepared by using the NMF precursor solution.
mapping (Ni, P, and S) of the Li$_3$PS$_4$ solid electrolyte-coated NiS-VGCF (SE-coated NiS-VGCF) composites. Phosphorus elements of Li$_3$PS$_4$ solid electrolyte layer were also detected on NiS-VGCF composites. From the EDX mapping in Figure 4-13, sulfide solid electrolyte was deposited on the NiS-VGCF composites by using the precursor solution.

All-solid-state cells using the prepared SE-coated NiS-VGCF composite (NiS-VGCF composite : SE layer = 92.5 : 7.5, wt.%) were fabricated. Figure 4-14 (a) shows the charge-discharge curves of the all-solid-state cells with the SE-coated NiS-VGCF composite prepared by using the precursor solution at the first, second, and 50th cycles under the current density of 3.8 mA cm$^{-2}$ (corresponding to ca. 1 C). In addition, Figure 4-14 (b) shows the cycle performance of the all-solid-state cells using the SE-coated NiS-VGCF composite prepared by using the precursor solution or pulsed laser deposition (PLD) at 3.8 mA cm$^{-2}$. For comparison, the cycle performance of the cell using the uncoated NiS-VGCF composite is also shown in Figure 4-14 (b). In the previous chapter 3, the all-solid-state cell using the SE-coated NiS-VGCF composite prepared by PLD showed the initial discharge capacity of 300 mAh g$^{-1}$, and exhibited better cycle performance than the cell using the uncoated NiS-VGCF composite at 3.8 mA cm$^{-2}$. The three composite electrodes consisted of the 40 wt.% SE-coated (or uncoated) NiS-VGCF composites, and 60 wt.% glass-ceramic electrolyte particles. The obtained capacity of the cell using the SE-coated (or uncoated) NiS-VGCF composite was normalized by the total weight of the SE-coated NiS-VGCF composite in the composite electrode. As shown in Figure 4-14 (a), the all-solid-state cell using the SE-coated NiS-VGCF composites prepared by using the precursor solution showed the initial discharge capacity of 68 mAh g$^{-1}$, and worked as a rechargeable battery at 3.8 mA cm$^{-2}$. In addition, the capacity of the all-solid-state cell with SE-coated NiS-VGCF composite prepared by using the precursor solution was smaller than that of the cell with uncoated and SE-coated NiS-VGCF composite prepared by PLD. This is because the ionic conductivity of the Li$_3$PS$_4$ crystal obtained from the precursor solution was lower than that of Li$_2$S-P$_2$S$_5$ amorphous solid electrolyte prepared by PLD [15]. In addition, considering that the capacity of the cell with SE-coated NiS-VGCF composite prepared by using the precursor solution was smaller than that of the cell with uncoated NiS-VGCF composite, the performance of the cell
Figure 4-13 (a) SEM and (b-d) EDX mapping (Ni, P, and S) of SE-coated NiS-VGCF composites prepared by using the NMF precursor solution. SE denotes the solid electrolyte.
Figure 4-14 (a) Charge-discharge curves of the all-solid-state cells with the SE-coated NiS-VGCF composite prepared by using the NMF precursor solution at the 1st, 2nd, and 50th cycles under the current density of 3.8 mA cm$^{-2}$ (ca. 1 C). (b) Cycle performance of the cells using the SE-coated NiS-VGCF composite prepared by using the precursor solution or pulsed laser deposition. Cycle performance of the cell using the uncoated NiS-VGCF composite is also shown.
(using the SE-coated NiS-VGCF composite) at a high current density of 3.8 mA cm\(^{-2}\) is strongly affected by the low ionic conductivity of solid electrolytes as a coating layer, compared to the performance of the cell (using SE-coated LiCoO\(_2\) particles) at a low current density of 0.13 mA cm\(^{-2}\) (in Figure 4-12). Therefore, the performance of all-solid-state cells at the high current density will be improved with increasing the ionic conductivity of the solid electrolytes prepared via a precursor solution. Future studies on electrolyte compositions and suitable solvents are needed to prepare amorphous or crystalline solid electrolytes with high lithium-ion conductivity via the precursor solution of sulfide solid electrolytes.

4.4. Summary

The Li\(_2\)S-P\(_2\)S\(_5\) solid electrolyte was prepared from \(N\)-methylformamide (NMF) solution of the 80Li\(_2\)S·20P\(_2\)S\(_5\) (mol %) glass solid electrolyte. The crystalline phase of the obtained powders was a mixture of Li\(_3\)PS\(_4\) and Li\(_2\)S, and the main structural unit was the same as that in the original 80Li\(_2\)S·20P\(_2\)S\(_5\) glass. The ionic conductivity of the prepared electrolyte was 2.6×10\(^{-6}\) S cm\(^{-1}\) at room temperature.

