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Development of high capacity all-solid-state lithium batteries using sulfur-rich amorphous transition metal sulfides TiS$_3$ and MoS$_3$

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Doctoral Thesis at Osaka Prefecture University
Development of high capacity all-solid-state lithium batteries using sulfur-rich amorphous transition metal sulfides TiS$_3$ and MoS$_3$

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1. General introduction

Currently, the demand for rechargeable batteries is increasing more and more. The most popular type, conventional lithium-ion secondary batteries are widely used in portable electronic devices such as cell phones and personal computers [1, 2]. Lithium-ion batteries have several advantages such as lightweight, no memory effect, high operating voltage and high energy density compared with other energy storage technologies. Increasingly they are also scaled up for large applications in hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) [3]. Moreover, the large batteries for power storage are used in power system linkage. Especially, the batteries for power storage are increasingly demanded after the Great East Japan Earthquake. The specific energy density of lithium-ion batteries needs to improve remarkably and battery performances need to meet the requirements for power storage applications. However, serious safety problems become obvious with the increase in battery size for vehicle application and power storage.

To reduce safety hazards of flammability and leakage, organic liquid electrolyte need to be replaced with inorganic solid electrolytes. It is expected that the use of all-solid-state lithium secondary batteries with inorganic solid electrolytes avoids the risk of fire and explosion. In addition, inorganic solid electrolytes have single ion conduction, which is difficult to realize in organic liquid electrolytes. For these reasons, all-solid-state lithium secondary batteries with inorganic solid electrolytes attract much attention as next generation batteries.

Two types of solid-state batteries have been studied; one is the thin-film battery, which is reported to show long cycle performance [4-6], and the other is bulk type battery, which consists of electrode and electrolyte powder compressed layers and thus high energy density of the batteries can be achieved. To improve the performance of bulk type solid-state batteries, there are two key points. One is the development of solid electrolytes with high lithium ion conductivity and the other is the application of suitable electrode active materials with high capacity and good cyclability.

For realizing the all-solid-state batteries, solid electrolytes with high Li ion conductivity are needed. Oxide solid electrolytes such as NASICON-type LATP(Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3) [7], Perovskite-type LLT(Li_{0.29}La_{0.57}TiO_3) [8], and Garnet-type LLZ(Li_7La_3Zr_2O_12) [9] have been reported to exhibit lithium-ion conductivities from 10^{-6} to 10^{-3} S cm^{-1} at room temperature. Oxide solid electrolytes have advantages of high chemical stability and easy handling.
However, to obtain dense oxide solid electrolytes and decrease their grain boundary resistances, high temperature sintering is needed.

On the other hand, sulfides solid electrolytes are known to exhibit higher ionic conductivity than oxide solid electrolytes because of higher polarizability of sulfide ions. Three types of sulfide-based solid electrolytes such as crystalline materials, glassy materials and glass-ceramic materials have been reported. Moreover, sulfide solid electrolytes are well densified even at cold-pressing [10]. High temperature sintering sometimes causes side reactions and generates large interfacial resistances between solid electrolytes and electrode active materials. Therefore, using sulfide solid electrolytes is desirable because all-solid-state batteries can be fabricated by pressing at room temperature without sintering processes.

Crystalline electrolytes in the system of $\text{Li}_{4-x}\text{M}_1\text{M'}_y\text{S}_4$ ($\text{M}=\text{Si, Ge and M'}=\text{P, Al, Zn, Ga}$) have high lithium ion conductive crystalline phases named thio-LISICON [11, 12], and among them, $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ with thio-LISICON II phase showed a lithium ion conductivity of $2.2 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature [13]. Glassy electrolytes have non-grain boundaries and random structure. $\text{Li}_2\text{Si}_2\text{S}_2-\text{Li}_x\text{MO}_y$ ($\text{Li}_x\text{MO}_y = \text{Li}_4\text{SiO}_4$, $\text{Li}_3\text{PO}_4$, $\text{Li}_3\text{BO}_3$ etc.) or $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glasses exhibited high conductivities over $10^{-4} \text{ S cm}^{-1}$ [14-18]. Especially, $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ (mol%) and $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ (mol%) glass-ceramics exhibited much higher lithium ion conductivities of about $10^{-3} \text{ S cm}^{-1}$ than the glasses due to precipitation of highly conductive crystals of thio-LISICON II analogous crystal [19] and $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal [20, 21], respectively. Therefore, sulfide solid electrolytes such as crystalline and glassy electrolytes showed higher lithium ion conductivity compared with oxide solid electrolytes. Especially, it is revealed that sulfide-based solid electrolytes such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ crystal [22] and $\text{Li}_7\text{P}_3\text{S}_{11}$ glass-ceramic [23] showed high lithium-ion conductivity over $10^{-2} \text{ S cm}^{-1}$ at room temperature, which is as high as that of conventional organic liquid electrolytes. In addition, the electrochemical voltage windows of sulfide solid electrolytes were over 5 V. Thus, the sulfide solid electrolytes could be applied to the all-solid-state batteries with high energy density. Actually, the all-solid-state lithium batteries with many kinds of positive and negative electrode active materials have been reported by many researchers [24-48]. Most of the all-solid-state batteries exhibit long cycle life. For example, the batteries $\text{In/ LiCoO}_2$ [49], $\text{Li-In/ Li}_4\text{Ti}_5\text{O}_{12}$ [49] and $\text{Li-In/V}_2\text{O}_5$ [50] using $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramics showed the excellent cyclability for several hundred cycles at current densities less than 1 mA cm$^{-2}$. However, due to limited capacity in both positive and negative electrodes, the specific energy density of
lithium-ion batteries needs to improve remarkably to meet the requirements for electric vehicles [51]. Current positive electrode materials have an actual capacity less than half of negative electrode materials such as graphite and silicon. Therefore, high-capacity positive electrode materials are required to realize lithium-ion batteries with higher-energy densities.

Sulfur is one of the most promising positive electrode materials because of its high theoretical specific capacity of 1672 mAh g$^{-1}$, which is at least 5 times higher than that of the transition metal oxides such as LiCoO$_2$ [52, 53]. Sulfur also has many other advantages such as low cost, abundant resource and environmental friendliness. However, fast capacity fading during cycling of Li/S batteries has been a major challenge toward its practical use [54, 55]. The poor cycle life is due to the dissolution of intermediate lithium polysulfides into organic liquid electrolytes, the volumetric expansion and contraction of sulfur during cycling and the insulating nature of sulfur. A well-designed sulfur electrode to clear these issues is required. The current approaches focus on confining sulfur active materials in porous nanostructures to capture the lithium polysulfides during charge-discharge reactions [56-59]. The cycle life and utilization of Li/S batteries are drastically improved by maintaining an electron conducting path to the sulfur active materials and physically inhibiting the dissolution of polysulfides into liquid electrolytes. Although an excellent structural electrode design mentioned above has led to the outstanding electrochemical performances, there are still a few soluble species escaping from the nanostructures as a matrix over numerous cycles, resulting in a consecutive capacity fading with cycling.

For fundamental improvement in inhibiting the dissolution of lithium polysulfides, the use of inorganic solid electrolytes instead of organic liquid electrolyte is an effective approach. The Li/S cells using sulfide solid electrolytes exhibited a good cycling performance because of completely eliminating the issue of polysulfides dissolution [25, 60-62]. Several attempts have been made to enhance utilization of sulfur active materials. For instance, composites of sulfur and electrically conducting materials such as copper [25, 63, 64] or nanocarbon [62, 64] were prepared by mechanical milling [25, 33, 63] and gas-phase mixing [62]. Furthermore, the construction of not only an electron conducting path but also a Li$^{+}$ ion conducting path to the sulfur active material is essential for improving the performance in all-solid-state Li/S batteries. Recently, Nagao et al. found that mechanical milling of a mixture of sulfur or Li$_2$S active material, acetylene black and Li$_2$S-P$_2$S$_5$ solid electrolytes was a powerful approach for enhancing the reversible capacity and the rate capability in all-solid-state Li/S batteries [65].
However, a large amount of conductive additive powders such as carbon was required for the Li/S batteries, because sulfur is an insulating material. Therefore, in order to achieve the batteries with high energy density, the amount of carbon needs to be decreased.

In this study, transition metal sulfide electrodes with the large sulfur content \((MS_x, x \geq 3)\) are a target material. The electrodes of \(MS_x\) would reduce the additional carbon in the working electrodes, because transition metal sulfides have a higher electronic conductivity than sulfur. In addition, the lithium batteries with the transition metal sulfides and liquid organic electrolytes showed reversible capacity [66-68]. Moreover, the transition metal sulfides such as \(\text{TiS}_2\), \(\text{Mo}_6\text{S}_8\), \(\text{Ni}_3\text{S}_2\), \(\text{NiS}\), \(\text{SnS}\), and \(\text{FeS}\) have been used as the electrode active materials in the all-solid-state lithium batteries using sulfide solid electrolytes [30-32, 44, 45, 47, 48, 69-76]. The all-solid-state batteries showed good cyclability. The transition metal sulfides are thus a suitable electrode active material for solid electrolytes. Here, it is well known that the advantage and disadvantage of transition metal sulfide and sulfur are presented as follows:

**The advantage/disadvantage of transition metal sulfides**
1. High electronic conductivity (Advantage)
2. Good cyclability (Advantage)
3. Low reversible capacity (Disadvantage)

**The advantage/disadvantage of elemental sulfur**
1. Low electronic conductivity (Disadvantage)
2. High reversible capacity (Advantage)

The purpose of this study is to prepare the sulfur-rich transition metal sulfide electrode active materials with the advantage of both transition metal sulfide and sulfur. All-solid-state batteries with sulfur-rich transition metal sulfides as an electrode would exhibit high capacity and good cyclability.

Lithium batteries with amorphous electrodes have been reported [77-96]. For example, the reversibility of amorphous \(\text{V}_2\text{O}_5\) electrode was superior to that of crystalline \(\text{V}_2\text{O}_5\) electrode and the chemical diffusion coefficient of \(\text{V}_2\text{O}_5\) was also increased by amorphization [77]. Delmer *et al.* have reported that amorphous \(\text{RuO}_2\) without long-range order was fairly tolerable for the charge-discharge process [80]. Amorphous \(\text{TiO}_2\) nanotubes showed higher capacities and better cycleability than crystalline \(\text{TiO}_2\) nanotubes [82]. The battery with amorphous \(\text{MoO}_2\) electrode also showed higher capacity and better rate capability than that of...
the battery with crystalline MoO$_2$ because the structural defects in amorphous MoO$_2$ acted as a Li$^+$ storage site [84]. Chae et al. have reported that amorphous V$_2$O$_5$ outperformed crystalline V$_2$O$_5$ with respect to reversible capacity and rate capability [86]. The remarkable battery performance was attributable to the enlarged accessible surface area for Li$^+$ ions and opened Li$^+$ diffusion pathways provided by the vacant sites in the amorphous V-O networks [86]. The batteries with amorphous SnS$_2$ showed the better reversibility and higher reversible capacity than the batteries with crystalline SnS$_2$ [93]. In addition, it has been reported that the fast Li$^+$ ion diffusion coefficient of amorphous SnS$_2$ is probably associated with the structural disorder of SnS$_2$. In the case of amorphous phosphorus electrodes, the batteries with amorphous P-carbon composites electrodes maintained the reversible capacity of about 1740 mAh g$^{-1}$ after the 100th cycle [95]. As mentioned above, the amorphous sulfur-rich transition metal sulfide electrode active materials are very attractive for the lithium batteries with high capacity and good cyclability.

Understanding the microstructural changes and electronic state changes of electrode active materials is extremely important in developing all-solid-state batteries with high capacity. Transmission electron microscope (TEM) observation is a powerful technique to reveal the microstructural changes of the electrode active materials before and after charge-discharge measurements. For example, Kim et al. have reported that structural changes of SnO$_2$ electrodes after cycling were examined by TEM [97]. TEM observations detected that the approximately 3 nm-sized SnO$_2$ nanoparticles did not aggregate into larger Sn clusters after during charge-discharge tests [97]. Sakuda et al. investigated the interface between LiCoO$_2$ electrodes and Li$_2$S-P$_2$S$_5$ solid electrolytes after charge tests by TEM observation, indicating that the interfacial resistance layer were formed by mutual diffusion of Co, P and S elements at the interface [98]. It is reported that TEM image of the 20th cycled charged FeS$_2$ solid-state electrode depicted nano-crystalline domains of 100-200 nm in diameter encased by an amorphous material [99]. The in-situ TEM observation confirmed that the charge-discharge process of CoS$_2$ in lithium batteries involved the reversible phase conversion between CoS$_2$ and Co/Li$_2$S [100]. Furthermore, TEM observation of the Li$_2$S electrodes in the all-solid-state batteries revealed that the crystalline Li$_2$S nanoparticles were changed to the amorphous sulfur by delithiation [101].

X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) measurements are also useful for observing the electronic structure changes of various
Electrode active materials during cycling in lithium-ion batteries [95-102]. For example, XPS measurements revealed that the CoO and Co metal coexisted during discharge process in Li/CoO batteries [102]. In addition, the amount of CoO decreased while that of Co metal increased during discharging. Yang et al. have reported that the common liquid electrolytes (1 M LiPF₆ in 1:1:1 EC:DMC:DEC) was not stable in the presence of LiNi₀.₅Mn₁.₅O₄ positive electrodes when charged above 4.5 V [103]. The electronic structure changes of Ti, P and S were clarified during discharge tests by XPS [106]. In the case of Li/S batteries, the electronic structure of sulfur positive electrodes after charge-discharge process was examined by S₂p XPS [107-111]. Diao et al. have reported that two S₂p peaks at 160.0 eV (Li₂S) and 161.5 eV (Li₂S₂) were observed in sulfur electrodes after the 1st discharge [107]. Helen et al. have reported that ex-situ S₂p XPS measurements were performed at various discharge and charge states during cycling; the single step transformation of sulfur to Li₂S₂ and Li₂S occurred during the charge-discharge tests in lithium-sulfur batteries [111]. Yabuuchi et al. have reported that the charge-discharge mechanisms of Li₂MnO₃-LiCo₁/₃Ni₁/₃Mn₁/₃O₂ composite electrodes were examined by XPS and X-ray absorption near edge structure (XANES) [112]. As a result, the manganese redox reaction (Mn³⁺/Mn⁴⁺) and the oxygen reduction reaction at the electrode surface were clarified. Takamatsu et al. have reported that the electronic and local structural changes of LiCoO₂ electrode thin films during charge-discharge measurements were investigated by XANES and Extended X-ray absorption fine structure (EXAFS); the redox of Co was examined during electrochemical tests [115, 116]. Recently, the reaction mechanism of lithium-sulfur battery was investigated by XANES [117-124]. For example, Gao et al. have reported that the effects of the electrolytes on the electrochemical performance of lithium-sulfur batteries were examined by in-situ S K-edge XANES [117]. Moreover, Cuisinier et al. have reported that the electronic changes of sulfur electrode in Li/S batteries during charge-discharge measurements were investigated by operando S K-edge XANES and the mechanisms of sulfur redox chemistry on cycling were revealed [118]. The above mentioned, TEM observation, XPS measurement and XAFS measurement are suitable for identifying the microstructural changes and electronic structure changes of electrode active materials.

The objectives of the present study focus on developing amorphous sulfur-rich transition metal sulfide electrodes with high capacities in the all-solid-state batteries and understanding of microstructural and electronic structure changes of the amorphous electrodes. This study
focuses on amorphous titanium sulfides and molybdenum sulfides. Crystalline titanium sulfide (TiS$_2$) is a well-known positive electrode active material in lithium-ion batteries [66, 67]. TiS$_2$ had been considered as the most promising electrode material before the appearance of LiCoO$_2$ because it possesses high conductivity and lithium diffusion rates. Whittingham et al. have reported that the liquid type cells with crystalline TiS$_2$ showed good cyclability with long cycle life [125]. In the case of the all-solid-state batteries with sulfide solid electrolytes, Li/TiS$_2$ batteries showed an excellent cyclability [69, 70]. Moreover, thin film batteries with a TiS$_2$ electrode prepared by chemical vapor deposition (CVD) have been reported [4]. On the other hand, crystalline molybdenum sulfide (MoS$_2$) for lithium-ion batteries are also of great interest due to its low cost and high safety [126]. It is reported that the lithium batteries with MoS$_2$ showed high reversible capacity with excellent cyclability. The theoretical capacity of crystalline TiS$_2$ and MoS$_2$ are about 240 and 170 mAh g$^{-1}$. This capacity was lower than the theoretical capacity of elemental sulfur (about 1670 mAh g$^{-1}$). For increasing the capacity of the electrode active materials, the electrodes have been prepared by combining sulfur and TiS$_2$ or MoS$_2$ in this study. These electrode active materials have been prepared by the pulsed laser deposition (PLD) and mechanical milling (MM) methods. Amorphous materials can be prepared by these techniques [18-21, 127, 128].

The PLD method has a benefit of preparing thin films with high density and smooth surface. In addition, the direct formation of the sulfide thin film electrodes on solid electrolytes by PLD is effective in achieving an favorable contact between electrode and electrolyte in all-solid-state lithium batteries. An ideal contact between electrode and electrolyte achieved by PLD contributes to elucidating the reaction mechanism from the fundamental point of view of structure and morphology of the interface. Moreover, it is possible to produce novel electrode materials by controlling the deposition conditions of PLD. Morphology and chemical composition of thin films are affected by deposition condition. Sulfur-rich amorphous titanium sulfide ($a$-TiS$_x$) electrode thin films can be namely prepared by PLD.

Sulfur-rich amorphous titanium sulfide and molybdenum sulfide electrode active materials have also been prepared by MM in order to apply to the bulk type all-solid-state lithium batteries. The advantages of the MM technique are room-temperature process and direct preparation of fine amorphous powders. In the case of the amorphous materials prepared by MM, TiS$_3$ has firstly been focused as working electrodes. The liquid type cells
using crystalline TiS$_3$ have been reported [129-131]. TiS$_3$ crystal has a higher theoretical capacity of 556 mAh g$^{-1}$ than TiS$_2$ crystal (240 mAh g$^{-1}$). The liquid-type cell with TiS$_3$ crystal exhibited high capacities of ca. 350 mAh g$^{-1}$ for the first few cycles, although the capacity decreased drastically after the fifth cycle [131]. The difference in cyclability between TiS$_2$ and TiS$_3$ crystals has not been clarified. A possible reason reported is the structural deterioration of TiS$_3$ crystal during cycles in cells with organic liquid electrolytes [131]. In this study, amorphous TiS$_3$ has been applied to all-solid-state cells and the comparison of electrochemical properties of amorphous and crystalline TiS$_3$ positive electrodes has been examined. The electrochemical reaction mechanism of amorphous TiS$_3$ has been investigated by XRD, Raman, HR-TEM, XPS and XAFS. For increasing the reversible capacity of bulk type all-solid-state batteries, amorphous titanium sulfide with the larger sulfur content than amorphous TiS$_3$ have been prepared by MM. However, the electronic conductivities of electrodes decrease with increasing the content of sulfur. Cycle life and utilization of Li/S batteries are improved by using the sulfur/carbon composite positive electrodes because of maintaining an electron conducting path to the sulfur active materials and physically inhibiting the dissolution of polysulfides into liquid electrolytes [56-59]. The decrease of electronic conductivity of electrodes has been prevented by using the sulfur/carbon composites. Therefore, sulfur-rich amorphous titanium sulfide has been prepared by MM from amorphous TiS$_3$ and sulfur/carbon composites.

Amorphous MoS$_3$ has also been prepared by MM. The electrochemical properties and microstructures of amorphous MoS$_3$ have been examined. The structure and electronic structure changes of amorphous MoS$_3$ during charge-discharge have been investigated by XRD, HR-TEM, XPS and XANES. Finally, the electrochemical reaction mechanisms of amorphous TiS$_3$ and amorphous MoS$_3$ in all-solid-state lithium batteries are discussed.

This doctoral thesis consists of five chapters indicated below:

Chapter 1
This chapter describes the background, the objectives and the contents of this thesis.

Chapter 2
This chapter describes that amorphous titanium sulfide (a-TiS$_x$) thin film electrodes are prepared by the pulsed laser deposition (PLD) method and their application to all-solid-state
lithium batteries with sulfide-based and oxide-based solid electrolytes. In the section 2-3-1, deposition conditions such as laser fluence, argon gas pressure and target-substrate distance are examined. Thin films of \( \alpha \)-TiS\(_x\) prepared by PLD are characterized by XRD, SEM, and TEM. In the section 2-3-2-1, \( \alpha \)-TiS\(_x\) thin films are directly formed on a pelletized 80Li\(_2\)S-20P\(_2\)S\(_5\) (mol\%) glass-ceramic electrolyte to construct all-solid-state cells. Electrochemical properties of the all-solid-state cells Li-In/80Li\(_2\)S-20P\(_2\)S\(_5\) glass ceramic/\( \alpha \)-TiS\(_x\) thin film are evaluated and compared to the solid-state cell using TiS\(_2\) active material particles instead of \( \alpha \)-TiS\(_x\) films. In addition, the all-solid-state lithium cells with pelletized LLZ and LLZ-Li\(_3\)BO\(_3\) solid electrolytes and amorphous TiS\(_4\) thin film electrodes are fabricated and evaluated their electrochemical performance in the section 2-3-2-2.

Chapter 3
In this chapter, the electrochemical performance and the structural changes of amorphous TiS\(_3\) (\( \alpha \)-TiS\(_3\)) electrode active materials in all-solid-state cells using Li\(_2\)S-P\(_2\)S\(_5\) solid electrolytes is investigated. First, \( \alpha \)-TiS\(_3\) electrode active materials are prepared by mechanical milling and applied to all-solid-state cells. Then, the comparison of electrochemical properties between amorphous and crystalline TiS\(_3\) electrodes in all-solid-state lithium cells is done. Moreover, the microstructural changes of these electrode active materials before and after charge-discharge measurements are investigated and the relationship between the battery performance and structural changes is discussed. The electrochemical mechanism of \( \alpha \)-TiS\(_3\) is considered from the results of \( \alpha \)-TiS\(_3\) electrodes examined by XRD, Raman, HR-TEM, XPS and XAFS. Finally, for developing of the electrode active materials with high capacity, composite electrodes of \( \alpha \)-TiS\(_3\)/S/carbon are prepared by mechanical milling from \( \alpha \)-TiS\(_3\) and S/carbon composites. The electrochemical properties of \( \alpha \)-TiS\(_3\)/S/carbon are examined in the coin-type cells with liquid electrolytes and all-solid-state cells with sulfide solid electrolytes.

