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Development of Novel Electrode Materials for All-Solid-State Lithium Secondary Batteries using Sulfide Solid Electrolyte

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1. General Introduction

Rechargeable lithium-ion secondary batteries are powerful energy storage systems used in various electronic devices such as laptop computer and mobile phone because of their high energy density and good cyclability [1-5]. These lithium-ion batteries also attract much attentions as power sources for plug-in hybrid vehicle (PHV) and battery electric vehicles (BEV). The demand for the batteries over the next several years is expected to grow rapidly. Under the circumstance, the development of safer lithium-ion batteries than the current battery systems is required. The commercialized lithium-ion secondary batteries generally consist of a lithium transition-metal oxide (e.g., LiCoO₂ or LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂) as positive electrode, graphite as negative electrode, and an organic electrolyte with lithium salts embedded in a separator felt. The flammability of the organic electrolyte is the main factor causing the low safety of the battery.

All-solid-state lithium secondary batteries using non-flammable inorganic solid electrolyte have been investigated for new technologies to the current battery systems with the organic electrolyte because of the high safety [6-12]. To develop the practical all-solid-state batteries, solid electrolytes with high lithium-ion conductivity have been explored [13-27]. In the solid electrolytes studied for the all-solid-state batteries recently, there are mainly two types: oxide and sulfide solid electrolytes. In the oxide solid electrolytes, perovskite-type Li_{0.34}La_{0.51}TiO_{2.94} [13], NASICON-type Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ [14], and garnet-type Li₇La₃Zr₂O₁₂ [17] solid electrolytes have been reported to show lithium-ion conductivity from more than 10^{-5} S cm⁻¹. Some garnet-type solid electrolytes with Zr^{4+} partially replaced by Ta^{5+} or Li^+ partially replaced by Ga^{3+} have the high lithium-ion conductivity of around 10^{-3} S cm⁻¹ [28,29] close to that of liquid electrolytes ($\sim 10^{-2}$ S cm⁻¹). To use the oxide solid electrolytes practically, sintering process at high temperature is required for the high density and the low grain boundary resistance. On the other hand, in the sulfide solid electrolytes, $Li_2S-P_2S_5$ systems [15,16], $Li_{10}GeP_2S_{12}$ (LGPS) [18], and Li_6PS_5C1 [20] have been reported to have high lithium-ion conductivity from more than 10^{-4} S cm⁻¹. $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$, which is one of the LGPS families, shows the highest lithium-ion conductivity of 2.5×10^{-2} S cm⁻¹ [10]. The higher polarization of sulfide ions compared with that of oxide ions leads to the high lithium-ion conductivity of the sulfide solid electrolytes. Since the sulfide solid electrolytes are much softer than the oxide solid electrolytes, the grain boundary can easily be decreased by a cold-pressing [7]. Many papers on the all-solid-state batteries using these sulfide solid electrolytes have been reported so far [7, 10, 18, 30-32].

For the practical all-solid-state batteries, another key material is active material. Lithium transition-metal oxides commercialized for the cathode materials in the lithium-ion secondary batteries (LiCoO₂ [33], LiMn₂O₄ [34], LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ [35], LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ [36], and LiFePO₄ [37]) have been studied in the all-solid-state batteries [38-46]. These oxide cathodes have the moderate capacity from 120 to 200 mAh g^{-1} . The advantages for the oxide cathodes are the insertion reaction derived from the layered structure and high discharge voltage based on the transition metal with high valence, resulting in high-power and high-energy density lithium-ion batteries. Moreover, the Li⁺ inclusions in the oxide cathodes allows the utilization of non-Li⁺ containing anode materials. However, in the all-solid-state batteries using the sulfide solid electrolytes, the oxide cathodes require the coating layer to form the favorable electrode-electrolyte interface with low resistance.

Since the interfacial layer with high resistance is formed by the elemental diffusion at the interface between the oxide electrode and the sulfide solid electrolyte during the charge cycle, the coting layer is required to suppress the formation of the interfacial layer [6,40]. However, the formation of the coating layer on the surface of the oxide cathodes can cause high cost and complexity under the manufacture. Thus, the favorable electrode-electrolyte interface with low resistance should be formed without the coating layer. Considering the elemental diffusion leading to the formation of the interfacial layer with high resistance, the elemental similarity between the electrode and the electrolyte can allow the formation of the favorable electrode-electrolyte interface without the coating layer. Thus, cathode materials with similar elements as the sulfide solid electrolytes or novel cathode materials are required for the formation of the favorable electrode-electrolyte interface without the coating layer.

Sulfur has been investigated as the cathode material for the all-solid-state batteries [47-49]. The sulfur cathode has lower discharge voltage (~ 2.1 V vs. Li). However, the theoretical capacity is 1672 mAh g⁻¹, which is 8 times higher than that of the commercialized oxide cathode materials. From this high theoretical capacity, sulfur is expected to improve the energy density of the lithium-ion batteries significantly. One of the disadvantages of the sulfur cathode material is its insulating nature (5×10^{-18} S cm⁻¹) [50]. The sulfur cathode needs large amounts of carbon additives, typically 30-60 wt% [51,52], to form sufficient electron conducting paths in the electrode. The large amounts of the additives decrease in the volumetric energy density of the batteries. Moreover, the large volume change of sulfur (~80 %) during the discharge-charge cycles based on the conversion reaction can lead to high interfacial resistance between the electrode and the electrolyte. Thus, the formation of the favorable electrode-electrolyte interface with low resistance is difficult for the sulfur cathode.

Some transition-metal sulfides such as NiS [53], MS_2 (M = Ti [54,55] and Mo [56]), and

amorphous MS_3 (M = Ti [55,57] and Mo [57,58]) also have been investigated as the cathode materials for the all-solid-state batteries. These sulfide cathodes can mainly be classified by the types of reactions: insertion and conversion reactions. TiS2 has been reported to show the insertion reaction based on the layered structure [59,60]. The theoretical capacity of the insertion reaction of TiS₂ is 239 mAh g^{-1} . One of the advantages for the insertion reaction is the small volume change during Li⁺ insertion/extraction. The volume change of TiS₂ is only 12 % [61], leading to possibly the prevention of the increase in the electrode-electrolyte interfacial resistance during the discharge-charge cycles. On the other hand, NiS has been reported to exhibit the conversion reaction [62,63]. FeS and CuS, which are investigated as the electrode materials in the lithium-ion batteries using liquid electrolytes [64,65], also show the conversion reaction. The theoretical capacity of NiS is 590 mAh g^{-1} based on the redox reactions of nickel. Since the conversion reaction suffers from the large volume change, the electrode-electrolyte interfacial resistance can be increased gradually during the discharge-charge cycles. MoS₂ shows both the insertion and conversion reactions [66]. NiS₂ and FeS₂, which are investigated as the cathode materials in the lithium-ion batteries [64,67], also exhibit both the insertion and conversion reactions. The theoretical capacity of MoS₂ is 670 mAh g⁻¹ attributable to the redox reaction of sulfur and molybdenum. Amorphous TiS₃ and Amorphous MoS₃ can react with Li⁺, but the discharge-charge reactions have not been identified. The theoretical capacity of TiS₃ is 670 mAh g^{-1} base on the sulfur redox reactions [55]. The theoretical capacity of MoS_3 is calculated to be 837 mAh g^{-1} in case of the reaction of 6 mol of Li^+ per MoS₃ base on the redox reactions of sulfur.

The discharge voltage of these sulfide cathodes is lower than that of the commercialized

oxide cathodes. Since the sulfide cathodes do not contain Li⁺, Li⁺ containing anodes are required to be used. One of the advantages for the sulfide cathodes is the high theoretical capacity. The theoretical capacity is higher than that of the oxide cathodes. Moreover, the similarity of sulfur between the sulfide cathodes and the sulfide solid electrolytes is expected to lead to the prevention of the increase in the electrode-electrolyte interfacial resistance without the coating layers. The sulfide cathodes showing the insertion reaction can particularly be attractive because of the small volume change during Li⁺ insertion/extraction, which can lead to keeping the favorable electrode-electrolyte interface.

Many materials have been studied as the cathodes for the all-solid-state batteries using the sulfide solid electrolytes so far, as described above. For further development of the all-solid-state batteries, novel sulfide cathodes, forming easily the favorable electrodeelectrolyte interface with the solid electrolytes, or the new cathode systems are needed to be explored. In the present study, sulfide materials such as NiPS₃, FePS₃, and FePS₃-S were investigated as the novel sulfide cathode materials for the all-solid-state batteries using the sulfide solid electrolytes. In addition, the application of the hybrid halide perovskite materials to the cathode materials for the all-solid-state batteries was examined.

NiPS₃ and FePS₃ have been studied as the electrode materials for the lithium-ion batteries using organic electrolytes since 1980s [68-71]. There are mainly two-step reactions: Li⁺ reversible insertion/extraction and irreversible conversion reactions, as shown in equations (1)-(3). In the insertion reaction (equation (1)) based on the layered structure, the theoretical reversible capacity of NiPS₃ and FePS₃ are 216 and 220 mAh g^{-1} , respectively, which corresponds to the insertion of 1.5 mol of Li⁺ per Ni or Fe [68]. MPS₃ + 1.5 Li⁺ + 1.5 e⁻ \rightleftharpoons Li_{1.5}MPS₃ (M = Ni and Fe) (1) The discharge voltages of NiPS₃ and FePS₃ are ~ 1.8 and ~ 1.5 V vs. Li. On the other hand, in conversion reactions (equation (2), (3)), NiPS₃ and FePS₃ undergo irreversible conversion reactions with up to 9 mol of Li⁺ per Ni or Fe [68]. The theoretical reversible capacity of NiPS₃ and FePS₃ are 1298 and 1316 mAh g⁻¹, respectively.

$$Li_{1.5}MPS_3 + 4.5 Li^+ + 4.5 e^- \rightarrow 3Li_2S + M + P \quad (M = Ni, Fe) \quad (2)$$

$$P + 3 Li^+ + 3 e^- \rightarrow 3Li_3P \quad (3)$$

The layered structure of NiPS₃ and FePS₃ is destroyed in the conversion reaction, causing the large volume change during the discharge-charge cycles. In contrast, in the insertion reaction, the layered structure is maintained. The small volume change derived from the insertion reaction can prevent from increasing the electrode-electrolyte interfacial resistance during the discharge-charge cycles. Thus, the insertion reaction, in which the layered structure is kept, is attractive in case of the use of NiPS₃ and FePS₃ as the cathode materials for the all-solid-state batteries. The similarity of the structural units between these sulfide materials (NiPS₃ and FePS₃) and the sulfide solid electrolytes can lead to the formation of the favorable electrode-electrolyte interface.

Moreover, NiPS₃ and FePS₃ are expected to show the high lithium-ion diffusion because of the layered structure. This property can allow the decrease of the solid electrolyte additives in the electrode, resulting in possibly improving the volumetric energy density of the batteries. In the all-solid-state batteries, the cathode materials usually need to be combined with the solid electrolytes and the carbon additives to compensate the insufficient lithium-ion and electronic paths in the electrode. The sufficient lithiumion and electronic paths formed by the solid electrolytes and the carbon additives lead to the favorable electrode-electrolyte interface with low resistance. However, these additives decrease the volume ratio of the cathode in the entire battery. The low volume ratio of the cathode can cause the low energy density per volume, even though the favorable electrode-electrolytes interface is formed by these additives. Thus, the favorable electrode-electrolyte interface with low resistance while keeping the high volume ratio of the cathode is required to prevent the decrease in the volumetric energy density of the all-solid-state batteries. Since the high lithium-ion diffusion of NiPS₃ and FePS₃ can form sufficient lithium-ion path in the electrode despite the small amount of solid electrolyte additives, the volumetric energy density of the all-solid-state batteries would be improved by the use of NiPS₃ and FePS₃. The moderate electronic conductivity of FePS₃ ($\sim 10^{-5}$ S cm⁻¹) [72], which is higher than that of NiPS₃ ($< 10^{-9}$ S cm⁻¹) [72], would form sufficient electronic path in the electrode without the large amount of carbon additives. FePS₃ has a potential to be used as the novel cathode materials without any solid electrolytes and carbon additives, which have not almost been reported [73]. In addition, the properties of FePS₃ such as the formation of sufficient lithium-ion and electronic paths can be useful to compensate the poor properties of other cathode materials.

Sulfide composite materials such as CuS-S [31], C-FeS₂-S [74] have been studied as the cathodes for the all-solid-state batteries. These sulfide additives such as CuS and FeS₂ compensate the low electronic conductivity of sulfur $(5 \times 10^{-18} \text{ S cm}^{-1})$ [50] to form the electronic path in the sulfur electrode. Moreover, the sulfide additives can work as the cathode materials, and contribute to the increase in the capacity. If FePS₃ is used as the additive for the sulfur electrode, FePS₃ is useful for the compensation of the electronic path and the contribution of the capacity. The small volume change of FePS₃ derived from the insertion reaction can suppress the large volume change of sulfur. On the other hand, the high capacity of sulfur (1672 mAh g⁻¹) can improve the capacity of FePS₃ (216 mAh

 g^{-1}) in the insertion reaction. Thus, FePS₃ is attractive as the additives for the sulfur cathode, and the potential of the FePS₃-S composite material as the cathode for the all-solid-state battery should be examined.

As for the new types of the cathode materials for the all-solid-state batteries, hybrid halide perovskites (HHPs) with the layered structure was studied. HHPs are well known materials for their incredible optical properties, which make them very attractive for light emitting diodes [75,76] and solar cells [77-79]. Their potential as electrode materials has recently been explored [80-85], and the lithium storage mechanism bv insertion/extraction, conversion, and alloying-dealloying has been proposed [86]. Their characteristic structure allows an efficient ionic diffusion (Li⁺, Na⁺). Actually, the coefficient of lithium-ion diffusion is as high as $\sim 10^{-7}$ cm² s⁻¹, implying that lithium-ion conductivity of lithiated HHP can reach $\sim 10^{-3}$ S cm⁻¹ [87]. This property makes them a potential alternative to be used as electrodes for all-solid-state batteries without the addition of any solid electrolytes. Nevertheless, there is no report on the investigation of the properties of HHPs as cathode materials for all-solid-state batteries. Among HHPs, (CH₃(CH₂)₂NH₃)₂(CH₃NH₃)₂Pb₃Br₁₀ with a layered structure (2D-HHP), which can lead to high lithium-ion diffusion, was evaluated as a cathode material for an all-solid-state battery.

In the present study, the all-solid-state batteries using NiPS₃, FePS₃, FePS₃-S, and 2D-HHP as the cathode materials and the sulfide solid electrolytes were fabricated, and the properties of these materials as the cathode materials were investigated. The reaction mechanism of these cathode materials was examined by evaluating the cathodes before and after discharge-charge cycles.

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

The properties of NiPS₃ and FePS₃ as the cathode materials for the all-solid-state batteries using the sulfide solid electrolytes and these reaction mechanisms in the allsolid-state batteries are described in this chapter. All-solid-state batteries using NiPS₃ and FePS₃ as the cathodes and the sulfide solid electrolytes were fabricated, and the dischargecharge behavior was investigated. To evaluate the interface between these sulfide cathodes (NiPS₃ and FePS₃) and the sulfide solid electrolytes, impedance spectra of the all-solid-state batteries were measured before and after discharge and charge. In the allsolid-state batteries using FePS₃, the effect of the amounts of the solid electrolytes and the carbon additives into the FePS₃ electrodes on the discharge-charge behavior was examined. The reaction mechanism of FePS₃ in all-solid-state batteries was investigated by X-ray diffraction patterns, X-ray absorption spectra, Raman spectra, and densityfunctional theory (DFT) calculations.