Li\(_3\)PS\(_4\) solid electrolyte was directly synthesized from Li\(_2\)S and P\(_2\)S\(_5\) by a liquid-phase reaction using NMF and \(n\)-hexane as a solvent. The presence of PS\(_4^{3-}\) ions was detected by Raman spectroscopy in a precursor solution including Li\(_2\)S, P\(_2\)S\(_5\), and NMF. Subsequent drying of the precursor solution at 180 °C for 3 h under vacuum gave the Li\(_3\)PS\(_4\) solid electrolyte. The ionic conductivity of the obtained Li\(_3\)PS\(_4\) solid electrolyte was 2.3×10\(^{-6}\) S cm\(^{-1}\) at room temperature, and was almost the same as that of the obtained solid electrolyte prepared form the NMF solution dissolved with the 80Li\(_2\)S·20P\(_2\)S\(_5\) glass.

Sulfide solid electrolyte (SE) was deposited on LiCoO\(_2\) particles and NiS-VGCF composites by using the NMF precursor solution. At a low current density of 0.13 mA cm\(^{-2}\), an all-solid-state cell using the SE-coated LiCoO\(_2\) particles as a positive electrode worked as a rechargeable battery without the addition of solid electrolyte particles in the positive electrode, suggesting that the favorable electrode-electrolyte interfaces with large contact area were formed by using the electrolyte solution. In addition, the all-solid-state cell using the SE-coated NiS-VGCF composites worked as a rechargeable battery at a high current density.
of 3.8 mA cm\(^{-2}\). However, the capacity of the all-solid-state cell with SE-coated NiS-VGCF composite prepared by using a NMF precursor solution was smaller than that of the cell with SE-coated NiS-VGCF composite prepared by pulsed laser deposition (PLD). This is because the ionic conductivity of the Li\(_3\)PS\(_4\) crystal obtained from the NMF precursor solution was lower than that of Li\(_2\)S-P\(_2\)S\(_5\) amorphous solid electrolyte prepared by PLD. In addition, the performance of the cell (using the SE-coated NiS-VGCF composite) at a high current density of 3.8 mA cm\(^{-2}\) is strongly affected by the ionic conductivity of solid electrolytes as a coating layer, compared to the performance of the cell (using SE-coated LiCoO\(_2\) particles) at a low current density of 0.13 mA cm\(^{-2}\). Therefore, the performance of all-solid-state cells at the high current density will be improved with increasing the ionic conductivity of the solid electrolytes prepared via a precursor solution.
4.5. References


5. General conclusions

In this thesis, a composite electrode with favorable solid-solid interfaces was prepared via liquid phase in order to develop high-performance all-solid-state batteries. We focused on these three topics:
(A) Synthesis of active materials with high capacity by a hot soap technique
(B) Morphology-design of composite electrodes with a high capacity and a high rate capability
(C) Liquid-phase synthesis of sulfide-based solid electrolytes

Metal phosphides and sulfides (SnP$_{0.94}$, NiP$_2$, SnS, and NiS) were selected as active materials with high capacity, and synthesized by a hot soap technique. The effects of the crystal phase and morphology on the electrochemical performance of all-solid-state cells were examined. The composite electrode with favorable solid-solid interfaces was prepared by a combination of the hot soap technique (liquid phase) and pulsed laser deposition method (gas phase). Furthermore, a precursor solution of sulfide solid electrolytes was prepared by using a liquid-phase reaction of Li$_2$S and P$_2$S$_5$ in N-methylformamide (NMF) in order to prepare the composite electrode via liquid phase. The following results and considerations were obtained.

1. SnP$_{0.94}$ and NiP$_2$ were synthesized by thermal decomposition of metal salts and trioctylphosphine (TOP) as a phosphorus source. Teardrop-shaped SnP$_{0.94}$ particles with the size of 500 nm were prepared by diffusion of phosphorus derived from TOP into spherical Sn particles. On the other hand, the obtained nickel phosphide particles changed from Ni$_5$P$_4$ particles (500 nm) to NiP$_2$ particles (200-500 nm) by increasing the reaction time and using hydrate nickel precursors such as nickel acetate tetrahydrate (Ni(Ac)$_2$·4H$_2$O). This result suggests that TOP molecules as a phosphorus source could possibly substitute for water molecules in the structure of Ni(Ac)$_2$·4H$_2$O, and thus Ni(Ac)$_2$·4H$_2$O could promote diffusion of phosphorus derived from TOP to nickel atoms.
2. SnS and NiS were synthesized by thermal decomposition of metal salts and 1-dodecanethiol (DT) as a sulfur source. Needlelike SnS particles were obtained by using TOP as a coordinating solvent, whereas platelike SnS particles were obtained by using OAm as a coordinating solvent. Needlelike SnS particles were formed by the diffusion of sulfur derived from DT into spherical Sn particles, and the aspect ratio of needlelike SnS particles was affected by the amount of DT. On the other hand, Ni$_9$S$_8$ nanorods with the size of 100 nm were obtained by using oleylamine (OAm) as a coordinating solvent, whereas NiS nanoparticles with the size of 50 nm were prepared by using 1-octadecene (ODE) as a noncoordinating solvent. Both Ni$_9$S$_8$ and NiS were formed via thermal decomposition of nickel(II) dodecanethiolate. Nickel sulfide crystals with different phases were obtained by selecting the solvent (OAm or ODE) as reaction media. This is because the excessive amount of OAm molecules has a strong capping ability to nickel ions in nickel(II) dodecanethiolate, and the OAm molecules prevent the diffusion of sulfur derived from nickel(II) dodecanethiolate and free DT.