Chapter 4
This chapter reports the electrochemical properties of all-solid-state lithium cells with amorphous MoS\(_3\) (\( \alpha \)-MoS\(_3\)) electrodes prepared by mechanical milling. The microstructural changes and electronic structures of \( \alpha \)-MoS\(_3\) during electrochemical reaction are investigated by XRD, SEM, HR-TEM XPS and XAFS. From the results of analyses, the electrochemical reaction mechanism is discussed. Finally, the difference of the charge-discharge mechanisms
between amorphous TiS$_3$ and amorphous MoS$_3$ is discussed.

**Chapter 5**

This chapter summarizes all the conclusions in this thesis.
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2. Preparation of amorphous TiS\textsubscript{x} thin film electrodes by the PLD method and their application to all-solid-state lithium batteries with sulfide and oxide solid electrolytes

2.1. Introduction

Crystalline TiS\textsubscript{2} (c-TiS\textsubscript{2}) is a well-known electrode material in lithium-ion batteries using organic liquid electrolytes [1, 2]. Whittingham \textit{et al.} performed considerable researches on c-TiS\textsubscript{2} as an electrode material for lithium-ion batteries with organic electrolytes and revealed that c-TiS\textsubscript{2} was a stable and high capacity electrode material with long cycle life [2]. Iwamoto \textit{et al.} [3] and Trevey \textit{et al.} [4] have demonstrated c-TiS\textsubscript{2} as a suitable positive electrode material on all-solid-state lithium secondary batteries using sulfide solid electrolytes; a Li/c-TiS\textsubscript{2} cell with sulfide solid electrolytes showed an excellent cyclability. However, the theoretical capacity of c-TiS\textsubscript{2} is about 240 mAh g\textsuperscript{-1}. This capacity was lower than the theoretical capacity of elemental sulfur (1672 mAh g\textsuperscript{-1}).

It is expected that the capacity of c-TiS\textsubscript{2} can be increased by combining sulfur and TiS\textsubscript{2}. Therefore, sulfur-rich amorphous titanium sulfide (a-TiS\textsubscript{x}, x \textgeq 3) were prepared by the PLD method in this chapter. The direct formation of the a-TiS\textsubscript{x} thin film electrodes on solid electrolytes by PLD is effective in achieving an favorable contact between electrode and electrolyte in all-solid-state lithium batteries. An ideal contact between electrode and electrolyte achieved by PLD contributes to enhancing their electrochemical performance. Moreover, it is possible to produce novel electrode materials by controlling the deposition conditions of PLD. Morphology and chemical composition of thin films are affected by deposition condition.

The a-TiS\textsubscript{x} thin film electrodes were deposited on the sulfide and oxide solid electrolytes.
Sulfide solid electrolytes are known to exhibit higher ionic conductivity than oxide solid electrolytes because of higher polarizability of sulfide ions. Various inorganic sulfide solid electrolytes such as Li$_2$S-SiS$_2$ glass [5], Li$_2$S-P$_2$S$_5$ glass-ceramics [6, 7] and thio-LISICONs in Li$_4$GeS$_4$-Li$_3$PS$_4$ system [8] with high Li$^+$ ion conductivity of over 10$^{-4}$ S cm$^{-1}$ at 25$^\circ$C have been explored as electrolytes in all-solid-state lithium batteries. Recent reports have described that sulfide-based solid electrolytes such as Li$_{10}$GeP$_2$S$_{12}$ crystals and Li$_7$P$_3$S$_{11}$ glass-ceramics have high lithium-ion conductivity of 1.2×10$^{-2}$ S cm$^{-1}$ [9] and 1.7×10$^{-2}$ S cm$^{-1}$ [10], respectively, at room temperature. Those values are as high as the conductivity of conventional organic liquid electrolytes.

Oxide solid electrolytes have advantages of high chemical stability and easy handling. To obtain dense oxide solid electrolytes and decrease grain boundary resistances, high temperature sintering is needed. Garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) has high lithium ion conductivity ($\sigma_{\text{total}}$>10$^{-4}$ S cm$^{-1}$) and chemical stability against lithium metal [11-14]. Although the bulk conductivity is close to 10$^{-3}$ S cm$^{-1}$, very high temperature at around 1200$^\circ$C is needed for sintering. These high temperatures cause a lithium loss and LLZ samples must be covered with mother powders during sintering to suppress a lithium loss. Low temperature synthesis of cubic LLZ is thus desired. Tadanaga et al. have reported that LLZ was prepared at a lower temperature of 900$^\circ$C by the sol-gel method [15, 16]. High lithium ion conductive composite electrolyte with LLZ and amorphous Li$_3$BO$_3$ was prepared from sol-gel derived precursor powders of LLZ and Li$_3$BO$_3$. The total electrical conductivity of the composite at 30$^\circ$C was 1×10$^{-4}$ S cm$^{-1}$, which is comparable to that of Al-doped LLZ pellet sintered at 1230$^\circ$C without Li$_3$BO$_3$.

Above the mentioned, sulfide solid electrolytes such as Li$_2$S-P$_2$S$_5$ glass-ceramics and oxide solid electrolytes such as LLZ and LLZ-Li$_3$BO$_3$ electrolytes are promising electrolytes.
for all-solid-state lithium batteries.

In the present chapter, $a$-$\text{TiS}_x$ thin film electrodes were prepared by PLD. Deposition conditions such as laser fluence, argon gas pressure and target-substrate distance were examined. Thin films prepared by PLD were characterized by XRD, SEM, and TEM. Thin film electrodes of $a$-$\text{TiS}_x$ were directly formed on a pelletized $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ (mol%) glass-ceramic electrolyte to construct all-solid-state cells. Electrochemical properties of the all-solid-state cells Li-In/$80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass ceramic/$a$-$\text{TiS}_x$ thin film were evaluated and compared to the solid-state cell using $\text{TiS}_2$ active material particles instead of $a$-$\text{TiS}_x$ films. In addition, the all-solid-state lithium cells with LLZ and LLZ-L$_3\text{BO}_3$ solid electrolytes and amorphous $\text{TiS}_4$ thin film electrodes were fabricated and evaluated their electrochemical performance.

2.2. Experimental

2.2.1. Preparation of the amorphous $\text{TiS}_x$ thin film electrodes

The target was prepared using reagent-grade $\text{TiS}_2$ (99.9%, Kojundo Chemical) as starting materials. $\text{TiS}_2$ powders were pulverized with dehydrated ethanol using ball milling for 60 hours. After the ball milling, the obtained powders were dried at 80°C for 24 hours. The powders were pressed into a pellet (20 mm in diameter) by cold press under 280 MPa without sintering process.

Thin film electrodes of amorphous $\text{TiS}_x$ ($a$-$\text{TiS}_x$) were fabricated using PLD with a KrF excimer laser ($\lambda=248$ nm, LPXPro; Lambda Physik). Thin film electrodes were prepared under various deposition conditions. The pulse energy was 200-600 mJ/pulse and the repeating frequency was 5 Hz. The energy density of the focused laser beam was estimated as about 2-6 J/cm$^2$ at the target. Argon gas (99.99%) was used as an ambient gas; various
pressures of the ambient argon gas (0.01-5 Pa) were used. The distance from the target to the substrate was 5-17 cm. The standard deposition condition was shown as follows: Ar gas pressure of 0.01 Pa, the pulse energy of 200 mJ/pulse, and the distance from the target to the substrate of 5 cm. Thin film electrodes of $a$-TiS$_x$ were deposited on a silicon substrate, a pelletized 80Li$_2$S·20P$_2$S$_5$ (mol%) glass-ceramic, a pelletized LLZ and a pelletized LLZ-Li$_3$BO$_3$. The deposition was carried out at room temperature. In a PLD vacuum chamber used for this study, target holders were attached to the upper side and substrates were set at the bottom side.

2.2.2. Cell configurations

The all-solid-state electrochemical cells with sulfide solid electrolytes using $a$-TiS$_x$ thin film electrodes were fabricated. The 80Li$_2$S·20P$_2$S$_5$ (mol%) glass-ceramic for a solid electrolyte was prepared by mechanical milling and subsequent heat treatment from starting materials of Li$_2$S (99.9%, Idemitsu Kosan) and P$_2$S$_5$ (99%, Aldrich) [17]. The stainless steel-304 powders (Kojundo Chemical) were pressed under 720 MPa as a current collector. A Li-In alloy as a counter electrode was put on the pelletized stainless steel (SUS304) and then the 80Li$_2$S·20P$_2$S$_5$ (mol%) glass-ceramic was added, and pressed under 120 MPa to form a three-layered pellet. Thin film electrodes of $a$-TiS$_x$ as a working electrode was directly formed on the surface of the sulfide glass-ceramic layer to form a pellet of SUS304/Li-In/80Li$_2$S·20P$_2$S$_5$ glass-ceramic/$a$-TiS$_x$.

Among $a$-TiS$_x$ thin film electrodes prepared by PLD, the amorphous TiS$_4$ ($a$-TiS$_4$) thin film electrodes showed the best electrochemical properties. Therefore, the $a$-TiS$_4$ thin film electrodes were used as the positive electrodes in the all-solid-state cells with oxide solid electrolytes. LLZ was prepared by a sol-gel process using LiNO$_3$ (Wako, Japan), La(NO$_3$)$_3$ ·
6H₂O (Wako, Japan), Zr(O-n-C₃H₇)₄ (Sigma-Aldrich), Al(O-sec-C₄H₹)₃, as starting materials [15, 16]. CH₃COCH₂COOC₂H₅ (EAcAc) was used as a stabilizing agent for the alkoxides. The mole ratio of LiNO₃ : La(NO₃)₃ · 6H₂O : Zr(O-n-C₃H₇)₄ : Al(O-sec-C₄H₉)₃ : EAcAc : ethanol is 7 : 3 : 2 : 0.3 : 1.6 : 50. LLZ particles were obtained by the calcinating process of the dry gel at 900°C for 5 hours. The obtained LLZ particles were ball-milled with zirconia balls for 12 hours. The milled powders were pressed into the pellets at a pressure of 360 MPa and sintered at 1230°C for 36 hours in an alumina crucible. The lithium ion conductivity of the prepared LLZ pellet (relative density of 92%) was 2-4×10⁻⁴ S cm⁻¹ at room temperature.

The LLZ-Li₃BO₃ composite electrolytes were also prepared by a sol-gel process. LLZ powders were prepared by the calcinating process of the dry gel at 600°C for 2 hours. The prepared LLZ powders were ball-milled with zirconia balls for 12h. Milled LLZ powders and Li₃BO₃ were mixed in an agate mortar. The weight ratio of the LLZ and Li₃BO₃ was 93.6 : 6.4. The mixtures were pressed into pellets at a pressure of 200 MPa and sintered at 900°C for 10 hours in an alumina crucible. The lithium ion conductivity of the LLZ-Li₃BO₃ pellet (relative density of 92%) was 1.0×10⁻⁴ S cm⁻¹ at room temperature.

Thin film electrode a-TiS₄ was deposited on a pelletized LLZ and LLZ-Li₃BO₃. The pulsed laser energy was 200 mJ/pulse and the repeating frequency was 5 Hz. The energy density of the focused laser beam was estimated about 2 J/cm² at the target. Ar gas was used as an ambient gas. The gas pressure was 0.01 Pa. The distance from the target to the substrate was 5 cm. Before depositing, the LLZ and LLZ-Li₃BO₃ pellets were polished by the sandpaper in order to form a smooth interface with the electrolyte pellets. The diameter of the LLZ and LLZ-Li₃BO₃ pellets was 10 mm. After preparing the a-TiS₄ thin film electrodes, the Au current collector was deposited on the a-TiS₄ thin film electrodes by the vacuum vapor deposition method. Then, the Li thin film electrodes were deposited on the other surface of
the LLZ and LLZ-Li$_3$BO$_3$ pellets by the same method. Finally, the Li foil as the negative electrode was put on the Li thin film electrode.

The prepared pellets were sandwiched with two stainless-steel rods to form two-electrode cells. All the processes described above were carried out in a dry Ar filled glove box.

2.2.2. Characterization

X-ray diffraction (CuK$\alpha$) of the thin films and LLZ powders were measured using a diffractometer (UltimaIV; Rigaku or XRD-6000; Shimadzu). The morphology of the thin films was observed using field-emission-type scanning electron microscope (FE-SEM, S4500; Hitachi), scanning electron microscope (SEM, JSM-5300; JEOL or SEM, JSM-6610A; JEOL) equipped with an energy-dispersive X-ray spectroscopy (EDX) system, and a transmission electron microscope (TEM, JEM-2100F; JEOL). The film thickness was measured using FE-SEM. The weight of the $a$-TiS$_x$ thin film electrodes formed on Si substrates was determined using a microbalance (MT5; Mettler-Toledo).

The electrochemical tests were conducted at 25°C in an Ar filled atmosphere using a charge-discharge measuring device (BTS-2004; Nagano Co.). AC impedance measurements were performed by an impedance analyzer (SI 1260; Solartoron) in frequency range from 0.1 to 1 MHz.

2.3. Results and discussion

2.3.1. Preparation of amorphous TiS$_x$ thin film electrodes

The amorphous TiS$_x$ ($a$-TiS$_x$) thin film electrodes were prepared by PLD under various deposition conditions. Figure 2-1 shows an FE-SEM image of cross-sectional titanium sulfide thin film deposited on a Si substrate using the standard deposition condition as mentioned in
Figure 2-1  Cross-sectional FE-SEM image of the $\alpha$-TiS$_x$ thin film electrode prepared under standard deposition condition on a Si substrate.
the experimental section 2.2.1. The thin film prepared by PLD was dense and its thickness was ca. 400 nm. The film was attached firmly to the substrate.

The XRD pattern of the titanium sulfide thin film on a Si substrate is presented in Figure 2-2. The titanium sulfide thin film showed no peaks in the XRD pattern.

A high-resolution TEM (HR-TEM) observation was carried out to clarify the microstructures of the titanium sulfide thin film in detail. The titanium sulfide thin film was prepared on a silicon nitride (Si₃N₄) membrane for the HR-TEM observation. Figure 2-3 shows a HR-TEM image of the titanium sulfide thin film electrode on a Si₃N₄ membrane. Both titanium and sulfur atoms were homogeneously dispersed in the titanium sulfide thin film. The HR-TEM image revealed that the titanium sulfide thin film showed no periodic lattice fringes, suggesting that the thin film prepared at room temperature was amorphous.

Table 1 presents the summary of thicknesses, deposition rates, chemical compositions and the results of the XRD measurements of titanium sulfide thin films prepared under various deposition conditions. The thicknesses and deposition rates were affected by the deposition conditions and they were in the range of 45-720 nm and 1.1-18 nm/min, respectively. The atomic ratios of S and Ti in the titanium sulfide thin films were determined by EDX. The atomic ratio of S/Ti of the pelletized TiS₂ target was confirmed to be 2.0. The atomic ratio of S/Ti of the films prepared under low Ar gas pressures was larger than that of the films prepared under high Ar gas pressures. Moreover, the atomic ratio of S/Ti of the films prepared under a low laser power and a long distance of target-substrate was larger than that of the films prepared under a high laser power and a short distance of target-substrate.

Sakuda et al. reported that the atomic ratio of Li/P of the Li₂S-P₂S₅ thin films prepared under low Ar gas pressures was larger than that of the target; the atomic ratio of Li/P of the thin film prepared under 5 Pa showed good agreement with that of the target [18]. Ambient Ar
Figure 2-2 XRD pattern of $\alpha$-TiS$_x$ thin film electrode prepared under standard deposition condition on a Si substrate.
Figure 2-3 HR-TEM image of $a$-TiS$_x$ thin film electrode prepared under standard deposition condition on a Si$_3$N$_4$ substrate.
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<th>Gas pressure (Pa)</th>
<th>Laser power (mJ / pulse)</th>
<th>Target-substrate distance (cm)</th>
<th>Thickness (nm)</th>
<th>Deposition rate (nm / min)</th>
<th>XRD S/Ti (atomic ratio)</th>
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This table presents the data on the thickness, deposition rate, chemical compositions, and XRD measurements of titanium sulfide thin films prepared under various deposition conditions. The results of the XRD measurements include the atomic ratios of S/Ti and the phase identification of the samples.
gas pressure during deposition, which was an important factor, affected the chemical composition of the sulfide electrolyte thin films. The origin of the relationship between chemical composition and deposition condition for the films has not been understood in detail, but an appropriate condition to form a TiS$_x$ film with a desired composition can be chosen on the basis of the data summarized in Table 1. XRD suggested that titanium sulfide thin films prepared under various deposition conditions were amorphous.

2.3.2. All-solid-state lithium cells

2.3.2.1. Sulfide solid electrolytes

Thin film electrodes of $a$-TiS$_x$ were prepared on the pelletized 80Li$_2$S·20P$_2$S$_5$ glass-ceramic electrolyte. Electrochemical performance of all-solid-state cells using $a$-TiS$_x$ thin films was evaluated. Figure 2-4 (a) shows the initial charge-discharge curves and (b) the cycling performances of all-solid-state cells Li-In/80Li$_2$S·20P$_2$S$_5$ glass-ceramic/$a$-TiS$_x$ ($S/ Ti = 1.7$ or $4$) thin film prepared by PLD. Charge-discharge measurements of the cells were carried out at the current density of 0.0064 mA cm$^{-2}$. In Figure 2-4 (a), the right side ordinate axis represents the electrode potential vs. Li$^+$/Li, as calculated based on the potential difference between the Li-In and Li electrode. Both the cells using $a$-TiS$_{1.7}$ and $a$-TiS$_{4.0}$ thin films operated as a lithium secondary battery at room temperature. The 1st charge capacities of the cells with $a$-TiS$_{1.7}$ and $a$-TiS$_{4.0}$ thin films were respectively 268 and 543 mAh g$^{-1}$. The cells were discharged and charged, but the charge capacities were higher than the discharge capacities. One possible reason for the capacity difference is the fact that lithium ions in the Li$_2$S-P$_2$S$_5$ electrolyte pellet are slightly doped to the $a$-TiS$_x$ thin films during film-deposition on the pellet. Further detailed analyses at the interfacial structure are needed to clarify the origin of the capacity-gap. As shown in Figure 2-4 (b), the capacity of the cells gradually
Figure 2-4  (a) Initial charge-discharge curves of all-solid-state cells Li-In/80 Li_2S·20 P_2S_5 glass-ceramic/α-TiS_x (S/Ti=1.7 or 4) thin film prepared by PLD and (b) cycling performances of all-solid-state cells with TiS_1.7 and TiS_4.0 thin films at room temperature.
decreased for 20 cycles. The 20th charge capacities of the cells using \( a\)-TiS\(_{1.7} \) and \( a\)-TiS\(_{4.0} \) thin films were respectively 155 and 284 mAh g\(^{-1}\). The cell using \( a\)-TiS\(_{4.0} \) thin film kept a higher capacity than the cell with \( a\)-TiS\(_{1.7} \) thin film for 20 cycles. Thin film electrodes of \( a\)-TiS\(_{x} \) prepared by PLD acted as an electrode of all-solid-state lithium secondary batteries.

It was reported that the 1st capacity of the all-solid-state battery using crystalline TiS\(_2\) (\( c\)-TiS\(_2\)) particles as an active material was 239 mAh g\(^{-1}\) [3], which was almost the same as the theoretical capacity of \( c\)-TiS\(_2\) (240 mAh g\(^{-1}\)). The average cell potential and the charge-discharge capacity of the cell using \( a\)-TiS\(_{1.7} \) thin film were similar to those of the cell using \( c\)-TiS\(_2\) particles [3]. Thus, the electrochemical reaction (1) proposed in the \( c\)-TiS\(_2\) would occur in the cell using \( a\)-TiS\(_{1.7} \) thin film electrode.

\[
\text{TiS}_2 + x\text{Li}^+ + xe^- \rightleftharpoons \text{Li}_x\text{TiS}_2 \quad (1)
\]

On the other hand, the cell using the \( a\)-TiS\(_{4.0} \) film with large amounts of sulfur showed the high capacity of 543 mAh g\(^{-1}\) at the 1st cycle and retained the high reversible capacity of 255 mAh g\(^{-1}\) after 20 cycles. The cell with \( a\)-TiS\(_{4.0} \) thin film exhibited a higher capacity than that with \( c\)-TiS\(_2\) particles [3] after the 20th cycle. This suggests that sulfur-rich \( a\)-TiS\(_{x} \) films have higher capacity than \( c\)-TiS\(_2\). This charge-discharge reaction would be affected by the presence of additional sulfur atoms in the thin film electrode. Since the cell using the \( a\)-TiS\(_{4.0} \) thin film had a higher potential than the cell using the \( a\)-TiS\(_{1.7} \) thin film, the charge-discharge mechanism of the \( a\)-TiS\(_{4.0} \) electrode is based on the redox of sulfur as well as the redox of titanium. The all-solid-state cell with \( a\)-TiS\(_{4.0} \) thin film prepared by PLD showed the 1st higher capacity than a liquid cell with \( c\)-TiS\(_2\) [2]. The capacity of the all-solid-state cell using \( a\)-TiS\(_{4.0} \) thin film was higher than the capacities of the solid-state cells using LiCoO\(_2\) (100 mAh g\(^{-1}\)) [19] and LiFePO\(_4\) (110 mAh g\(^{-1}\)) [20] active material particles. It is noteworthy that the titanium sulfide \( a\)-TiS\(_{4.0} \) electrode with a higher capacity than \( c\)-TiS\(_2\) was successfully
prepared by the PLD method. Recently, Sakuda et al. have reported that $a$-TiS$_4$ electrodes prepared by mechanical milling showed the 1st discharge capacity of about 560 mAh g$^{-1}$ in all-solid-state lithium batteries using sulfide solid electrolytes [21]. Therefore, the all-solid-state cells with $a$-TiS$_4$ prepared by PLD showed the similar capacity to that with $a$-TiS$_4$ prepared by mechanical milling.