Chapter 3

In this chapter, the performance of the all-solid-state batteries using FePS₃-S as the cathode material and the sulfide solid electrolytes are described. Three types of FePS₃-S with the different compositions (FePS₃:S = 100:0, 70:30, and 50:50 wt%) were synthesized, the crystalline structures of FePS₃-S with the different compositions were identified. To investigate the properties of FePS₃-S as the cathode material, all-solid-state

batteries using FePS₃-S and the sulfide solid electrolytes were fabricated, and the effect of the composition change and the temperature change (25-100 °C) on the dischargecharge performance was investigated. The S K-edge X-ray absorption near edge structure (XANES) spectra of the FePS₃-S electrode in the all-solid-state batteries were measured before and after discharge/charge to reveal the redox reaction of the FePS₃-S electrode during discharge-charge cycles.

Chapter 4

This chapter reports the evaluation of 2D-HHP (CH₃(CH₂)₂NH₃)₂(CH₃NH₃)₂Pb₃Br₁₀ as the cathode material for the all-solid-state batteries using the sulfide solid electrolytes. The 2D-HHP powders were synthesized by the slow solvent evaporation of the precursor solution consisted of CH₃NH₃Br, CH₃(CH₂)₂NH₃Br and PbBr₂ (2:2:3 molar ratio) dissolved with Dimethyl sulfoxide in N,N-dimethylformamide. The all-solid-state batteries using the 2D-HHP and the sulfide solid electrolytes were constructed, and the discharge-charge performance was investigated at different temperatures (25, 60, and 100 °C). Impedance spectra of the all-solid-state batteries were measured before and after discharge and charge to evaluate the interface between the 2D-HHP and the sulfide solid electrolytes. Based on ex-situ XRD measurements at different stages of the dischargecharge processes, the mechanism of the lithium storage into the 2D-HHP electrode was investigated.

Chapter 5

This chapter summarizes all the conclusions in this thesis.

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2. NiPS₃ and FePS₃ electrodes for all-solid-state lithium secondary batteries

2.1. Introduction

All-solid-state lithium-ion secondary batteries with sulfide solid electrolytes have much attention as powerful energy storage systems with high safety. One of the key materials for the development of the high-performance all-solid-state batteries is the cathode material. Various cathode materials such as lithium transition-metal oxides (LiCoO₂ [1-4] and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ [4,5]), sulfur [6,7], and transition-metal sulfides (NiS [8,9], TiS₂ [10,11], MoS₂ [12], amorphous TiS₃ [11,13], amorphous MoS₃ [13,14]) have been previously studied in the all-solid-state batteries. However, the lithium transition-metal oxides need the coating layer at the interface between the oxide electrode and the sulfide solid electrolyte because of the interfacial layer with high resistance, which is formed by the elemental diffusion during the charge cycle [15]. Sulfur and the transition-metal sulfides are not expected to need the coating layer owing to the similarity of sulfur between them and the sulfide solid electrolyte. However, the large volume change of sulfur and the transition-metal sulfides derived from the conversion reaction can cause the increase in the electrode-electrolyte interfacial resistance. Among these transitionmetal sulfides, TiS₂ is the only cathode material showing the small volume change derived from the insertion reaction, resulting in possibly the low electrode-electrolyte interface resistance. Thus, novel sulfide cathodes forming the favorable electrode-electrolyte interface with the sulfide solid electrolytes are required for the development of the highperformance all-solid-state batteries.

NiPS₃ and FePS₃ have been investigated as the electrode materials in the lithium-ion batteries with liquid electrolytes [16,17], and these electrodes have been reported to show

the insertion reaction (MPS₃ + 1.5 Li⁺ + 1.5 e⁻ \Rightarrow Li_{1.5}MPS₃ (M = Ni and Fe)) [17]. The insertion reaction is expected to lead to the small volume change during the dischargecharge cycles. In addition, the similarity of sulfur and phosphorus can result in keeping the low electrode-electrolyte interface resistance without the coating layer. Thus, in this chapter, NiPS₃ and FePS₃ were investigated as the cathode materials for the all-solid-state lithium secondary batteries based on the sulfide solid electrolytes.

NiPS₃ and FePS₃ were synthesized by heating the mixture composed of Ni or Fe, P, and S. [17]. The X-ray diffraction (XRD) patterns, the morphologies, and the compositions of the obtained samples were examined. The all-solid-state batteries were fabricated using NiPS₃ or FePS₃ as the cathode material, Li₂S-P₂S₅ glassy powder as the solid electrolyte, and a Li-In sheet as the anode material [18]. The discharge-charge performance and impedance spectra of these batteries were measured. In the all-solid-state batteries using FePS₃, the effect of the amounts of the solid electrolytes and the carbon additives into the FePS₃ electrodes on the discharge-charge behavior was examined. The reaction mechanism of NiPS₃ and FePS₃ was examined based on the NiPS₃ and FePS₃ electrodes before and after discharge and charge using X-ray diffraction (XRD) measurements. The reaction mechanism in detail of FePS₃ was investigated by XANES spectra, Raman spectra, and density-functional theory (DFT) calculations.

2.2. Experimental

2.2.1. Synthesis and characterization of battery materials

NiPS₃ was synthesized from elemental nickel powder (Nilaco, 99.8%), red phosphorus (Kanto Chemical, 98.0%), and sulfur (Kanto Chemical, 99.5%) [17]. Red phosphorus and sulfur were used in approximately 15 wt% excess of the stoichiometric amounts. These

powders were mixed using an agate mortar and pestle, and the mixture was heated in an evacuated quartz tube at 998 K for 24 h. To remove excess red phosphorus and sulfur, the obtained sample was heated at 598 K for 20 min, under vacuum. The product was ground in an agate mortar, and then, particles larger than 100 μ m were removed using a 100 μ m sieve.

FePS₃ was synthesized by the same process as NiPS₃ using elemental iron powder (Wako Chemical, 99.9%), red phosphorus (Kanto Chemical, 98.0%), and sulfur (Kanto Chemical, 99.5%) [17]. The powders with the particle size less than 100 μ m were obtained.

XRD patterns of the prepared NiPS₃ and FePS₃ powders were recorded using an X-ray diffractometer (RINT-2000 and MiniFlex600, Rigaku) with CuKa radiation source. The morphologies and the compositions of the obtained NiPS₃ and FePS₃ powders were investigated by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX; JEOL JSM-6390 LVS and JSM-6510).

Li₂S-P₂S₅ glassy powders were prepared via mechanical milling of mixtures of reagentgrade Li₂S (Mitsuwa Chemical, 99.9%) and P₂S₅ (Aldrich, 99%) powders with a molar ratio of 80:20 or 75:25 in a dry Ar atmosphere [19,20]. First, Li₂S and P₂S₅ powders were mixed together using an agate mortar. The mixtures were placed into ZrO₂ pots (45 mL) with 500 ZrO₂ balls ($\phi = 4$ mm). The pots were set in a planetary ball mill apparatus (Fritsch, Pulverisette 7), and the mechanical milling was performed at 510 rpm for 10 or 24 h. The 75Li₂S·25P₂S₅ (mol%) glass was used mainly for the investigation of the reaction mechanism of FePS₃, because the stoichiometric ratio of the 75Li₂S·25P₂S₅ glass (Li₃PS₄) is advantageous for the analysis of the mechanism. The 80Li₂S·20P₂S₅ (mol%) glass was utilized for the other measurements. These obtained powders were pelletized, and the resistance of the pellets was estimated using electrochemical impedance spectroscopy (EIS). Based on the resistance and the thickness of the pellets, the lithium-ion conductivity of the obtained powders was calculated.

2.2.2. Battery construction and electrochemical measurements of the all-solid-state batteries

Laboratory-scale, all-solid-state batteries were fabricated using NiPS₃ or FePS₃ as the cathode active material, the Li₂S-P₂S₅ glassy powder as the solid electrolyte, and a Li-In sheet as the anode active material [18]. A NiPS₃ electrode was prepared by mixing NiPS₃, the 80Li₂S·20P₂S₅ glass, and vapor grown carbon fiber (VGCF, Showa Denko), in a weight ratio of 69:29:2. On the other hand, FePS₃ electrodes were prepared using only FePS₃, or mixtures of FePS₃ with the Li₂S-P₂S₅ glass or vapor grown carbon fibers, according to the composition and weight data shown in Table 2-1. These prepared electrodes (10 or 30 mg) and the Li₂S-P₂S₅ glass (120 mg) were pressed under 360 MPa in a polycarbonate tube ($\phi = 10$ mm) to obtain bilayer pellets. The Li-In alloy foil was pressed under 120 MPa on the prepared bilayer pellets. The obtained three-layer pellets were sandwiched between two stainless-steel disks serving as the current collectors.

The discharge-charge performance of the batteries was investigated under a constant current density from 0.064 to 0.64 mA cm⁻² at room temperature, using a charge-discharge measuring device (Scribner Associates, 580 battery-type system). To evaluate the electrode-electrolytes interface, impedance spectra of the all-solid-state batteries were measured before and after discharge and charge.

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	Composition of electrode	Weight of electrode / mg
	FePS3:SE:VGCF (wt. ratio)	
Battery A	69:29:2	10
Battery B	100:0:0	10
Battery C	100:0:0	30
Battery D	90:10:0	10
Battery E	80:20:0	10
Battery F	98:0:2	10
Battery G	96:0:4	10

Table 2-1 Composition and weight of the FePS₃ electrode.

SE: 75Li_2S·25P_2S_5 glass or $80Li_2S\cdot20P_2S_5$ glass solid electrolytes.

2.2.3. Reaction mechanisms of NiPS3 and FePS3 in all-solid-state batteries

To investigate the reaction mechanism of NiPS₃ in the all-solid-state batteries, ex-situ XRD patterns of the NiPS₃ composite electrode with the solid electrolytes and the carbon additives were measured using a XRD diffractometer (Rigaku, MiniFlex 600) before and after discharge and charge. For the XRD measurement, a Kapton film was used to cover the sample holder in Ar atmosphere.

As for the investigation of the reaction mechanism of FePS₃, not only XRD measurement but also other measurements were performed. In discharge-charge measurements, the effect of the amount of inserted Li⁺ in FePS₃ on the discharge-charge behavior was investigated. In order to examine the change in the crystalline structures of FePS₃ during discharge-charge cycles, ex-situ XRD patterns of the FePS₃ composite electrodes before and after the discharge and charge were recorded using synchrotron Xray sources at the SPring-8 BL02B2 beam line. Raman spectra of the FePS₃ composite electrodes before and after discharge and charge were measured using a Raman spectrometer (XploRA, Horiba) with a green laser (Wavelength: 532 nm) to investigate the change in the $P_2S_6^{4-}$ units in FePS₃ during discharge-charge cycles. In the XRD and Raman measurements, evacuated capillary glass tubes were used to seal the samples. The X-ray absorption near-edge structure (XANES) spectra were measured before and after discharge and charge. The spectra of Fe-K-edge were measured using the FePS₃ composite electrodes and those of S K-edge were measured using the FePS₃ electrodes without solid electrolytes. XANES spectra were measured at the BL5S1 and BL6N1 of the Aichi Synchrotron Center, Aichi Science & Technology Foundation. Redox reactions of iron and sulfur in FePS₃ during the discharge-charge process were investigated. Based on the results obtained for the above-mentioned measurements, first-principle

calculations were performed using the Vienna Ab initio Simulation Package (VASP). The equilibrium voltage of the reaction of FePS₃ with Li⁺ and density of states (DOSs) of FePS₃ and Li⁺-inserted FePS₃ were calculated using the optimized structure models of FePS₃ and Li⁺-inserted FePS₃. Structure models of FePS₃ before and after discharge and charge were illustrated using VESTA.

2.3. Results and discussion

2.3.1. NiPS₃ electrode material

Figure 2-1 shows the XRD pattern of NiPS₃ synthesized by heating the mixture of nickel powder, red phosphorus, and sulfur in an evacuated quartz tube. The XRD peaks were indexed as NiPS₃: ICDD#33-952. These peaks showed a preferred orientation along the (00l) plane. The molar ratio of the synthesized NiPS₃ was semi-quantitatively determined as Ni:P:S = 1:1:3. A 100 μ m sieve was used because NiPS₃ particles of several hundred micrometers were included in the ground sample. NiPS₃ particles with sizes smaller than 100 μ m, as shown in Figure 2-2, were incorporated as the active material for fabricating all-solid-state batteries with the sulfide solid electrolytes.

Figure 2-3 shows the discharge-charge curves of the all-solid-state Li-In/80Li₂S·20P₂S₅ glass/NiPS₃ battery, under a current density of 64 μ A cm⁻² at room temperature. The lithium-ion conductivity of the 80Li₂S·20P₂S₅ glass used as the solid electrolyte was around 10⁻⁴ S cm⁻¹ similar to that previously reported [21]. The open-circuit voltage (OCV) of the battery was initially 1.8 V. The battery was first discharged to a capacity of 216 mAh g⁻¹, which corresponds to the insertion of 1.5 mol of Li⁺ per Ni, therefore allowing for the introduction of sufficient lithium ions into the NiPS₃ electrode. Then, the battery was charged to a value of 2.5 V (vs. Li-In). The cut-off voltage was 0.8–2.5V (vs.



Figure 2-3 Discharge-charge curves of the all-solid-state battery $Li-In/80Li_2S\cdot 20P_2S_5$ glass/NiPS₃.

Li-In) from the second cycle onwards. The first charge capacity was 102 mAh g⁻¹, roughly corresponding to the insertion of 0.7 mol of Li⁺ per Ni. The all-solid-state battery exhibited reversible behavior after the first cycle, and a stable reversible capacity for 30 cycles. During the first cycle, the battery showed a discharge plateau at about 1.2 V (vs. Li-In), which is similar to that observed for Li/NiPS₃ batteries using conventional liquid electrolytes [17,22]. At the second cycle, the discharge plateau was observed at about 1.5 V (vs. Li-In). This plateau disappeared at the 30th cycle. As it has been previously reported that the discharge potential in this kind of systems is influenced by the crystalline state of NiPS₃ [23], the above-mentioned change in the discharge curves can be due to the change in the electrode crystallinity with cycling.

Figure 2-4 presents the cycle performance of the all-solid-state battery. The all-solidstate battery exhibited a capacity of about 80 mAh g⁻¹ for 30 cycles; this capacity accommodates the insertion of about 0.5 mol of Li⁺ per Ni. The all-solid-state battery showed this stable reversible capacity for 30 cycles. Thus, these results demonstrate that NiPS₃ can be utilized as an electrode active material in all-solid-state batteries with sulfide solid electrolytes. Although the capacity of this battery is lower than those of the batteries using NiP₂ or NiS electrodes [8,9,24], fabrication of nanocomposites of NiPS₃ and Li₂S-P₂S₅ electrodes can further improve the discharge-charge performance.

Figure 2-5 exhibits the impedance spectra of the all-solid-state battery using the NiPS₃ electrode (a) before discharge and charge and (b) after first charge. Before the discharge and charge, the part of the semicircle with the peak top at the frequency of about 100 kHz was observed, but obvious semicircles were not confirmed to identify the resistance components. Based on the part of the semicircle, the total resistance of the all-solid-state battery with the NiPS₃ electrode before discharge and charge and charge was estimated to be ~1200



Figure 2-4 Cycle performance of the all-solid-state battery $Li-In/80Li_2S\cdot 20P_2S_5$ glass/NiPS₃.



Figure 2-5 Impedance spectra of the all-solid-state battery using the NiPS₃ electrode (a) before discharge and charge and (b) after first charge.

 Ω . After first charge, the resistance components can be identified according to a reference [15]. The resistance at high frequency (>100 kHz) can be attributed to the solid electrolyte layer, and the semicircle with the peak top at the frequency of about 100 Hz can be identified to the interfacial resistance between NiPS₃ and the Li₂S-P₂S₅. The total resistance of the all-solid-state battery after first charge was estimated to be ~550 Ω . After the first charge, the total resistance of the all-solid-state battery using the NiPS₃ electrode decreased. This suggests that the combination of the NiPS₃ electrode and the LiS₂-P₂S₅ solid electrolyte is favorable.

