Conventional lithium-ion batteries using organic liquid electrolytes have been used extensively as power sources for mobile devices and personal computers.1,2 Increasingly, they have been scaled up for use in large applications for electric vehicles and smart grids.3 However, traditional lithium ion batteries containing a transition metal oxide cathode and a graphite anode are not able to satisfy energy density demands for many applications.4,5

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 LiCoO₂.6,7 In addition, sulfur has many other advantages of which is at least 5 times higher than that of the transition metal oxides such as LiCoO₂. In our previous studies, sulfur-rich transition metal sulfides such as amorphous TiS₂ (a-TiS₂), amorphous MoS₂ (a-MoS₂) were reported.31–33 These active materials exhibited higher reversible capacity than TiS₂ and MoS₂ in all-solid-state cells. In addition, it was reported that all-solid-state cells using a-TiS₂ electrodes maintained better cyclability than cells using c-TiS₃ electrodes.34 Sakuda et al. have also shown that amorphous TiS₃ electrodes showed reversible capacities of about 700 mAh g⁻¹ in lithium batteries using liquid electrolytes.35 This capacity was higher than that of a-TiS₂ (560 mAh g⁻¹). These results suggest that amorphous sulfur-rich transition metal sulfides have a high capacity owing to additional sulfur content in the redox. Moreover, it is reported that the dissolution of polysulfide into the electrolyte was significantly suppressed by amorphous TiS₃, because of the chemical binding between Ti and S.36

For increasing the capacity beyond TiS₂, electrode active materials such as amorphous TiS₄ (x = 4) (a-TiS₄) are promising. However, although one might expect that the electronic conductivity of a-TiS₄ would decrease with increasing sulfur content, we show here that a-TiS₄ electrodes with high capacity and good cyclability can be realized by combining a-TiS₃ and sulfur/carbon composites.

To inhibit the dissolution of lithium polysulfides, the use of inorganic solid electrolytes instead of organic liquid electrolytes is an effective approach. Among many types of lithium ion conductive solid electrolytes, sulfide materials are known to exhibit higher ionic conductivity than oxide materials because of the higher polarizability of sulfide ions.36–38 Sulfide-based solid electrolytes such as crystalline Li₉GeP₂S₁₂39 and Li₂S-P₂S₅ glass-ceramics40 have a high lithium-ion conductivity of almost 10⁻² S cm⁻¹ at room temperature, which is comparable to the conductivity of conventional organic liquid electrolytes. LiS cells using Li₃S-P₂S₅ solid electrolytes have exhibited good cycling performance,41–43 so sulfide electrolytes are suitable for application to all-solid-state batteries with a-TiS₃ electrodes. In this study, we have prepared a-TiS₃/S/carbon composites by mechanical milling mixtures of a-TiS₃ and S/several carbon composites. The electrochemical properties of coin type cells utilizing organic liquid electrolytes, and all-solid-state cells using sulfide solid electrolytes with a-TiS₃/S/carbon composite electrodes were examined. Four types of carbons encompassing Ketjen black (KB), CMK-3, CMK-4, and CMK-5 were used as carbon materials.

Amorphous TiS₃/S/C Composite Positive Electrodes with High Capacity for Rechargeable Lithium Batteries

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Composite electrodes of a-TiS₃/S/carbon (Ketjen black; KB) with high capacity were prepared by mechanical milling from a-TiS₃ and S/KB composites. The composites were fabricated into coin type liquid cells and all-solid-state cells and operated as rechargeable batteries at room temperature. The reversible capacity of the coin type liquid cells decreased from 484 to 33 mAh g⁻¹ over 50 charge-discharge cycles, because the polysulfides formed from the redox reactions of a-TiS₃/S dissolved in the liquid electrolyte. On the other hand, the all-solid-state cells showed higher reversible capacity and better cyclability than the coin type liquid cells. In order to improve their cycle performance, solid electrolyte (SE) powders were added to the composite electrodes to serve as lithium-ion conduction paths to the active materials. The cell using the a-TiS₃/S/KB composite with 30 wt% SE exhibited the highest reversible capacity of about 850 mAh g⁻¹ at the 1st cycle and retained a reversible capacity of about 650 mAh g⁻¹ after the 50th cycle. Owing to their relatively high sulfur content, composite positive electrodes of a-TiS₃/S/KB are attractive positive electrodes with high capacities for all-solid-state lithium secondary batteries.