2.3.2.1. Oxide solid electrolytes

Among $a$-TiS$_x$ thin film electrodes, $a$-TiS$_4$ thin film electrodes showed the best electrochemical properties. Therefore, $a$-TiS$_4$ thin film electrode was deposited on the pelletized oxide solid electrolytes such as LLZ and LLZ-Li$_3$BO$_3$. Figure 2-5 (a) shows the XRD pattern of the LLZ pellet sintered at 1230$^\circ$C. Only the diffraction peaks of cubic LLZ were observed. The calculated lattice parameter of the cubic LLZ is 12.96 Å, which corresponds to that of LLZ prepared by the solid phase method (12.968 Å) [11]. Figure 2-5 (b) shows the XRD pattern of the $a$-TiS$_4$/LLZ pellet where the $a$-TiS$_4$ thin film was deposited on the LLZ pellet. All of the diffraction peaks were assigned to cubic-LLZ and the TiS$_4$ thin film electrodes was amorphous. Figure 2-6 shows the cross-sectional SEM images of the interface between $a$-TiS$_4$ thin film electrode and LLZ electrolyte pellet. The thin film prepared by PLD was dense and its thickness was $ca.$ 400 nm. The film was attached firmly to the pellet.

The charge-discharge curves of the all-solid-state cell Li/cubic-LLZ/$a$-TiS$_4$ thin film electrodes are shown in Figure 2-7. Charge-discharge measurements of the cell were carried out at the current density of 0.010 mA cm$^{-2}$ between the 1st cycle and the 10th cycle as shown in Figure 2-7 (a). The current density was increased to 0.020 mA cm$^{-2}$ after the 11th cycle as shown in Figure 2-7 (b). The 10th charge-discharge curves are shown in Figure 2-7 (b) as
Figure 2-5 XRD patterns of prepared (a) LLZ pellet and (b) $a$-TiS$_4$/LLZ pellet.
Figure 2-6  Cross-sectional SEM image of $a$-TiS$_4$ thin film electrodes on LLZ pellet.
Figure 2-7 Charge-discharge curves of the all-solid-state cell Li/cubic-LLZ/a-TiS$_4$ at the current density of 0.010 mA cm$^{-2}$ for initial 10 cycles (a) and at 0.020 mA cm$^{-2}$ after the 11th cycle (b).
comparison. The cell Li/cubic-LLZ/a-TiS$_4$ operated as a lithium secondary battery at room temperature for the first time. The 1st charge capacity was about 510 mAh g$^{-1}$ and the capacity fading was not observed at 0.010 mA cm$^{-2}$ for 10 cycles. The reversible capacity was decreased by about 40 mAh g$^{-1}$ with an increase of the current density from 0.010 mA cm$^{-2}$ to 0.020 mA cm$^{-2}$.

Figure 2-8 shows the Nyquist plots of (a) the symmetrical cell Li/LLZ/Li and (b) the cell Li/LLZ/a-TiS$_4$ after the 1st discharge, 2nd discharge and 10th discharge. The only one semicircle was observed in Figure 2-8 (a). The semicircle (characteristic frequency of 0.8 kHz) was attributed to the interfacial resistance of Li/LLZ ($R_{Li/LLZ}$). The value of the $R_{Li/LLZ}$ was about 340 Ω cm$^2$. The Li/LLZ/a-TiS$_4$ cell also showed the only one semicircle at the lower frequency region. The characteristic frequency of the observed semicircle was 0.3 kHz, which is similar to that of the Li symmetrical cell of the $R_{Li/LLZ}$. The semicircle would include interfacial resistances of both Li/LLZ ($R_{Li/LLZ}$) and a-TiS$_4$/LLZ ($R_{a-TiS_4/LLZ}$), although it is difficult to separate these two components. The $R_{a-TiS_4/LLZ}$ was roughly calculated to be about 740 Ω cm$^2$, which was the difference in resistance of two semicircles as shown in (a) and (b). The value of $R_{a-TiS_4/LLZ}$ was higher than that of $R_{Li/LLZ}$. In addition, the difference of the LLZ electrolytes resistance ($R_{LLZ}$) was observed in Figure 2-8 (a) and (b). The thickness of the LLZ pellets used in both the cells was about 1 mm. The difference of $R_{LLZ}$ between Li/LLZ/Li and Li/LLZ/a-TiS$_4$ cells would be affected by lithium ion conductivities of the LLZ pellet used, because the range of the lithium ion conductivities of the LLZ pellets was 2-4×10$^{-4}$ S cm$^{-1}$. The total resistance of the cell will be reduced by decreasing the thickness of the solid electrolyte pellets. An alternative technique is heat-treatment for electrode-electrolyte interfaces. For example, Iriyama et al. have reported that the reactivity of the film battery (Li/LiPON/LiCoO$_2$) was markedly improved by the thermal treatment [22]. Therefore, the
Figure 2-8 Nyquist plots of (a) the symmetrical cell Li/LLZ/Li, (b) the cell Li/LLZ/a-TiS\textsubscript{4} after the 1st discharge, 2nd discharge and 10th discharge.
interface resistances of the cells may be reduced by heat-treatment at temperatures without crystallization of the electrodes. The total resistance did not change with increasing the charge-discharge cycle number. Therefore, the good cycle performance of the all-solid-state cell Li/LLZ/a-TiS$_4$ was obtained.

The LLZ-Li$_3$BO$_3$ composite electrolytes synthesized at a lower temperature 900°C were applied to all-solid-state batteries with a-TiS$_4$. The charge-discharge curves of the cell Li/LLZ-Li$_3$BO$_3$/a-TiS$_4$ at the different current densities of 0.010 mA cm$^{-2}$ and 0.020 mA cm$^{-2}$ are shown in Figure 2-9. The cell with LLZ-Li$_3$BO$_3$ electrolytes operated as a lithium secondary battery at room temperature. The reversible capacities at the current densities of 0.010 mA cm$^{-2}$ and 0.020 mA cm$^{-2}$ were about 500 mAh g$^{-1}$ and 470 mAh g$^{-1}$, respectively. The capacity fading was not observed for 15 cycles. The LLZ-Li$_3$BO$_3$ electrolytes are thus useful for all-solid-state lithium batteries with Li metal and a-TiS$_4$ electrodes.

2.4. Summary

Amorphous titanium sulfide (a-TiS$_x$) thin film electrodes were prepared by the pulsed laser deposition (PLD) method. Deposition conditions such as ambient gas, laser fluence and target-substrate distance affected the chemical compositions of the thin films determined by EDX. XRD and TEM analyses revealed that the TiS$_x$ thin films were amorphous. The all-solid-state cell using the a-TiS$_{4.0}$ thin film electrode on the Li$_2$S-P$_2$S$_5$ solid electrolyte showed the charge capacity of 543 mAh g$^{-1}$, which was higher than the theoretical capacity of TiS$_2$.

Among the a-TiS$_x$ thin film electrodes prepared by PLD, a-TiS$_4$ thin film electrodes were deposited on a pelletized LLZ and LLZ-Li$_3$BO$_3$. The thin film prepared by PLD was dense and its thickness was ca. 400 nm. The film was attached firmly to the pellet. The
Figure 2-9 Charge-discharge curves of the all-solid-state cell Li/LLZ-Li$_3$BO$_3$/α-TiS$_4$ at the current densities of 0.010 mA cm$^{-2}$ and 0.020 mA cm$^{-2}$. 
all-solid-state lithium cells with $a$-TiS$_4$ thin film electrodes and LLZ or LLZ-Li$_3$BO$_3$ electrolytes were prepared. The both cells operated as lithium secondary batteries at room temperature and their reversible capacities were about 500 mAh g$^{-1}$. The capacity fading was not observed for 15 cycles in both the cells using LLZ and LLZ-Li$_3$BO$_3$ pellets used as the solid electrolytes. The thin film electrodes of $a$-TiS$_4$ without heating process are an attractive positive electrodes with high capacity for all-solid-state lithium batteries with LLZ and LLZ-Li$_3$BO$_3$ electrolytes.

The thin film electrode of $a$-TiS$_4$ showed the reversible capacity of over 500 mAh g$^{-1}$ in the all-solid state cells using sulfide and oxide solid electrolytes. It is concluded that sulfur redox in the $a$-TiS$_4$ film was utilized in addition to the redox chemistry for TiS$_2$. 
2.5. References


3. Preparation of amorphous TiS$_3$ electrodes for all-solid-sate lithium batteries and investigation of their electrochemical reaction mechanism

3.1. Introduction

In the previous chapter, sulfur-rich amorphous titanium sulfide ($a$-TiS$_x$) thin film electrodes were prepared by PLD. The electrochemical properties of $a$-TiS$_x$ were examined in all-solid-sate batteries. In order to increase energy density of the batteries, bulk type all-solid-state batteries are promising. Bulk type all-solid-state batteries are composed of electrode and electrolyte particles. Energy density of the batteries can be improved by increasing the amount of electrode active materials in the electrode layer. In order to further increase energy density of the all-solid-state batteries, electrode active materials with high capacity need to be developed.

In this chapter, titanium trisulfide, TiS$_3$ was focused as sulfur-rich transition metal sulfides. Crystalline TiS$_3$ ($c$-TiS$_3$) has a higher theoretical capacity of 556 mAh g$^{-1}$ than crystalline TiS$_2$ ($c$-TiS$_2$, 240 mAh g$^{-1}$) because the redox reaction of additional sulfur would contribute to the higher capacity. The electrochemical properties of $c$-TiS$_3$ were examined in liquid-electrolyte cells [1-3]. However, the capacity of the $c$-TiS$_3$ cell drastically decreased after the fifth cycle [3]. The difference in cyclability between $c$-TiS$_2$ and $c$-TiS$_3$ has not been clarified; one possible reason is structural deterioration of $c$-TiS$_3$ crystal during cycles with organic liquid electrolytes.

To improve the cycle performance of $c$-TiS$_3$, amorphization of $c$-TiS$_3$ is an effective approach. Actually, it is reported that amorphous V$_2$O$_5$ and MoO$_2$ exhibited better rechargeability than crystalline V$_2$O$_5$ or MoO$_2$ did [4, 5]. It is thus expected that the electrochemical properties of $a$-TiS$_3$ shows better cyclability than $c$-TiS$_3$. The comparison of
electrochemical properties of amorphous and crystalline TiS$_3$ positive electrodes in all-solid-state lithium batteries is important for clarifying the superiority of $\alpha$-TiS$_3$.

Moreover, in order to understand the electrochemical reaction mechanism of $\alpha$-TiS$_3$ electrodes in all-solid-state lithium cells, the structural changes and electronic structure changes of $\alpha$-TiS$_3$ during cycling tests need to be investigated. There are many observation techniques to examine the microstructure of electrode active materials. For example, high-resolution transmission electron microscopy (HR-TEM) observation of the Li$_2$S electrodes in the all-solid-state batteries revealed that the crystalline Li$_2$S nanoparticles were changed to the amorphous sulfur by delithiation [6]. Therefore, TEM observation is powerful techniques to reveal the microstructural changes of the electrode active materials before and after charge-discharge measurements.

To examine the electronic structure changes in $\alpha$-TiS$_3$ during cycling, X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) analysis have been used. Previously, the electronic structure of sulfur positive electrodes after charge-discharge process was examined by S$_{2p}$ XPS [7-11]. Diao et al. have reported that two S$_{2p}$ peaks at 160.0 eV (Li$_2$S) and 161.5 eV (Li$_2$S$_2$) were observed in sulfur electrodes after the 1st discharge [7]. Helen et al. have reported that ex-situ S$_{2p}$ XPS measurements were performed at various discharge and charge states during cycling; the single step transformation of sulfur to Li$_2$S$_2$ and Li$_2$S occurred during the charge-discharge tests in lithium-sulfur batteries [11].

In addition, XANES is a promising probe for reaction mechanism of lithium-sulfur battery [12-19]. For example, Gao et al. have reported that the effects of the electrolytes on the electrochemical performance of lithium-sulfur batteries were examined by in-situ sulfur K-edge XANES [12]. Moreover, Cuisinier et al. have reported that the electronic changes of sulfur electrode in Li/S batteries during charge-discharge measurements were investigated by
operando sulfur K-edge XANES and the mechanisms of sulfur redox chemistry on cycling were revealed [13]. As mentioned above, XPS and XANES measurements are powerful techniques to reveal the electronic structure changes of the sulfur-based electrode active materials during charge-discharge cycles.

Recently, electrochemical performance of amorphous TiS$_4$ ($a$-TiS$_4$) was reported by Sakuda et al [20, 21]. Lithium batteries using liquid electrolytes using $a$-TiS$_4$ electrodes showed the reversible capacities of about 700 mAh g$^{-1}$ [20]. This capacity was higher than the capacity of $c$-TiS$_3$ of about 560 mAh g$^{-1}$. Moreover, it is reported that the dissolution of polysulfide into the electrolyte was significantly suppressed by amorphization of TiS$_4$, because the chemical bonding between Ti and S was formed by amorphization [20].

Further increasing the capacity of TiS$_4$, the electrode active materials such as amorphous TiS$_x$ ($x$>4) ($a$-TiS$_x$) are promising. However, the electronic conductivity of $a$-TiS$_x$ would decrease with increasing of sulfur content. In this study, $a$-TiS$_3$ electrodes with high capacity and good cyclability are expected to be prepared by combining $a$-TiS$_3$ and sulfur/carbon composites. Sulfur/carbon composites to capture lithium polysulfides during charge-discharge reactions have been used as positive electrodes in Li/S batteries with liquid electrolytes [22-33]. For example, a sulfur-porous hollow carbon composite electrode showed the reversible capacity of 974 mAh g$^{-1}$ after 100 cycles [22]. The sulfur/carbon nanotube composites delivered the 1st discharge capacity of about 1100 mAh g$^{-1}$, and capacity retention of 85% even after the 100th cycle at 1C [33]. It is reported that sulfur/highly ordered nanostructured mesoporous carbon (CMK-3) positive electrodes exhibited the reversible capacity of 1320 mAh g$^{-1}$ [24]. Sulfur/porous carbon nanospheres (PCNSs) positive electrode materials with stable cycling capacity for 100 cycles is reported [32]. As described above, the cycle life and utilization of Li/S batteries are improved by using the sulfur/carbon composite
positive electrodes, because of maintaining an electron conducting path to the sulfur active materials and physically inhibiting the dissolution of polysulfides into liquid electrolytes. Therefore, the degradation of the electronic conductivity of \( a \)-TiS\(_3\) would be suppressed by combining \( a \)-TiS\(_3\) and sulfur/carbon composites.

In this chapter, \( a \)-TiS\(_3\) electrode particles were prepared by mechanical milling and applied to all-solid-state cells. The electrochemical properties of \( a \)-TiS\(_3\) were compared to those of \( c \)-TiS\(_2\) and \( c \)-TiS\(_3\). The structural changes and electronic structure changes of \( a \)-TiS\(_3\) during cycling were examined. Moreover, \( a \)-TiS\(_3\)/S/carbon composites were prepared by mechanical milling. Further details are described below.

Firstly, \( a \)-TiS\(_3\) was mechanochemically prepared from the mixture of \( c \)-TiS\(_2\) and S, and then characterized. The obtained active materials were applied to all-solid-state cells with the Li\(_2\)S-P\(_2\)S\(_5\) electrolytes. Electrochemical performance of the cells was compared to that of the cell using \( c \)-TiS\(_2\) electrodes. Structural changes of \( a \)-TiS\(_3\) electrode in all-solid-state cells after the initial few cycles were investigated. XRD patterns and Raman spectra of the electrode after cycles were compared with those before cycling. Furthermore, the electrode properties of the equimolar mixture of \( c \)-TiS\(_2\) and sulfur, which were used as the starting materials of \( a \)-TiS\(_3\), were examined and compared to those of \( a \)-TiS\(_3\) electrode.

Secondary, the comparison of electrochemical properties of amorphous and crystalline TiS\(_3\) positive electrodes in all-solid-state lithium batteries was examined. Microstructures and morphologies of \( a \)-TiS\(_3\) and \( c \)-TiS\(_3\) electrodes before and after charge-discharge measurements were investigated by XRD and HR-TEM. In addition, the electronic structure changes of sulfurs in \( a \)-TiS\(_3\) for all-solid-state lithium batteries with sulfide solid electrolytes during cycling were examined by XPS and XANES.

Finally, \( a \)-TiS\(_3\)/S/carbon composites were prepared by mechanical milling for the mixture
of $a$-TiS$_3$ and S/several carbon composites. The electrochemical properties of the coin type cells using organic liquid electrolytes and all-solid-state cells using sulfide solid electrolytes with $a$-TiS$_3$/S/carbon composite electrodes were examined. Four kinds of carbons such as ketjen black (KB), CMK-3, PCNS and graphite were used. Because the cell with the composite with KB showed the best cell performance and thus this paper mainly reports the results of the composite electrodes with KB.

3.2. Experimental

3.2.1.1. Preparation of the amorphous TiS$_3$ electrodes

Amorphous TiS$_3$ ($a$-TiS$_3$) electrode active materials were prepared using the mechanical milling method. Reagent-grade crystalline TiS$_2$ ($c$-TiS$_2$, 99.9%; Kojundo Chemical) and sulfur (99.98%; Aldrich) were used as starting materials. The equimolar mixture of these materials was milled mechanically at ambient temperature using a planetary ball mill apparatus (Pulverisette 7; Fritsch) with zirconia pot (volume of 45 ml) and 500 zirconia balls (4 mm in diameter). The rotational speed was set to 370 rpm. The milling time was 40 hours.

The electrode active materials of $a$-TiS$_3$ were also prepared from crystalline TiS$_3$ ($c$-TiS$_3$) by the mechanical milling method. Titanium metal (99.9%; Kojundo Chemical) and sulfur (99.98%; Aldrich) were used as starting materials to prepare $c$-TiS$_3$. The atomic ratio of Ti to S in the starting mixture was 1/3. Titanium metal and sulfur were mixed and put into a carbon-coated quartz glass ampule and then sealed under vacuum. The glass ampule was heated at 500$^\circ$C for 8 days, and then cooled in a furnace to form $c$-TiS$_3$ [34]. The obtained $c$-TiS$_3$ was mechanically milled at ambient temperature using a planetary ball mill apparatus (Pulverisette 7; Fritsch) with zirconia pot (volume of 45 ml) and 500 zirconia balls (4 mm in diameter). The rotational speed was set to 370 rpm. The milling time was 40 hours to form
3.2.1.2. Preparation of the amorphous TiS₃/S/C electrodes

A 70 wt% sulfur containing composite (S/KB) was prepared by a melt diffusion technique in Ketjen Black (KB) at 155°C [24, 32]. Sulfur and KB were mixed with an agate mortar. Then, the powders were pressed into a pellet by cold press. The pelletized S/KB composite was heated at 155°C for overnight in air. After heating, the composite was crushed with an agate mortar. Composites of S/CMK-3 [24], S/PCNS [32] and S/graphite were prepared in the same manner.

Amorphous TiS₃/S/KB (a-TiS₃/S/KB) electrodes were prepared by mechanical milling. Prepared a-TiS₃ prepared from c-TiS₃ and the S/KB composite were used as the starting materials with the molar ratio of 1/2. The mixture of the materials was milled mechanically at ambient temperature using a planetary ball mill apparatus (Pulverisette 7; Fritsch) with zirconia pot (volume of 45 ml) and 500 zirconia balls (4 mm in diameter). The rotational speed was set to 370 rpm and the milling time was 20 hours.

3.2.2. Cell configurations

3.2.2.1. All-solid-state cells with sulfide solid electrolytes

All-solid-state electrochemical cells were fabricated as follows. The 80Li₂S·20P₂S₅ (mol%) solid electrolyte was prepared by the mechanical milling and then heated at 210°C for 1 hour [35]. The a-TiS₃ prepared by milling and the equimolar mixture of c-TiS₂ and sulfur crystals (before milling) were used as active materials. The a-TiS₃ prepared from c-TiS₃ and c-TiS₃ were also used as active materials. The working electrode was prepared by mixing of the active materials, the 80Li₂S·20P₂S₅ solid electrolyte and acetylene black with the weight
ratio of 40/60/6.

On the other hand, in the case of XPS and XANES measurements, the working electrodes of $a$-TiS$_3$ without conductive additives and solid electrolytes were used.

The $a$-TiS$_3$/S/KB electrodes were used as active materials. The working electrode was prepared by mixing of the active materials and the solid electrolyte. The weight ratios of electrodes were 100/0, 70/30 or 40/60. The S/KB and $a$-TiS$_3$ without sulfide solid electrolyte and acetylene black were also used as working electrodes for comparisons.

The working electrode (10 mg) and the solid electrolyte (80 mg) were placed in polycarbonate tube (10 mm in diameter) and pressed together under 360 MPa. A Li-In alloy was put on the solid electrolyte layer as a counter-reference electrode. A pressure of 120 MPa was then applied to the three-layered pellet. Finally, bulk type all-solid-state cells sandwiched with two stainless-steel disks as a current collector were obtained. All processes described above were conducted in a dry Ar filled glove box.

### 3.2.2.2. Coin-type cells with liquid electrolytes

Coin cells with 2325 type using organic liquid electrolytes were fabricated as follows. The S/KB, $a$-TiS$_3$ or $a$-TiS$_3$/S/KB electrodes onto a carbon-coated aluminum or carbon paper current collector were formed by drop casting from N, N-dimethylformamide, and drying the electrodes at 60°C overnight. The 80 wt% of S/KB composite, 10 wt% Super P and 10 wt% poly(vinylidene fluoride) (PVDF) were mixed with N, N-dimethylformamide. On the other hand, the coin type cells using of $a$-TiS$_3$ and $a$-TiS$_3$/S/KB were used with the different composite ratios. The 70 wt% of $a$-TiS$_3$ or $a$-TiS$_3$/S/KB composite, 20 wt% Super P and 10 wt% PVDF were mixed with N, N-dimethylformamide. The electrolyte was 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixed solvent of 1,2-dimethoxyethane.
(DME) and 1,3-dioxolane (DOL) (v/v = 1:1), with 2 wt% of LiNO₃. Lithium metal foil was used as the negative electrode, and was physically isolated using 2 sheets of Celgard 3501 separators. All the processes described above were conducted in a dry Ar filled glove box.

3.2.3. Characterization

To examine crystal structures of prepared samples, X-ray diffraction experiment was carried out using a X-ray diffractometer (CuKα, UltimaIV; Rigaku Corp.) and a laser Raman spectrometer (He-Ne laser, LabRAM HR-800; Horiba Ltd.). The morphologies of the prepared samples were observed using scanning electron microscope (SEM, JSM-5300; JEOL), a field emission scanning electron microscopy (FE-SEM, SU8220; HITACHI) and a high-resolution transmission electron microscope (HR-TEM, JEM-2100F; JEOL).