Figure 2-6 shows the ex-situ XRD patterns of the NiPS₃ composite electrodes before and after discharge and charge. Before the discharge, the peaks due to NiPS₃ and Li₂S were observed; the peaks of Li₂S can be attributed to the 80Li₂S·20P₂S₅ electrolyte [25]. After the initial discharge, the peaks attributable to NiPS₃ disappeared, and no other peaks from Ni (44.5 and 51.8°) were observed. Thus, discharge of NiPS₃ formed a lowcrystalline or amorphous phase(s). Note that a very weak peak at $2\theta = 16.5^{\circ}$, which can be attributed to the Li₂NiPS₃ phase [16], is detected. The subsequent charge resulted in the peaks attributed to NiPS₃. Hence, the discharge-charge reaction of the NiPS₃-80Li₂S·20P₂S₅ glass composite was based on NiPS₃ and an amorphous/low-crystalline phase(s) possibly including the Li₂NiPS₃ phase, as shown in below:

NiPS₃ + 1.5 Li⁺ + 1.5 e⁻ \rightleftharpoons amorphous/low-crystalline phase(s) including Li₂NiPS₃



Figure 2-6 Ex-situ XRD patterns of the NiPS₃ composite electrode before and after charge-discharge cycles. An arrow indicates the peak at ca. 16.5°, which is possibly attributed to Li₂NiPS₃ [16].

2.3.2. FePS₃ electrode material

Figure 2-7 shows the XRD pattern of the FePS₃ powder synthesized from elemental iron powder, red phosphorus, and sulfur. This XRD pattern is indexed to FePS₃ (ICDD#633087). Figure 2-8 presents the SEM image of the prepared FePS₃ powders after grinding and passing through a 100 μ m sieve. The particle size of the FePS₃ powders was approximately 10 μ m. The molar ratio of the elements in FePS₃, semi-quantitatively estimated by EDX, was found to be Fe:P:S = 1:1:3.

Figure 2-9 shows the discharge-charge curves of the all-solid-state battery using the FePS₃ composite electrode with solid electrolytes and carbon additives (Battery A), under a current density of 0.13 mA cm⁻² at room temperature. For this measurement, the 75Li₂S·25P₂S₅ glass was used as the solid electrolyte. The insertion reaction ranging from 0 to 1.5 mol Li⁺ per Fe has been reported to be reversible in a cell using an organic electrolyte [17]. Hence, the battery was initially discharged to a capacity of 220 mAh g^{-1} , corresponding to the insertion of 1.5 mol Li⁺ per unit FePS₃, Subsequently, the battery was charged to 2.2 V (vs. Li-In). From the second cycle onwards, the cut-off voltage was set to 0.91 V (vs. Li-In) for discharging and 2.2 V (vs. Li-In) for charging. The battery showed a first charge capacity of 203 mAh g^{-1} , roughly corresponding to the extraction of 1.4 mol Li⁺ per Fe. This capacity was higher than that of the all-solid-state battery using NiPS₃ even though the higher current density (0.13 mA cm⁻²) is used in this measurement. The battery exhibited reversible discharge-charge behavior for 30 cycles. The reversible capacity at the 30th cycle was 119 mAh g^{-1} . A discharge plateau was observed at approximately 0.9 V (vs. Li-In) during the first cycle, similar to the case of an FePS₃ cell using liquid electrolytes [17]. From the second cycle onwards, the plateau disappeared and the discharge voltage increased. This behavior is similar to that of a cell



Figure 2-7 XRD pattern of FePS₃ powders synthesized from elemental iron powders, red phosphorus, and sulfur.



Figure 2-8 SEM image of FePS₃ powders used for all-solid-state batteries.


Figure 2-9 Discharge-charge curves of the all-solid-state battery using the FePS₃ composite electrode with solid electrolytes and carbon additives (Battery A).

based on isostructural NiPS₃, which can be explained by the decrease in crystallinity [23]. Thus, voltage change of FePS₃ may also be ascribed to the decrease in the crystallinity of FePS₃ during discharging.

Figure 2-10 exhibits the impedance spectra of the all-solid-state battery using the FePS₃ composite electrode (a) before discharge and charge and (b) after first charge. The enlarged spectrum (b) after first charge is also shown. Before the discharge and charge, the part of the semicircle with the peak top at the frequency of about 100 kHz was observed, and this impedance profile was similar to that of the all-solid-state battery using the NiPS₃ electrode (Figure 2-5 (a)). Based on the part of the semicircle, the total resistance of the all-solid-state battery using the FePS₃ composite electrode before discharge and charge was estimated to be $\sim 2550 \Omega$. After first charge, the semicircle with the peak top at the frequency of about 100 Hz, which is attributed to the interfacial resistance between the FePS₃ electrode and the LiS₂-P₂S₅ solid electrolyte, cannot be confirmed. The resistance component at high frequency (>100 kHz) can attributed to the solid electrolyte layer according to a reference [15]. The total resistance of the all-solidstate battery after first charge was estimated to be ~300 Ω , which was mainly ascribed to the solid electrolyte layer. After first charge, the total resistance of the all-solid-state battery using the FePS₃ composite electrode decreased, indicating that the favorable interface between the FePS₃ electrode and the LiS₂-P₂S₅ solid electrolyte was formed.

To investigate the additive amounts in the electrodes on the discharge-charge behavior, the performance of the batteries with different additive amounts was compared. For these discharge-charge measurements, the $80Li_2S \cdot 20P_2S_5$ glass was used as the solid electrolyte.

Figure 2-11 shows (a) the discharge-charge curves and (b) cycle performance of the allsolid-state battery using the FePS₃ electrode (10 mg) without the solid electrolytes and



Figure 2-10 Impedance spectra of the all-solid-state battery using the FePS₃ composite electrode (a) before discharge and charge and (b) after first charge. The enlarged spectrum (b) after first charge is also shown.

the carbon additives (Battery B). The discharge-charge performance was measured under 0.13 mA cm⁻² at room temperature. The measured open-circuit voltage (OCV) of the battery was approximately 1.3 V (vs. Li-In). As is evident from Figure 2-11 (a), the battery showed a first charge capacity of 171 mAh g⁻¹ despite no solid electrolytes and carbon additives for the formation of lithium-ion and electronic paths in the FePS₃ electrode. This charge capacity corresponds to the extraction of 1.2 mol Li⁺ per Fe. As seen in Figure 2-11 (b), the battery exhibited reversible capacities of more than 107 mAh g⁻¹ for 30 cycles, corresponding to the insertion of about 0.7 mol Li⁺ per Fe. These results reveal that the battery with the FePS₃ electrode can be operated without the addition of solid electrolytes and carbon additives. That can be because FePS₃ has the high lithium-ion diffusion derived from the layered structure and the moderate electronic conductivity (~10⁻⁵ S cm⁻¹).

Figure 2-12 shows the discharge-charge curves of the all-solid-state battery using a thick FePS₃ electrode layer (30 mg), without any solid electrolytes or carbon additives (Battery C). The discharge-charge performance of Battery C was measured under 0.13 mA cm⁻² at room temperature. Battery C exhibited an initial charge capacity of 156 mAh g⁻¹, corresponding to the extraction of 1.1 mol Li⁺ per Fe. The capacity per unit volume was calculated to be 483.6 mAh cm⁻³ using the theoretical density of FePS₃ = 3.1 g cm⁻³ from ICSD #633087. The discharge capacity subsequently decreased to 93 mAh g⁻¹ at the 10th cycle. The battery using a thick FePS₃ electrode layer also showed reversible charge-discharge behavior, indicating that the battery capacity can be increased by increasing the amount of FePS₃ used for fabricating the electrode.

The discharge-charge behavior of the FePS₃ electrode mixed with different amounts of solid electrolytes was investigated to confirm the rather high lithium-ion diffusion in this

electrode. Figure 2-13 shows the first and second discharge-charge curves of Battery B and those of the batteries with 10 and 20 wt% of the solid electrolyte (Battery D and Battery E, respectively) under a constant current density of 0.13 mA cm⁻² at room temperature. Although these batteries exhibited a slightly different charge behavior near 2.1 V (vs. Li-In) during the first and second charging, the discharge-charge behavior was not significantly affected by the addition of solid electrolytes. These comparable discharge-charge behaviors of Batteries B, D, and E suggest that the FePS₃ electrode has adequate lithium-ion conduction.

Figure 2-14 displays the first and second discharge-charge curves of Battery B, and the curves for the batteries with 2 and 4 wt% of the carbon additives (Battery F and Battery G, respectively), under a constant current density of 0.13 mA cm⁻² at room temperature. The discharge-charge behavior did not change significantly during the first and second cycles. This suggests that the FePS₃ electrode has sufficient electron conducting paths to enable discharge-charge under the current density of 0.13 mA cm⁻².

Figure 2-15 shows the rate performance of Batteries B, D, and F. The batteries showed discharge capacities ranging from 138 mAh g^{-1} to 152 mAh g^{-1} at the 5th cycle under a current density of 0.13 mA cm⁻². Further, the batteries exhibited discharge capacities ranging from 82 mAh g^{-1} to 95 mAh g^{-1} at the 10th cycle under a current density of 0.64 mA cm⁻². The discharge capacities were not significantly changed by the addition of solid electrolytes and carbon additives under the current density of 0.64 mA cm⁻², suggesting that the FePS₃ electrodes show sufficient lithium-ion and electron conducting paths even in the absence of solid electrolytes and carbon additives.

To investigate the reaction mechanism of the FePS₃ electrode in the all-solid-state batteries, XRD, XANES, and Raman measurements and density-functional theory (DFT)



Figure 2-11 (a) Discharge-charge curves and (b) cycle performance of the all-solid-state battery using FePS₃ electrode (10 mg) without solid electrolytes and carbon additives (Battery B).



Figure 2-12 Discharge-charge curves of the all-solid-state battery using FePS₃ electrode (30 mg) without solid electrolytes and carbon additives (Battery C).



Figure 2-13 First and second discharge-charge curves of the all-solid state batteries using FePS₃ electrodes mixing 0 wt% (Battery B : red solid line), 10 wt% (Battery D : blue dashed line) and 20 wt% (Battery E : green dashed-dotted line) of solid electrolytes.



Figure 2-14 First and second discharge-charge curves of the all-solid state batteries using FePS₃ electrodes with mixing 0 wt% (Battery B : red solid line), 2 wt% (Battery F : dark blue dashed line) and 4 wt% (Battery G : purple dashed-dotted line) of carbon additives.



Figure 2-15 Rate performance of all-solid-state batteries using FePS₃ electrodes without solid electrolytes and carbon additives (Battery B : red circles •), with 10 wt% of solid electrolytes (Battery D : blue diamonds •) and with 2 wt% of carbon additives (Cell F : dark blue squares •) under a constant current density of 0.13 mA cm⁻² and 0.64 mA cm⁻².

calculations were performed. Moreover, the effect of the amount of the inserted Li⁺ in FePS₃ on the discharge-charge behavior also examined. Figure 2-16 shows (a) first and discharge-charge of all-solid-state of Li-(b) second curves batteries In/75Li₂S·25P₂S₅/FePS₃ at 0.13 mA cm⁻² at room temperature. The FePS₃ composite electrode used for this measurement was prepared by mixing FePS₃, 75Li₂S·25P₂S₅ glass, and VGCF with a weight ratio of 69:29:2. Based on the reported reaction of FePS₃ with 0-1.5 mol Li⁺ [17], 0.5-mol (solid lines), 1.0-mol (dashed lines), and 1.5-mol (dasheddotted lines) Li⁺ were first inserted into FePS₃ in the first discharge cycle. Then, the discharge-charge cycles were repeated between 0.91-2.2 V vs. Li-In. The batteries showed similar discharge-charge behaviors, indicating that the same discharge-charge reaction occurred with a range below 1.5-mol Li⁺ per FePS₃. Thus, the reaction mechanism with the insertion of 1.5 mol of Li⁺ was further investigated. To discuss the overvoltage of the batteries, the open-circuit voltage (OCVs) were measured at several points shown in Figure 2-16 (a) (A)-(D). The OCVs (A) before discharge and charge, (B) after the first discharge, (C) at 1.5 V vs. Li-In during charge, and (D) after the first charge were 1.28 V, 0.92 V, 1.48 V, 2.14 V vs. Li-In, respectively. These results suggest a small overvoltage of the batteries.

Figure 2-17 shows XRD patterns of the FePS₃ composite electrode (a) before discharge and charge, (b) after the first discharge, (c) first charge, and (d) second discharge cycles. Before the discharge and charge, the diffraction peaks due to FePS₃ were observed. After the first discharge, the intensity of the peaks due to FePS₃ became significantly weak, and only broad peaks were observed. After the first charge, strong peaks due to FePS₃ were observed. After the subsequent second discharge, the intensity of the peaks due to FePS₃ again became weak. The change in intensity of the peaks owing to FePS₃ reveals that Li⁺- inserted FePS₃ with low crystallinity is formed after the discharge and crystalline FePS₃ is formed after the charge. Similar crystallinity changes by the Li⁺ insertion/extraction were confirmed even in the NiPS₃ electrode, as shown in Figure 2-6. Although the peak position at 6.42 Å, which corresponded to 001 diffraction, was unchanged (a) before discharge and charge and (c) after the first charge, the peak had a tail toward the higher angle after the first charge. This tail can be explained by the insertion of Li⁺ into the interlayer of FePS₃. Thus, Li⁺ would be (at least partially) inserted and extracted into and from the interlayer of FePS₃ during the discharge-charge process.

Figure 2-18 presents Raman spectra of the FePS₃ composite electrode (a) before discharge and charge, (b) after the first discharge, (c) first charge, and (d) second discharge cycles. The Raman bands that are attributed to $P_2S_6^{4-}$ were observed before and after the discharge and charge [26]. This indicates that $P_2S_6^{4-}$ units in FePS₃ are not destroyed during discharge-charge cycles, even in the low-crystallinity phase detected by XRD. The peak position shifted to a higher wavenumber after the second discharge, indicating that the symmetry of $P_2S_6^{4-}$ changes after the second discharge. The peak width increased after the discharge. This indicates a local disordering in Li⁺-inserted FePS₃ after discharge. This result is in good agreement with that obtained for the formation of a low-crystallinity phase during discharge cycles in the XRD patterns.

Fe K-edge XANES spectra of the FePS₃ composite electrode (a) before discharge and charge, (b) after the first discharge, (c) first charge, and (d) second discharge cycles are shown in Figure 2-19. For comparison, the spectrum of (e) Fe metal that is used as a reference is also shown. The oxidation state of iron in FePS₃ has reported to be 2+ [17]. After the first and second discharge, the spectrum of the FePS₃ electrode shifted to the low energy side, indicating that the valence of iron in FePS₃ decreased during the

discharge process. These spectra were different from that of Fe metal, indicating the valence of iron is above zero. In contrast, the spectrum of the FePS₃ electrode shifted to the high-energy side after the first charge although this is not the same as pristine spectra. This indicates that the valence of iron in FePS₃ increases but below 2+ during the charge process. These results reveal that iron is reduced and oxidized during discharge-charge cycles. Although the quantitative analysis of Fe valence is difficult to be determined, the spectrum change between discharge and charge is smaller if one assume the oxidation and reduction between 0.5+ and 2+. This indicates that sulfur can also be oxidized at the first charge cycle and reduced at the second discharge cycle. To investigate the redox reaction of sulfur before and after discharge and charge, S K-edge XANES spectra of the FePS₃ electrode without solid electrolytes were measured (Figure 2-20). In sulfur K-edge spectra of the FePS₃ electrode, a peak at 2471.2 eV was observed before discharge and charge. After the first discharge, the peak intensity was decreased, and the profile shape changed slightly. This profile was different to that of elemental sulfur [27]. After the first charge, the peak intensity at 2471.2 eV was increased, and the profile shape was similar to that before discharge and charge. After the second discharge, the peak intensity was decreased again. The profile shape was similar to that after the first discharge. The similar change of the peak intensity before and after discharge and charge was confirmed in S Kedge XANES spectra of the Li₃PS₄-carbon during charge-discharge cycles [28]. These results suggest that the chemical state of sulfur in FePS₃ changes reversibly during discharge-charge cycles although there was no evidence of the sulfur redox.