3. The all-solid-state cells were fabricated using the obtained SnP$_{0.94}$, NiP$_2$, SnS, and NiS particles. All the cells showed the large discharge capacity (about 800-1000 mAh g$^{-1}$) at the 1st cycle under the current density of 0.13 mA cm$^{-2}$. The initial discharge capacity of the all-solid-state cell using needlelike SnS particles as an active material was larger than that of the cell using platelike SnS particles. This result suggests that the use of needlelike particles as an active material increases contact area among the three components (SnS active materials, solid electrolytes, and conductive additives), and then forms a continuous lithium-ion conducting paths in composite electrodes. However, after 15 cycles, the discharge capacity of the cells is almost the same because of a large volume change and contact loss with solid electrolyte particles during charge-discharge cycles. On the other hand, the cell using NiS nanoparticles with the size of 50 nm exhibited high capacity retention during 20 cycles, and shows an excellent cycle performance. It was difficult to synthesize one-dimensional NiS active material by a hot soap technique. Therefore, in order to form one-dimensional lithium-ion and electron
conduction paths in a composite electrode, morphology-design of the composite electrode was needed as an alternative to synthesis of one-dimensional NiS active material.

4. Nanocomposites including NiS nanoparticles, carbon fibers, and solid electrolytes were prepared by a combination of the hot soap technique and the pulsed laser deposition (PLD). Firstly, NiS-VGCF (VGCF: vapor grown carbon fiber) composites were synthesized by a hot soap technique. NiS nanoparticles of 50 nm in diameter were formed on the VGCF surface. The all-solid-state cell using NiS-VGCF composite retained a discharge capacity of 520 mAh g\(^{-1}\) after 30 cycles, and exhibited better cycle performance than the cell using the electrode prepared by hand-grinding of a mixture of NiS nanoparticles, solid electrolyte, and VGCF at a current density of 1.3 mA cm\(^{-2}\) (ca. 1/3 C). This result suggests that the formation of intimate NiS-VGCF interfaces gave favorable electron conduction paths to NiS active materials. Next, composite materials (SE-coated NiS-VGCF composites) including NiS-VGCF composites and sulfide solid electrolytes were prepared by deposition of the Li\(_2\)S-P\(_2\)S\(_5\) solid electrolyte thin films onto NiS-VGCF composites using PLD. An amorphous solid electrolyte thin film with the thickness of ca. 5 nm was observed on NiS nanoparticles. At a high current density of 3.8 mA cm\(^{-2}\) (ca. 1 C), the all-solid-state cell using the SE-coated NiS-VGCF composite showed the initial discharge capacity of 300 mAh g\(^{-1}\), and exhibited better cycle performance than the cell using the uncoated NiS-VGCF composite. These results suggest that the formation of intimate interfaces among NiS, VGCF, and solid electrolyte gives favorable electron and lithium-ion conduction paths to NiS active materials.

5. Sulfide solid electrolytes and composite electrodes were prepared via liquid phase. Firstly, the sulfide solid electrolyte powders were reprecipitated via liquid phase. Powders of 80Li\(_2\)S-20P\(_2\)S\(_5\) (mol %) glass solid electrolyte originally prepared by mechanical milling were dissolved into N-methylformamide (NMF) and a homogeneous solution was obtained. The crystalline phase of the obtained powders was a mixture of Li\(_3\)PS\(_4\) and Li\(_2\)S, and the main structural unit (PS\(_4^{3-}\) unit) was the same as that in the
original 80Li₂S:20P₂S₅ glass. The ionic conductivity of the prepared electrolyte was 2.6×10⁻⁶ S cm⁻¹ at room temperature. Moreover, the sulfide solid electrolyte was directly synthesized from the Li₂S and P₂S₅ by a liquid-phase reaction using NMF and n-hexane as reaction media. In this process, the precursor solution of sulfide solid electrolytes was directly prepared from Li₂S, P₂S₅, and NMF; the preparation of solid electrolytes in advance by mechanical milling is unnecessary. The presence of PS₄³⁻ ions was detected by Raman spectroscopy in the precursor solution, and subsequent drying of the precursor solution at 180 °C for 3 h under vacuum produced the Li₃PS₄ crystal. The ionic conductivity of the obtained Li₃PS₄ solid electrolyte was 2.3×10⁻⁶ S cm⁻¹ at room temperature, and was almost the same as that of the obtained solid electrolyte prepared form the NMF solution dissolved with the 80Li₂S:20P₂S₅ glass.