Surface areas of KB, S/KB and α-TiS₃/S/KB were determined from nitrogen adsorption and desorption isotherms performed on an instrument (Autosorb-1; Quantachrome) at 77 K. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. Differential thermal analysis (DTA) and thermogravimetric analyses (TGA) of the sample were performed using a thermal analyzer (Thermo Plus TG8110; Rigaku or SDT Q600; TA Instruments) at a heating rate of 10°C min⁻¹.

The electronic structures of α-TiS₃ and c-TiS₃ were characterized by the X-ray photoelectron spectroscopy (XPS, K-Alpha; Thermo Fisher Scientific) with a Monochromatic AlKα source (1486.6 eV). The observed binding energies were calibrated with the adventitious C1s peak to 284.7 eV. The samples were mounted on a sample stage in a dry Ar filled glove box and they were transferred to an analysis chamber using an Ar filled transfer vessel.

The electrochemical tests of all-solid-state cells were conducted at 25°C in Ar filled
atmosphere using a charge-discharge measuring device (BTS-2004; Nagano Co.).

The coin type cells with S/KB with an organic liquid electrolyte were discharged and charged at the 1st cycle in the potential window of 1.9-3.0 V vs. Li at the current density of 0.084 mA cm\(^{-2}\). The potential window of 1.8-3.0 V vs. Li was set at the current density of 0.84 mA cm\(^{-2}\) after the 2nd cycle. The coin type cells with \(a\)-TiS\(_3\) and \(a\)-TiS\(_3\)/S/KB were cycled in the potential window of 1.8-3.0 V vs. Li with the current density of 0.064 mA cm\(^{-2}\). Electrochemical studies were performed using a charge-discharge measuring device (BT-2000; Arbin) in galvanostatic mode at room temperature.

To analyze the structure of the working electrode, XRD, Raman spectroscopy, cross-sectional FE-SEM with an energy dispersive X-ray spectroscopy system (EDX, EMAXEvolution X-Max; Horiba, Ltd.) and HR-TEM observations for the working electrode before and after cycling were done. For Raman spectroscopy, the laser beam was focused on \(a\)-TiS\(_3\) particles at the surface of the working electrode, which was placed in a vessel packed with Ar gas. The cross sections of the working electrodes were prepared by using an ion milling system (IM4000; HITACHI). For HR-TEM observations of the working electrodes using \(a\)-TiS\(_3\) and \(c\)-TiS\(_3\) before and after charge-discharge, the cells were disassembled and then \(a\)-TiS\(_3\) and \(c\)-TiS\(_3\) composite electrodes were scratched in an Ar filled glove box. The obtained powders were placed on a grid for TEM observation without any ion-milling treatments. These powders were packed in a folder to maintain inert atmosphere, and were then transferred to a TEM apparatus.

The electronic structures of \(a\)-TiS\(_3\) electrodes before and after charge-discharge tests were analyzed by XPS and XANES. XANES spectra at S K-edge were measured at BL-13 of the Synchrotron Radiation Center, Ritsumeikan University. The spectra were collected in total electron yield mode, wherein the sample current produced due to excitation of all electrons of
different energies was measured. The sample for S K-edge XANES measurements were mounted on a sample stage in a dry Ar filled glove box and they were transferred to the chamber using an Ar filled transfer vessel. Ti K-edge XANES measurements were also carried out at beamlines BL14B2 at SPring-8, Japan. The electrodes were sealed in laminated packets in an Ar filled glove box. The measurements were performed in a transmission mode.

3.3. Results and discussion

3.3.1. Preparation of amorphous TiS$_3$ particles and their electrochemical performance

Amorphous TiS$_3$ (α-TiS$_3$) electrode particles were prepared by mechanical milling from the equimolar mixture of crystalline TiS$_2$ (c-TiS$_2$) and sulfur. Then, α-TiS$_3$ particles were applied to the all-solid-state cells. Figure 3-1 shows XRD patterns of the prepared samples milled for several periods of time. The diffraction peaks attributable to sulfur disappeared by milling for 1 hour. On the other hand, the intensity of the peaks attributable to c-TiS$_2$ gradually decreased with an increase in the milling time and a halo pattern was almost dominant after milling for more than 20 hours. XRD measurements of the titanium sulfide prepared by milling of equimolar mixture of c-TiS$_2$ and S for 40 hours produced a halo pattern, suggesting that an amorphous material was obtained. However, the possibility remains that the milled material includes nanocrystals that are undetectable using XRD. Therefore, high-resolution transmission electron microscope (HR-TEM) observation was conducted to clarify the microstructures of the milled material. Figure 3-2 shows a HR-TEM image of the titanium sulfide prepared by milling for 40 hours. The inset shows an electron diffraction pattern. The HR-TEM image showed no periodic lattice fringes, indicating that the milled material did not have fine crystals with nanometer size. The diffraction pattern also supports the prepared titanium sulfide is amorphous. It is concluded that amorphous titanium sulfides
Figure 3-1 XRD patterns of the equimolar mixtures of $c$-Ti$_2$S$_2$ and sulfur, which were ball-milled for several periods of time.
Figure 3-2 HR-TEM image of the TiS$_3$ sample prepared using mechanical milling. The inset shows an electron diffraction pattern of the sample.
were synthesized by milling of the equimolar mixture of \( c \)-TiS\(_2\) and S crystal.

The SEM image of the equimolar mixture of \( c \)-TiS\(_2\) and S before milling indicated that the mixture consisted of plate-like \( c \)-TiS\(_2\) particles of \( ca. \) 500 nm in size and sulfur particles of \( ca. \) 50 \( \mu \)m. The SEM image and EDX maps of S and Ti elements for the sample milled for 40 hours are shown in Fig. 3-3. Secondary particles of several microns in size, which were formed by agglomeration of submicron-sized ordinary particles, were mainly observed in the SEM image (a). The EDX map of sulfur element (b) for the SEM image almost overlapped the map of Ti element (c), suggesting that sulfur and \( c \)-TiS\(_2\) particles were not separately present but TiS\(_x\) particles were prepared. The DTA curve of the sample milled for 40 hour exhibited no endothermic peaks attributable to melt of crystalline sulfur, which were observed at around 115\(^\circ\)C in the equimolar mixture of \( c \)-TiS\(_2\) and S before milling (0 hour) as shown in Fig. 3-4. It is noted by XRD, SEM-EDX and DTA that amorphous TiS\(_x\) would be prepared.

**Figure 3-5** shows the Raman spectra of the samples milled for 0 or 40 hours. Two broad bands at 335 cm\(^{-1}\) and 230 cm\(^{-1}\) appeared in the Raman spectrum of the sample before milling (0 hour); the bands were observed for \( c \)-TiS\(_2\), and the band at 230 cm\(^{-1}\) was also observed for crystalline sulfur. After milling for 40 hours, the intensity of the two bands decreased and two new bands at 375 and 303 cm\(^{-1}\), which were observed for crystalline TiS\(_3\) (\( c \)-TiS\(_3\)) [36], appeared. This suggests that \( c \)-TiS\(_2\) and S were reacted to form \( a \)-TiS\(_3\), and thus the prepared sample is called \( a \)-TiS\(_3\) in the following discussion.

The \( a \)-TiS\(_3\) was applied as an active material to all-solid-state lithium cells. **Figure 3-6 (a)** shows the initial charge-discharge curves of the all-solid-state cells at 25\(^\circ\)C. The working electrode was prepared by mixing of \( a \)-TiS\(_3\), the 80Li\(_2\)S-20P\(_2\)S\(_5\) glass-ceramic and acetylene black with the weight ratio of 40/60/6. The active materials of \( c \)-TiS\(_2\), the TiS\(_2\) milled for 40 hours and the equimolar mixture of \( c \)-TiS\(_2\) and S were used for comparisons. **Figure 3-6 (b)**
Figure 3-3  SEM image (a) and EDX maps of S (b) and Ti (c) elements for the equimolar mixture of c-TiS$_2$ and sulfur milled for 40 hours.
Figure 3-4  DTA curves of the equimolar mixtures of $c$-TiS$_2$ and sulfur milled for 0 or 40 hours.
Figure 3-5  Raman spectra of the equimolar mixtures of \( c \)-TiS\(_2\) and sulfur milled for 0 or 40 hours.
Figure 3-6  (a) Initial charge-discharge curves of all-solid-state cells Li-In/80Li$_2$S·20P$_2$S$_5$ glass-ceramic/TiS$_x$ or equimolar mixture of c-TiS$_2$ and S and (b) cycling performances of the cells with a-TiS$_3$ or equimolar mixture of c-TiS$_2$ and S at room temperature.
shows the cycle performances of the cells with $a$-TiS$_3$ or equimolar mixture of $c$-TiS$_2$ and S. A current density was 0.064 mA cm$^{-2}$ and a potential window was 0.9-2.4 V vs. Li-In. The Li-In alloy was used as a counter electrode because Li-In alloy exhibits a stable potential plateau at 0.62 V vs. Li$^+/\text{Li}$ in an all-solid-state cell using a sulfide solid electrolyte. In Fig. 3-6 (a), the right side ordinate axis represents the electrode potential vs. Li$^+/\text{Li}$, as calculated based on the potential difference between the Li-In and Li electrode (0.62 V). All the cells worked as a secondary battery at 25$^\circ$C. The cell with $c$-TiS$_2$ exhibited a reversible capacity of $ca.$ 230 mAh g$^{-1}$, which was close to the theoretical capacity of 240 mAh g$^{-1}$. The particles of $c$-TiS$_2$ were pulverized by milling for 40 hours (not to be amorphous), but the cell with the milled TiS$_2$ exhibited a similar charge-discharge profile to the cell with $c$-TiS$_2$ without milling-treatment. The 1st reversible capacity of the cell with the equimolar mixture of $c$-TiS$_2$ and S was approximately 150 mAh g$^{-1}$. When only $c$-TiS$_2$ in the equimolar mixture of $c$-TiS$_2$ and S acted as active materials, the capacity normalized by the weight of $c$-TiS$_2$ was $ca.$ 210 mAh g$^{-1}$, which was close to the theoretical capacity of $c$-TiS$_2$. This fact suggests that S itself would not function as an active material in the working electrode prepared by simple mixing of $c$-TiS$_2$ and S because S is insulative and is not activated as an electrode material. On the other hand, the $a$-TiS$_3$ prepared by milling showed a higher capacity of about 400 mAh g$^{-1}$ than the other electrodes at the 1st cycle. It is noteworthy that the reaction between $c$-TiS$_2$ and S to form $a$-TiS$_3$ is useful to obtain electrode materials with high capacity. Figure 3-6 (b) shows that the all-solid-state cell with the $a$-TiS$_3$ retained a higher capacity of more than 320 mAh g$^{-1}$ after 10 cycles than the cell with the mixture. The cyclability of the TiS$_3$ electrode mentioned above was compared to that of a cell with an organic liquid electrolyte. The active material of $c$-TiS$_3$ showed the 1st discharge capacity of $ca.$ 350 mAh g$^{-1}$ at 0.003 mA cm$^{-2}$, but its capacity rapidly decreased after several cycles and a limited capacity of $ca.$ 50 mAh g$^{-1}$
was only obtained after 10 cycles [3]. Moreover, the 1st coulombic efficiency of the solid-state cell with the $a$-TiS$_3$ (95.4 %) was higher than that of a liquid-type cell with $c$-TiS$_3$ (71.8%) [3]. Compared to the liquid electrolyte cell, the $a$-TiS$_3$ electrode in the all-solid-state cell with the sulfide solid electrolyte exhibited the higher capacity and better cyclability at 0.064 mA cm$^{-2}$ as mentioned above. The average operating voltages of the two cells were comparable, suggesting that a similar electrochemical reaction basically occurred during charge-discharge processes. The excellent electrochemical performance observed in the solid-state cell would be brought about by the use of inorganic sulfide electrolytes and/or amorphization of TiS$_3$ active material. The comparison of electrochemical performance of $a$-TiS$_3$ and $c$-TiS$_3$ in all-solid-state cells will be discussed later.

**Figure 3-7** shows the XRD patterns of the $a$-TiS$_3$ electrodes before (a) and after the 1st (b) and the 10th (c) charge-discharge measurements. The XRD pattern of a simple mixture of $c$-TiS$_2$ and S is also depicted in **Fig. 3-7 (d)** for comparison. Silicon was used as an internal standard in XRD measurements. The Li$_2$S-P$_2$S$_5$ solid electrolyte used for this study, partially included Li$_2$S crystal and thus the peaks attributable to Li$_2$S were observed slightly in the XRD pattern for the electrode before cycling. A halo pattern was observed mainly because the TiS$_3$ active material was amorphous. The XRD patterns of the electrodes after the 1st (b) and the 10th (c) charge-discharge measurements were similar to the pattern before the measurement (a). Crystalline peaks attributable to TiS$_2$ or S as shown in (d) were not observed during cycling. The XRD measurements revealed that the $a$-TiS$_3$ maintained its amorphous structure for 10 cycles.

**Figure 3-8** shows the Raman spectra of the $a$-TiS$_3$ electrodes before (a) and after the 1st (b) and the 10th (c) charge-discharge measurements. The electrode before the charge-discharge measurement showed Raman bands at 303, 335, and 375 cm$^{-1}$, which were
Figure 3-7 XRD patterns of the $a$-TiS$_3$ electrode before (a) and after the 1st (b) and the 10th (c) charge-discharge measurements. The XRD pattern of a simple mixture of $c$-TiS$_2$ and S is also depicted in Fig. 3-7 (d) for comparison.
Figure 3-8 Raman spectra of the $\alpha$-TiS$_3$ electrodes before (a) and after the 1st (b) and the 10th (c) charge-discharge measurements.
observed in the \( \alpha \)-TiS\(_3\) (Fig. 3-5). The Raman spectra of the electrodes after the 1st and 10th cycles resembled the spectrum before the measurement. These results suggest that the structure of \( \alpha \)-TiS\(_3\) electrode did not change greatly during the 1st charge-discharge process. The all-solid-state cells with the \( \alpha \)-TiS\(_3\) electrode showed higher 1st coulombic efficiency because the \( \alpha \)-TiS\(_3\) active material retained its structure during the 1st electrochemical tests.

3.3.2. Comparison of electrochemical properties between amorphous and crystalline TiS\(_3\) electrode active materials

The comparison of electrochemical properties of amorphous and crystalline TiS\(_3\) positive electrodes in all-solid-state lithium batteries was examined. Microstructures and morphologies of \( \alpha \)-TiS\(_3\) and \( c \)-TiS\(_3\) electrodes before and after charge-discharge measurements were investigated by XRD and HR-TEM. Figure 3-9 shows the XRD patterns of the \( c \)-TiS\(_3\) prepared by the solid-phase method and \( \alpha \)-TiS\(_3\) prepared by ball-milling from \( c \)-TiS\(_3\). The peaks attributable to \( c \)-TiS\(_3\) (JCPDS: 080-0924) were observed before ball-milling. On the other hand, the intensity of the peaks attributable to \( c \)-TiS\(_3\) were not observed after milling for 40 hours. A halo pattern was obtained. These results suggested that \( \alpha \)-TiS\(_3\) was prepared by mechanical milling from \( c \)-TiS\(_3\). HR-TEM observation was conducted to clarify microstructures of the \( c \)-TiS\(_3\) and \( \alpha \)-TiS\(_3\). HR-TEM images of \( c \)-TiS\(_3\) (a) and \( \alpha \)-TiS\(_3\) (b) are shown in Fig. 3-10. The electron diffraction patterns obtained from HR-TEM images are also shown in the inset of Fig. 3-10. The TEM image of the sample prepared by the solid-phase method showed periodic lattice fringes attributable to \( c \)-TiS\(_3\). The electron diffraction pattern showed the strong spots identified to \( c \)-TiS\(_3\). However, the periodic lattice fringes were not observed in HR-TEM image of the milled material. It suggested that the milled material did not have fine crystals with nanometer size. The diffraction pattern also supports the prepared
Figure 3-9 XRD patterns of $c$-TiS$_3$ (MM 0 hour) and $a$-TiS$_3$ (MM 40 hours).
Figure 3-10  HR-TEM images and electron diffraction patterns of c-TiS$_3$ (a) and a-TiS$_3$ (b).
titanium sulfide is amorphous. It is concluded that \( a\)-TiS\(_3\) was synthesized by milling of \( c\)-TiS\(_3\). Figure 3-11 shows the SEM images of \( c\)-TiS\(_3\) (a) and \( a\)-TiS\(_3\) (b). Before milling, \( c\)-TiS\(_3\) consisted of needle-like TiS\(_3\) particles of about 2 \( \mu \)m in size. This particle shape was similar to that reported in the literature [1]. After milling for 40 hours, secondary particles of several \( \mu \)m in size, which were formed by agglomeration of submicron-sized particles, were obtained in the milled sample.

Figure 3-12 shows the \( S_{2p} \) XPS spectra of \( c\)-TiS\(_3\) and \( a\)-TiS\(_3\) prepared. The \( S_{2p} \) spectrum of \( c\)-TiS\(_3\) was composed of two sets of doublet peaks (\( S_{2p3/2} \) and \( S_{2p1/2} \)). The peak energy separation (1.2 eV) in each doublet was set during peak fitting. The \( S_{2p} \) spectrum of \( c\)-TiS\(_3\) showed two \( S_{2p3/2} \) peaks at 161.7 eV and 162.9 eV, respectively. The peak at 161.7 eV was characteristic of \( S^{2-} \) and the peak at 162.9 eV was characteristic of \( S_2^{2-} \) [34]. The \( S_{2p} \) spectrum of \( a\)-TiS\(_3\) consisted of two \( S_{2p3/2} \) peaks at 161.3 eV and 162.5 eV, respectively. The two \( S_{2p3/2} \) peak positions of \( a\)-TiS\(_3\) were similar to those of \( c\)-TiS\(_3\), suggesting that \( a\)-TiS\(_3\) consisted of \( S^{2-} \) and \( S_2^{2-} \) species. The fitted peak ratios of \( S^{2-}/S_2^{2-} \) in \( c\)-TiS\(_3\) and \( a\)-TiS\(_3\) were 1/1.7 and 1/1.8, respectively. Therefore, the electronic structure of sulfur in \( a\)-TiS\(_3\) prepared by mechanical milling from \( c\)-TiS\(_3\) was almost the same as that in \( c\)-TiS\(_3\).

Figure 3-13 shows the charge-discharge curves of all-solid-state cells Li-In/80Li\(_2\)S·20P\(_2\)S\(_5\) glass-ceramic/\( c\)-TiS\(_3\) (a) or \( a\)-TiS\(_3\) (b) at the potential window of 0.6-2.4 V vs. Li-In. The 1st, 2nd, 3rd, 5th and 10th charge-discharge curves are shown in Fig. 3-13. The working electrode was prepared by mixing of \( c\)-TiS\(_3\) or \( a\)-TiS\(_3\), the 80Li\(_2\)S·20P\(_2\)S\(_5\) glass-ceramic and acetylene black with the weight ratio of 40/60/6. Charge-discharge measurements of the cells were conducted at the current density of 0.064 mA cm\(^{-2}\) (C/40) at 25°C. The 1st discharge capacity of the cell with \( c\)-TiS\(_3\) was about 556 mAh g\(^{-1}\), which was the same as the theoretical capacity of \( c\)-TiS\(_3\) (556 mAh g\(^{-1}\); the capacity corresponding to the
Figure 3-11 SEM images of $c$-Ti$_3$S$_3$ (a) and $a$-Ti$_3$S$_3$ (b).
Figure 3-12  $S_{2p}$ XPS spectra of $c$-TiS$_3$ and $a$-TiS$_3$. 
Figure 3-13  Charge-discharge curves of the all-solid-state cells with $c$-TiS$_3$ (a) and $a$-TiS$_3$ (b).
insertion of 3 mol Li to TiS\textsubscript{3}). However, the irreversible capacity was observed at the 1st charge process. The possible reason of the irreversible capacity observed is the structural deterioration of $c$-TiS\textsubscript{3} reported in the literature [3]. The structural changes of $c$-TiS\textsubscript{3} after cycle tests were analyzed and will be discussed later. The operating potential of the cell using $c$-TiS\textsubscript{3} gradually increased from the 2nd to 10th cycle, although the charge-discharge profiles were almost the same during cycles. On the other hand, $a$-TiS\textsubscript{3} showed the reversible capacity of about 556 mAh g\textsuperscript{-1} for the 1st charge-discharge process. In addition, the cell exhibited similar charge-discharge curves from the 2nd to 10th cycle. The cycle performance of the cells with $c$-TiS\textsubscript{3} and $a$-TiS\textsubscript{3} are shown in Fig. 3-14. The cell using $c$-TiS\textsubscript{3} showed the reversible capacity of about 400 mAh g\textsuperscript{-1} for 10 cycles at the current density of 0.064 mA cm\textsuperscript{-2}. The reversible capacity decreased with increasing the current density. The reversible capacity of the cell with $c$-TiS\textsubscript{3} exhibited about 320 mAh g\textsuperscript{-1} at the current density of 0.13 mA cm\textsuperscript{-2}. On the other hand, the cell with $a$-TiS\textsubscript{3} showed the higher reversible capacity than the cell with $c$-TiS\textsubscript{3}. The reversible capacity of the cell using $a$-TiS\textsubscript{3} was about 550 mAh g\textsuperscript{-1} for 10 cycles at the current density of 0.064 mA cm\textsuperscript{-2} and 500 mAh g\textsuperscript{-1} at the current density of 0.13 mA cm\textsuperscript{-2}. This suggests that $a$-TiS\textsubscript{3} electrode active materials retained higher reversible capacities than $c$-TiS\textsubscript{3}.

The XRD patterns for working electrodes of $c$-TiS\textsubscript{3} before and after the 10th charge test are shown in Fig. 3-15 (a). Silicon was used as an internal standard in XRD measurements. The Li\textsubscript{2}S-PbS\textsubscript{5} solid electrolyte used in this study partially included Li\textsubscript{2}S crystal and thus the peaks attributable to Li\textsubscript{2}S were observed slightly in the XRD pattern for the electrode after the 10th charge. The XRD peaks attributable to $c$-TiS\textsubscript{3} were not observed and Li\textsubscript{3}TiS\textsubscript{3} peaks were observed after the 10th charge process. The reason of the disappearance of $c$-TiS\textsubscript{3} peaks in XRD would be amorphization of $c$-TiS\textsubscript{3} during cycles. HR-TEM observation was conducted.
Figure 3-14  Cycle performance of the all-solid-state cells with $c$-TiS$_3$ and $a$-TiS$_3$. 
Figure 3-15  XRD patterns of $c$-TiS$_3$ electrodes before and after the 10th charge (a) and HR-TEM image of $c$-TiS$_3$ electrode after the 10th charge (b).
to clarify the microstructures of $c$-TiS$_3$ electrode after the 10th charge. **Figure 3-15 (b)** shows the HR-TEM image of $c$-TiS$_3$ electrode active material after the 10th charge. The HR-TEM image partially showed amorphous areas (yellow dot ring).

