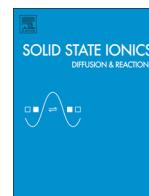




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Composite positive electrode based on amorphous titanium polysulfide for application in all-solid-state lithium secondary batteries

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ABSTRACT

Composite electrodes composed of amorphous titanium polysulfide (a-TiS_x) and titanium disulfide (TiS₂) were designed for application in all-solid-state batteries. The conductivity of the a-TiS_x/TiS₂-based working electrode was higher than that of the amorphous TiS₄ (a-TiS₄); the reversible capacity of the cell using a-TiS_x/TiS₂ electrode was higher than that of the cell using a-TiS₄. Designing nanocomposite materials such as the a-TiS_x/TiS₂ described in this paper is an effective way to improve the performance of all-solid-state batteries.

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1. Introduction

Development of high-energy-density rechargeable lithium batteries is highly desirable. Lithium–sulfur batteries are promising candidates for high-energy-density rechargeable lithium batteries because lithium–sulfur batteries exhibit high theoretical energy density [1–4]. However, several challenges must be overcome before sulfur-based electrodes can be practically used in lithium–sulfur batteries. The challenges include (i) improving the electrical conductivity of sulfur, which is intrinsically an insulator and (ii) suppressing the dissolution of polysulfides into the electrolyte. The polysulfides are formed when a battery is discharged and charged, and they reduce the coulomb efficiency through the well-known polysulfide shuttle mechanism [5].

Crystalline metal sulfides have also been studied as materials for preparing positive electrodes [6–9]. Such metal sulfides generally show high electronic conductivity and low solubility in electrolytes, and these properties make using metal sulfides advantageous for constructing Li/metal-sulfide batteries. However, the theoretical capacity of metal sulfides is significantly lower than that of elemental sulfur. Therefore, using a hybrid of metal sulfides and elemental sulfur would be a promising approach for developing an electrode material that can be applied in rechargeable batteries that satisfy the high-energy-density requirement. We have focused on amorphous metal polysulfide

materials toward that goal [10–13]. Although there are only a few crystalline metal polysulfides that have high sulfur content, materials with a wide range of compositions, including sulfur-rich materials, can be obtained through amorphization. Thus, amorphous metal polysulfides are promising candidates as electrode materials for application in the above-mentioned Li/metal-sulfide batteries.

Electrodes prepared using amorphous titanium trisulfide particles were recently reported to have a high reversible capacity of ca. 400 mAh g⁻¹ in all-solid-state batteries [11]. This reversible capacity was beyond that reported for crystalline TiS₃ (ca. 350 mAh g⁻¹) in the 2 V vs. Li/Li⁺ region [12]. The reversible capacity of metal-sulfide-based electrodes can be further increased by increasing the sulfur content in metal sulfides such as TiS_x (x > 3), assuming that the electrochemical reaction is mainly responsible for the redox reaction of sulfur atoms. However, the high sulfur content in amorphous TiS_x (a-TiS_x) increases the solubility of the material in electrolytes and decreases the conductivity of the material, which usually decreases the cycle performance and capacity of electrodes prepared using amorphous TiS_x. Thus, it is necessary to design composites that exhibit high conductivity. We have previously reported that electrodes prepared using nanocomposites consisting of a-TiS_x and acetylene black showed high capacity in ether-based liquid electrolytes [13]. The nanocomposite-based electrodes showed a high capacity of ca. 700 mAh g⁻¹ around the 2 V vs. Li/Li⁺ region and low solubility in liquid electrolytes.

In contrast to the above-mentioned liquid-electrolyte batteries, all-solid-state batteries require the design of alternative materials so that metal polysulfides can be used as electrodes. Although polysulfides do not dissolve in the electrolytes used in all-solid-state batteries,

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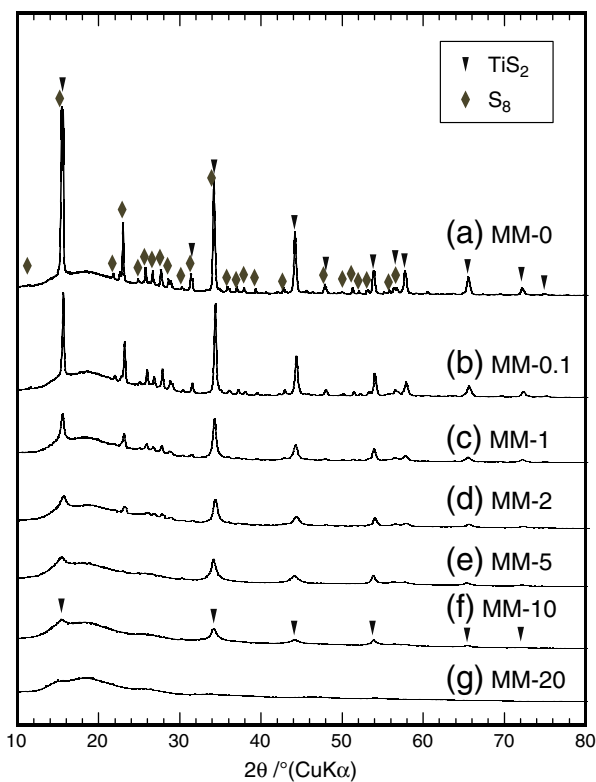


Fig. 1. XRD patterns for composites prepared by mechanically milling mixture of TiS_2 and S_8 for (a) 0, (b) 0.1, (c) 1, (d) 2, (e) 5, (f) 10, or (g) 20 h. Atomic ratio of Ti to S in composites is fixed at 1:4.

electronic and ionic conduction at the interparticle contacts in such batteries are absolutely essential in order for the batteries to exhibit superior electrochemical performance [14].