6. Sulfide solid electrolyte was deposited on LiCoO₂ particle and NiS-VGCF composite by using a precursor solution including Li₂S powders, P₂S₅ powders, and N-methylformamide (NMF). Firstly, all-solid-state cells using the prepared SE-coated or uncoated LiCoO₂ particle as a positive electrode were fabricated. At a low current density of 0.13 mA cm⁻², the cell using SE-coated LiCoO₂ particle worked as a rechargeable battery without the addition of solid electrolyte and conductive additive particles to the positive electrode, and showed an initial discharge capacity of 32 mAh g⁻¹. This result suggests that the favorable electrode-electrolyte interfaces with large contact area were formed by using the precursor solution of the solid electrolyte. Moreover, all-solid-state cells using the SE-coated NiS-VGCF composite were fabricated. At a high current density of 3.8 mA cm⁻², the capacity of the all-solid-state cell with SE-coated NiS-VGCF composite prepared by using a precursor solution was smaller than that of the cell with SE-coated NiS-VGCF composite prepared by pulsed laser deposition (PLD). This is because the ionic conductivity of the Li₃PS₄ crystal obtained from the precursor solution was lower than that of Li₂S-P₂S₅ amorphous solid electrolyte prepared by PLD. In addition, the performance of the cell (using the SE-coated NiS-VGCF composite) at a high current density of 3.8 mA cm⁻² is strongly affected by the ionic conductivity of solid electrolytes.
as a coating layer, compared to the performance of the cell (using SE-coated LiCoO$_2$
particles) at a low current density of 0.13 mA cm$^{-2}$. As described herein, SE-coated
NiS-VGCF composites were synthesized by using a precursor solution as the first step
toward a liquid-phase synthesis of nanocomposites consisting of active materials, sulfide
solid electrolytes and conductive additives. In order to improve the electrochemical
performance of the all-solid-state cells using the nanocomposites, future studies on
electrolyte compositions and suitable solvents are needed to prepare amorphous or
crystalline solid electrolytes with high lithium-ion conductivity via a precursor solution of
sulfide solid electrolytes.
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List of Publications

Original articles regarding this study are as follows:

1. “SnP\textsubscript{0.94} active material synthesized in high-boiling solvents for all-solid-state lithium batteries”
   Aso, K.; Kitaura, H.; Hayashi, A.; Tatsumisago, M.

2. “Phase-selective synthesis of nickel phosphide in high-boiling solvent for all-solid-state lithium secondary batteries”
   Aso, K.; Hayashi, A.; Tatsumisago, M.

3. “Synthesis of needlelike and platelike SnS active materials in high-boiling solvents and their application to all-solid-state lithium secondary batteries”
   Aso, K.; Hayashi, A.; Tatsumisago, M.

4. “Synthesis of nanosized nickel sulfide in high-boiling solvent for all-solid-state lithium secondary batteries”
   Aso, K.; Kitaura, H.; Hayashi, A.; Tatsumisago, M.

5. “Preparation conditions of NiS active material in high-boiling solvents for all-solid-state lithium secondary batteries”
   Aso, K.; Hayashi, A.; Tatsumisago, M.
6. “Synthesis of NiS-carbon fiber composites in high-boiling solvent to improve electrochemical performance in all-solid-state lithium secondary batteries”
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(Chapter 3)

7. “All-solid-state lithium secondary batteries using NiS-carbon fiber composite electrodes coated with Li$_2$S-P$_2$S$_5$ solid electrolytes by pulsed laser deposition”
   Aso, K.; Sakuda, A.; Hayashi, A.; Tatsumisago, M.

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8. “Formation of Li$_2$S-P$_2$S$_5$ solid electrolyte from N-methylformamide solution”
   Teragawa, S.; Aso, K.; Tadanaga, K.; Hayashi, A.; Tatsumisago, M.

(Chapter 4)

9. “Preparation of Li$_2$S-P$_2$S$_5$ solid electrolyte from N-methylformamide solution and application for all-solid-state lithium battery”
   Teragawa, S.; Aso, K.; Tadanaga, K.; Hayashi, A.; Tatsumisago, M.

(Chapter 4)

10. “Liquid-phase synthesis of Li$_3$PS$_4$ solid electrolyte using N-methylformamide for all-solid-state lithium batteries”
    Teragawa, S.; Aso, K.; Tadanaga, K.; Hayashi, A.; Tatsumisago, M.

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