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PCNS and graphite were used. Because the cell with the KB composite showed the best cell performance, we primarily report these results.

Experimental

Amorphous TiS$_3$ (\textit{a}-TiS$_3$) electrode active materials were prepared using mechanical milling of crystalline TiS$_3$ (\textit{c}-TiS$_3$) prepared by solid-state reaction. The starting material, \textit{c}-TiS$_3$, was milled mechanically at ambient temperature using a planetary ball mill apparatus (Pulverisette 7, Fritsch) with an zirconia pot (volume of 45 ml) and 500 zirconia balls (4 mm diameter). The rotational speed was set to 370 rpm and the milling time was 40 h. A 70 wt% sulfur containing composite (S/KB) was prepared by via a melt diffusion technique at 155 °C. Composites of S/CMK-3, S/PCNS$^{23}$ and S/graphite were prepared in the same manner.

Amorphous TiS$_3$/S/KB (\textit{a}-TiS$_3$/S/KB) electrodes were prepared by mechanical milling. Prepared \textit{a}-TiS$_3$ and the S/KB composite were used as the starting materials in a molar ratio of 1/2. The mixture of the materials was milled mechanically at ambient temperature using the ball milling parameters were as above and the milling time was 20 h.

To examine the crystallinity of the prepared samples, X-ray diffraction was carried out using a X-ray diffractometer (CuK$_\alpha$, UltimaIV; Rigaku Corp.). Surface areas of KB, S/KB and \textit{a}-TiS$_3$/S/KB were determined from nitrogen adsorption and desorption isotherms performed on an Autosorb-1; Quantachrome at 77 K. Surface areas were determined from nitrogen adsorption and desorption isotherms performed on an Autosorb-1; Quantachrome at 77 K. Surface areas of the S/KB and \textit{a}-TiS$_3$/S/KB composites were evaluated using a field emission scanning electron microscopy (FE-SEM, SU8220; HITACHI).

Coin cells with 2325 type using organic liquid electrolytes were fabricated as follows: the S/KB, \textit{a}-TiS$_3$ or \textit{a}-TiS$_3$/S/KB electrodes were formed by drop casting a slurry onto a carbon-coated aluminum or carbon paper current collector, and drying the electrodes at 60 °C overnight. In these experiments, 80 wt% of S/KB composite, 10 wt% Super P and 10 wt% poly(vinylidene fluoride) (PVDF) were mixed with N, N-dimethylformamide to form the slurry for drop coating. Different electrode ratios were also examined: coin type cells consisting of \textit{a}-TiS$_3$ and \textit{a}-TiS$_3$/S/KB were fabricated with electrodes consisting of 70 wt% of \textit{a}-TiS$_3$ or \textit{a}-TiS$_3$/S/KB composite, 20 wt% Super P and 10 wt% PVDF (also mixed with N, N-dimethylformamide to form a slurry). The mass loading of the electrode was 1 mg cm$^{-2}$. 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 LiNO$_3$. Lithium metal foil was used as the negative electrode, and was electronically isolated using 2 sheets of Celgard 3501 separators. All the processes described above were conducted in a dry Ar glove box. The coin type cells with S/KB were discharged and charged on the 1st cycle in a voltage window between 1.9 and 3.0 V at a current density of 0.084 mA cm$^{-2}$. The voltage was set between 1.8 and 3.0 V at a current density of 0.84 mA cm$^{-2}$ after the 2nd cycle. Coin cells with \textit{a}-TiS$_3$ and \textit{a}-TiS$_3$/S/KB were cycled in a voltage window between 1.8 and 3.0 V at a current density of 0.064 mA cm$^{-2}$. Electrochemical studies were performed using a cycler (BT-2000; Arbin) in galvanostatic mode at room temperature.