The results obtained so far reveal that Li^+ can be inserted and extracted into and from the interlayer of FePS₃ during the discharge-charge cycle with a range below 1.5-mol Li^+ per 1.0 mol of FePS₃. While Li^+ -inserted FePS₃ with low crystallinity was formed during



Figure 2-16 (a) First and (b) second discharge-charge curves of all-solid-state Li-In/75Li₂S·25P₂S₅ glass/FePS₃ batteries at 0.13 mA cm⁻² at room temperature. In the first discharge cycle, 0.5 mol (black solid lines), 1.0 mol (blue dashed lines), and 1.5 mol (red dashed-dotted lines) of Li⁺ was inserted per unit FePS₃. The open-circuit voltages (OCVs) were measured (A) before discharge and charge, (B) after first discharge, (C) at 1.5 V vs. Li-In during charge, and (D) after first charge.



Figure 2-17 XRD patterns of the FePS₃ composite electrode (a) before discharge and charge, (b) after first discharge, (c) first charge, and (d) second discharge cycles. Solid circles denote peaks due to FePS₃.



Figure 2-18 Raman spectra of the FePS₃ composite electrode (a) before discharge and charge, (b) after first discharge, (c) first charge, and (d) second discharge cycles. Solid inverted triangles denote Raman bands attributable to $P_2S_6^{4-}$.



Figure 2-19 Fe K-edge XANES spectra of the FePS₃ composite electrode (a) before discharge and charge, (b) after first discharge, (c) first charge, and (d) second discharge cycles. For comparison, the spectrum of (e) Fe metal that is used as a reference is also shown.



Figure 2-20 S K-edge XANES spectra of the FePS₃ electrode without solid electrolytes (a) before discharge and charge, (b) after first discharge, (c) first charge, and (d) second discharge cycles.

the discharge cycle, crystalline FePS₃ was formed during the charge cycle. However, the $P_2S_6^{4-}$ units in FePS₃ were not destroyed during discharge-charge cycles. In terms of redox reactions, only iron was reduced during the first discharge cycle. In contrast, not only iron but also sulfur may be oxidized and reduced from the first charge cycle onward.

The reaction mechanism of FePS₃ on the above results using density functional theory (DFT) calculations was further investigated. The initial structural model was constructed with the assumption that the layered structure of $FePS_3$ with the $P_2S_6^{4-}$ unit does not significantly change during discharge-charge cycles according to the repeated appearance of the layered FePS₃ phase and undestroyed $P_2S_6^{4-}$ structural unit. It has been reported that transition-metal dichalcogenides, which have layer structures that are similar to that of FePS₃, have two different coordination geometries of $P_2S_6^{4-}$ units, namely trigonal prismatic and octahedral coordination geometries [29,30]. Hence, the coordination geometry of $P_2S_6^{4-}$ units in FePS₃ can change during the discharge-charge process. Four structure models of FePS₃ and Li_{1.5}FePS₃ with octahedral and trigonal prismatic symmetries were constructed by Li⁺ insertion between FePS₃ layers. Because the crystallinity of Li⁺-inserted FePS₃ after discharge was low, these crystalline structural models were not consistent with the experimental structure. Nonetheless, some local structures would be represented in the model because these structural models are based on the experimental characterization and the local structural transition with octahedral and trigonal prismatic symmetries. Antimagnetic state within the layered structures were assumed [31]. The structure models that have been described were optimized using a firstprinciples calculation.

Figure 2-21 shows the optimized structures of (a) $FePS_3$ with octahedral $P_2S_6^{4-}$ units (octahedral FePS₃), (b) $Li_{1.5}FePS_3$ with octahedral $P_2S_6^{4-}$ units (octahedral $Li_{1.5}FePS_3$),

(c) FePS₃ with trigonal $P_2S_6^{4-}$ units (trigonal FePS₃), and (d) Li_{1.5}FePS₃ with trigonal $P_2S_6^{4-}$ units (trigonal Li_{1.5}FePS₃). These optimizations showed some local structural change without changing the framework of octahedral FePS₃, octahedral Li_{1.5}FePS₃, and trigonal FePS₃. However, trigonal $Li_{1.5}$ FePS₃ changes significantly owing to the structural optimization, and a rock salt-type structure that is attributable to bonds between sulfur and lithium was confirmed. As previously described, the experimental results showed the formation of a low-crystallinity phase which would be composed of various local structures. Thus, the local structures of the experimental low-crystallinity phase can be represented by those of computationally calculated octahedral and/or trigonal Li_{1.5}FePS₃. Table 2-2 shows the equilibrium voltage of the lithium intercalation reactions of FePS₃. At the first discharge cycle, the reaction corresponds to the formation of trigonal Li_{1.5}FePS₃ from octahedral FePS₃ (Table 2-2 (B)) because the discharge plateau of around 0.9 V vs. Li-In at the first discharge cycle corresponded to the equilibrium voltage of the reaction between octahedral FePS₃ and trigonal Li_{1.5}FePS₃ (Table 2-2 (B)). At the first charge cycle, no charge plateau was observed (Figure 2-16 (a)). Hence, the reaction may correspond to two reactions between octahedral FePS₃ and trigonal Li_{1.5}FePS₃ (Table 2-2 (B)) and between trigonal FePS₃ and trigonal Li_{1.5}FePS₃ (Table 2-2 (D)). At the second discharge cycle, no discharge plateau was observed (Figure 2-16 (b)). The discharge voltage at the second discharge cycle was higher than that at the first discharge cycle. Hence, the reaction of the second discharge cycle represents to two reactions between octahedral FePS₃ and trigonal Li_{1.5}FePS₃ (Table 2-2 (B)), and between trigonal FePS₃ and trigonal Li_{1.5}FePS₃ (Table 2-2 (D)). The calculated equilibrium voltages of these reactions at the first charge and the second discharge cycles were underestimated to the experimental charge and discharge voltages; there is little difference between charge and

discharge voltages and OCV (Figure 2-16). A possible reason for the underestimated voltage is the difference between experimental $Li_{1.5}FePS_3$ and simplified models for DFT calculation. These computational models are constructed assuming Li^+ insertion between FePS₃ layers and the coordination change between octahedral and trigonal coordination. However, the experimental XRD patterns showed low-crystalline phase(s), which was not completely represented by the computational structures. Thus, the redux reactions between FePS₃ and trigonal $Li_{1.5}FePS_3$ would be more complicated than computational ones.

Figure 2-22 presents density-of-states (DOSs) of (a) FePS₃ with octahedral $P_2S_6^{4-}$ units (octahedral FePS₃), (b) Li_{1.5}FePS₃ with octahedral $P_2S_6^{4-}$ units (octahedral Li_{1.5}FePS₃), (c) FePS₃ with trigonal $P_2S_6^{4-}$ units (trigonal FePS₃), and (d) Li_{1.5}FePS₃ with trigonal $P_2S_6^{4-}$ units (trigonal Li_{1.5}FePS₃). In octahedral and trigonal FePS₃, the states at the fermi level (E_f) were mainly composed of the states of iron (see Figure 2-22 (a), (c)). In contrast, in octahedral and trigonal Li_{1.5}FePS₃, the states at E_f were composed of those of iron and sulfur (see Figure 2-22 (b), (d)). Thus, the redox reaction of FePS₃ during discharge-charge cycles would be due to not only iron but also sulfur.

These simulation results indicate that only iron is reduced at the first discharge cycle, and that not only iron but also sulfur is oxidized and reduced from the first charge cycle onwards. The results of the redox of iron corresponded to the change in chemical states shown by the experimental results of Fe and S K-edge XANES spectra of the FePS₃ electrode.



Figure 2-21 Optimized structures of (a) FePS₃ with octahedral $P_2S_6^{4-}$ units (octahedral FePS₃), (b) Li_{1.5}FePS₃ with octahedral $P_2S_6^{4-}$ units (octahedral Li_{1.5}FePS₃), (c) FePS₃ with trigonal $P_2S_6^{4-}$ units (trigonal FePS₃), and (d) Li_{1.5}FePS₃ with trigonal $P_2S_6^{4-}$ units (trigonal Li_{1.5}FePS₃).

Table 2-2 Calculated equilibrium voltage vs. Li-In for lithium intercalation reactions of FePS₃.

Reaction formula	Equilibrium voltage / V vs. Li-In*
(A) FePS_3 (O) + 1.5 Li^+ + 1.5 $\text{e}^ \rightleftharpoons$ Li _{1.5} FePS_3 (O)	0.62
(B) FePS_3 (O) + 1.5 Li^+ + 1.5 $\text{e}^ \rightleftharpoons$ $\text{Li}_{1.5}\text{FePS}_3$ (T)	0.88
(C) $FePS_3(T) + 1.5Li^+ + 1.5e^- \rightleftharpoons Li_{1.5}FePS_3(O)$	1.02
(D) $\text{FePS}_3(T) + 1.5\text{Li}^+ + 1.5\text{e}^- \rightleftarrows \text{Li}_{1.5}\text{FePS}_3(T)$	1.27

FePS₃ (O): FePS₃ with octahedral $P_2S_6^{4-}$ units.

FePS₃ (T): FePS₃ with trigonal $P_2S_6^{4-}$ units.

Li_{1.5}FePS₃ (O): Li_{1.5}FePS₃ with octahedral $P_2S_6^{4-}$ units.

Li_{1.5}FePS₃ (T): Li_{1.5}FePS₃ with trigonal $P_2S_6^{4-}$ units.

*The calculated equilibrium voltage versus Li was converted to the equilibrium voltage versus Li-In using the potential of Li-In at 0.62 V vs. Li^+/Li .



Figure 2-22 Density-of-states (DOSs) of (a) FePS₃ with octahedral $P_2S_6^{4-}$ units (octahedral FePS₃), (b) Li_{1.5}FePS₃ with octahedral $P_2S_6^{4-}$ units (octahedral Li_{1.5}FePS₃), (c) FePS₃ with trigonal $P_2S_6^{4-}$ units (trigonal FePS₃), and (d) Li_{1.5}FePS₃ with trigonal $P_2S_6^{4-}$ units (trigonal Li_{1.5}FePS₃).

2.4. Summary

In the all-solid-state lithium-ion batteries using the sulfide solid electrolytes, NiPS₃ and FePS₃ were investigated as the novel sulfide cathode materials possibly forming easily the favorable electrode-electrolyte interface.

The all-solid-state battery using the NiPS₃ composite electrode exhibited the reversible discharge-charge behavior, and the discharge capacity of the battery after 30 cycles was about 80 mAh g⁻¹. After the first charge, the total resistance decreased, suggesting that the combination the NiPS₃ electrode and the LiS₂-P₂S₅ solid electrolyte is favorable. While after the first discharge the peaks attributable to NiPS₃ disappeared and the very weak peak, which can be assigned as Li₂NiPS₃, appeared, after the first charge the peaks attributable to NiPS₃ appeared. From this result, the discharge-charge reaction of the NiPS₃ electrode can be described as the equation (NiPS₃ + 1.5 Li⁺ + 1.5 e⁻ \rightleftharpoons amorphous/low-crystalline phase(s) including Li₂NiPS₃).

The all-solid-state battery using the FePS₃ composite electrode showed the reversible discharge-charge behavior. The discharge capacity of the battery at the 30th cycle was 119 mAh g^{-1} , which was higher than that of the battery using the NiPS₃ electrode. After the first charge, the total resistance decreased, and the interfacial resistance between the FePS₃ electrode and the LiS₂-P₂S₅ solid electrolyte cannot be confirmed. Thus, the favorable interface between the FePS₃ electrode and the FePS₃ electrode and the EiS₂-P₂S₅ solid electrolyte was formed after the first charge cycle.

Moreover, FePS₃ can be used as an electrode (10 mg) for an all-solid-state battery without the addition of solid electrolytes and carbon additives. Even the all-solid-state battery using the large amount of the FePS₃ electrode (30 mg) without the additives exhibited the discharge-charge behavior. The addition of small amounts of solid

electrolytes (10 and 20 wt%) and carbon additives (2 and 4 wt%) into the FePS₃ electrodes did not significantly affect the discharge-charge behavior of the batteries operated at the current density of 0.13 mA cm⁻². The discharge capacities were not significantly changed by the addition of solid electrolytes and conductive additives under the current density of 0.64 mA cm⁻². These results suggest that the FePS₃ electrode without any solid electrolytes or conductive additives have adequate paths of lithium-ion and electron conduction to show discharge behavior at 0.64 mA cm⁻².

The discharge-charge reaction of the FePS₃ electrode was described by the equation $(FePS_3 + xLi^+ + xe^- \rightleftharpoons Li_xFePS_3, 0 \le x \le 1.5)$. In this reaction, $P_2S_6^{4-}$ units were not destroyed during the first discharge cycle, but the crystalline phase of FePS₃ disappeared with the reduction of iron at the discharge cycle, and FePS₃ appeared along with the oxidation of iron at the charge cycle. This crystalline change was similar to that of NiPS₃. The reversible change in chemical states of iron and sulfur was confirmed by X-ray absorption measurement. The first-principle calculation explained the experimental results of the change of crystalline phase and the increase in the discharge voltage. Further, the calculation results indicated that not only iron but also sulfur was oxidized and reduced from the first charge cycle onwards.

2.5. References

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3. FePS₃-S electrode for all-solid-state lithium secondary batteries

3.1. Introduction

Sulfur has been investigated one of the promising cathode materials for the all-solidstate batteries using the sulfide solid electrolytes because of the high theoretical capacity (1672 mAh g^{-1}) despite its low discharge voltage (~ 2.1 V vs. Li) [1-6]. However, sulfur has mainly two disadvantages as the cathode material: the insulating nature (5×10^{-18} S cm⁻¹) [7] and the large volume change (~80 %) during discharge-charge cycles [8]. Because of the insulating nature, sulfur needs to be mixed with the large carbon additives, which can decrease the volumetric energy density. The large volume change can cause the degradation of the battery. To compensate the insulating nature and the large volume change, sulfide composite materials such as CuS-S [9], C-FeS₂-S [10] have been developed as the cathode materials for the all-solid-state batteries. The additives such as CuS and FeS₂ help the electronic conduction of the sulfur cathode. Since these additives work as the electrode materials, the capacity of the sulfur cathode can be enhanced. The enhanced capacity should lead to the improvement of the volumetric energy density of the battery. The volume changes of CuS and FeS₂ is calculated to be less than 12 % based on the density of CuS (4.76 g cm⁻³), Cu (8.96 g cm⁻³), Li₂S (1.66 g cm⁻³), FeS₂ with pyrite structure (4.98 g cm⁻³), and Fe (7.87 g cm⁻³). Since these volume changes were smaller than that of sulfur (~80 %), the additives can mitigate the large volume change of the sulfur cathode during the discharge-charge cycles.

FePS₃ has been investigated as the cathode material showing the insertion reaction (FePS₃ + 1.5 Li⁺ + 1.5 e⁻ \rightleftharpoons Li_{1.5}FePS₃) in the lithium-ion batteries [11]. FePS₃ has the moderate electronic conductivity (~10⁻⁵ S cm⁻¹) [12], and the layered structure of FePS₃ can lead to the high lithium-ion diffusion. These characteristic properties can form the lithium-ion and electron conduction in the sulfur cathode, when FePS₃ is used as the additive for the sulfur cathode. The small volume change of FePS₃ derived from the insertion reaction can prevent the large volume change of sulfur during the discharge-charge cycles. Moreover, similarity of the constituent elements between FePS₃ and sulfide solid electrolytes can lead to the favorable electrode-electrolyte interface. Thus, FePS₃ is attractive as the additive for the sulfur cathode.