The XRD patterns of $a$-TiS$_3$ electrodes before (a), after the 1st discharge (b), after the 1st charge (c) and after the 10th charge (d) are shown in **Fig. 3-16**. Silicon was used as an internal standard in XRD measurements. The Li$_2$S in the Li$_2$S-P$_2$S$_5$ solid electrolyte was observed in the XRD patterns for the electrodes. A halo pattern was mainly observed and new crystalline peaks were not observed during 10 cycles. The XRD pattern of the working electrode after the 10th charge measurement was similar to that before the measurement. The XRD measurements revealed that $a$-TiS$_3$ maintained its amorphous structure for 10 cycles.

HR-TEM observations were carried out to clarify microstructures of the working electrodes. **Figure 3-17** shows the HR-TEM images of $a$-TiS$_3$ electrodes after the 1st discharge (a), after the 1st charge (b) and after the 10th charge (c). The electron diffraction patterns obtained from HR-TEM images are respectively shown in the inset of the HR-TEM images. The HR-TEM images after charge-discharge tests showed no periodic lattice fringes, indicating that the $a$-TiS$_3$ electrode for 10 cycles did not have fine crystals with nanometer in size. All the diffraction patterns were halo pattern. Therefore, the most part of $a$-TiS$_3$ electrode after charge-discharge measurements maintained the amorphous structure. Based on the results of the structural analyses, the structure did not change greatly during charge-discharge cycles.

Finally, the relationship of the capacity and structural changes of $c$-TiS$_3$ and $a$-TiS$_3$ are discussed. In the case of $c$-TiS$_3$, the XRD peaks of $c$-TiS$_3$ were not observed after the 10th charge, because amorphization occurred during charge-discharge process. The diffraction peaks due to Li$_2$TiS$_3$, which is formed after the discharge process (lithiation process), were
Figure 3-16 XRD patterns of $a$-TiS$_3$ electrodes before (a), after the 1st discharge (b), after the 1st charge (c) and after the 10th charge (d).
Figure 3-17  HR-TEM images of $a$-TiS$_3$ electrodes after the 1st discharge (a), after the 1st charge (b) and after the 10th charge (c).
still observed after the 10th charge process (delithiation process). From the HR-TEM observation, the amorphous areas in the $c$-$\text{TiS}_3$ were formed. These irreversible structural changes of $c$-$\text{TiS}_3$ during charge-discharge tests might be responsible for the irreversible capacity at the 1st cycle. On the other hand, partial amorphization of $c$-$\text{TiS}_3$ would contribute to good cyclability from the 2nd to 10th cycle.

The cells with $a$-$\text{TiS}_3$ showed the higher reversible capacity and better cyclability, compared to the cells with $c$-$\text{TiS}_3$. The reversible structural changes of $a$-$\text{TiS}_3$ during charge-discharge cycles were observed in XRD and HR-TEM. Therefore, $a$-$\text{TiS}_3$ electrode active materials are more attractive electrodes than $c$-$\text{TiS}_3$. Amorphization of $\text{TiS}_3$ electrodes is effective in developing all-solid-state lithium batteries with higher reversible capacity and better cyclability.

### 3.3.3. Investigation of the electrochemical reaction mechanism of amorphous $\text{TiS}_3$ electrodes

In order to understand the reaction mechanisms of $a$-$\text{TiS}_3$ electrodes in all-solid-state cells, the electronic structure changes of $a$-$\text{TiS}_3$ during cycling tests were examined by XPS and XANES. **Figure 3-18 (a)** shows the 1st and 10th charge-discharge curves of all-solid-state cell with $a$-$\text{TiS}_3$ and **(b)** shows the $S_{2p}$ XPS spectra of $a$-$\text{TiS}_3$ before charge-discharge, after the 1st discharge, after the 1st charge and after the 10th charge. The working electrode of $a$-$\text{TiS}_3$ without conductive additives and solid electrolytes was used. Charge-discharge measurements of the cell with $a$-$\text{TiS}_3$ were conducted at the current density of 0.013 mA cm$^{-2}$ (1 mA g$^{-1}$) at 25°C. The cell using $a$-$\text{TiS}_3$ showed the reversible capacity of about 510 mAh g$^{-1}$ for 10 cycles. This capacity corresponded to the storage of about 3 molar Li to $a$-$\text{TiS}_3$. The cells shown in **Fig. 3-13 (b)** and **Fig. 3-18 (a)** gave similar charge-discharge curves. Therefore,
Figure 3-18 (a) The 1st and 10th charge-discharge curves of the all-solid-state cell with $a$-TiS$_3$. (b) S$_{2p}$ XPS spectra of $a$-TiS$_3$ before charge-discharge, after the 1st discharge, after the 1st charge, and after the 10th charge.
the all-solid-state cells using $a$-TiS$_3$ working electrodes without the addition of solid electrolytes successfully operated as a secondary battery.

As shown in Fig. 3-12, $a$-TiS$_3$ consisted of $S^{2-}$ and $S_2^{2-}$ species. The S$_{2p}$ XPS spectrum of $a$-TiS$_3$ after the 1st discharge was shifted to the lower binding energy side. This is because Li$^+$ ions reacted with sulfurs in $a$-TiS$_3$ electrode active materials during discharge process. The spectrum was composed of two sets of doublet peaks. Two S$_{2p3/2}$ peaks at 160.0 and 161.2 eV would be respectively attributable to $S^{2-}$ and $S_2^{2-}$ components interacted with both lithium and titanium. After the 1st and 10th charge, the S$_{2p3/2}$ peak positions of $S^{2-}$ and $S_2^{2-}$ were almost the same as those before charge-discharge tests. The additional doublet peak (purple dot line) was observed slightly after the 1st and 10th charge and it would be attributable to bridging sulfurs. It is revealed that the $a$-TiS$_3$ after the 10th charge mainly consisted of $S^{2-}$ and $S_2^{2-}$ species.

S K-edge XANES spectra of $a$-TiS$_3$ before charge-discharge, after the 1st discharge processes to 1 and 2 mol Li$^+$ storage, after the 1st full discharge (3 mol Li$^+$ storage), after the 1st charge and after the 10th charge are shown in Fig. 3-19. The peak intensity of the spectra at about 2471 eV decreased during the 1st discharge process to 2 mol Li$^+$ storage. The peak position at about 2471 eV was similar to that of $S_2^{2-}$ in c-TiS$_3$ [34], suggesting that the fraction of $S_2^{2-}$ in $a$-TiS$_3$ decreased. On the other hand, after the 1st full discharge (3 mol Li$^+$ storage), the spectrum profile changed significantly. Moreover, the new broad peak at about 2478 eV was observed after the 1st full discharge. This peak might be derived from sulfurs interacted with both lithium and titanium, but the detailed assignment has not been clarified yet. After the 1st and 10th charge, the profiles of the spectra were similar to that before measurements, although the peak intensity at 2471 eV became smaller. The reversible electronic structure changes of sulfur were mainly observed during charge-discharge process.
Figure 3-19  S K-edge XANES spectra of α-TiS₃ before charge-discharge, after the 1st discharge process to 1 and 2 mol Li⁺ storage, after the 1st full discharge (3 mol Li⁺ storage), after the 1st charge and after the 10th charge.
**Figure 3-20 (a)** shows Ti K-edge XANES spectra of \( a\text{-TiS}_3 \) before cycles, after the 1st discharge and after the 1st charge, and (b) shows the magnification of the XANES spectra. In addition, the spectrum of Ti metal as a reference is also shown for comparison in **Fig. 3-20**. The profiles of the spectra for \( a\text{-TiS}_3 \) after the 1st discharge and charge were similar to that of \( a\text{-TiS}_3 \) before charge-discharge. Moreover, a pre-edge peak was hardly observed in the spectra of \( a\text{-TiS}_3 \) before and after tests, while the spectrum of Ti metal exhibited a sharp pre-edge peak at 4964.5 eV. It is suggested that Ti metal was not observed and the electronic structure of titanium did not change during charge-discharge. The charge-discharge curves (**Fig. 3-18 (a)**) showed 3 mol Li\(^+\) ions reversibly reacted with \( a\text{-TiS}_3 \) for 10 cycles. S\( _{2p} \) XPS spectra (**Fig. 3-18 (b)**) and S K-edge XANES spectra (**Fig. 3-19**) indicated that sulfur electronic structures in \( a\text{-TiS}_3 \) exhibited almost reversible changes during charge-discharge tests. Based on the structure analyses of \( a\text{-TiS}_3 \) during charge-discharge process, its reaction mechanism is proposed as follows:

\[
\text{discharge} \quad a\text{-TiS}_3 + 3\text{Li}^+ + 3\text{e}^- \quad \leftrightarrow \quad \text{charge} \quad a\text{-Li}_3\text{TiS}_3 \quad (1)
\]

Because the discharge plateau potential for the first 2 mol Li\(^+\) storage was close to the reaction potential of elemental sulfur with Li\(^+\), S\(^{2-}\) in \( a\text{-TiS}_3 \) reacted with 2 mol Li\(^+\). This agrees with the spectral changes in S K-edge XANES. Then, the other 1 mol Li\(^+\) reacted with S\(^{2-}\) to form Li\(_3\)TiS\(_3\) after the full discharge. Because the lattice fringes were not observed in HR-TEM image after the 1st full discharge (**Fig. 3-17 (b)**), Li\(_3\)TiS\(_3\) was in amorphous state. Almost 3 mol Li\(^+\) ions were extracted from \( a\text{-Li}_3\text{TiS}_3 \) and \( a\text{-TiS}_3 \) was formed again after the charge process. The similar reversible reaction occurred from the 2nd to 10th cycles.
Figure 3-20 (a) Ti K-edge XANES spectra of α-TiS₃ before, after the 1st discharge and after the 1st charge, and (b) the magnification of the XANES spectra. The spectrum of Ti metal as reference is also shown for comparison.
3.3.4. Preparation of amorphous Ti$_x$S$_3$/S/C electrode active materials

Further increasing the capacity of $a$-TiS$_3$, the electrode active materials such as amorphous Ti$_x$S$_3$ ($x>3$) ($a$-TiS$_x$) are promising. However, the electronic conductivity of $a$-TiS$_x$ would decrease with increasing of sulfur content. Therefore, the purpose of this section is that $a$-TiS$_x$ electrodes with high capacity and good cyclability were prepared by combining $a$-TiS$_3$ and sulfur/carbon composites. Figure 3-21 (a) shows the XRD patterns of S/KB samples before and after heating and $a$-TiS$_3$/S/KB prepared by mechanical milling. The peaks attributable to sulfur were observed for the S/KB sample before heating. The intensity of sulfur peaks decreased after heating. This result suggests that the elemental sulfur was incorporated into pores in KB [24]. Figure 3-21 (b) shows the thermogravimetric analysis (TGA) curve of S/KB sample after heating. The weight of S/KB sample decreased drastically at the temperature range from 200 to 300$^\circ$C. A weight loss was attributable to the evaporation of the sulfur in KB’s pore, indicating that S/KB sample after heating included 70 wt% sulfur. A halo pattern was observed in the XRD of TiS$_3$/S/KB and thus TiS$_3$/S/KB was amorphous. In addition, the specific surface areas of the prepared samples were examined by the BET measurements. The results are listed in Table 3-1. The specific surface area of KB was 1117 m$^2$ g$^{-1}$. The specific surface area of S/KB reduced to 21.6 m$^2$ g$^{-1}$ by the occupation of sulfur inside porous KB. The specific surface area of $a$-TiS$_3$/S/KB was 4.6 m$^2$ g$^{-1}$. FE-SEM images of S/KB sample after heating (a) and $a$-TiS$_3$/S/KB (b) are shown in Fig. 3-22. FE-SEM image of S/KB sample indicated that the particle sizes were about 100 nm. Secondary particles of several microns in size, which were formed by agglomeration of submicron-sized ordinary particles, were mainly observed in the FE-SEM image of $a$-TiS$_3$/S/KB composite (Fig. 3-22 (b)). The agglomeration decreased the specific surface area of $a$-TiS$_3$/S/KB.

Figure 3-23 shows (a) the initial charge-discharge curves and (b) the cycle performance
Figure 3-21  (a) XRD patterns of S/KB samples before and after heating and of $a$-TiS$_3$/S/KB prepared by mechanical milling and (b) TGA curve of S/KB sample after heating.
Table 3-1  Specific surface area of KB, S/KB and $a$-Ti$_3$/S/KB

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
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<tbody>
<tr>
<td>KB</td>
<td>1117</td>
</tr>
<tr>
<td>S/KB</td>
<td>21.6</td>
</tr>
<tr>
<td>$a$-Ti$_3$/S/KB</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Figure 3-22 FE-SEM images of S/KB sample (a) and $\alpha$-TiS$_3$/S/KB composite (b).
of the coin type liquid cells with S/KB, $a$-TiS$_3$ and $a$-TiS$_3$/S/KB. The cell with S/KB operated at the current density of 0.084 mA cm$^{-2}$ (at the 1st cycle) and 0.84 mA cm$^{-2}$ (from the 2nd to 100th cycle). The charge-discharge measurements of the cells with $a$-TiS$_3$ and $a$-TiS$_3$/S/KB were conducted at the current density of 0.064 mA cm$^{-2}$ at 25°C. The coin type cell using S/KB showed the reversible capacities of about 1200 mAh g$^{-1}$ and 800 mAh g$^{-1}$ at the 1st and the 100th cycle. This electrochemical performance of the cell with S/KB is similar to that of the previous reports [31]. On the other hand, the 1st reversible capacities of the cells using $a$-TiS$_3$ and $a$-TiS$_3$/S/KB were about 400 and 500 mAh g$^{-1}$, respectively. The cell with $a$-TiS$_3$/S/KB showed higher reversible capacity than the cell with $a$-TiS$_3$, because the additional sulfur in S/KB reacted with Li$^+$ ions during charge-discharge process. The cycle performance of the liquid cells with $a$-TiS$_3$ and $a$-TiS$_3$/S/KB deteriorated during the electrochemical tests. It is suggested that the polysulfides produced during discharge process were dissolved in liquid electrolytes. Sakuda et al. have reported that the coin cell using liquid electrolytes and amorphous TiS$_4$ ($a$-TiS$_4$)/AB composite showed the stable cyclability [20]. They mentioned the chemical bonding between Ti and S formed by amorphization suppressed the dissolution of polysulfide into the electrolyte and the dispersion of AB inside $a$-TiS$_4$ particles were effective in improving the cycle performance of the cell [20]. In this study, the dispersion of KB inside TiS$_3$ might be insufficient and thus the liquid cell with $a$-TiS$_3$/S/KB showed unstable cycle performance. Similarly, we prepared the S/carbon composites using the other carbon materials such as CMK-3 [24], PCNS [32] and graphite. The charge-discharge curves and cycle performance of the coin type liquid cells with $a$-TiS$_3$/S/CMK-3, $a$-TiS$_3$/S/PCNS and $a$-TiS$_3$/S/graphite are shown in Fig. 3-24 (a-d). In addition, the results of the cell with $a$-TiS$_3$/S/KB are also shown for comparison in Fig. 3-24 (e-f). The 1st and the 50th charge and discharge capacities of those cells are also summarized in Table 3-2. The
Figure 3-23  (a) Initial charge-discharge curves of the coin type liquid cells with $\alpha$-Ti$_3$S$_3$, S/KB and $\alpha$-Ti$_3$S$_3$/S/KB and (b) cycle performance of their cells.
Figure 3-24 Charge-discharge curves of the coin type liquid cells with \( a \)-\( \text{TiS}_3 / S / \text{CMK-3} \) (a), \( a \)-\( \text{TiS}_3 / S / \text{PCNS} \) (b) and \( a \)-\( \text{TiS}_3 / S / \text{graphite} \) (c) and (d) cycle performance of the cell with \( a \)-\( \text{TiS}_3 / S / \text{graphite} \). The charge-discharge curves (e) and cycle performance (f) of the cell using \( a \)-\( \text{TiS}_3 / S / \text{KB} \) are also shown for comparison.
Table 3-2 1st and the 50th charge and discharge capacities of the coin type liquid cells with \(a\)-TiS\(_3\)/S/KB, \(a\)-TiS\(_3\)/S/CMK-3, \(a\)-TiS\(_3\)/S/PCNS and \(a\)-TiS\(_3\)/S/graphite composite electrodes

<table>
<thead>
<tr>
<th></th>
<th>1st discharge</th>
<th>1st charge</th>
<th>50th discharge</th>
<th>50th charge</th>
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</thead>
<tbody>
<tr>
<td>(a)-TiS(_3)/S/KB</td>
<td>673</td>
<td>484</td>
<td>52</td>
<td>33</td>
</tr>
<tr>
<td>(a)-TiS(_3)/S/CMK-3</td>
<td>780</td>
<td>666</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(a)-TiS(_3)/S/PCNS</td>
<td>774</td>
<td>498</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(a)-TiS(_3)/S/graphite</td>
<td>642</td>
<td>400</td>
<td>260</td>
<td>250</td>
</tr>
</tbody>
</table>
capacity degradation of the cell $a$-TiS$_3$/S/graphite was also observed. The cells using $a$-TiS$_3$/CMK-3/S and $a$-TiS$_3$/PCNS/S showed the shuttle phenomenon [37] at the 2nd charging process. On the other hand, the cells using the S/CMK-3, S/PCNS and S/graphite respectively showed the 1st reversible capacity of about 1250, 900 and 800 mAh g$^{-1}$ in a potential window of 1.9-3.0 V vs. Li at the current density of 0.084 mA cm$^{-2}$. The 2nd reversible capacities of the cells with S/CMK-3, S/PCNS and S/graphite in the potential window of 1.8-3.0 V vs. Li at the current density of 0.84 mA cm$^{-2}$ were about 780, 650 and 470 mAh g$^{-1}$, respectively. The reversible capacities of the cells using S/CMK-3, S/PCNS and S/graphite after the 50th cycle were about 770, 500 and 380 mAh g$^{-1}$, respectively and the S/carbon samples (carbon: KB, CMK-3, PCNS and graphite) in the cells with liquid electrolytes showed the stable cycle performances in this study. Therefore, the degradation of the cells with liquid electrolytes and $a$-TiS$_3$/S/carbon composites would be due to the dissolution of polysulfides derived from $a$-TiS$_3$.

It is expected that $a$-TiS$_3$/S/carbon composites in all-solid-state cells with sulfide solid electrolytes will have good cyclability because the dissolution of polysulfides is suppressed by using solid electrolytes. **Figure 3-25** shows the initial charge-discharge curves of the all-solid-state cells with $a$-TiS$_3$/S/KB, $a$-TiS$_3$/S/CMK-3, $a$-TiS$_3$/S/PCNS and $a$-TiS$_3$/S/graphite. The working electrodes of their composites without conductive additives and solid electrolytes were used. The charge-discharge measurements of the cells were conducted at the current density of 0.064 mA cm$^{-2}$ at 25°C. The $a$-TiS$_3$/S/carbon composites were used as a working electrode. The all-solid-state cells operated as secondary batteries at room temperature. Specifically, the all-solid-state cell with $a$-TiS$_3$/S/KB showed the highest reversible capacity of about 650 mAh g$^{-1}$ in the cells. The performance of the cell with $a$-TiS$_3$/S/KB was compared with that of the cell with S/KB or $a$-TiS$_3$. **Figure 3-26** shows the
Figure 3-25  Initial charge-discharge curves of the all-solid-state cells with a-TiS$_3$/S/KB, a-TiS$_3$/S/CMK-3, a-TiS$_3$/S/PCNS and a-TiS$_3$/S/graphite.
initial charge-discharge curves (a) and cycle performance (b) of the all-solid-state cells with $a$-TiS$_3$/S/KB, S/KB, $a$-TiS$_3$ and $a$-TiS$_5$ electrodes. Amorphous TiS$_5$ ($a$-TiS$_5$) was prepared by mechanical milling from $a$-TiS$_3$ and S. The cells with S/KB showed the 1st discharge capacity of about 150 mAh g$^{-1}$ and the obtained capacity in this study was lower than that of our previous results [38], because the Li$^+$ ion conduction paths were insufficient; the cell with S/KB needs the addition of sulfide solid electrolytes in the working electrode. The cell using S/KB did not have a capacity at the 1st charge. On the other hand, $a$-TiS$_3$ showed the reversible capacity in the all-solid-state cell using $a$-TiS$_3$ electrode without solid electrolyte and conductive additive powders. The reversible capacity of the cell with $a$-TiS$_3$ was about 500 mAh g$^{-1}$. The solid-state cell with $a$-TiS$_5$ exhibited about 490 mAh g$^{-1}$ at the 1st discharge, but the cell was not charged. A lower electronic conductivity of $a$-TiS$_5$ (about $10^{-6}$ S cm$^{-1}$ at 25$^\circ$C) than that of $a$-TiS$_3$ (over $10^{-3}$ S cm$^{-1}$ at 25$^\circ$C) is one reason for the irreversibility. The cell with $a$-TiS$_3$/S/KB exhibited the highest 1st capacity of about 650 mAh g$^{-1}$. The electronic conductivity of $a$-TiS$_3$/S/KB prepared from $a$-TiS$_3$ and S/KB was about $10^{-3}$ S cm$^{-1}$, which is similar to the conductivity of $a$-TiS$_3$. Both all-solid-state cells with $a$-TiS$_3$ and $a$-TiS$_3$/S/KB showed a better cyclability than the coin type liquid cells. Especially, the cell using $a$-TiS$_3$ showed the reversible capacity of about 450 mAh g$^{-1}$ at the 50th cycle without capacity fading. However, the capacity degradation of the cell with $a$-TiS$_3$/S/KB was observed, and the 50th reversible capacity was about 250 mAh g$^{-1}$. This reason will be mentioned later.