All-solid-state electrochemical cells were fabricated as follows: an 80Li$_2$S·20P$_2$S$_5$ (mol%) solid electrolyte was prepared by mechanical milling and then heated at 210 °C for 1 h. The S/KB, \textit{a}-TiS$_3$ and \textit{a}-TiS$_3$/S/KB electrodes were used as active materials. The working electrode was prepared by mixing the active materials and the solid electrolyte. The weight ratios of electrodes were 100/0, 70/30, or 40/60. The obtained working electrode (10 mg) and the solid electrolyte were placed in a polycarbonate tube (10 mm diameter) and pressed together under 360 MPa of pressure. A Li–In alloy was placed on the solid electrolyte layer to serve as a counter and reference electrode, and a pressure of 120 MPa was applied to the three-layered pellet. Finally, two electrode cells sandwiched by two stainless-steel disks that functioned as a current collector were obtained. All the processes described above were conducted in a dry Ar glove box. The electrochemical tests were conducted at 25 °C in an Ar atmosphere using a cycler (BTS-2004; Nagano Co.). To analyze the structure of the working electrode, XRD measurements and cross-sectional FE-SEM observations were carried out with an energy dispersive X-ray spectroscopy system (EDX, MAXEvolution X-Max; Horiba, Ltd.) for the working electrodes before and after electrochemical testing. The cross sections of the working electrodes were thinned down for analysis using an ion milling system (IM4000; HITACHI).

Results and Discussion

Figure 1a shows the XRD patterns of S/KB samples before and after heating, and \textit{a}-TiS$_3$/S/KB prepared by mechanical milling. Peaks attributable to sulfur were observed for the S/KB sample before heating, but their intensity decreased after heating. This suggests that elemental sulfur was incorporated into the pores of KB. Figure 1b shows the thermogravimetric analysis (TGA) profile of the S/KB sample. The weight loss between 200 to 300 °C indicates a sulfur content of 70 wt%. A halo pattern was observed in the XRD pattern of TiS$_3$/S/KB indicating it is amorphous. In addition, specific surface areas of the prepared samples were examined by BET measurements. The results are listed in Table I. The specific surface area of KB was 1117 m$^2$ g$^{-1}$. The specific surface area of S/KB was reduced to 21.6 m$^2$ g$^{-1}$.

![Figure 1](https://example.com/figure1.png)

Figure 1. (a) XRD patterns of S/KB samples before and after heating and of \textit{a}-TiS$_3$/S/KB prepared by mechanical milling and (b) TGA curve of the S/KB sample after heating.
Table I. Specific surface area of KB, S/KB and α-TiS$_3$/S/KB.

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<th>Samples</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
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<tr>
<td>KB</td>
<td>1117</td>
</tr>
<tr>
<td>S/KB</td>
<td>21.6</td>
</tr>
<tr>
<td>α-TiS$_3$/S/KB</td>
<td>4.6</td>
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by the inclusion of sulfur within the pores, whereas the specific surface area of α-TiS$_3$/S/KB was 4.6 m$^2$ g$^{-1}$. FE-SEM images of S/KB sample after heating (a) and α-TiS$_3$/S/KB (b) are shown in Fig. 2. The FE-SEM image of the S/KB sample indicated that the particle sizes were about 100 nm. Secondary particles of several microns in size, formed by agglomeration of submicron-sized ordinary particles, were mainly observed in the FE-SEM image of the α-TiS$_3$/S/KB composite (Fig. 2b). The agglomeration decreased the specific surface area of α-TiS$_3$/S/KB.