In this chapter, sulfide composite material FePS₃-S was synthesized and investigated as the cathode materials, which have a potential to form the favorable electrodeelectrolyte interface, for the all-solid-state lithium secondary batteries using the sulfide solid electrolytes. FePS₃-S cathode materials were synthesized by mechanical milling of the mixture of FePS₃ and S with different composition ratios (FePS₃:S = 100:0, 70:30, and 50:50 wt%). The crystal structure, the structural units, the stability at high temperature, and the morphologies of the FePS₃-S cathode material were investigated by XRD, Raman spectroscopy, the TG-DTA, and the SEM. The all-solid-state batteries were fabricated using the FePS₃-S cathode materials, a Li₂S-P₂S₅ glass as the solid electrolyte, and a Li-In sheet as the anode material [13]. To compare the performance of the all-solidstate battery with that of the battery using liquid electrolytes, the battery using the FePS₃-S cathode material and a liquid electrolyte was also constructed. In the all-solid-state batteries, the effect of the composition ratios (FePS₃:S = 100:0, 70:30, and 50:50 wt%) and the operating temperature (25, 60, 80, and 100 °C) on the discharge-charge performance was investigated. Rate performance of the all-solid-state battery of the 70FePS₃·30S composite electrode was examined. To investigate the redox reaction of sulfur, the S K-edge XANES spectra of the 70FePS₃·30S composite electrode with solid

electrolytes and carbon additives in the all-solid-state batteries were measured before and after discharge and charge.

3.2. Experimental

3.2.1. Synthesis and characterization of battery materials

FePS₃-S cathode materials were synthesized by mechanical milling of FePS₃ and sulfur (Kanto Chemical, 99.5%). FePS₃ was synthesized by heating a mixture of iron powder (Wako Chemical, 99.9%), red phosphorus (Kanto Chemical, 98.0%), and sulfur (Kanto Chemical, 99.5%) [11]. The synthesized FePS₃ and elemental sulfur were mixed using an agate mortar with weight ratio of 100:0, 70:30, and 50:50, respectively. Then, the mixtures were mechanically milled using a planetary ball mill (Fritsch, Pulverisette 7) with a zirconia pot (45 mL volume) and 500 zirconia balls ($\phi = 4$ mm) in a dry Ar atmosphere at 510 rpm for 24 h.

To identify the crystalline phases of the resultant powder of the 70FePS₃·30S cathode material, X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (Miniflex 600, Rigaku) under Cu-Kα radiation. For this measurement, a sample stage was covered with Kapton film to avoid undesired reaction of the sample with air. Raman spectra of the milled powder of the 70FePS₃·30S cathode material were measured using a Raman spectrometer (XploRA, Horiba) with a green laser (Wavelength: 532 nm) to identify the structural units. For the Raman measurements, the sample was sealed in an evacuated capillary glass tube. The morphology and elemental mapping were studied using focused ion beam–scanning electron microscopy (FIB-SEM; JIB-4600, JEOL) and scanning transmission electron microscopy (STEM; HD-2000, Hitachi) in conjunction with an energy dispersive spectroscopy (EDS) system. The stability of the 70FePS₃·30S

cathode material at high temperature was evaluated by thermogravimetric and differential thermal analysis (TG-DTA; Thermo Plus TG 8120, Rigaku). The electronic conductivity of the 70FePS₃·30S cathode material was measured using a symmetric stainless steel/70FePS₃·30S/stainless steel cell.

3.2.2. Battery construction and electrochemical measurements of the all-solid-state batteries

All-solid-state batteries (Li-In/75Li₂S·25P₂S₅ (mol%) glass/FePS₃-S) were assembled as described in a reference [13]. 75Li₂S·25P₂S₅ (mol%) glass solid electrolytes were prepared by mechanical milling of Li₂S (Mitsuwa Chemical, 99.9%) and P₂S₅ (Aldrich, 99%) [14]. Cathode composite electrodes were prepared by mixing the FePS₃-S cathode samples, 75Li₂S·25P₂S₅ (mol%) glass, and vapor-grown carbon fibers (VGCF, Showa Denko) in a weight ratio of 69:29:2 (wt%). To measure the electronic conductivity of the composite electrode, a symmetric stainless steel/composite electrode/stainless steel cell was constructed. The composite electrodes (10 mg) and the $75Li_2S \cdot 25P_2S_5$ (mol%) glass solid electrolytes (120 mg) were placed into a polycarbonate tube ($\phi = 10$ mm), and pressed under 360 MPa. A Li-In alloy foil was attached to the bilayer pellet consisting of the cathode composite electrode and the solid electrolyte layers by uniaxially pressing them together at 120 MPa. These pellets were sandwiched by two stainless-steel disks as current collectors. The assembled all-solid-state batteries were discharged and charged under a constant current density of 0.51 mA cm^{-2} at different temperature (25, 60, 80, and 100 °C) using a discharge-charge measuring device (Scribner Associates, 580 batterytype system). The discharge-charge measurement was initiated with discharge. To evaluate the rate performance of the battery, the constant current densities from 0.51 to

 8.15 mA cm^{-2} were used for the discharge cycles.

To compare the performance of the all-solid-state battery with that of the battery using liquid electrolytes, the battery (Li/FePS₃-S) using liquid electrolytes was also constructed. In a typical processing, the FePS₃-S cathode sample of 70FePS₃·30S, polyvinylidene fluoride (PVDF), and Super P were mixed using an agate mortar in a weight ratio of 75:15:10 (wt%). Subsequently, 1-methyl-2-pyrrolidone (NMP) was added to the mixture to prepare a slurry. This slurry was loaded onto a copper foil and dried at 100 °C for 24 h in a vacuum. A CR2016 coin-cell battery was constructed using the dried composite cathode foil as a working electrolyte, porous propylene separator (Celgard 2500), 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, wt/wt/wt%) as a liquid electrolyte, and a Li foil as reference and counter electrodes. The weight of the 70FePS₃·30S sample was 0.575 mg cm⁻². The battery was discharged and charged under a constant current density of 65.6 mA g⁻¹ (~0.1 C) at room temperature (typically 25–30 °C), using a discharge-charge measuring device (LANHE CT2001A).

3.2.3. Reaction mechanism of FePS₃-S in all-solid-state batteries

To examine the reaction mechanism of the 70FePS₃·30S cathode material, the products of the 70FePS₃·30S cathode composite electrode after the first charge cycle were investigated by the XRD measurement. To reveal the redox reaction of the 70FePS₃·30S cathode material during discharge-charge cycles, the S K-edge XANES spectra of the cathode composite electrode in the all-solid-state batteries were measured before and after discharge and charge. XANES spectra were measured at the BL6N1 (proposal No. 201705058) of the Aichi Synchrotron Center, Aichi Science & Technology Foundation. K₂SO₄ was used as a standard sample for XANES measurement to calibrate the spectra data. Their intensity was normalized as zero and one for the intensity at 2466.4 eV and 2489.5 eV, respectively. These processes were all performed under a dry Ar atmosphere.

3.3. Results and discussion

Figure 3-1 shows XRD pattern of the FePS₃-S cathode material of 70FePS₃·30S. For comparison, the patterns of pyrite FeS₂, reagent-grade sulfur, and the prepared FePS₃ are also shown in Figure 3-1. The diffraction peaks of the XRD pattern of 70FePS₃·30S were attributed to pyrite FeS₂ (ICSD #316) without peak shift. Considering the composition of the 70FePS₃·30S cathode material, this result indicates that the 70FePS₃·30S cathode material is composed of the pyrite FeS₂ phase and amorphous phase(s) containing phosphorus and sulfur.

Figure 3-2 shows the Raman spectrum of the 70FePS₃·30S cathode material. Raman bands present at 337 and 373 cm⁻¹ were similar to those attributed to S²⁻ in FeS₂ [15]. These results were in agreement with the XRD result, in which only the FeS₂ pyrite phase was detected. In the Raman spectrum, a band at 412 cm⁻¹ was also noted. It has been reported that P-S bonds in $P_2S_6^{4-}$, $P_2S_7^{4-}$, and PS_4^{3-} units show Raman bands at 390, 410, and 425 cm⁻¹, respectively [16,17]. Therefore, the observed band at 412 cm⁻¹ could be attributed to the P-S bond of the $P_2S_7^{4-}$ unit in amorphous phase(s) containing phosphorus and sulfur.

Figure 3-3 (a) through (e) present an SEM and a HAADF-STEM image, and EDS mapping of Fe, P, and S, respectively, of the 70FePS₃·30S cathode material. The particle size of the 70FePS₃·30S cathode was in the range of $1-5 \mu m$ (Figure 3-3 (a)). In the STEM image of the 70FePS₃·30S cathode particle, bright and dark parts were observed (Figure 3-3 (b)), suggesting that the 70FePS₃·30S particle is composed of two or more component



Figure 3-1 XRD patterns of the FePS₃-S cathode material of 70FePS₃·30S, FePS₃ before mechanical milling, reagent-grade pure sulfur and PDF file of FeS₂.



Figure 3-2 Raman spectrum of the 70FePS₃·30S cathode material.


Figure 3-3 (a) SEM image, (b) HAADF-STEM image, and EDS mapping of (c) Fe, (d) P, and (e) S of the 70FePS₃·30S cathode material.

phases. Indeed, in the 70FePS₃·30S particle, iron and phosphorus were non-uniformly distributed (Figure 3-3 (c) and (d)) while sulfur was uniformly distributed (Figure 3-3 (e)). In the mapping image of iron (Figure 3-3 (c)), the distribution of iron corresponded mainly to the bright regions of the HAADF-STEM image (Figure 3-3 (b)), with an average size of approximately 30 nm. Considering SEM and STEM images, and the XRD results, 70FePS₃·30S can contain FeS₂ with a particle size of approximately 30 nm. However, the possibility of P doping into FeS₂ cannot be denied because a very similar case of P-doped CoS₂, isostructural to FeS₂, has been reported [18,19]. Other components in the 70FePS₃·30S particle, which corresponded to darker regions in Figure 3-3 (b), were amorphous phase(s) composed of phosphorus and sulfur. The electronic conductivity of the 70FePS₃·30S electrode was 3×10^{-7} S cm⁻¹ at room temperature and 6×10^{-6} S cm⁻¹ at 100 °C, which were much higher than that of sulfur (5×10^{-18} S cm⁻¹ at 20 °C) [7].

To measure the stability of the 70FePS₃·30S cathode at high temperature, the TG-DTA was performed. Figure 3-4 shows TG-DTA curves of the 70FePS₃·30S cathode material measured at a heating rate of 5 °C min⁻¹. No significant change in weight and heat were confirmed below 120 °C, suggesting that the 70FePS₃·30S cathode material neither show evaporation and melt.

Figure 3-5 shows discharge-charge curves of (a) the all-solid-state battery using the 70FePS₃·30S electrode at 25 °C and (b) the battery with 70FePS₃·30S and the liquid electrolytes at room temperature (typically 25–30 °C). The current densities were set to 0.51 mA cm⁻² (~0.1 C) for the all-solid-state battery and 65.6 mA g⁻¹ (~0.1 C) for the battery with liquid electrolytes. The all-solid-state battery exhibited discharge-charge capacities of less than 1 mAh g⁻¹ at 25 °C. The low capacity can be attributed to the low electronic conductivity of 5×10^{-7} S cm⁻¹ of the composite electrode with the sulfide



Figure 3-4 TG-DTA curves of the 70FePS₃·30S cathode material measured at a heating rate of 5 $^{\circ}$ C min⁻¹.



Figure 3-5 Discharge-charge curves of (a) all-solid-state battery using the 70FePS₃·30S electrode at 25 °C and (b) battery with the 70FePS₃·30S and liquid electrolytes at room temperature (typically 25–30 °C). In the all-solid-state battery, the cut-off voltage was set to -0.62 V vs. Li-In for discharging and 3.0 V vs. Li-In for charging. On the other hand, the battery with liquid electrolytes was firstly discharge to a capacity of 656 mAh g⁻¹. From the first charge cycle onwards, the cut-off voltage was set to 1.78 V vs. Li-In for charging and 0.58 V vs. Li-In for discharging.

electrolytes and 2 wt% carbon additives. In contrast, the first charge capacity of the battery using the liquid electrolyte was 414 mAh g⁻¹, and its capacity, however, degraded rapidly with repetition of the discharge-charge cycles. Note that the capacity of the battery with liquid electrolytes cannot be directly compared with that of the all-solid-state battery because of the different amounts of carbon additives. More importantly, its capacity, however, degraded rapidly with repetition of the discharge capacity was less than 15 mAh g⁻¹ because of the dissolution of the polysulfide [20].

In order to achieve large discharge-charge capacity at a reasonable rate, the dischargecharge performance of the all-solid-state battery was examined at higher temperature (60, 80, and 100 °C). Figure 3-6 shows the first discharge-charge curves of all-solid-state batteries using the 70FePS₃·30S electrode at different temperature (25, 60, 80, and 100 °C) under a current density of 0.51 mA cm⁻². The battery heated at 100 °C exhibited the high reversible capacity of 625 mAh g⁻¹ for the first cycle. This can be because the electronic conductivity of the composite electrode at 100 °C is 1×10^{-5} S cm⁻¹, which is higher than that at 25 °C (5×10^{-7} S cm⁻¹).

Figure 3-7 (a) shows discharge-charge curves of the all-solid-state battery with the 70FePS₃·30S electrode at 100 °C, under a current density of 0.51 mA cm⁻² (~0.1 C). 1 Crate was defined as 5.8 mA cm⁻² required to (dis)charge the battery in 1 hour. In the discharge-charge measurement, the battery was firstly discharged with a capacity of 656 mAh $g^{-1}_{(FePS3-S)}$. Subsequently, the battery was charged to 3.0 V vs. Li-In. The capacity of 656 mAh $g^{-1}_{(FePS3-S)}$ was calculated by using the theoretical capacities of FePS₃ (220 mAh g^{-1}) and sulfur (1672 mAh g^{-1}) with the weight ratio of 70:30, but the theoretical capacity (656 mAh



Figure 3-6 First discharge-charge curves of all-solid-state batteries using the 70FePS₃·30S electrode at 25 °C (black lines), 60 °C (blue lines), 80 °C (green lines), 100 °C (red lines) under a current density of 0.51 mA cm⁻². First, the battery was discharged to the capacity of 656 mAh g^{-1} ; this was calculated based on the theoretical capacities of FePS3 (220 mAh g^{-1}) and sulfur (1672 mAh g^{-1}). The cut-off voltage was set to -0.62 V vs. Li-In for discharging and 3.0 V vs. Li-In for charging.



Figure 3-7 (a) Discharge-charge curves and (b) cycle performance of the all-solid-state battery using the 70FePS₃·30S electrode at 100 °C under a current density of 0.51 mA cm⁻² (~0.1 C). Discharge and charge capacities are represented by blue and red dots, respectively. For discharging, the cut-off voltage was set to 0.9 V vs. Li-In and the cut-off capacity was set to 656 mAh g⁻¹. For charging, the cut-off voltage was set to 3.0 V vs. Li-In for charging.

 g^{-1}). The theoretical capacity can be estimated based on final products of FeS₂ and amorphous P-S. If 70 wt% FePS₃ and 30 wt% sulfur (1 mol FePS₃ and 2.4 mol sulfur) in the original composite completely react by mechanical milling process, the weight ratio of FeS₂ and amorphous P-S can be estimated to be 46:54 (wt%) based on this reaction. The theoretical capacity of FeS₂ is 894 mAh g⁻¹. In regarding to the amorphous P-S, the composition of P and S can be estimated to be 1:3.4 (mol) based on the reaction of 70 wt% FePS₃ with 30 wt% sulfur. If the amorphous PS_{3.4} completely reacts with Li, and Li₃P and Li₂S are formed, the theoretical capacity can be calculated to be 1876 mAh g⁻¹. By using the estimated weight ratio (46:54 (wt%)) and these theoretical capacities (FeS₂: 894 mAh g⁻¹ and PS_{3.4}: 1876 mAh g⁻¹), the theoretical capacity of the 70FePS₃·30S electrode would be 1423 mAh g⁻¹(FePS₃·S). The all-solid-state battery showed stable reversible discharge-charge behavior for 50 cycles in spite of the low content of the carbon additive (2 wt%) in the 70FePS₃·30S composite electrode.