In order to improve the cycle performance of the cell with $a$-TiS$_3$/S/KB, the working electrodes were prepared with sulfide solid electrolyte powders as lithium-ion conduction paths to active materials. The working electrodes were prepared by hand-mixing of $a$-TiS$_3$/S/KB and the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic solid electrolyte (SE). The weight ratios of electrodes were 100/0, 70/30 or 40/60. Figure 3-27 shows (a) the initial charge-discharge
Figure 3-26 (a) Initial charge-discharge curves and (b) cycle performance of the all-solid-state cells with $a$-TiS$_3$/S/KB, S/KB, $a$-TiS$_3$, and $a$-TiS$_5$. 
curves and (b) the cycle performance of the all-solid-state cells with \(a\)-TiS\(_3\)/S/KB composites. The cell using the \(a\)-TiS\(_3\)/S/KB composites with the addition of 30 wt% SE exhibited the highest reversible capacity of about 850 mAh g\(^{-1}\) at the 1st cycle. It is suggested that forming favorable contacts among electrode components of \(a\)-TiS\(_3\)/S/KB and sulfide solid electrolytes would be effective in improving the reversible capacity of all-solid-state cells. However, the 1st reversible capacity of the cell with \(a\)-TiS\(_3\)/S/KB composite with 60 wt% SE decreased to 650 mAh g\(^{-1}\). This reason might be less electron conduction paths among the electrode active materials by adding the large amount of sulfide solid electrolytes. After the 50th cycle, the all-solid-state cells using the electrodes with 0, 30, and 60 wt% SE showed the capacity of about 250, 650 and 370 mAh g\(^{-1}\), respectively. Although the capacity degradation was observed in all the cells, the cell using \(a\)-TiS\(_3\)/S/KB composite with 30 wt% SE retained higher reversible capacity than the cell using \(a\)-TiS\(_3\) after the 50 cycles.

Figure 3-28 shows XRD pattern of the \(a\)-TiS\(_3\)/S/KB working electrodes without electrolytes before cycling and after the 50th charge-discharge measurements. The peaks of silicon as an internal standard were observed in all XRD patterns. A halo pattern due to the \(a\)-TiS\(_3\)/S/KB active material was mainly observed even after the 50th charge process. This result implied that the amorphous state of the \(a\)-TiS\(_3\)/S/KB active materials was maintained during the electrochemical tests.

Figure 3-29 shows the cross-sectional FE-SEM images and their EDX elemental mapping images for S, Ti and C of the \(a\)-TiS\(_3\)/S/KB working electrodes without electrolytes (a) before cycling and (b) after the 50th charge-discharge measurements. Pores and grain boundaries were observed in the FE-SEM image (a) for the working electrode before cycles. On the other hand, the working electrode after the 50th cycle (b) was denser than that before measurements. This is because the volumetric changes of the sulfur in \(a\)-TiS\(_3\)/S/KB composite occurred by
**Figure 3-27** (a) Initial charge-discharge curves and (b) cycle performance of the all-solid-state cells using α-TiS<sub>3</sub>/S/KB composites with 0, 30 and 60 wt% SE.
Figure 3-28  XRD patterns of the $a$-TiS$_3$/S/KB working electrodes without electrolytes before cycling and after the 50th charge-discharge measurements.
Figure 3-29  Cross-sectional FE-SEM images and EDX elemental mapping images for S, Ti and C of the $a$-TiS$_3$/S/KB working electrodes without electrolytes before cycling (a) and after the 50th charge-discharge measurements (b).
charge-discharge process. He et al. have reported that the thickness of sulfur composite electrode expanded during discharging (lithiation process) [39]. The EDX mappings of all elemental signals of S, Ti and C were observed in entire area of the electrode before and after charge-discharge, suggesting that $a$-TiS$_3$/S/KB was homogeneously dispersed during cycles. In order to understand the capacity degradation of the all-solid-state cell using $a$-TiS$_3$/S/KB, the change of the electronic structures of titanium and sulfur during charge-discharge tests is needed to investigate, and XAFS and XPS analyses for $a$-TiS$_3$/S/KB electrodes will be done in the near future.

3.4. Summary

In this chapter, amorphous TiS$_3$ ($a$-TiS$_3$) electrode particles for all-solid-sate lithium batteries were prepared by mechanical milling and their electrochemical reaction mechanism was investigated by XRD, Raman, TEM, XPS and XANES. Further increasing the capacity of $a$-TiS$_3$, $a$-TiS$_3$/S/carbon electrodes were also prepared by combining $a$-TiS$_3$ and sulfur/carbon composites. The summary of each section is shown as follows.

1. Preparation of $a$-TiS$_3$ particles and their electrochemical performance

The electrode particles of $a$-TiS$_3$ were prepared by mechanical milling of crystalline TiS$_2$ ($c$-TiS$_2$) and sulfur. Then, $a$-TiS$_3$ particles were applied to the all-solid-state lithium cells. The cell with $a$-TiS$_3$ at the cell potential window of 0.9-2.4 V vs. Li-In showed the 1st reversible capacity of about 400 mAh g$^{-1}$ and retained capacity of about 320 mAh g$^{-1}$ for 10 cycles. The obtained capacity was higher than the equimolar mixture $c$-TiS$_2$ and sulfur, which were used as starting materials of the $a$-TiS$_3$. This fact suggests that the high capacity resulted from the amorphization of TiS$_3$. 
2. Comparison of electrochemical properties between amorphous and crystalline TiS₃ electrode active materials

The all-solid-state lithium cells with crystalline and amorphous TiS₃ at the cell potential window of 0.6-2.4 V vs. Li-In showed the 1st discharge capacity of about 560 mAh g⁻¹, corresponding to the theoretical capacity of TiS₃. However, the cell using c-TiS₃ had an irreversible capacity at the 1st cycle. The cell showed the reversible capacity of about 400 mAh g⁻¹ from the 2nd to 10th cycle. On the other hand, irreversible capacities were not observed for 10 cycles in the cell with a-TiS₃. The structural changes of crystalline and amorphous TiS₃ were observed by XRD and HR-TEM during cycling. The electrode of c-TiS₃ became partially amorphous during the cycling. The electrode of a-TiS₃ maintained amorphous state for 10 cycles.

3. Investigation of the electrochemical reaction mechanism of a-TiS₃ electrodes

Electronic structure changes of sulfurs in a-TiS₃ were examined by XPS and XANES. The electrode of a-TiS₃ consisted of S²⁻ and S₂²⁻ species. From the XPS and XANES results, it was revealed that the reversible sulfur redox of both S²⁻ and S₂²⁻ in a-TiS₃ mainly occurred during charge-discharge process for 10 cycles. Therefore, the all-solid-state cell using a-TiS₃ electrodes shows the stable cycle performance for 10 cycles.

4. Preparation of amorphous TiS₃/S/C electrode active materials

Composite electrodes of a-TiS₃/S/KB with high capacity were prepared by mechanical milling from a-TiS₃ and S/KB composites. Coin type liquid cells and
all-solid-state cells with $a$-TiS$_3$/S/KB electrodes operated as the secondary batteries at room temperature. The reversible capacity of coin type liquid cell using $a$-TiS$_3$/S/KB composites decreased from 484 to 33 mAh g$^{-1}$ during 50 charge-discharge cycles, because the polysulfides formed in $a$-TiS$_3$/S/KB were dissolved in liquid electrolytes. On the other hand, the all-solid-state cells showed higher reversible capacity of about 650 mAh g$^{-1}$ and better cyclability than the coin type liquid cells. The composite positive electrodes of $a$-TiS$_3$/S/KB with the large sulfur contents are attractive positive electrodes with high capacities for all-solid-state lithium secondary batteries.
3.5. References


4. Preparation of amorphous MoS$_3$ electrodes for all-solid-state lithium batteries and investigation of their electrochemical reaction mechanism

4.1. Introduction

High capacity of lithium batteries can be achieved by using active materials with a large content of sulfur. Elemental sulfur is one of the most promising positive electrode materials because of its high theoretical specific capacity of 1672 mAh g$^{-1}$, which is at least 5 times higher than that of the transition metal oxides such as LiCoO$_2$ [1, 2]. Sulfur also has many other advantages of low cost, abundant resource and environmental friendliness. However, low electronic conductivity is a drawback of sulfur. In the chapter 3, amorphous TiS$_3$ ($a$-TiS$_3$) with high electronic conductivity and larger sulfur content than TiS$_2$ as a typical transition-metal sulfide electrode was studied. The all-solid-state with $a$-TiS$_3$ exhibited the higher reversible capacity of about 550 mAh g$^{-1}$ and better cyclability than crystalline TiS$_2$ for 10 cycles. It is suggested that the redox reaction of additional sulfur was attributable to high capacity. Therefore, $a$-TiS$_3$ electrode active materials are effective in developing all-solid-state lithium batteries with higher reversible capacity and better cyclability.

Molybdenum sulfide was selected to achieve the higher capacity than $a$-TiS$_3$. The valence states of molybdenum atom would have more than those of titanium atom. Therefore, the redox of the molybdenum atom can be used as the capacities. The all-solid-state batteries with molybdenum sulfide would thus achieve high capacity. In addition, the use of crystalline molybdenum disulfide ($c$-MoS$_2$) as positive electrode active materials for lithium batteries is of great interest because of its low cost and high safety [3]. The lithium batteries with $c$-MoS$_2$ showed high reversible capacity with excellent cyclability.

Electrode properties of amorphous MoS$_3$ ($a$-MoS$_3$) prepared by pyrolysis of (NH$_4$)$_2$MoS$_4$
have also been investigated in an organic liquid electrolyte [4]. A liquid-type cell with \( a \)-MoS\(_3\) electrode shows the reversible capacity of 400 mAh \( g^{-1} \). The capacity of \( a \)-MoS\(_3\) electrode active materials has thus a higher reversible capacity than that of \( c \)-MoS\(_2\). Moreover, it is reported that MoS\(_3\) was prepared by a variety of synthesis processes [5-12]. All the prepared MoS\(_3\) materials were in amorphous state [5-12]. Therefore, crystalline MoS\(_3\) has not been synthesized so far. In addition, the thermal decomposition of \( a \)-MoS\(_3\) to \( c \)-MoS\(_2\) was studied by XRD, and a model for the crystallization process is proposed [5]. In this chapter, the electrochemical properties of \( a \)-MoS\(_3\) electrode active materials were firstly examined in all-solid-state cells.

In order to understand the reaction mechanisms of \( a \)-MoS\(_3\) electrodes in all-solid-state lithium cells, the structural changes and electronic structure changes of \( a \)-MoS\(_3\) during cycling tests need to be investigated. In the chapter 3, the structural changes and electronic structure changes of \( a \)-TiS\(_3\) during electrochemical tests were clarified by XRD, Raman, SEM, HR-TEM, XPS and XANES. The electrochemical reaction mechanism of \( a \)-TiS\(_3\) was proposed based on the structural analyses. Therefore, these analyses techniques are powerful to reveal the electrochemical reaction mechanism of \( a \)-MoS\(_3\) electrode active materials in all-solid-state lithium batteries.

In this chapter, \( a \)-MoS\(_3\) has successfully been prepared by mechanical milling from the mixtures of molybdenum metal and sulfur. Both microstructures and electrochemical properties of \( a \)-MoS\(_3\) in all-solid-state cells with sulfide solid electrolytes have been investigated. Electrochemical performances in \( a \)-MoS\(_3\) and \( c \)-MoS\(_2\) positive electrodes in all-solid-state cells have been examined. It is revealed that \( a \)-MoS\(_3\) had a higher capacity and superior cyclability.

In order to understand the electrochemical reaction mechanisms of \( a \)-MoS\(_3\) electrodes in
all-solid-state lithium cells, the structural changes and electronic structure changes of \( a \)-MoS\(_3\) during cycling tests have been investigated by XRD, SEM, HR-TEM, XPS and XANES. Finally, the difference of the charge-discharge mechanisms between \( a \)-TiS\(_3\) and \( a \)-MoS\(_3\) will be discussed.

4.2. Experimental

4.2.1. Preparation of the amorphous MoS\(_3\) electrodes

Amorphous MoS\(_3\) (\( a \)-MoS\(_3\)) electrode active materials were prepared by mechanical milling. Reagent-grade Mo metal (99.9+%; Aldrich) and sulfur (99.98%; Aldrich) were used as starting materials. The atomic ratio of Mo to S in the starting mixture was 1/3. The mixture of these materials was mechanically milled at ambient temperature using a planetary ball mill apparatus (Pulverisette 7; Fritsch) with zirconia pot (volume of 45 ml) and 500 zirconia balls (4 mm in diameter). The rotational speed was set to 370 rpm. The milling time was 80 hours.

4.2.2. Cell configurations

All-solid-state electrochemical cells were fabricated as follows. The 80Li\(_2\)S·20P\(_2\)S\(_5\) (mol\%) solid electrolyte was prepared by the mechanical milling and then heated at 210°C for 1 hour [13]. The \( a \)-MoS\(_3\) prepared by milling and the crystalline MoS\(_2\) (\( c \)-MoS\(_2\), 99%; Aldrich) were used as active materials. The working electrode was prepared by mixing of the active materials, the 80Li\(_2\)S·20P\(_2\)S\(_5\) solid electrolyte and acetylene black with the weight ratio of 40/60/6. The solid electrolyte and acetylene black were respectively added to secure lithium-ion and electron conduction paths to the active material in the working electrode.

On the other hand, in the case of XPS and XANES measurements, the working electrodes of \( a \)-MoS\(_3\) without conductive additives and solid electrolytes were used. The working
electrode (10 mg) and the solid electrolyte (80 mg) were placed in polycarbonate tube (10 mm in diameter) and pressed together under 360 MPa. A Li-In alloy was put on the solid electrolyte layer as a counter-reference electrode. A pressure of 120 MPa was then applied to the three-layered pellet. Finally, bulk type all-solid-state cells sandwiched with two stainless-steel disks as a current collector were obtained. All processes described above were conducted in a dry Ar filled glove box.

4.2.3. Characterization

To examine crystal structures of $a$-MoS$_3$ prepared by mechanical milling, X-ray diffraction experiment was carried out using an X-ray diffractometer (CuK$\alpha$, UltimaIV; Rigaku Corp.). Differential thermal analysis (DTA) was performed by using a thermal analyzer (Thermo Plus TG8110; Rigaku) at a heating rate of 10°C min$^{-1}$. The morphology of the $a$-MoS$_3$ was examined using a scanning electron microscopy (SEM, JSM-6610A; JEOL) and a high-resolution transmission electron microscope (HR-TEM, JEM-2100F; JEOL). The electronic structure of $a$-MoS$_3$ was characterized by the X-ray photoelectron spectroscopy (XPS, K-Alpha; Thermo Fisher Scientific) with a Monochromatic AlK$\alpha$ source (1486.6 eV). The observed binding energies were calibrated with the adventitious C1s peak to 284.7 eV. The samples were mounted on a sample stage in a dry Ar filled glove box and they were transferred to an analysis chamber using an Ar filled transfer vessel.

The electrochemical tests were conducted at 25°C in Ar filled atmosphere using a charge-discharge measuring device (BTS-2004; Nagano Co.) and a cyclic voltammetry device (CV, HSV10; Hokuto Denkou Co.).

To analyze the structure of the working electrode, XRD, SEM and HR-TEM for the working electrode after the charge-discharge tests were done. The cross sections of the
working electrodes were prepared by using an ion milling system that employs an Ar ion beam (E-3500; Hitachi High-Technologies). Ion milling to obtain a smooth cross-section was conducted for the samples transferred with an Ar filled vessel to prevent exposing the samples to air. For HR-TEM observation of the working electrodes before discharge, after the 1st discharge, 1st charge, 10th discharge and 10th charge, the cells were disassembled and then the $\alpha$-MoS$_3$ composite electrodes were scratched in an Ar filled glove box. The obtained powders were placed on a carbon grid for TEM observation without any ion-milling treatments. These powders were packed in a folder to maintain inert atmosphere, and were then transferred to the TEM apparatus.

The electronic structures of sulfur in $\alpha$-MoS$_3$ electrodes before and after charge-discharge tests were analyzed by XPS and XANES. XANES spectra at S K-edge were measured at BL-13 of the Synchrotron Radiation Center, Ritsumeikan University. The spectra were collected in total electron yield mode, wherein the sample current produced due to excitation of all electrons of different energies was measured. The sample for S K-edge XANES measurements were also mounted on a sample stage in a dry Ar filled glove box and they were transferred to the chamber using an Ar filled transfer vessel. Mo K-edge XANES measurements were also carried out at beamlines BL14B2 at SPring-8, Japan. The electrodes were sealed in laminated packets in an Ar filled glove box. The measurements were performed in a transmission mode.

4.3. Results and discussion

4.3.1. Preparation of amorphous MoS$_3$ particles and their electrochemical performance

For increasing capacity of the all-solid-state cells, sulfur-rich molybdenum sulfide such as amorphous MoS$_3$ ($\alpha$-MoS$_3$) electrode particles were prepared by mechanical milling. Then,
a-MoS\(_3\) particles were applied to the all-solid-state cells. **Figure 4-1** shows the XRD patterns of the molybdenum sulfide prepared by milling of the mixtures of Mo and S at various milling periods of time. In the mixtures, the diffraction peaks belonging to the starting materials, Mo metal and sulfur, were detected. The diffraction peaks due to octahedral ring structure of sulfur disappeared by milling for 20 hours. On the other hand, the intensities of the diffraction peaks due to Mo metal gradually decreased as the milling time is longer. After milling for 80 hours, all the diffraction peaks due to Mo metal and sulfur disappeared. In addition to a halo pattern due to the amorphous structure, it is a broad peak at about 15\(^\circ\) that appeared in the diffraction pattern obtained in MM 80 hours. We analyzed the position of the broad peak around 15\(^\circ\) and found that the position corresponds to the (002) diffraction peak of crystalline MoS\(_2\) (c-MoS\(_2\), JCPDS No. 070-9264). Thus, to clarify microstructures in some milled materials, high-resolution TEM (HR-TEM) observation was conducted. **Figure 4-2** shows (a) a HR-TEM image, (b) electron diffraction pattern and (c) its intensity profile of the molybdenum sulfide prepared by milling for 80 hours. The inset in (a) shows magnified image of (a). The HR-TEM image revealed that microstructure in the milled sample was characterized as random distribution of nano-sized domains with the size of 2~3 nm, which consist of c-MoS\(_2\) with the layered structure. Note that lattice spacing due to the (002) plane of c-MoS\(_2\) was approximately 6 Å, which was almost coincident with spacing of the lattice fringes in **Fig. 4-2 (a)**. Electron diffraction patterns obtained in the milled sample showed debye rings without diffraction spots. **Figure 4-2 (c)** shows the intensity profile obtained along the dotted line in the ED pattern of **Fig. 4-2 (b)** and the origin at the horizontal axis corresponds to the direct 000 spot. The peak positions of the intensity profile almost corresponded to those of c-MoS\(_2\). From these considerations, it is suggested that the prepared sample should include clusters consisting of MoS\(_2\) with the layered structure. It is noted that
Figure 4-1  XRD patterns of the mixture products prepared by mechanical milling (MM) of Mo metal and sulfur for different periods time.
Figure 4-2  HR-TEM image (a), electron diffraction pattern (b) and its intensity profile (c) of the molybdenum sulfide prepared by milling for 80 hours. The inset in (a) shows magnified image of (a).
the prepared material including the clusters is called amorphous MoS$_3$ ($a$-MoS$_3$) in the following discussion.

The DTA curve of the sample milled for 80 hours exhibited no endothermic peaks attributable to melt of crystalline sulfur whereas endothermic peaks were observed at around 115$^\circ$C in the DTA curve obtained in the mixture of Mo metal and S before milling (0 hour), as shown in Fig. 4-3. This implies that chemical reaction between Mo metal and sulfur occurred completely.

The SEM images of the sample before and after milling are shown in Fig. 4-4. The SEM image of the mixture of Mo metal and S before mechanical milling indicated that the mixture consisted of Mo metal particles of $ca$. 20 $\mu$m in size and sulfur particles of $ca$. 100 $\mu$m. After milling for 80 hours, the milled sample consisted of submicron-sized particles. The staring materials as Mo metal and sulfur particles were not observed.

Figure 4-5 shows the S$_{2p}$ and Mo$_{3d}$ XPS spectra of $a$-MoS$_3$ prepared by ball milling. In addition, the spectra of $c$-MoS$_2$, crystalline Na$_2$S$_4$, elemental sulfur (S$_8$) and MoO$_3$ are also shown for comparison in Fig. 4-5. Each doublet was comprised of S$_{2p3/2}$ and S$_{2p1/2}$ components. The peak energy separation (1.2 eV) of each doublet was set during peak fitting. The S$_{2p}$ XPS spectra of $c$-MoS$_2$ and elemental sulfur (S$_8$) showed the only one S$_{2p3/2}$ peak contribution at 162.5 eV and 164.0 eV, respectively. The S$_{2p3/2}$ peak of $c$-MoS$_2$ at 162.5 eV was characteristic of S$^{2-}$, agreeing well with a literature reported [14]. Similarly, the S$_{2p3/2}$ peak positioned at 164.0 eV was attributable to elemental sulfur (S$_8$) [15]. On the other hand, the S$_{2p}$ XPS spectrum of $a$-MoS$_3$ before charge-discharge showed the two S$_{2p3/2}$ peaks at 162.2 and 163.4 eV. The peak at 162.2 eV was almost same as the peak at 162.5 eV attributable to S$^{2-}$ in $c$-MoS$_2$ [14]. The S$_{2p}$ spectrum for reference sample of Na$_2$S$_4$ has been also examined. The S$_{2p}$ XPS spectra of Na$_2$S$_4$ showed the two S$_{2p3/2}$ peaks at 161.3 and 162.9
Figure 4-3  DTA curves of the mixture and product of Mo metal and sulfur prepared by MM for 0 and 80 hours.
Figure 4-4  SEM images of the mixture and product of Mo metal and sulfur prepared by MM for 0 and 80 hours.
Figure 4-5 $S_{2p}$ and $Mo_{3d}$ XPS spectra of $\alpha$-MoS$_3$, crystalline MoS$_2$, crystalline MoO$_3$, crystalline Na$_2$S$_4$ and sulfur.
eV. Crystalline Na$_2$S$_4$ has two sulfur species of terminal non-bridging S$^-$ (161.3 eV) and bridging sulfur S$^0$ in S-S bond (162.9 eV). The peak of $a$-MoS$_3$ at 163.4 eV exhibited between the S$_{2p3/2}$ peak at 162.9 eV of bridging sulfur in the S-S bond combined with S$^-$ in Na$_2$S$_4$ and the S$_{2p3/2}$ peak at 164.0 eV of bridging sulfur with long chain in S$_8$. The S$_{2p3/2}$ peak of $a$-MoS$_3$ at 163.4 eV to bridging sulfur with longer chain than S-S (S$_2$) having partial negative charge has thus been assigned. The S$_{2p3/2}$ peak of $a$-MoS$_3$ at 163.4 eV is expressed as S$^{\delta-}$ in the following discussion. The fitted S$^{2-}$/S$^{\delta-}$ peak ratio was 2.2/1. As a result, $a$-MoS$_3$ consisted of S$^{2-}$ in MoS$_2$ nano-clusters detected by HR-TEM and S$^{\delta-}$.