Figure 3 shows (a) the initial charge-discharge curves and (b) the cycle performance of the liquid electrolyte coin cells with S/KB, α-TiS$_3$ and α-TiS$_3$/S/KB. The cell with S/KB was run at a 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 α-TiS$_3$ and α-TiS$_3$/S/KB were conducted at a current density of 0.064 mA cm$^{-2}$ at 25°C. The cell with S/KB showed reversible capacities of about 1200 mAh g$^{-1}$ and 800 mAh g$^{-1}$ at the 1st and the 100th cycle. This electrochemical performance is similar to that of previous reports. On the other hand, the initial reversible capacities of the cells using α-TiS$_3$ and α-TiS$_3$/S/KB were about 400 and 500 mAh g$^{-1}$, respectively. The cell with α-TiS$_3$/S/KB showed higher reversible capacity than the cell with α-TiS$_3$, because the additional sulfur in the S/KB reacted with Li during the discharge process. The cycling performance of the liquid cells with α-TiS$_3$ and α-TiS$_3$/S/KB deteriorated during the electrochemical tests, however. We assume this is due to dissolution of polysulfides produced from α-TiS$_3$ during discharge process. To clarify detailed reaction process, electronic structures of sulfur and titanium elements in α-TiS$_3$ during cycling need to be analyzed. Sakuda et al. have reported that coin cells using liquid electrolytes and α-TiS$_4$/acetylene black (AB) composite showed stable cyclability. They explained that the chemical binding between Ti and S formed by the amorphization procedure suppressed the dissolution of polysulfide into the electrolyte. Furthermore, the dispersion of AB inside the α-TiS$_4$ was effective in improving the cycle performance. In our study, ineffective dispersion of KB inside TiS$_3$ might have led to unstable cycling performance. We prepared S/carbon composites using the other carbon materials such as CMK-3, PCNS and graphite in a similar manner. The initial and the 100th charge and discharge capacities of the coin type liquid cells with α-TiS$_3$/S/CMK-3, α-TiS$_3$/S/PCNS and α-TiS$_3$/S/graphite are summarized in Table II. The capacities of the cell with α-TiS$_3$/S/KB are also shown for comparison in


<table>
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<th>Capacity (mAh g$^{-1}$)</th>
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<tr>
<td></td>
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<tr>
<td>1st discharge 1st charge 100th discharge 100th charge</td>
</tr>
<tr>
<td>a-TiS$_3$/S/KB</td>
</tr>
<tr>
<td>a-TiS$_3$/S/CMK-3</td>
</tr>
<tr>
<td>a-TiS$_3$/S/PCNS</td>
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<tr>
<td>a-TiS$_3$/S/graphite</td>
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Figure 2. FE-SEM images of (a) S/KB; (b) the α-TiS$_3$/S/KB composite.
Figure 4. Initial charge-discharge curves of the all-solid-state cells with α-TiS_{3}/S/KB, α-TiS_{3}/S/CMK-3, α-TiS_{3}/S/PCNS and α-TiS_{3}/S/graphite.

Table II. Capacity degradation of the all-solid-state cells with α-TiS_{3}/S/KB, α-TiS_{3}/S/CMK-3, α-TiS_{3}/S/PCNS and α-TiS_{3}/S/graphite in the voltage window between 1.9 and 3.0 V at a current density of 0.084 mA cm\(^{-2}\). The 2nd reversible capacities of the cells with S/CMK-3, S/PCNS and S/graphite are shown in Table II. The initial charge-discharge curves and (b) the cycling performance of the all-solid-state cells with α-TiS_{3}/S/KB, α-TiS_{3}/S/TiS_{3}/S-1 and α-TiS_{3}/S/TiS_{3}/S-2 at 25°C, 0.064 mA cm\(^{-2}\) from 25°C to 30°C.