During the first discharge curve, three plateaus around at 0.9, 1.7, and 1.8 V vs. Li-In were observed. Sulfur has been reported to show two plateaus [21,22]. The plateau at ~2.3 V vs. Li was attributed to the reduction of sulfur to Li_2S_n (n > 4). The another plateau at ~2.1 V vs. Li corresponded to the further reduction of Li_2S_n to Li_2S_2 or Li_2S . The observed plateaus at around 1.7 and 1.8 V vs. Li-In in a range of capacities from 0 to ~280 mAh g⁻¹ can be attributed to the redox reaction of sulfur in amorphous phase(s) containing phosphorus and sulfur. On the other hand, the plateaus at ~1.0 V vs. Li-In in a range of capacities from ~280 to ~660 mAh g⁻¹ can correspond to the redox reactions of S₂²⁻ (Eq. 1) and Fe²⁺ (Eq. 2) in FeS₂ because FeS₂ exhibits a discharge plateau at around 1.7 and 1.5 V vs. Li, corresponding to around 1.1 and 0.9 V vs. Li-In, in the redox reactions of Fe²⁺ and S₂²⁻, as shown in the following equations [23-25].

$FeS_2 + 2Li^+ + 2e^- \rightarrow Li_2FeS_2$	(1)
$Li_2FeS_2 + 2Li^+ + 2e^- \rightarrow Fe + 2Li_2S$	(2)

After the first cycle, the discharge capacity based on the redox reaction of sulfur in the amorphous phase(s) was around 280 mAh g⁻¹, roughly corresponding to 2.7 mol of Li⁺ per 70FePS₃·30S. The sulfur utilization based on the additional amount of sulfur was 56%. A possible reason for the moderate sulfur utilization is that the electron path in the composite electrode is still insufficient to drastically increase the sulfur utilization; the electronic conductivity of the composite electrode was 1×10^{-5} S cm⁻¹ at 100 °C. On the other hand, the discharge capacity attributable to the redox reactions of S₂²⁻ and Fe²⁺ in FeS₂ was around 380 mAh g⁻¹, which corresponds to ~3.7 mol of Li⁺ per 70FePS₃·30S. The utilization based on the amount of FeS₂ was 92%.

From the 1st to 10th cycle, the discharge profile gradually changed, and the discharge voltage in a range of capacities from ~220 to ~450 mAh g⁻¹ slightly increased. For the batteries using FeS₂, the discharge voltage has been reported to increase from the second cycle onwards because of the complex reaction of FeS₂ forming FeS_x and S in the first charge cycle, [23,24,26-28]. The proposed first charge reactions (Eq. 3–5) can be described as the following equations.

$$Fe + Li_2S \rightarrow Li_2FeS_2 + 2Li^+ + 2e^-$$
(3)

$$Li_2FeS_2 \rightarrow Li_{2-x}FeS_2 + xLi^+ + xe^- (0.5 < x < 0.8)$$
 (4)

$$Li_{2-x}FeS_2 \rightarrow FeS_y + (2-y)S + (2-x)Li^+ + (2-x)e^-$$
 (5)

The proposed first charge reactions would cause the discharge profile change from the 1st to 10th cycle.

In the XRD pattern of the 70FePS₃·30S electrode composite electrode after the first charge cycle (Figure 3-8), the peaks can be assigned as S, Fe₇S₈, Li₂FeS₂, Li₄P₂S₆, and



Figure 3-8 XRD pattern of the 70FePS₃ \cdot 30S composite electrode after the first charge cycle.

the unknown phase(s) were observed. This result for the products of S, Fe_7S_8 , and Li_2FeS_2 was consistent with the previously reported complex reaction of FeS_2 forming FeS_x and S [23,24,26-28]. $Li_4P_2S_6$ and unknown phase(s) could be formed by the reaction of the amorphous P-S with Li^+ . These possible reactions (Eq. 6 and 7) can be described as the following equations.

1st discharge: amorphous
$$P-S + zLi^+ + ze^- \rightarrow$$
 unknown $Li-P-S + Li_4P_2S_6$ (6)
1st charge: unknown $Li-P-S \rightarrow$ amorphous $P-S + zLi^+ + ze^-$ (7)

Figure 3-7(b) shows the cycle performance of the all-solid-state battery using the 70FePS₃·30S electrode. The reversible capacity was more than 625 mAh g^{-1} , and the charge capacity at the 50th cycle was 653 mAh g^{-1} . The battery at 100 °C showed no drastic degradation and better cycle performance than at 25 °C. This superior performance indicates that the favorable interface between the FePS₃-S cathode and the sulfide solid electrolyte is formed and kept during the discharge-charge cycles.

Figure 3-9 shows (a) discharge curves and (b) cycle performance of the all-solid-state battery using the 70FePS₃·30S electrode at 100 °C under the constant current densities from 0.51 to 8.15 mA cm⁻² for discharging. The battery exhibited the discharge capacity of larger than 581 mAh g⁻¹ at the current density of 2.03 mA cm⁻² while the battery hardly showed discharge-charge behavior at the current density of equal or higher than 4.07 mA cm⁻². The effect of composition ratios of FePS₃ and S on the capacities of all-solid-state batteries operated at 100 °C was also investigated, and the battery using the 70FePS₃·30S electrode showed higher capacity than those of the 100FePS₃·0S and 50FePS₃·50S electrode (Figure 3-10).

To clarify the discharge-charge behavior, the redox reaction of sulfur in the 70FePS₃·30S electrode was further investigated. Figure 3-11 shows the sulfur K-edge XANES spectra



Figure 3-9 (a) Discharge curves and (b) cycle performance of all-solid-state battery using the 70FePS₃·30S electrode at 100 °C under the constant current densities from 0.51 to 8.15 mA cm⁻² for discharging. First, the battery was discharged to the capacity of 656 mAh g⁻¹ under the cut-off voltage of 0.9 V vs. Li-In. For charging, the current density was set to 0.51 mA cm⁻², and the cut-off voltage was set to 3.0 V vs. Li-In.



Figure 3-10 First discharge-charge curves of all-solid-state batteries using the FePS₃-S electrodes of 100FePS₃·0S (green lines), 70FePS₃·30S (red lines), and 50FePS₃·50S (blue lines) at 100 °C under a current density of 0.51 mA cm⁻². First, the batteries of 100FePS₃·0S, 70FePS₃·30S and 50FePS₃·50S were discharged to the capacities of 220, 656, and 946 mAh g⁻¹, respectively; these were calculated based on the theoretical capacities of FePS₃ (220 mAh g⁻¹) and sulfur (1672 mAh g⁻¹). The cut-off voltage was set to 0.62 V vs. Li-In for discharging. For charging, the cut-off voltages of 100FePS₃·0S, 70FePS₃·50S were set to 2.2, 3.0, and 4.0 V vs. Li-In respectively.



Figure 3-11 Sulfur K-edge XANES spectra of the 70FePS₃·30S composite electrode (a) before discharge and charge, (b) at 1.1 V vs. Li-In during the first discharge, (c) after the first discharge, and (d) after the first charge cycle. For comparison, the spectra of (A) the 75Li₂S·25P₂S₅ glass solid electrolytes and (B) sulfur are shown. The brown dotted line indicates the energy at 2471.8 eV corresponding to the sulfur component. First discharge-charge curve of the all-solid-state battery using the 70FePS₃·30S electrode is also shown in the right upper figure. Colored circles are from the S K-edge XANES spectra of the 70FePS₃·30S composite electrode, as measured (a) before discharge and charge, (b) at 1.1 V vs. Li-In during the first discharge, (c) after the first discharge, and (d) first charge cycles. Intensities at 2471.8 eV at each discharge-charge condition are shown in the right lower panel.

of the 70FePS₃·30S composite electrode at different discharge-charge conditions marked as colored circles in a first discharge-charge curve of the all-solid-state battery using the 70FePS₃·30S electrode. For comparison, the spectra of the 75Li₂S·25P₂S₅ glass solid electrolyte (Figure 3-11 (A)) and sulfur (Figure 3-11 (B)) are also shown. Moreover, the intensity of the sulfur component at 2471.8 eV, at which showed a strong absorption of elemental sulfur, is shown on the lower right side in Figure 3-11 to discuss the chemical state of the sulfur component during the discharge-charge cycle. The samples contain some amounts of 75Li₂S·25P₂S₅ glass of a solid electrolyte layer. The absorption at 2471.8 eV was attributed to sulfur, whereas the absorption at 2470.8 eV was probably attributable to the 75Li₂S·25P₂S₅ glass. The absorption of the 75Li₂S·25P₂S₅ glass cannot be used for discussion in detail, because some amount of 75Li₂S·25P₂S₅ glass of a solid electrolyte layer was unintentionally mixed in the composite electrode samples when the measurement samples were collected. Before discharge and charge, the sulfur component was confirmed (left side in Figure 3-11 (a)). At 1.1 V vs. Li-In during the first discharge, the peak intensity of the sulfur component decreased, as shown in the intensity at 2471.8 eV (right lower side in Figure 3-11). This suggests that the sulfur component is chemically reduced during the discharge cycle up to 1.1 V vs. Li-In. After the first discharge, the peak intensity of the sulfur component was not significantly changed. This means the chemical state of sulfur is not significantly altered during the discharge from 1.1 V vs. Li-In to after the first discharge. After the first charge, the peak intensity of the sulfur component became stronger, as shown in the intensity at 2471.8 eV (right lower side in Figure 3-11). The change of peak intensity indicates that the sulfur component is oxidized during the charge cycle. Note that the profile before discharge and charge was not completely consistent with that after the first charge. This suggests that the initial state of sulfur is

not totally recovered after the charge cycle. The absorption edge energy, which was estimated at the energy of the normalized absorption intensity of 0.5, was between 2469.4 and 2469.6 eV in the spectra of the 70FePS₃·30S composite electrodes at the all dischargecharge conditions. The absorption edge energy was almost the same as that of $75Li_2S \cdot 25P_2S_5$ glass (2469.6 eV). This is because the samples contain some amounts of 75Li₂S·25P₂S₅ glass. Considering the effect of the solid electrolyte inclusion on the absorption edge energy, the redox reaction of the sulfur cannot be discussed based on the absorption edge energy. In the post-edge region of the 70FePS₃·30S composite electrodes, the peak was observed at 2478.6 eV before discharge and charge, which is similar to that of (B) sulfur [29]. On the other hand, at 1.1 V vs. Li-In during the first discharge, the peak was observed at 2476.0 eV, which was consistent with that of (A) 75Li₂S·25P₂S₅ glass. These results indicate the sulfur component is chemically reduced during the discharge cycle up to 1.1 V vs. Li-In. After the first discharge and the first charge cycles, the same peak at 2476.0 eV was observed. This suggests that the sulfur component does not show the redox reaction from the discharge cycle below 1.1 V vs. Li-In to the end of the first charge cycle. Note that this result may be affected by the solid electrolyte inclusion in the samples. From the change of the absorption of sulfur K-edge XANES spectra, it was reasonable to conclude that the sulfur component was reduced and oxidized during the discharge-charge cycles.

To compare with other all-solid-state lithium-sulfur batteries previously reported, Table 3-1 shows details of the battery using the 70FePS₃·30S electrode and these batteries. The discharge capacity of 625 mAh $g^{-1}_{(FePS_3-S)}$ in the battery using the 70FePS₃·30S electrode was lower than those of some other all-solid-state batteries shown in Table 3-1 since the 70FePS₃·30S electrode can contain partially inactive phosphorus. Note that the difference

of the construction conditions of the batteries prevents the quantitative comparison of these electrochemical properties. On the other hand, the battery using the 70FePS₃·30S electrode showed the reasonably good moderate rate performance (~0.1 C) and the moderate discharge capacity (625 mAh g⁻¹) at 100 °C in spite of not only low carbon content but also high cathode material content. In addition, because of extremely low carbon content and introduction of phosphorus, which presumably help lithium-ion conductivity, the battery using the 70FePS₃·30S electrode exhibited high energy density based on volume of the composite electrode even after repeated discharge-charge cycles.

Active	Weight of active	Carbon	Temperature / °C	C-rate / C	Discharge Capacity	Discharge	Energy density*	Reference
material	material / mg	content / wt%)		$/ mAh g^{-1}$ (Active material)	Capacity / mAh	/ Wh cm^{-3} (Composite electrode)	
Cu-S	3.8	6	R.T.	0.02	650	2.5 (at 20th cycle)	~1.1 (at 20th cycle)	[30]
Sulfur	1.6	20	25	0.02	1050	1.6 (at 50th cycle)	~2.1 (at 1st cycle)	[3]
Sulfur	0.7	37	25	0.15	500	0.33 (at 10th cycle)	~0.90 (at 1st cycle)	[4]
Sulfur	3.8	10	25	0.18	~1500	~5.6 (at 100 cycle)	~1.5 (at 1st cycle)	[31]
Sulfur	1.5	10	25	0.1	1288	1.9 (at 1st cycle)	~2.1 (at 1st cycle)	[32]
FeS ₂ -S	6.6	15	25	0.02	~710	~4.7 (at 5th cycle)	~0.99 (at 5st cycle)	[10]
FePS ₃ -S	6.9	2	100	~0.1	625	4.3 (at 50th cycle)	~2.2 (at 50th cycle)	This study

Table 3-1. Properties of all-solid-state lithium-sulfur batteries using sulfur or sulfur composite active materials.

^{*}The energy density per the volume of the composite electrodes is calculated by assuming that each density of the solid electrolyte and the carbon additives was 1.9 g cm⁻³ and 1.8 g cm⁻³, respectively, and molecular weight of the solid electrolytes is 180 g mol⁻¹. This molecular weight corresponds to that of Li₃PS₄. The average discharge voltages, which are used for the calculation, are assumed to be the voltages at the middle point of discharge capacity per the weight of the active materials. Assuming that lithium metal is used as the negative electrodes, the energy density was calculated.

3.4. Summary

FePS₃-S cathode materials were synthesized by mechanical milling of FePS₃ and elemental sulfur. The resultant 70FePS₃·30S powder with particles of about 1–5 μ m diameter was composed of FeS₂ with the size of 30 nm, and the amorphous P-S inclusions. In the discharge-charge measurement at 100 °C, at which liquid electrolytes are unstable, the all-solid-state battery using the 70FePS₃·30S composite electrode, containing only 2 wt% carbon additives, showed excellent reversible discharge-charge behavior. The reversible capacity was more than 625 mAh g⁻¹(FePS₃·S) for 50 cycles at 0.51 mA cm⁻² (~0.1 C) in spite of the low content of carbon additive in the composite electrode. This superior performance indicates the favorable interface between the 70FePS₃·30S cathode and the sulfide solid electrolyte is formed and kept during the discharge-charge cycles. The discharge-charge reactions of the amorphous P-S phase(s) and FeS₂ can be described as the following equations.

amorphous P-S: (1st discharge) amorphous P-S + zLi^+ + ze^- → unknown Li-P-S + $Li_4P_2S_6$

(1st charge) unknown Li-P-S \rightarrow amorphous P-S + zLi⁺ + ze⁻

FeS₂: (1st discharge) FeS₂ + $2Li^+$ + $2e^- \rightarrow Li_2FeS_2$

 $Li_2FeS_2 + 2Li^+ + 2e^- \rightarrow Fe + 2Li_2S$

(1st charge) Fe + $Li_2S \rightarrow Li_2FeS_2 + 2Li^+ + 2e^-$

 $Li_2FeS_2 \rightarrow Li_{2-x}FeS_2 + xLi^+ + xe^-$ (0.5 < x < 0.8)

$$Li_{2-x}FeS_2 \rightarrow FeS_y + (2-y)S + (2-x)Li^+ + (2-x)e^-$$

These reactions can be based on the redox reactions of sulfur component in the amorphous P-S phase(s) and sulfur and iron components in FeS₂. The redox reaction of the sulfur component during the discharge-charge cycle was confirmed by the XANES measurement. The addition of an iron-based metal sulfide to elemental sulfur can provide

moderate electronic conductivity to sulfur, and the carbon additive content in the sulfur composite electrode can be thereby decreased. The FePS₃-S electrode with low content of carbon would be useful for a high-capacity electrode for all-solid-state lithium-sulfur batteries.