The Mo$_{3d}$ XPS spectra of $a$-MoS$_3$, $c$-MoS$_2$ and crystalline MoO$_3$ were observed. Each doublet was comprised of Mo$_{3d5/2}$ and Mo$_{3d3/2}$ components. The peak energy separation (3.1 eV) of each doublet was set during peak fitting. The Mo$_{3d5/2}$ peak of $c$-MoS$_2$ at 229.4 eV was characteristic of Mo$^{4+}$ [14]. The Mo$_{3d5/2}$ peak positioned at 229.4 eV was also observed in $a$-MoS$_3$ sample. In addition, the one peak of S$_{2s}$ was observed at 226.7 eV in $a$-MoS$_3$ and $c$-MoS$_2$ samples. On the other hand, Mo$_{3d5/2}$ peak of crystalline MoO$_3$ at 233.1 eV was attributable to Mo$^{6+}$ [16]. It is suggested that the electronic state of molybdenum in $a$-MoS$_3$ was not Mo$^{6+}$ but Mo$^{4+}$. XPS measurements of $a$-MoS$_3$ prepared by mechanical milling revealed that the electronic state of molybdenum was Mo$^{4+}$ and the electronic states of sulfur were S$^{2-}$ and S$^{\delta-}$.

**Figure 4-6** shows (a) the charge-discharge curves and (b) the rate performance of all-solid-state cells Li-In/80Li$_2$S·20P$_2$S$_5$ glass-ceramic/$a$-MoS$_3$ or $c$-MoS$_2$. The working electrode was prepared by mixing of $a$-MoS$_3$ or $c$-MoS$_2$, the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic and acetylene black with the weight ratio of 40/60/6. In **Fig. 4-6** (a), charge-discharge measurements of the cells were conducted at the current density of 0.064 mA cm$^{-2}$ (C/50) at 25°C. The right side ordinate axis represents the electrode potential vs. Li$^+$/Li, as calculated
Figure 4-6 Charge-discharge curves (a) and rate performance (b) of the all-solid-state cells with $\alpha$-MoS$_3$ and $\varepsilon$-MoS$_2$. 
based on the potential difference between the Li-In and Li electrode (0.62 V). The Li-In alloy was used as a counter electrode, because Li-In alloy exhibits a stable potential plateau at 0.62 V vs Li\textsuperscript{+/}/Li in an all-solid-state cell using a sulfide solid electrolyte. The 1st discharge capacity of the cell using c-MoS\textsubscript{2} was approximately 270 mAh g\textsuperscript{-1}. The obtained discharge capacity was larger than 167 mAh g\textsuperscript{-1} (the capacity corresponding to the insertion of 1 molar Li to MoS\textsubscript{2}). The electrode of c-MoS\textsubscript{2} was practically used as the positive electrode in lithium metal batteries with liquid organic electrolyte [3]. Electrochemical reaction mechanism of c-MoS\textsubscript{2} with lithium is reported as follows:

\[
\begin{align*}
\alpha\text{-MoS}_2 + x\text{Li}^+ + xe^- & \rightarrow \alpha\text{-Li}_x\text{MoS}_2 \quad (2.1 \text{ V-1.1 V vs. Li}) \quad (1) \\
\alpha\text{-Li}_x\text{MoS}_2 + y\text{Li}^+ + ye^- & \rightarrow \beta\text{-Li}_{x+y}\text{MoS}_2 \quad (1.1 \text{ V vs. Li}) \quad (2)
\end{align*}
\]

The intercalation reaction of Li\textsuperscript{+} ions to \(\alpha\text{-MoS}_2\) was observed at the potential window of 2.1-1.1 V vs. Li in the 1st discharge process. The discharge plateau due to the two phase reaction between \(\alpha\text{-MoS}_2\) and \(\beta\text{-MoS}_2\) appeared at 1.1 V vs. Li. The charge-discharge reaction after the 1st discharge process proceeded in \(\beta\text{-MoS}_2\) because the structure change to \(\alpha\text{-MoS}_2\) did not occur [3]. Recently, Du \textit{et al.} and Fang \textit{et al.} reported that the cell with c-MoS\textsubscript{2} exhibited a higher capacity of approximately 670 mAh g\textsuperscript{-1} (the capacity corresponding to the insertion of 4 molar Li to MoS\textsubscript{2}) than 167 mAh g\textsuperscript{-1} [17, 18]. The following reaction is suggested on the discharge process to 0 V vs. Li:

\[
\beta\text{-LiMoS}_2 + 3 \text{Li}^+ + 3 e^- \rightarrow 2\text{Li}_2\text{S} + \text{Mo} \quad (1.1-0 \text{ V vs. Li}) \quad (3)
\]

The all-solid-state cell with c-MoS\textsubscript{2} showed a higher capacity than 167 mAh g\textsuperscript{-1} because the excess Li\textsuperscript{+} would react with \(\beta\text{-LiMoS}_2\) due to the reaction (3) occurring at the potential window of 1.1-0 V vs. Li. Because the discharge cut-off potential was 0.62 V vs. Li, the all-solid-state cell did not show a higher discharge capacity than the cell with an organic electrolyte reported by Du \textit{et al.} and Fang \textit{et al.} The 1st charge capacity was about 180 mAh
The 1st coulombic efficiency of the cell with \( c\text{-MoS}_2 \) was 69.3%. This capacity was close to 167 mAh g\(^{-1}\). Additionally, the charge-discharge curve of the all-solid-state cell with \( c\text{-MoS}_2 \) was similar to that of the cell using an organic liquid electrolyte, suggesting that electrochemical reaction mechanism of the \( c\text{-MoS}_2 \) electrode in all-solid-state cells is almost the same as that in the cell with an organic liquid electrolyte.

On the other hand, the \( a\text{-MoS}_3 \) electrode in the all-solid-state cell with the sulfide solid electrolyte exhibited higher capacity and better cyclability, compared to the \( c\text{-MoS}_2 \) in the all-solid-state cell. The 1st discharge and charge capacities of the cell with \( a\text{-MoS}_3 \) were about 760 mAh g\(^{-1}\) and 720 mAh g\(^{-1}\), respectively. The 1st coulombic efficiency of the cell using \( a\text{-MoS}_3 \) was 93.4%. The obtained discharge capacity was higher than 670 mAh g\(^{-1}\) (the capacity corresponding to the insertion of 4 molar Li to \( \text{MoS}_2 \)). The capacity loss was observed at the second cycle and a possible reason for it is a partial contact loss in the working electrode by a volume change of \( a\text{-MoS}_3 \). The cell maintained the capacity of about 670 mAh g\(^{-1}\) up to the 10th cycle. The cell with \( a\text{-MoS}_3 \) did not show well-defined discharge plateaus and this is a typical behavior of amorphous electrode materials. Cyclic voltammogram (CV) of the cell is shown in Fig. 4-7 and three broad peaks observed in CV almost corresponded to the discharge profile as shown in Fig. 4-6 (a). The discharge potential of the cell using \( a\text{-MoS}_3 \) was higher than that of the cell using \( c\text{-MoS}_2 \). This suggested that the additional sulfur reacted with Li\(^+\) during discharge process to 1.6 V vs. Li. The electrochemical reaction at \textit{ca.} 2.0 V vs. Li at the 1st discharge process would be based on the additional sulfur redox because this electrochemical potential was similar to that of elemental sulfur. The electrochemical reaction mechanism of the \( a\text{-MoS}_3 \) below 1.6 V vs. Li is similar to that of \( \text{MoS}_2 \).

The rate performance of the cells with \( a\text{-MoS}_3 \) and \( c\text{-MoS}_2 \) are shown in Fig. 4-6 (b). The
Figure 4-7  Cyclic voltammogram of the all-solid-state cell with $\alpha$-MoS$_3$ electrode.
cell using \( c \)-MoS\(_2\) showed the reversible capacity about 180 mAh g\(^{-1}\) for 10 cycles at the current density of 0.064 mA cm\(^{-2}\). The reversible capacity decreased gradually with increasing the current density. The reversible capacity of the cell with \( c \)-MoS\(_2\) exhibited about 75 mAh g\(^{-1}\). On the other hand, the cell with \( a \)-MoS\(_3\) showed the higher reversible capacity than the cell with \( c \)-MoS\(_2\). The reversible capacity of the cell using \( a \)-MoS\(_3\) was about 670 mAh g\(^{-1}\) for 10 cycles at the current density of 0.064 mA cm\(^{-2}\). After the 2nd cycle, the coulombic efficiency of the cell was about 100%. The capacity fading was not observed with increasing the current density from 0.064 mA cm\(^{-2}\) to 0.13 mA cm\(^{-2}\). However, the reversible capacity of the cell with \( a \)-MoS\(_3\) was about 400 mAh g\(^{-1}\) at the current density of 1.3 mA cm\(^{-2}\). This suggests that sulfur-rich molybdenum sulfide electrode active materials such as \( a \)-MoS\(_3\) have higher reversible capacity than the \( c \)-MoS\(_2\) even at the high current density.

4.3.2. Investigation of the electrochemical reaction mechanism of amorphous MoS\(_3\) electrodes

In order to understand the electrochemical reaction mechanism of \( a \)-MoS\(_3\) electrodes, the structural changes and electronic structure changes of \( a \)-MoS\(_3\) during cycling were examined by XRD, HR-TEM, XPS and XANES measurements. The 1st and 10th charge-discharge curves of the all-solid-state cell Li-In/80Li\(_2\)S·20P\(_2\)S\(_5\) glass-ceramic/\( a \)-MoS\(_3\) and the XRD patterns of working electrodes with \( a \)-MoS\(_3\) before and after the 1st charge-discharge cycle and after the 10th charge are shown in Fig. 4-8 (a) and (b), respectively. The working electrode was prepared by mixing of \( a \)-MoS\(_3\), the 80Li\(_2\)S·20P\(_2\)S\(_5\) glass-ceramic and acetylene black with the weight ratio of 40/60/6. Charge-discharge measurements of the cells were conducted at the current density of 0.064 mA cm\(^{-2}\) at 25°C. The cell using \( a \)-MoS\(_3\) showed the 1st reversible capacity of about 720 mAh g\(^{-1}\). The about 5 mol Li\(^+\) was intercalated and
Figure 4-8  (a) The 1st and 10th charge-discharge curve of the cell with $a$-MoS$_3$, (b) the XRD patterns of the working electrodes using $a$-MoS$_3$ before and after the 1st discharge, after the 1st charge and after the 10th charge.
deintercalated in $a$-MoS$_3$ active materials at the 1st cycling test. The reversible capacity decreased gradually with increasing cycle number. The cell using $a$-MoS$_3$ showed the reversible capacity of about 670 mAh g$^{-1}$ (4.8 mol Li$^+$) at the 10th cycle.

The silicon peaks were observed in all XRD patterns. Silicon was used as an internal standard in XRD measurements. The Li$_2$S-P$_2$S$_5$ solid electrolyte used in this study, partially included Li$_2$S crystal and thus the peaks attributable to Li$_2$S were observed slightly in all the XRD patterns for the electrodes before and after the 1st cycle and after the 10th charge. In addition, a halo pattern due to the $a$-MoS$_3$ active material was mainly observed in all the XRD patterns. By comparing the XRD patterns of the electrodes after the 1st charge-discharge measurement with that before the measurement, it is revealed that no diffraction peaks due to crystalline Mo and S were observed. These results implied that the amorphous state of the $a$-MoS$_3$ active materials should remain intact during the 10 cycles.

The cross-sectional SEM images of the working electrodes using $a$-MoS$_3$ (a) before and (b) after the 1st charge-discharge measurements are shown in Fig. 4-9. As understood in Fig. 4-9 (a) and (b), there were no morphology changes of $a$-MoS$_3$ after the 1st charge-discharge measurement. Bright parts were observed in $a$-MoS$_3$ before and after the 1st charge-discharge process and the origin of the contrast in $a$-MoS$_3$ has not been identified. Moreover, good contacts between $a$-MoS$_3$ and solid electrolytes were kept during the 1st cycle.

Figure 4-10 shows the HR-TEM images of $a$-MoS$_3$ in the intermediate states of (a) 1.0 V, (b) 0.5 V and (c) 0 V (full discharge) vs. Li-In during the 1st discharge process. The electron diffraction patterns are shown in the inset of Fig. 4-10 (a-c). Lattice fringes due to MoS$_2$ layer structures (yellow dotted circles) were observed in the HR-TEM images of $a$-MoS$_3$ electrode active materials during the 1st discharge process. However, the number of regions with the lattice fringes observed in the HR-TEM images decreased gradually with increasing the depth.
Figure 4-9 Cross-sectional SEM images of the working electrodes with $a$-MoS$_3$ (a) before and (b) after the 1st charge-discharge test.
Figure 4-10 HR-TEM images of $\alpha$-MoS$_3$ in the intermediate states of (a) 1.0 V, (b) 0.5 V and (c) 0 V. The insets show the electron diffraction patterns of $\alpha$-MoS$_3$. (d) STEM-HAADF image of $\alpha$-MoS$_3$ after the 1st discharge.
of discharge. After the 1st discharge to 0 V (Fig. 4-10 (c)), the lattice fringes due to the MoS$_2$ layer structures disappeared in $\alpha$-MoS$_3$ electrodes and a halo pattern due to the amorphous state was observed in the electron diffraction pattern. These results suggest that the local nano-scaled regions with the lattice fringes changed gradually into the amorphous state during the discharge process. In addition, it was found that the HR-TEM image obtained in the $\alpha$-MoS$_3$ electrodes after the 1st full discharge showed regions with bright and dark contrast separately, as shown in Fig. 4-10 (c). Moreover, the STEM-HAADF image displaying in Fig. 4-10 (d) shows separated regions with bright and dark contrast. It is significant that in the STEM-HAADF image regions consisting of elements with larger Z number should be observed as a bright contrast, suggesting that regions with a large amount of Mo can be seen as bright contrast and, on the other hand, regions with a large amount of S can be seen as a dark contrast. The $\alpha$-MoS$_3$ electrode material was separated into two distinct nano-scaled regions; one with a large amount of Mo (blue) and the other with a large amount of S (red) after the 1st discharge, as shown Fig. 4-10 (d).

Figure 4-11 shows (a) HR-TEM image, (b) electron diffraction pattern and (c) its intensity profile of $\alpha$-MoS$_3$ electrode after the 1st charge. The HR-TEM image showed random distribution of nano-scaled domains with curved lattice fringes in the $\alpha$-MoS$_3$ electrode after the 1st charge. The microstructures obtained in the $\alpha$-MoS$_3$ electrode after the 1st charge almost coincided with those of $\alpha$-MoS$_3$ before charge-discharge process. On the other hand, in the electron diffraction pattern, diffraction spots due to the crystalline was not observed, as shown in Fig. 4-11 (b). Debye rings without diffraction spots were observed in the electron diffraction pattern. It is noteworthy that Fig. 4-11 (c) shows the intensity profile obtained along the dotted line in the ED pattern of Fig. 4-11 (b) and the origin in the horizontal axis in Fig. 4-11 (c) corresponds to the direct 000 spot in the ED pattern. The peak
Figure 4-11 (a) HR-TEM image, (b) electron diffraction pattern and (c) its intensity profile of $a$-MoS$_3$ electrode after the 1st charge.
positions of the intensity profile can be identified as those of the \(c\)-MoS\(_2\). The present HR-TEM observation suggested that the reversible structural changes of \(a\)-MoS\(_3\) occurred during the 1st charge-discharge process.

The HR-TEM image (a), electron diffraction pattern (b) and its intensity profile (c) of \(a\)-MoS\(_3\) electrode active material after the 10th discharge process are shown in Fig. 4-12. There is no random distribution of nano-scaled domains with curved lattice fringes in the \(a\)-MoS\(_3\) electrode after the 10th charge in the HR image of Fig. 4-12 (a). On the contrary, there appeared nano-scaled regions with lattice fringes, as indicated by yellow circles in Fig. 4-12 (a). This result suggests that \(a\)-MoS\(_3\) after the 10th discharge had nano crystals. Debye rings with weak intensity were observed in the electron diffraction pattern (Fig. 4-12 (b)). Fig. 4-12 (c) shows the intensity profile obtained along the dotted line in the ED pattern of Fig. 4-12 (b) and the origin of the intensity profile in Fig. 4-12 (c) corresponds to the direct 000 spot. The peak positions of the intensity profile were consistent with peak positions calculated based on the lattice parameters of the crystalline Li\(_2\)S with space group of Fm\(\bar{3}\)m.

In addition, there is a possibility of forming Mo-doped Li\(_2\)S crystal. It is expected that the intensity of 220 peak increases with an increase of substitution of Mo for Li in Li\(_2\)S crystal. Because an intense 220 peak was not observed in Fig. 4-12 (c), Li\(_2\)S or its solid solutions where a small amount of Mo is substituted for Li was precipitated after the 10th discharge process.

Figure 4-13 shows the (a) cross-sectional SEM image of working electrode using \(a\)-MoS\(_3\) and (b) HR-TEM image of \(a\)-MoS\(_3\) electrode after the 10th charge process. The electron diffraction pattern is shown in Fig. 4-13 (b). There was no drastic change of the morphology of \(a\)-MoS\(_3\), as displayed in Fig. 4-13 (a). In addition, the good interface contact between \(a\)-MoS\(_3\) electrode and sulfide solid electrolyte remained after the 10th charge-discharge test.
Figure 4-12 (a) HR-TEM image, (b) electron diffraction pattern and (c) its intensity profile of $\alpha$-MoS$_3$ electrode after the 10th discharge.
Figure 4-13  (a) Cross-sectional SEM image of working electrode with $\alpha$-MoS$_3$ and (b) HR-TEM image of $\alpha$-MoS$_3$ electrode after the 10th charge.
The lattice fringes attributable to both Li$_2$S nano crystal and MoS$_2$ with layer structure in $a$-MoS$_3$ electrodes were not observed in HR-TEM image of Fig. 4-13 (b). Halo pattern was observed in the electron diffraction pattern. Thus, the electrodes after the 10th charge were completely amorphous. These results revealed that amorphization of the electrodes gradually proceeded with increasing the cycle number.

In order to examine electronic structure changes of $a$-MoS$_3$ electrodes during cycling, the all-solid-state cells using $a$-MoS$_3$ working electrodes without the addition of solid electrolytes were assembled and the cells operated as a secondary battery at 25°C.

**Figure 4-14 (a)** shows the 1st and 10th charge-discharge curves of all-solid-state cell with $a$-MoS$_3$ and (b) shows the S$_{2p}$ XPS spectra of $a$-MoS$_3$ before cycles, after the 1st discharge, after the 1st charge and after the 10th charge. Charge-discharge measurements of the cell with $a$-MoS$_3$ were conducted at the current density of 0.013 mA cm$^{-2}$ (1 mA g$^{-1}$) at 25°C. The 1st discharge and charge capacities of the cell with $a$-MoS$_3$ were about 760 and 720 mAh g$^{-1}$, respectively. The irreversible capacity was observed at the 1st cycle. After the 10th cycle, the cell using $a$-MoS$_3$ showed the reversible capacity of about 670 mAh g$^{-1}$.

As shown in **Fig. 4-5**, $a$-MoS$_3$ consisted of S$^{2-}$ and S$^{5-}$ species before charge-discharge measurements. The S$_{2p}$ XPS spectrum of $a$-MoS$_3$ after the 1st discharge was shifted to lower binding energy side. This is because Li$^+$ ions reacted with sulfur in $a$-MoS$_3$ electrode active materials during discharge process. Two S$_{2p3/2}$ peaks at 159.9 and 161.4 eV are possibly assigned to S$^{5-}$ and S$^{2-}$ interacted with both lithium and molybdenum. The peak positions of two S$_{2p3/2}$ peaks after the 1st and 10th charge were different from those before charge-discharge and almost the same as those after the 1st discharge.

**Figure 4-15** shows the S K-edge XANES spectra of $a$-MoS$_3$ before charge-discharge, after the 1st discharge, after the 1st charge and after the 10th charge. The peak sharpness of
Figure 4-14 (a) The 1st and 10th charge-discharge curves of all-solid-state cell with $a$-MoS$_3$ and (b) the S$_{2p}$ XPS spectra of $a$-MoS$_3$ before charge-discharge, after the 1st discharge, after the 1st charge and after the 10th charge.
Figure 4-15 S K-edge XANES spectra of α-MoS₃ before charge-discharge, after the 1st discharge, after the 1st charge and after the 10th charge.
a-MoS$_3$ before charge-discharge at about 2471 eV was different from that of $a$-TiS$_3$. It is suggested that the electronic structure of sulfur in $a$-MoS$_3$ was not the same as that in $a$-TiS$_3$. After the 1st discharge, the profile of S K-edge XANES spectrum changed drastically. It is suggested that the electronic structures of sulfur changed by lithiation process. The profiles of the S K-edge XANES spectra of $a$-MoS$_3$ after the 1st and 10th charge were not the same as that of $a$-MoS$_3$ itself. Consequently, the electronic structures of sulfur did not change reversibly. However, the profiles of the spectra after the 1st and 10th charge were similar to those after the 1st discharge. Moreover, the peak at about 2473 eV was observed in the spectra except for $a$-MoS$_3$ before test. This peak is attributable to S$^{2-}$ in Li$_2$S [19-26]. The new broad peak at about 2476 eV was observed after the 1st discharge, 1st charge and 10th charge. This peak might be derived from sulfurs interacted with both lithium and molybdenum, but detailed assignment has not been clarified yet.

**Figure 4-16 (a)** shows Mo K-edge XANES spectra of $a$-MoS$_3$ before cycles, after the 1st discharge and after the 1st charge and (b) shows the magnification of the XANES spectra. In addition, the spectrum of Mo metal is also shown for comparison in **Fig. 4-16.** Mo K-edge XANES spectra after discharge shifted to the lower energy side, which indicates the reduction of molybdenum. However, the profile of the spectrum for $a$-MoS$_3$ after the 1st discharge did not coincide with that of Mo metal as a reference, suggesting that molybdenum was not metallic state. After the 1st charge, the spectrum was similar to that before tests. The reversible change of electronic structure in molybdenum was observed.