Figure 5. (a) Initial charge-discharge curves and (b) cycling performance of the all-solid-state cells with α-TiS_{3}/S/KB, α-TiS_{3}/S/TiS_{3}/S-1, α-TiS_{3}/S/TiS_{3}/S-2 and α-TiS_{3}/S/S-1. The capacity degradation of α-TiS_{3}/S/KB prepared from α-TiS_{3} and S/KB was about 10\(^{-3}\) S cm\(^{-2}\), which is similar to the conductivity of α-TiS_{3} itself. The α-TiS_{3}/S/KB electrode exhibited a higher capacity than the α-TiS_{3} electrode, suggesting that additional sulfurs in S/KB were used as active material in the α-TiS_{3}/S/KB electrode. The additional sulfurs in α-TiS_{3}/S/KB electrode thus contribute to a reversible capacity because of the conductive feature of α-TiS_{3}. Both all-solid-state cells with α-TiS_{3} and α-TiS_{3}/S/KB showed better cyclability than the liquid electrolyte cells. In particular, the cell comprised of α-TiS_{3} alone showed a promising reversible capacity of about 450 mAh g\(^{-1}\) at the 50th cycle without significant capacity fading. However, capacity degradation of α-TiS_{3}/S/KB was observed, with a reversible capacity of only 250 mAh g\(^{-1}\) being attained on the 50th cycle. This is explained below.

In order to improve the cycle performance of the cell with α-TiS_{3}/S/KB, working electrodes were prepared with a sulfide solid electrolyte. These were assembled by hand-mixing α-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 6 shows (a) the initial charge-discharge curves and (b) the cycling performance of the all-solid-state cells with α-TiS_{3}/S/KB composites. The cell using the α-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. Forming favorable contacts among the electrode components of α-TiS_{3}/S/KB and the sulfide solid electrolytes should clearly be effective in improving the reversible capacity of all-solid-state cells. However, the initial irreversible capacity of the cell with the α-TiS_{3}/S/KB composite with 60 wt% SE decreased to 650 mAh g\(^{-1}\) over cycling. After the 50th cycle, the all-solid-state cells using the electrodes with 0, 30, and 60 wt% SE showed a capacity of about 250, 650 and 370 mAh g\(^{-1}\), respectively. Although capacity degradation was observed in all the cells, the cell using α-TiS_{3}/S/KB composite with 30 wt% SE retained higher reversible capacity than the cell using α-TiS_{3} after the 50 cycles.

Figure 7 shows the XRD pattern of the α-TiS_{3}/S/KB working electrodes without solid electrolytes before cycling and after the 50th
Figure 6. (a) Initial charge-discharge curves and (b) cycle performance of the all-solid-state cells using α-TiS$_3$/S/KB composites with 0, 30 and 60 wt% solid electrolyte.

Figure 8. Cross-sectional FE-SEM images and EDX elemental mapping images for S, Ti and C of the α-TiS$_3$/S/KB working electrodes without solid electrolytes (a) before cycling; and (b) after the 50th charge-discharge.

Conclusions

Novel α-TiS$_3$/S/KB electrode active materials were prepared. The reversible capacity of coin cells using a liquid electrolyte and an α-TiS$_3$/S/KB cathode decreased from 484 to 33 mAh g$^{-1}$ during 50 charge-discharge cycles, because polysulfides formed from α-TiS$_3$/S/KB were dissolved in the electrolyte. Capacity degradation of α-TiS$_3$/S/graphite cells was also observed. The cells using...
all-solid-state cells using α-TiS₃/PCNS/S also showed a shuttle phenomenon as early as the 2nd charging process. On the other hand, all-solid-state cells using α-TiS₃/KB composite electrodes showed a higher reversible capacity and better cyclability. In addition, all-solid-state cells with α-TiS₃/KB/S showed a higher reversible capacity (650 mAh g⁻¹) than the cell with α-TiS₃. We believe this is because the additional sulfur in KB/S can be utilized as an active material, while maintaining the amorphous state of the α-TiS₃/KB/S. That makes this material, with a high sulfur content, attractive as a high capacity positive electrode for all-solid-state lithium secondary batteries.

Acknowledgments

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