3.5. References

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4. Hybrid halide perovskite electrode for all-solid-state lithium secondary batteries

4.1. Introduction

Inorganic-organic hybrid halide perovskites (HHPs) have been investigated as the materials for solar cells because of the suitable bandgap and the high carrier mobility [1-6]. The application of the HHPs for the electrode material in the lithium-ion batteries has been recently examined [7-13]. The HPPs such as CH₃NH₃PbBr₃ have been reported to show the three-step reactions: Li⁺ insertion, conversion, and alloying-dealloying processes [13]. The insertion reaction derives the lithiated phases $Li_xCH_3NH_3PbBr_3$ (0 < x < 1). The conversion reaction leads to methylammonium bromide (CH₃NH₃Br), lithium bromide (LiBr), and lead metal (Pb). The alloying-dealloying reaction gives rise to lithium-lead alloys. This indicates the potential of the HHPs as the new cathode materials for the all-solid-state batteries. The lithium-ion diffusion coefficient in the HHPs has been reported to achieve $\sim 10^{-7}$ cm² s⁻¹ [14], leading to the application of the HHPs for solid electrolytes. Based on the lithium-ion diffusion coefficient, the lithium-ion conductivity of the lithiated HHP can be calculated to be $\sim 10^{-3}$ S cm⁻¹ [14]. The characteristic property can allow the HHPs to be used as the cathode material for the all-solid-state batteries without mixing any solid electrolytes, even though general cathode materials need to be mixed with the solid electrolytes to form the lithium-ion path in the electrodes [15,16]. There are still very few reports on cathode materials with no requiring to mix the solid electrolytes [17].

In this chapter, the application of the HHPs to the cathode materials for the all-solidstate lithium secondary batteries was investigated. The HHPs have been reported to be able to take zero- (0D), 1-(1D), 2-(2D), and 3-dimensions (3D) [17]. The 2D-HHP (CH₃(CH₂)₂NH₃)₂(CH₃NH₃)₂Pb₃Br₁₀ was evaluated as the cathode material because of the expected high lithium-ion diffusion derived from the layered structure. The 2D-HHP was synthesized using methylammonium bromide (CH₃NH₃Br), n-propylammonium bromide (CH₃(CH₂)₂NH₃Br), and lead bromide (PbBr₂). The structural change before and after heating, the morphology, and the elemental distribution of the 2D-HHP were evaluated by XRD, FE-SEM, STEM, and EDS. All-solid-state batteries were constructed using the 2D-HHP as the cathode material and a Li₂S-P₂S₅ glass as the solid electrolyte, and the discharge-charge performance of the batteries was investigated at different temperatures (25, 60, and 100 °C). To evaluate the resistance change of the batteries before and after discharge and charge, the impedance spectra of the batteries were measured. The crystal phases of the products in the 2D-HHP electrodes were examined, and the reaction mechanism of the 2D-HHP in the all-solid-state batteries was proposed.

4.2. Experimental

4.2.1. Synthesis and characterization of battery materials

The 2D-HHP (CH₃(CH₂)₂NH₃)₂(CH₃NH₃)₂Pb₃Br₁₀ was synthesized according to a previous report [12]. Methylammonium bromide (CH₃NH₃Br) and n-propylammonium bromide (CH₃(CH₂)₂NH₃Br) from Dyesol were used as organic cations. Dimethyl sulfoxide (DMSO, Sigma Aldrich) and N,N-dimethylformamide (DMF, Alfa Aesar) were used as solvents, and lead bromide (PbBr₂) (Alfa Aesar) as lead source. The precursor solution consisted of CH₃NH₃Br, CH₃(CH₂)₂NH₃Br and PbBr₂ (2:2:3 molar ratio) dissolved with 71.05 µL DMSO in 560 µL DMF. The 2D-HHP powder was obtained by slow solvent evaporation of the precursor solution at 100°C inside a dry box with relative humidity below 10%. The resulting orange precipitate was then hand milled to obtain the

perovskite powder.

The morphology and elemental mapping of the obtained 2D-HHP powder were examined using field emission scanning electron microscopy (FE-SEM; JIB-4600, JEOL) and scanning transmission electron microscopy (STEM; HD-2000, Hitachi) in conjunction with an energy dispersive spectroscopy (EDS) system. To investigate the stability of the 2D-HHP powder to heat, the structure change of the 2D-HHP powder was examined before and after heating. The XRD patterns were measured before heating and after heating at 100 °C for 6 and 14 days.

4.2.2. Battery construction and electrochemical measurements of the all-solid-state batteries

All-solid-state battery batteries were fabricated using a composite electrode as a cathode, a 75Li₂S·25P₂S₅ (mol%) glass as a solid electrolyte, and Li-In as an anode. The composite electrode was prepared by mixing the synthesized 2D-HHP and vapor-grown carbon fibers (VGCF, Showa Denko) with a weight ratio of 90:10. The 75Li₂S·25P₂S₅ glass solid electrolyte was prepared by mechanical milling process of Li₂S (Mitsuwa Chemical, 99.9%) and P₂S₅ (Aldrich, 99%) [19]. The obtained composite electrode (10 mg) and the 75Li₂S·25P₂S₅ glass solid electrolyte (120 mg) were loaded into polycarbonate tube with the diameter of 10 mm. These powders were pressed at 360 MPa to obtain the binary pellet. The Li-In foil was placed on the solid electrolyte side of the binary pellet and pressed together at 120 MPa. The resultant three-layer pellet was sandwiched by two stainless-steel disks. These processes were performed in a dry Ar atmosphere.

The discharge-charge performance of the all-solid-state batteries with the 2D-HHP was measured at 25, 60, and 100 °C under a current density of 0.13 mA cm⁻² using a discharge-

charge measuring device (Scribner Associates, 580 battery-type system). In this measurement, firstly, the discharge process for Li^+ insertion was started. Impedance spectra of the all-solid-state battery before discharge and charge and after the 30th charge at 100 °C were measured. The cross-section of the interface between the composite electrode and the $Li_2S-P_2S_5$ solid electrolyte after the 30th charge was observed using field emission scanning electron microscopy (FE-SEM; JIB-4600, JEOL).

4.2.3. Reaction mechanism of (CH₃(CH₂)₂NH₃)₂(CH₃NH₃)₂Pb₃Br₁₀ in all-solid-state batteries

The structural change of the 2D-HHP during the first discharge-charge cycle was investigated. Ex-situ X-ray diffraction (XRD) patterns of the composite electrodes were recorded using an X-ray diffractometer (Rigaku, MiniFlex600) with CuK α radiation source. In the XRD measurement, the composite electrodes were put on a sample stage, which was covered with Kapton film, to prevent exposure to air. The composite electrodes were mixed with Si powders to correct measured XRD patterns based on peaks due to Si.

4.3. Results and discussion

Figure 4-1 shows (a) SEM image and (b) enlarged SEM image of the prepared 2D-HHP. The particle size of the 2D-HHP was approximately ten micrometers. A sheet-like structure, in agreement with the 2D structure of the HHP, was observed, as indicated in Figure 4-1 (b). The constituent elements (C, N, Pb, and Br) of the 2D-HHP were distributed uniformly in nanoscale (STEM images shown in Figure 4-2 (a)-(e)).

Figure 4-3 shows the XRD pattern of the 2D-HHP before heating and after heating at 100 °C for 6 and 14 days. The low angle peaks corresponding to the reflection planes



Figure 4-1 (a) SEM image and (b) enlarged SEM image of the prepared 2D-HHP. Red dotted circles indicate the sheet-like structure.



Figure 4-2 (a) STEM image, and EDS mappings of (b) C, (c) N, (d) Pb, and (e) Br of the 2D-HHP.



Figure 4-3 (c) XRD pattern of the 2D-HHP before heating and after heating at 100 °C for 6 and 14 days.

(040), (060) and (080) matched well with the experimental and theoretical XRD patterns of the 2D-HHP previously reported [12]. The additional peak around $2\theta = 9.8^{\circ}$ should correspond to a 2D perovskite with a different dimensionality, but still a 2D material. The crystal phase of the obtained perovskite did not change by heating at 100 °C for 14 days, evidencing high chemical stability that could be useful for its application in batteries operated at extreme working conditions such as high temperatures.

Figure 4-4 shows discharge-charge curves of the all-solid-state batteries using the 2D-HHP at (a) 25, (b) 60, and (c) 100 °C. In Figure 4-4, (d) cyclability, (e) coulomb efficiency and (f) capacity retention of the all-solid-state batteries with the 2D-HHP at the different temperatures (25, 60, and 100 °C) are also shown. In the discharge-charge measurement, the cut-off voltage was set to -0.52 V vs. Li-In alloy for discharge and 2.58 V vs. Li-In alloy for charging. The current density was set to 0.13 mA cm⁻², and the batteries were firstly discharged (lithium insertion). The capacity retention, described in Figure 4-4 (f), was calculated using the equation shown in below:

$C_{retention} = C_n / C_i \times 100$

(where C_{retention}: Capacity retention, C_n; Charge capacity at each cycle, and C_i: Charge capacity at the first cycle)

The battery operated at 25 °C showed discharge-charge behavior, but the reversible capacity was only 12 mAh g⁻¹ at the first cycle. The battery operated at 60 °C showed a higher reversible capacity of 93 mAh g⁻¹ at the first cycle compared with that of the battery operated at 25 °C. From the second cycle onwards, the battery retained a discharge capacity of more than 46 mAh g⁻¹. At the higher temperature operation of 100 °C, the battery performance was further improved compared with those at 25 and 60 °C. The reversible capacity was increased to 249 mAh g⁻¹ at the first cycle, and the discharge



Figure 4-4 Discharge-charge curves of the all-solid-state batteries using the prepared 2D-HHP at (a) 25, (b) 60, and (c) 100 °C. (d) Cyclability, (e) coulombic efficiency, and (f) capacity retention of the all-solid-state batteries with the 2D-HHP at different temperature (25, 60, and 100 °C).

capacity was more than 242 mAh g⁻¹ for 30 cycles even though the composite electrode did not contain solid electrolyte. The Coulombic efficiency of the batteries was more than 90 % after initial cycles (~8 cycles) onwards (Figure 4-4 (e)), in the case of the battery operated at 100 °C after the initial third cycle. The large irreversible capacity observed at the initial cycle can be attributed to irreversible reactions between 2D-HHP electrode and solid electrolyte. The capacity retention (lithium extraction) of the battery operated at 25 °C and 60 °C showed a continuous capacity fade, while the battery operated at 100 °C displayed a significant improvement in the lifetime of the battery achieving a capacity retention close to 100 % after 30 cycles. The clear temperature dependence of the battery performance of the 2D-HHP was attributed to a better lithium-ion diffusion in the 2D-HHP electrode promoted by the heating of the battery. This behavior has also been observed in similar systems with others composite electrode not containing lithium (conversion materials) [20]. In addition, lithium-ion batteries using LiCoO₂ have also shown a similar temperature dependence of the discharge behavior [21], in which faster lithium-ion diffusion into the LiCoO₂ structure was obtained at higher temperatures, resulting in the better discharge performance. Thus, a temperature of 100 °C was high enough to promote a faster lithium-ion diffusion ($\sim 10^{-7}$ cm² s⁻¹) [14] into 2D-HHP structure resulting in adequate and superior battery performance. Note that the operating temperature of the battery at 100 °C is expected not to cause a huge negative effect on the 75Li₂S·25P₂S₅ solid electrolyte used as the separator layer because this temperature is low enough not to produce the structural changes such as crystallization, which have been reported to be in the range from 220 °C to 260 °C [22]. Moreover, the conductivity of the $75Li_2S \cdot 25P_2S_5$ glass electrolyte at 100 °C is expected to be in the order of 10^{-3} S cm⁻¹ (~10⁻⁴ S cm⁻¹ at 25 °C) ensuing the lithium ionic conductivity during discharge and

charge processes [22,23].

Figure 4-5 shows Nyquist plots of the all-solid-state battery with the 2D-HHP (a) before discharge and charge, and (d) after the 30th charge at 100 °C. The enlarged Nyquist plots are also included in Figure 4-5 (b)–(c), (e)–(f) to differentiate the individual contributions at higher frequencies. In the Nyquist plots, three resistance components followed of the capacitive tail at low frequency (0.1-0.01 Hz), which was ascribed to electrode impedance (Li-In alloy and electrode composite with current collectors of stainless steel), were confirmed. The resistive components were identified according to previous reports [24,25]. The resistance (R_1) observed at high frequency (1 MHz), corresponding to the interception with the real axis, was attributed to the solid electrolyte separator layer. The resistance (R₂) at middle frequency (200–100 kHz), shown as green semicircles in Figure 4-5 (c) and (f), corresponded to the interfacial resistance between the 2D-HHP electrode and the 75Li₂S·25P₂S₅ solid electrolyte. A resistance (R₃) at low frequency (500–50 Hz), shown as orange semicircles in Figure 4-5 (c) and (f), was attributed to the interface with the Li-In alloy electrode. To assess the value of each resistance, the impedance profiles were fitted to equivalent circuits illustrated in Figure 4-5 (g) and (h). The constant phase elements (CPE), CPE1 and CPE2, are used to simulate the capacitive behavior of R₂ and R₃ resistances, respectively. The Warburg element (Wo) and CPE3 were used to simulate the diffusive behavior at low frequency range. In the fitting of the impedance profile of the battery after the 30th charge at 100 °C (Figure 4-5 (h)), a constant phase element was used instead of a Warburg element to reduce the error since limited data at low frequency were obtained, even when the data were collected until 0.01 Hz. This behavior was attributed to the high resistance of the composite electrode (before discharge-charge) because of the deficiency of the charges in the 2D-HHP electrode, which was visibly

reduced after the 30th charge where the lithium pathway to the inside of the electrode composite is expected.

Table 4-1 shows resistance values extracted from the fitting results (solid red line in Figure 4-5). After the 30th charge, the R₁ resistance increased from 7.5 to 16.6 Ω . This suggests that the lithium-ion conductivity of the solid electrolyte decreases by extended heating at 100 °C, but the solid electrolyte is relatively stable even at 100 °C. Actually, an all-solid-state battery using the Li₂S-P₂S₅ solid electrolyte system has been reported to show stable discharge-charge behavior at high temperature such as 120 °C [20]. The R₂ resistance increased from 13.0 to 33.7 Ω after the 30th charge, which corresponded to a slight increase of ~20 Ω . This resistance, associated to the elemental diffusion at the electrode-electrolyte interface, is reported to achieve higher values up to ~300 Ω in an all-solid-state battery using LiCoO₂ electrode and Li₂S-P₂S₅ solid electrolyte [25]. This suggests that a favorable interface can be formed in all-solid-state batteries using the 2D-HHP. The R₃ resistance was not changed significantly over cycling, keeping a value around 50 Ω .

It can be inferred that the interface formed between 2D-HHP electrode and sulfide solid electrolyte in the all-solid-state battery was electrochemically stable even at the high operating temperature of 100 °C. Moreover, the high capacity retention of the all-solid-state battery using the 2D-HHP has not been observed in the lithium-ion batteries prepared with the 2D or 3D hybrid perovskites and organic liquid electrolytes [7,26].

In addition, the interface between the solid electrolyte and 2D-HHP composite electrode, and the 2D-HHP electrode after the 30th charge were evaluated by SEM-EDS analysis (Figure 4-6 (a)–(e)), where the composite electrode was observed to be sufficiently attached to the solid electrolyte layer without any evidence of an elemental diffusion, in



Figure 4-5 Nyquist plots of the all-solid-state battery with the 2D-HHP (a) before discharge and charge, and (d) after the 30th charge at 100 °C. These enlarged Nyquist plots (b)–(c) before discharge and charge and (e)–(f) after the 30th charge are also shown. Equivalent Circuit models used to fit the impedance profiles of the all-solid-state battery with the 2D-HHP (g) before discharge and charge and charge and (h) after the 30th charge at 100 °C, respectively.