On the basis of the results of charge-discharge curves (**Fig. 4-14 (a)**), $a$-MoS$_3$ reacted with about 6 mol Li$^+$ ions at the 1st discharging process, while about 5 mol Li$^+$ ions were extracted at the 1st charging process. The reversible reaction with about 5 mol Li$^+$ ions occurred during 10 cycles. From the result of Mo K-edge XANES (**Fig. 4-16**), the electronic structures of
Figure 4-16  (a) Mo $K$-edge XANES spectra of $\alpha$-MoS$_3$ before, after the 1st discharge and after the 1st charge, and (b) the magnification of the XANES spectra. The spectrum of Mo metal is also shown for comparison.
molybdenum changed reversibly during electrochemical tests. From the results of $S_{2p}$ XPS (Fig. 4-14 (b)) and S K-edge XANES (Fig. 4-15), the irreversible electronic structure changes of sulfur were observed during the 1st charge-discharge process. This is a possible reason for the 1st irreversible capacity of the cell using $a$-MoS$_3$. The electronic structure of sulfur after the 10th charge was similar to that after the 1st charge. Based on the structure analyses of $a$-MoS$_3$ during charge-discharge process, its reaction mechanism is proposed as follows:

$$a$-MoS$_3 + 6Li^+ + 6e^- \rightarrow a$-Li$_2$S (Li$_{2-x}$Mo$_x$S) + $a$-Li$_x$MoS$_2$ \hspace{1cm} \text{(1st discharge process)} \hspace{1cm} (4)$$

$$a$-LiMoS$_3 + 5Li^+ + 5e^- \rightarrow a$-Li$_2$S (Li$_{2-x}$Mo$_x$S) + $a$-Li$_x$MoS$_2$ \hspace{1cm} \text{(After the 1st discharge)} \hspace{1cm} (5)$$

The discharge plateau potential of the cell using $a$-MoS$_3$ at about 2.0 V vs. Li as shown in Fig. 4-14 (a) was higher than that of the cell using $c$-MoS$_2$ at about 1.0 V vs. Li (Fig. 4-6 (a)). This suggests that $S^{6-}$ ions in $a$-MoS$_3$ would firstly react with Li$^+$ ions during discharge process from 2.0 to 1.6 V vs. Li. The cell using $a$-MoS$_3$ operated near the electrochemical potential of sulfur. After reacted with 2 mol Li$^+$ ions at about 2.0 V, Li$_2$S and/or its solid solutions (Li$_{2-x}$Mo$_x$S$_2$), where a small amount of Mo is substituted for Li, were formed. Because $S^{2-}$ in $c$-MoS$_2$ reacted with Li$^+$ ions below 1.6 V vs. Li, 4 mol Li$^+$ ions reacted with $S^{2-}$ in $a$-MoS$_3$ to form Li$_x$MoS$_2$ at the 1st lithiation process below 1.6 vs. Li. HR-TEM analyses indicated these discharge products were amorphous state (Fig. 4-10 (c)). After the 1st charge, about 5 mol Li$^+$ ions were extracted from the discharge products and thus amorphous LiMoS$_3$ would be formed. As shown in $S_{2p}$ XPS (Fig. 4-14 (b)) results, the $S_{2p}$ XPS spectrum was shifted to lower binding energy side after the 1st full discharge, suggesting that $S^{2-}$ and $S^{6-}$ species interacted with both lithium and molybdenum. The S K-edge XANES spectrum (Fig. 4-15)
and Mo K-edge XANES spectrum (Fig. 4-16) changed during the 1st discharge process. These results agree with the reaction mechanism of the 1st discharge process mentioned above. The 1st irreversible capacity was observed because the electronic structures of sulfur in $a$-MoS$_3$ after the 1st charge were not similar to those before cycling. The electronic structures of sulfur after the 10th charge were similar to those after the 1st charge. Thus, the all-solid-state cell with $a$-MoS$_3$ showed relatively good cyclability after the 1st cycle.

**4.3.3. Difference of the charge-discharge reaction mechanisms between amorphous TiS$_3$ and amorphous MoS$_3$ electrodes**

Comparison of the electrochemical reaction mechanisms between $a$-TiS$_3$ (shown in chapter 3) and $a$-MoS$_3$ was done in this section. The differences of the obtained capacity are discussed from the viewpoint of density of states (DOS) of $a$-TiS$_3$ and $a$-MoS$_3$. The cell with $a$-TiS$_3$ showed the reversible capacity of about 510 mAh g$^{-1}$ for 10 cycles. This capacity was mainly attributable to the redox of sulfur during charge-discharge tests. On the other hand, the 1st charge capacity of the cell with $a$-MoS$_3$ was about 720 mAh g$^{-1}$ and the irreversible capacity of 40 mAh g$^{-1}$ was observed. The cell maintained the capacity of about 670 mAh g$^{-1}$ up to the 10th cycle. Charge-discharge capacity of $a$-MoS$_3$ was based on the redox of both sulfur and molybdenum.

The DOS of crystalline TiS$_3$ ($c$-TiS$_3$) and $a$-MoS$_3$ have already been reported, as shown in Fig. 4-17 [27, 28]. The S3p electrons in $c$-TiS$_3$ are occupied near the Fermi level [27], indicating that the redox of sulfur mainly occurs for $c$-TiS$_3$. In this study, $a$-TiS$_3$ was prepared from $c$-TiS$_3$ and it seems that the DOS of $a$-TiS$_3$ is similar to that of $c$-TiS$_3$. As the result, the redox of sulfur mainly takes place for $a$-TiS$_3$. On the other hand, the S3p and Mo4s electrons are occupied near the Fermi level in $a$-MoS$_3$ [28]. Therefore, the redox of both sulfur and
Figure 4-17 DOS of $c$-TiS$_3$ (a) and $a$-MoS$_3$ (b).
molybdenum occurs. The electrochemical redox species considered from XPS and XANES results agree with those from DOS of \( a \)-TiS\(_3\) and \( a \)-MoS\(_3\). The 1st irreversible capacity of the cell using \( a \)-MoS\(_3\) was observed. The cut-off potential of all-solid-state cell with \( a \)-MoS\(_3\) was lower than that of \( a \)-TiS\(_3\) and the difference of cut-off potential is a possible reason for the irreversible capacity in \( a \)-MoS\(_3\). The electrochemical test for the cell with \( a \)-MoS\(_3\) has thus been demonstrated at the same cut-off of 0.5 V as the cell with \( a \)-TiS\(_3\).

**Figure 4-18** shows (a) the 1st charge-discharge curves of all-solid-state cell with \( a \)-MoS\(_3\) at the cut-off potential of 0.5 V vs. Li-In and (b) the S\(_{2p}\) XPS spectra of \( a \)-MoS\(_3\) after the 1st charge. The cell with \( a \)-MoS\(_3\) showed the discharge capacity of about 550 mAh g\(^{-1}\), which was similar to the capacity of the cell with \( a \)-TiS\(_3\). However, the cell with \( a \)-MoS\(_3\) showed the 1st irreversible capacity of 60 mAh g\(^{-1}\). The S\(_{2p}\) XPS spectrum of \( a \)-MoS\(_3\) after the 1st charge mainly showed the two S\(_{2p3/2}\) peaks at 159.9 and 161.4 eV. These two S\(_{2p3/2}\) peaks were the same position as that after the 1st full discharge (cut-off of 0 V) (**Fig. 4-14** (b)). It was found that the irreversible structure changes of \( a \)-MoS\(_3\) occurred even though the cut-off potential of the cell with \( a \)-MoS\(_3\) was the same as that with \( a \)-TiS\(_3\).

Finally, the difference of the 1st reversibility of \( a \)-TiS\(_3\) and \( a \)-MoS\(_3\) is discussed. The electrode of \( a \)-TiS\(_3\) was composed of S\(^{2-}\) and S\(^{2-}\) species and the electronic structures of sulfurs were similar to those in \( c \)-TiS\(_3\). The electronic structures of these sulfur species changed reversibly during the 1st charge-discharge tests and thus the coulombic efficiency of the cell with \( a \)-TiS\(_3\) was almost 100%. The reversible changes of sulfur electronic structures in \( a \)-TiS\(_3\) were observed up to the 10th cycle and this brought about good cyclability of \( a \)-TiS\(_3\). On the other hand, the electronic structures of sulfurs in \( a \)-MoS\(_3\) were S\(^{2-}\) and S\(^{δ-}\). The S\(_{2p}\) XPS spectrum was shifted to lower binding energy side after the 1st full discharge. The peak positions of two S\(_{2p3/2}\) peaks after the 1st charge were different from those before tests and
Figure 4-18 (a) The 1st charge-discharge curve of all-solid-state cell with α-MoS₃ at the cut-off voltage of 0.5 V and (b) the S₂p XPS spectra of α-MoS₃ after the 1st charge.
almost the same as those after the 1st full discharge. As a result, the 1st reversibility of the cell with $a$-MoS$_3$ was inferior compared to that with $a$-TiS$_3$. Because the $S_{2p}$ XPS and $S$ K-edge XANES profiles after the 10th charge were similar to those after the 1st full discharge, the electronic structures of sulfur after the 10th charge were similar to those after the 1st charge. Therefore, the cell showed good cyclability up to the 10th cycle. As described above, $a$-TiS$_3$ showed a superior initial reversibility. Sulfurs ($S^{2-}$ and $S_2^{2-}$) and titanium atoms in $a$-TiS$_3$ have chemical bonding similar to that in $c$-TiS$_3$ and strong interactions between the sulfurs and titanium would retain during the 1st cycle. On the other hand, $S^{δ-}$ in $a$-MoS$_3$ may have weaker interactions to molybdenum atoms than $S^{2-}$ in MoS$_2$ nano-clusters. One of the reason is the fact that $a$-MoS$_3$ was prepared by milling of crystalline sulfur and molybdenum metal. The difference in sulfur electronic structures is a possible reason for the 1st irreversible capacity in $a$-MoS$_3$. Sulfurs species lithiated at the 1st discharge process have similar electronic structures as sulfurs after the 1st and 10th charge, and thus sulfurs formed at the 1st discharge would have strong interactions to molybdenum atoms. In order to design the sulfur-rich transition metal sulfide electrodes with high capacity as well as good cyclability, sufficient interactions between sulfur and transition metal in the electrodes is important.

### 4.4. Summary

Amorphous MoS$_3$ ($a$-MoS$_3$) was successfully prepared by ball milling of the mixture of Mo metal and sulfur. The present XRD, DTA, SEM, HR-TEM, XPS and XANES experiments revealed that $a$-MoS$_3$ is characterized by the random distribution of the nano-sized domains consisting of clusters of crystalline MoS$_2$ ($c$-MoS$_2$). The XPS measurements revealed that amorphous MoS$_3$ should consist of Mo$^{4+}$, S$^{2-}$, and S$^{δ-}$. The 1st discharge capacity of the all-solid-state cell with the $a$-MoS$_3$ was approximately 760 mAh g$^{-1}$. The capacity was higher
than 670 mAh g⁻¹ (the capacity corresponding to the insertion of 4 molar Li to MoS₂). The cell with a-MoS₃ electrode retained discharge capacity of about 670 mAh g⁻¹ for 60 cycles. The a-MoS₃ had higher capacity than the c-MoS₂. In the XRD patterns of the a-MoS₃ electrodes after the 1st discharge and charge tests for 10 cycles, only the halo patterns due to the amorphous state were observed without the crystalline diffraction peaks. These imply that MoS₃ electrodes after the 10th charge-discharge measurements were characterized as the amorphous state. In addition, good interface contacts between a-MoS₃ electrodes and sulfide solid electrolytes retained during 10 cycles. The HR-TEM observations of a-MoS₃ electrodes during the 1st discharge test revealed that the lattice fringes due to MoS₂ layer structure disappeared gradually. After the 1st full discharge, the lattice fringes were not observed and the electron diffraction showed halo pattern. However, the lattice fringes like MoS₂ were observed again after the 1st charge. These results of HR-TEM observations suggested that the reversible structural changes of a-MoS₃ occurred. The HR-TEM image after the 10th charge showed no lattice fringes of MoS₂. It is concluded that MoS₃ after the 10th charge was completely amorphous. The S₂p XPS and S K-edge XANES profiles after the 1st and 10th charge process were similar to those after the 1st discharge and were different from those before charge-discharge measurements. The irreversible sulfur redox of both S²⁻ and S⁵⁻ in a-MoS₃ was observed, while the reversible electronic structure changes of molybdenum were observed at the 1st cycle. The all-solid-state cell with a-MoS₃ showed relatively good cyclability except for the 1st cycle. Electrochemical performance of the cells using a-MS₃ (M: Ti and Mo) was affected by electronic structures of sulfurs in a-MS₃.
4.5. References


5. General conclusions

In this thesis, amorphous TiS\textsubscript{x} (a-TiS\textsubscript{x}) thin film electrodes were prepared by the pulsed laser deposition (PLD) method and their application to all-solid-state lithium batteries with sulfide-based and oxide-based solid electrolytes. The electrochemical performance and the structural changes of amorphous TiS\textsubscript{3} (a-TiS\textsubscript{3}) and amorphous MoS\textsubscript{3} (a-MoS\textsubscript{3}) electrode particles in all-solid-state cells using Li\textsubscript{2}S-P\textsubscript{2}S\textsubscript{5} solid electrolytes were investigated.

The following results and considerations were obtained.

1. Thin film electrodes of a-TiS\textsubscript{x} (x=0.71~9) were prepared by PLD. Deposition conditions such as ambient gas, laser fluence and target-substrate distance affected the chemical compositions of the thin films determined by EDX. XRD and TEM analyses revealed that the TiS\textsubscript{x} thin films were amorphous. Among a-TiS\textsubscript{x} thin film electrodes, the all-solid-state cell with a-TiS\textsubscript{3} thin film electrodes and Li\textsubscript{2}S-P\textsubscript{2}S\textsubscript{5} sulfide solid electrolytes showed the highest capacity of 543 mAh g\textsuperscript{-1}.

2. The all-solid-state lithium cells with a-TiS\textsubscript{4} thin film electrodes and Li\textsubscript{3}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (LLZ) or LLZ-Li\textsubscript{3}BO\textsubscript{3} electrolytes were fabricated. The both cells operated as lithium secondary batteries at room temperature and their reversible capacities were about 500 mAh g\textsuperscript{-1}. The rate performances of the cells with LLZ and LLZ-Li\textsubscript{3}BO\textsubscript{3} solid electrolytes were examined. The thin film electrode of a-TiS\textsubscript{4} showed the reversible capacity of over 500 mAh g\textsuperscript{-1} in the all-solid state cells using sulfide and oxide solid electrolytes. It is concluded that sulfur redox in the a-TiS\textsubscript{4} film was utilized in addition to the redox chemistry for TiS\textsubscript{2}.

3. The positive electrode particles of a-TiS\textsubscript{3} were prepared by mechanical milling of the equimolar mixture of crystalline TiS\textsubscript{2} (c-TiS\textsubscript{2}) and sulfur. The 1st capacity of the all-solid-state cell with the a-TiS\textsubscript{3} at the cell potential window between 0.9-2.4 V vs. Li-In was about 400 mAh g\textsuperscript{-1}. The a-TiS\textsubscript{3} had higher capacity than the equimolar mixture c-TiS\textsubscript{2} and sulfur crystals, which were used as starting materials of the a-TiS\textsubscript{3}. It is suggested that the high capacity resulted from the amorphization of TiS\textsubscript{3}. 

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4. The all-solid-state lithium cells with crystalline and amorphous TiS$_3$ at the cell potential window of 0.6-2.4 V vs. Li-In showed the 1st discharge capacity of about 560 mAh g$^{-1}$, corresponding to the theoretical capacity of TiS$_3$. However, the cell using c-TiS$_3$ had irreversible capacity at the 1st charge process. The cell showed reversible capacity of about 400 mAh g$^{-1}$ from the 2nd to 10th cycle. On the other hand, the irreversible capacities were not observed for 10 cycles in the cell with a-TiS$_3$. The structural changes of crystalline and amorphous TiS$_3$ were observed by XRD and HR-TEM during cycling. The electrode of c-TiS$_3$ became partially amorphous during the cycling. The electrode of a-TiS$_3$ maintained amorphous state for 10 cycles and thus had better cyclability compared to c-TiS$_3$.

5. The electrochemical reaction mechanism of a-TiS$_3$ electrodes was clarified. From the XPS and XANES results, it was revealed that the reversible sulfur redox of both S$^{2-}$ and S$_2^{2-}$ in a-TiS$_3$ mainly occurred during charge-discharge process for 10 cycles. Therefore, the all-solid-state cell using a-TiS$_3$ electrodes shows the stable cycle performance for 10 cycles.

6. Novel a-TiS$_3$/S/KB composite electrode active materials were prepared. The reversible capacity of the coin type liquid cell with a-TiS$_3$/S/KB decreased from 484 to 33 mAh g$^{-1}$ during 50 charge-discharge cycles because the polysulfides formed from a-TiS$_3$/S/KB were dissolved in liquid electrolytes. On the other hand, the all-solid-state cells using a-TiS$_3$/S/KB composite electrodes showed higher reversible capacity and better cyclability, compared to the coin type cells with liquid electrolytes. In addition, the all-solid-state cell using a-TiS$_3$/KB/S showed a higher reversible capacity of about 650 mAh g$^{-1}$ than the cell with a-TiS$_3$. The higher capacity was achieved because the additional sulfur in KB/S was used as an active material.

7. The electrode particles of a-MoS$_3$ were successfully prepared by mechanical milling of the mixture of Mo metal and sulfur. A halo pattern was observed in the XRD of a-MoS$_3$ after milling for 80 hours. The XPS measurements revealed that a-MoS$_3$ should consist of Mo$^{4+}$, S$^{2-}$, and S$^{6-}$. The all-solid-state cell with the a-MoS$_3$ showed the 1st
reversible capacity of about 760 mAh g\(^{-1}\) and retained capacity of about 670 mAh g\(^{-1}\) for 60 cycles. The cell using \(a\)-MoS\(_3\) exhibited higher capacity than the cell using \(c\)-MoS\(_2\).

8. The electrochemical reaction mechanism of \(a\)-MoS\(_3\) electrodes was clarified. Random distribution of the nano-sized domains consisting of clusters of crystalline MoS\(_2\) (\(c\)-MoS\(_2\)) was observed in \(a\)-MoS\(_3\) before the electrochemical tests by HR-TEM. The HR-TEM observations of \(a\)-MoS\(_3\) electrodes during the 1st discharge test revealed that the lattice fringes due to MoS\(_2\) layer structure disappeared gradually. After the 1st full discharge, the lattice fringes were not observed and the electron diffraction showed halo pattern. However, the lattice fringes like MoS\(_2\) were observed again after the 1st charge. These results of HR-TEM observations suggested that the reversible structural changes of \(a\)-MoS\(_3\) occurred. The HR-TEM image after the 10th charge showed no lattice fringes of MoS\(_2\). It is concluded that MoS\(_3\) after the 10th charge was completely amorphous. The S\(_{2p}\) XPS and S \(K\)-edge XANES profiles after the 1st and 10th charge process were similar to those after the 1st discharge and were different from those before charge-discharge measurements. The irreversible sulfur redox of both S\(^{2-}\) and S\(^{5-}\) in \(a\)-MoS\(_3\) was observed at the 1st cycle, while the reversible electronic structure changes of molybdenum were observed. The all-solid-state cell with \(a\)-MoS\(_3\) showed relatively good cyclability except for the 1st cycle. Electrochemical performance of the cells using \(a\)-MS\(_3\) (M: Ti and Mo) was affected by electronic structures of sulfurs in \(a\)-MS\(_3\).
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List of Publications

Original articles regarding this study are as follows:

1. “Preparation of amorphous TiS$_x$ thin fil electrodes by the PLD method and their application to all-solid-state lithium secondary batteries”
   T. Matsuyama, A. Sakuda, A. Hayashi, Y. Togawa, S. Mori and M. Tatsumisago,
   (Chapter 2)

2. “Fabrication of all-solid-state lithium secondary batteries with amorphous TiS$_4$ positive electrodes and Li$_7$La$_3$Zr$_2$O$_{12}$ solid electrolytes”
   T. Matsuyama, R. Takano, K. Tadanaga, A. Hayashi and M. Tatsumisago,
   (Chapter 2)

3. “Amorphous titanium sulfide electrode for all-solid-state rechargeable lithium batteries with high capacity”
   A. Hayashi, T. Matsuyama, A. Sakuda and M. Tatsumisago,
   (Chapter 3)

4. “Electrochemical properties of all-solid-state lithium batteries with amorphous titanium sulfide electrodes prepared by mechanical milling”
   T. Matsuyama, A. Sakuda, A. Hayashi, Y. Togawa, S. Mori and M. Tatsumisago,
   (Chapter 3)

5. “Improved electrochemical performance of amorphous TiS$_3$ electrodes compared to its crystal for all-solid-state rechargeable lithium batteries”
   T. Matsuyama, A. Hayashi, T. Ozaki, S. Mori and M. Tatsumisago,
   (Chapter 3)
6. “Amorphous TiS$_3$/S/C composite positive electrodes with high capacity for rechargeable lithium batteries”
   T. Matsuyama, A. Hayashi, C. J. Hart, L. F. Nazar and M. Tatsumisago,
   (Chapter 3)

7. “Structure analyses using X-ray photoelectron spectroscopy and X-ray absorption near edge structure for amorphous MS$_3$ (M: Ti, Mo) electrodes in all-solid-state lithium batteries”
   T. Matsuyama, M. Deguchi, K. Mitsuhara, T. Ohta, T. Mori, Y. Orikasa, Y. Uchimoto, Y. Kowada, A. Hayashi and M. Tatsumisago,
   *J. Power Sources*, submitted.
   (Chapter 3, 4)

8. “Electrochemical properties of all-solid-state lithium batteries with amorphous MoS$_3$ electrodes prepared by mechanical milling”
   T. Matsuyama, A. Hayashi, T. Ozaki, S. Mori and M. Tatsumisago,
   (Chapter 4)

9. “Structure analyses of amorphous MoS$_3$ active materials in all-solid-state lithium batteries”
   T. Matsuyama, M. Deguchi, A. Hayashi, M. Tatsumisago, T. Ozaki, Y. Togawa and S. Mori,
   (Chapter 4)