Table 4-1 Fitting results of the impedance spectra of the all-solid-state battery with the 2D-HHP (a) before discharge and charge and (d) after the 30th charge at 100 °C.

	R_1 / Ω	R_2 / Ω	R_3 / Ω
Before discharge and charge	7.5	13.0	56.9
After the 30th charge	16.6	33.7	49.6


Figure 4-6 (a) Cross-sectional SEM image, and EDS mapping of (b) Br and (c) P of the electrode-electrolyte interface of the all-solid-state battery after the 30th charge. (d) SEM images details of the interface between 2D-HHP electrode and solid electrolyte and (e) the 2D-HHP electrode.

good agreement with the low interfacial resistance (34 Ω) of the all-solid-state battery determined by the impedance analysis (Figure 4-5 (d)–(f)).

To inquire about the mechanism of lithium storage of the all-solid-state battery using the 2D-HHP material, a series of ex-situ XRD measurements at different stages of the discharge-charge processes were carried out. Figure 4-7 shows (a) the first dischargecharge curve of the all-solid-state battery using the 2D-HHP and (b) the XRD patterns of the composite electrodes at different voltage during the first discharge-charge process. The colored circles in the discharge-charge curve indicate the measurement points of the XRD patterns (A) before discharge and charge, (B) at 1.43 V and (C) at 0 V vs. Li-In alloy during the first discharge process, (D) after the first discharge at -0.52 V vs. Li-In alloy, and (E) after the first charge at 2.58 V vs. Li-In alloy. To correct the XRD patterns, Si powders were used as a standard material for the composite electrodes. In the XRD pattern at 1.43 V vs. Li-In alloy during the discharge process, the peaks due to Pb meal (31.2 and 36.2 °) and LiBr (28.0 and 32.5 °) were confirmed, and unknown peaks (22.0 and 38.7 °) were also observed. This result indicates that the conversion reaction can occur during the early stage of the discharge process (Figure 4-7 (a), between (A) and (B) points). It has been reported that batteries using CH₃NH₃PbBr₃, which is 3D-HHP, show the discharge plateau at ~ 2.3 V vs. Li, corresponding to ~ 1.7 V vs. Li-In alloy, through the formation of the Li⁺-inserted CH₃NH₃PbBr₃ [13]. In case of the all-solid-state battery prepared with 2D-HHP, a similar discharge plateau was observed at ~1.5 V vs. Li-In alloy. In contrast, this discharge plateau was not observed at the first cycle in a lithium-ion battery using PbO, where only conversion and alloying-dealloying processes have been reported [27]. Thus, conversion and Li⁺ insertion reactions in the 2D-HHP are expected to occur during the early stage of the discharge process. The possible Li⁺ insertion and



Figure 4-7 (a) First discharge-charge curve of the all-solid-state battery using the 2D-HHP and (b) XRD patterns of the composite electrodes at different voltage during the first discharge-charge process. The colored circles in the discharge-charge curve indicates the measurement points of the XRD patterns (A) before discharge and charge, (B) at 1.43 and (C) at 0 V vs. Li-In alloy during the first discharge process, (D) after the first discharge at -0.52 V vs. Li-In alloy, and (E) after the first charge at 2.58 V vs. Li-In alloy. To correct the XRD patterns, Si powders as a standard material were mixed into the composite electrodes.

conversion reactions are shown below:

 $(PA)_{2}(MA)_{2}Pb_{3}Br_{10} + xLi^{+} + xe^{-} \rightarrow \text{amorphous } Li_{x}(PA)_{2}(MA)_{2}Pb_{3}Br_{10} \qquad (1)$ amorphous $Li_{x}(PA)_{2}(MA)_{2}Pb_{3}Br_{10} + (6-x)Li^{+} + (6-x)e^{-} \rightarrow 3Pb + 6LiBr + (PA)_{2}(MA)_{2}Br_{4}$ (2)

where $MA = CH_3NH_3$ and $PA = CH_3(CH_2)_2NH_3$. In these reactions, Pb^{2+} can be reduced to Pb^0 . The unknown peaks would be attributed to an organic component such as $(CH_3(CH_2)_2NH_3)_2(CH_3NH_3)_2Br_4$. In the XRD pattern (C) at 0 V vs. Li-In alloy during the discharge process, the peaks due to Pb meal and LiBr and unknown peaks (22.0° and 38.7°) were again observed, suggesting that the conversion reaction (equation (2)) proceeded in the discharge process between (B) at 1.43 and (C) at 0 V vs. Li-In alloy. In the XRD pattern (D) after the discharge at -0.52 V vs. Li-In alloy, the peaks due to LiBr, Li₈Pb₃ (22.2°, 24.2°, 25.0°, 29.1°, and 37.7°), and Li₃Pb (23.0°, 26.6°, and 38.0°) and unknown peaks (22.0°, 31.3°, and 38.7°) were confirmed. This result indicates that the alloying reactions occur during last stage of the discharge process (Figure 4-7 (a), between (C) and (D)), as shown below:

$$3Pb + 8Li^+ + 8e^- \rightarrow Li_8Pb_3 \qquad (3)$$

$$Li_8Pb_3 + Li^+ + e^- \rightarrow 3Li_3Pb \qquad (4)$$

The unknown peak at 31.3° would be attributed to the Li-Pb alloy component. The XRD pattern (E) after the first charge showed almost the same diffraction peaks that those observed in the XRD patterns of (B) at 1.43 V and (C) at 0 V vs. Li-In alloy during the discharge process. Thus, the dealloying reactions occur during the charge process. In the charge process, the plateau was observed at ~1.7 V vs. Li-In alloy. Considering the discharge plateau observed at ~1.5 V vs. Li-In alloy in the first discharge cycle, which can correspond to the Li⁺ insertion reaction, this charge plateau can be attributed to the

Li⁺ extraction reaction from the Li⁺-inserted 2D-HHP. Since the peaks due to the 2D-HHP were not detected after the charge cycle, 2D-HHP with amorphous feature may be formed in the Li⁺ extraction reaction. Therefore, not only the dealloying but also the Li⁺ extraction reactions may occur during the charge cycle. The possible first charge reactions are the following:

 $3Li_3Pb \rightarrow Li_8Pb_3 + Li^+ + e^-$ (5)

$$\mathrm{Li}_8\mathrm{Pb}_3 \to 3\mathrm{Pb} + 8\mathrm{Li}^+ + 8\mathrm{e}^- \qquad (6)$$

amorphous $Li_x(PA)_2(MA)_2Pb_3Br_{10} \rightarrow amorphous (PA)_2(MA)_2Pb_3Br_{10} + xLi^+ + xe^-$ (7)

where $MA = CH_3NH_3$ and $PA = CH_3(CH_2)_2NH_3$. Thus, the mechanism of the lithium storage into the 2D-HHP electrode material is suggested, consisting of three-step reactions: Li⁺ insertion/extraction, conversion, and alloying–dealloying reactions. The favorable electrochemical performance of the battery can be attributed to both the high lithium-ion diffusion of the 2D-HHP structure facilitated at high temperatures and the formation of LiBr during the first discharge process. LiBr, known as an additive to increase Li⁺ conductivity of polymers and glasses [28], can enhance the lithium pathway into the composite electrode.

Finally, the 2D-HHP electrode material can be more effective than other inorganic materials based on Pb or their mixture with additives such as LiBr because the organic component in the unique 2D-HHP structure (organic cation: $(CH_3(CH_2)_2NH_3)_2(CH_3NH_3)_2^{4+})$ is expected to prevent or minimize the large volume change of the electrode during the discharge-charge process (lithium insertion/disinsertion) which coincides with the observed electrochemical behavior of the all-solid-state battery where a negligible capacity degradation after the second cycle was

obtained. It is anticipated that the chemical structure of the 2D-HHP material strongly affects the interfacial reactions with the solid electrolyte, and therefore the electrochemical performance of the battery is expected to be improved by the change in the structure of the metal halide perovskite, such as the use of Sn or Ni instead of Pb, Cl instead of Br, and the volume of organic cation.

4.4. Summary

All-solid-state lithium 2D-HHP secondary battery using (CH₃(CH₂)₂NH₃)₂(CH₃NH₃)₂Pb₃Br₁₀ (electrode material), sulfide solid electrolyte (separator layer), and the Li-In alloy (negative electrode) was successfully prepared and evaluated at different temperatures from 25 to 100 °C in a potential range between -0.52 V to 2.58 V vs. Li-In alloy. In the higher temperature operation at 100 °C, the all-solidstate battery performance was further improved compared with those at 25 and 60 °C because of a faster lithium-ion diffusion into 2D-HHP structure and its high chemical stability verified by the XRD measurement. The all-solid-state battery operated at 100 °C achieved a high reversible capacity of more than 242 mAh g^{-1} for 30 cycles at 0.13 mA cm⁻², even though the absence of solid electrolyte additives in the composite electrode. Moreover, a low interfacial resistance between 2D-HHP and sulfide solid electrolyte of only 34 Ω after the 30th charge was determined, which showed the high electrochemical stability of the battery. These results revealed that the potential of the 2D-HHP as a new electrode system for all-solid-state batteries. The mechanism of the lithium storage into the 2D-HHP electrode material was investigated by ex-situ XRD measurements of composite electrode at different stages of the discharge-charge processes. The results suggest that the lithium storage of the battery consists of three-step reactions: Li⁺ insertion/extraction, conversion, and alloying-dealloying reactions.

4.5. References

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5. General conclusions

In this thesis, sulfide materials NiPS₃, FePS₃, and FePS₃-S were examined as novel cathode materials, which can form the favorable electrode-electrolyte interface, in the all-solid-state lithium secondary batteries using the sulfide solid electrolytes. In addition, 2D-HHP (CH₃(CH₂)₂NH₃)₂(CH₃NH₃)₂Pb₃Br₁₀ was investigated as a new cathode system for the all-solid-state batteries. The following results and considerations were obtained.

- 1. NiPS₃ and FePS₃ were examined as cathode materials for all-solid-state batteries using Li₂S-P₂S₅ solid electrolytes because these materials have P-S structural units, similar to the solid electrolytes. The all-solid-state batteries with the NiPS₃ or FePS₃ electrodes containing Li₂S-P₂S₅ glass solid electrolytes and carbon additives showed the discharge-charge behavior, and NiPS₃ and FePS₃ were found to be used as the cathode materials for the all-solid-state batteries. The resistance of the batteries decreased after the first charge, suggesting that the combination of the NiPS₃ and FePS₃ cathodes with the sulfide solid electrolyte are favorable. Thus, the similarity between the electrode and the electrolyte must be important for the formation of the favorable electrolyte interface.
- 2. Although most of cathode materials in all-solid-state batteries require solid electrolytes and conductive additives for sufficient lithium-ion and electron conducting paths in the electrode, FePS₃ was found to function as an electrode material without mixing the solid electrolyte and conductive additives. This indicates that the FePS₃ electrode has sufficient lithium-ion and electron conducting paths even in the absence of solid electrolytes and carbon additives.

3. The investigation on the reaction mechanism of NiPS₃ by XRD revealed that the crystallinity of NiPS₃ was decreased after the discharge reaction. The following reaction mechanism was proposed:

 $NiPS_3 + 1.5 Li^+ + 1.5 e^- \rightleftharpoons$ amorphous/low-crystalline phase(s) including Li_2NiPS_3

 Discharge-charge measurements, XRD, Raman spectroscopy, and XANES revealed the reversible discharge-charge reaction as follows

 $FePS_3 + xLi^+ + xe^- \rightleftharpoons Li_xFePS_3 \quad (0 \le x \le 1.5)$

In this reaction, the crystallinity of FePS₃ was decreased after the discharge reaction, similar to NiPS₃, and the chemical states of iron and sulfur reversibly changed. The change in the chemical states of iron and sulfur is supported by the computational result.

5. The 70FePS₃·30S powder synthesized by mechanical milling was composed of FeS₂ and the amorphous phase(s) containing phosphorus and sulfur, and the all-solid-state batteries using the 70FePS₃·30S powder as the cathode material showed discharge-charge behavior without the drastic capacity degradation. The 70FePS₃·30S powder worked as the cathode material for the all-solid-state batteries, and the good performance of the battery suggests that the favorable interface between the 70FePS₃·30S cathode and the sulfide solid electrolyte is formed and kept during the discharge-charge cycles. In addition, this performance indicates that the addition of FePS₃ to elemental sulfur can provide moderate electronic conductivity to sulfur and suppress the large volume change of sulfur during the discharge-charge cycle,

leading to no capacity degradation of the battery.

The all-solid-state battery using the 2D-HHP (CH₃(CH₂)₂NH₃)₂(CH₃NH₃)₂Pb₃Br₁₀ 6. as the new electrode system showed the discharge-charge behavior, and the 2D-HHP was found to function as a new electrode system for all-solid-state batteries. The interfacial resistance between the 2D-HHP and the sulfide solid electrolyte was low even after the discharge-charge cycle, suggesting that the combination of the 2D-HHP and the sulfide solid electrolyte is favorable. The investigation of the lithium storage mechanism of the 2D-HHP by XRD indicated that the reaction proceeded Li^+ with three-step processes, insertion/extraction, conversion, and alloying-dealloying reactions.

These results revealed that the sulfide materials NiPS₃, FePS₃, and FePS₃-S function as the novel cathode materials for the all-solid-state battery using the sulfide solid electrolyte, and the combination of sulfide cathode materials with sulfide solid electrolytes is useful for the formation of the favorable electrode-electrolyte interface with low resistance. In addition, the results clarified that the 2D-HHP is the new electrode system for the allsolid-state battery. The present study proposed new concepts for designing the cathode materials for all-solid-state battery using Li₂S-P₂S₅ solid electrolyte, and for designing favorable electrode/electrolyte interfaces. The present study must contribute to further development of all-solid-state batteries.

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List of Publications

Original articles regarding this study are as follows:

 "Development of All-solid-state Lithium Secondary Batteries Using NiPS₃ Electrode and Li₂S-P₂S₅ Solid Electrolyte" <u>Fujii, Y.;</u> Suto, Y.; Miura, A.; Higuchi, M.; Tadanaga, K. *Chem. Lett.* 2016, 45, 652-654.

(Chapter 2)

 "FePS₃ electrodes in all-solid-state lithium secondary batteries using sulfidebased solid electrolytes"
 <u>Fujii, Y.;</u> Miura, A.; Rosero-Navarro, N. C.; Higuchi, M.; Tadanaga, K. *Electrochim. Acta* 2017, 241, 370-374.

(Chapter 2)

 "Reaction Mechanism of FePS₃ Electrodes in All-Solid-State Lithium Secondary Batteries Using Sulfide-Based Solid Electrolytes" <u>Fujii, Y.;</u> Miura, A.; Rosero-Navarro, N. C.; Mizuguchi, Y.; Moriyoshi, C.; Kuroiwa, Y.; Higuchi, M.; Tadanaga, K. *J. Electrochem. Soc.* 2018, 165, A2948-A2954.

(Chapter 2)

4. "Fe-P-S electrodes for all-solid-state lithium secondary batteries using sulfide-based solid electrolytes"
<u>Fujii, Y.</u>; Kobayashi, M.; Miura, A.; Rosero-Navarro, N. C.; Li, M.; Sun, J.; Kotobuki, M.; Lu, L.; Tadanaga, K. J. Power Sources 2020, 449, 227576.

(Chapter 3)

 5. "Two-Dimensional Hybrid Halide Perovskite as Electrode Materials for All-Solid-State Lithium Secondary Batteries Based on Sulfide Solid Electrolytes" <u>Fujii, Y.;</u> Ramirez, D.; Rosero-Navarro, N. C.; Jullian, D.; Miura, A.; Jaramillo, F.; Tadanaga, K. *ACS Appl. Energy Mater.* 2019, 2, 6569-6576.

(Chapter 4)