In this study, composite electrodes composed of amorphous titanium polysulfide (a-TiS_x) and titanium disulfide (TiS_2) were designed for application in all-solid-state batteries. The composites were prepared by mechanically milling a mixture consisting of TiS_2 and elemental sulfur

(S_8) for various lengths of time. The structure, electronic conductivity, and electrochemical performance of the electrodes were investigated using all-solid-state cells prepared using $\text{Li}_2\text{S-P}_2\text{S}_5\text{-LiI}$ solid electrolytes.

2. Experimental

The titanium polysulfide composites composed of a-TiS_x and TiS_2 ($\text{a-TiS}_x/\text{TiS}_2$) were prepared using mechanical milling (MM). Crystalline TiS_2 (99.8%; Wako) and sulfur (99.9%; Wako) were used as the starting materials. The atomic ratio of Ti to S in the starting mixture was 1:4. Zirconia pots (45 mL) and 500 zirconia balls (4 mm in diameter) were used to ball-mill the mixture, and the planetary ball-mill apparatus (P-7, Fritsch) was operated at 370 rpm. A composite consisting of a-TiS_4 and acetylene black (AB) ($\text{a-TiS}_4/\text{AB}$) was prepared by mechanically milling a mixture consisting of a-TiS_4 (90 wt.%) and AB (10 wt.%) in the ball mill for 20 h. The starting materials and the obtained samples were treated in an Ar-filled glove box. X-ray diffraction (XRD) patterns were measured using an X-ray diffractometer (Rotaflex RU-200B/RINT, Rigaku). The samples used for the measurements were covered with Kapton® film in an Ar-filled glove box to prevent exposure to air.

Conductivities of the prepared samples were measured with a two electrode cell in an Ar-filled glove box. The pellets for the conductivity measurements were prepared by pressing the sample powder under 360 MPa at 25 °C.

The all-solid-state cells were constructed as follows. The active materials ($\text{a-TiS}_x/\text{TiS}_2$ mechanically milled for various lengths of time), $70(0.75\text{Li}_2\text{S} \cdot 0.25\text{P}_2\text{S}_5) \cdot 30\text{LiI}$ glass electrolyte, and AB were mixed in a weight ratio of 73:20:7 in an agate mortar to prepare the positive electrode material. $\text{Li}_2\text{S-P}_2\text{S}_5\text{-LiI}$ glass electrolyte exhibits a high ionic conductivity of more than $10^{-3} \text{ S cm}^{-1}$ [15–17]. A lithium–indium alloy was used as a counter electrode. Bilayer pellets consisting of the positive electrode material (10 mg) and the glass electrolyte (70 mg) were pressed under 360 MPa ($\varphi = 10 \text{ mm}$); an indium foil ($t = 0.3$, $\varphi = 9 \text{ mm}$) and a lithium foil ($t = 0.1$, $\varphi = 8 \text{ mm}$) were then attached to the bilayer pellets by pressing them all together under 100 MPa. The pellets were pressed using two stainless steel rods, which were used as current collectors for both the positive and negative electrodes. All the processes for preparing the electrochemical cells were performed in a dry Ar-filled glove box ($[\text{H}_2\text{O}] < 1 \text{ ppm}$).

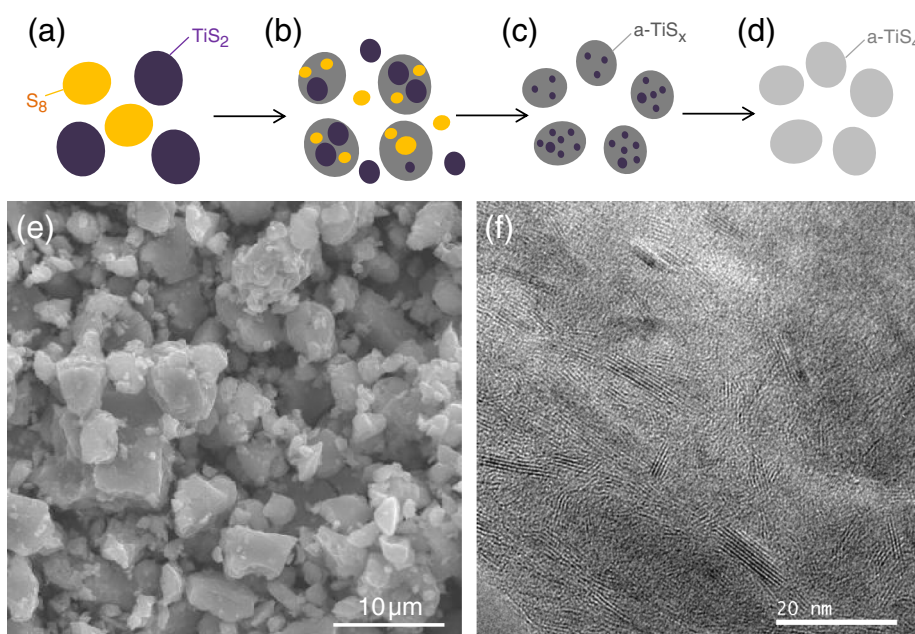


Fig. 2. (a–d) Schematics of composites ball-milled for various lengths of time. (a) TiS_2/S_8 mixture (MM-0), (b) $\text{a-TiS}_x/\text{TiS}_2/\text{S}_8$ nanocomposites (MM-1 and MM-2), (c) $\text{a-TiS}_x/\text{TiS}_2$ nanocomposites (MM-5 and MM-10), and (d) a-TiS_4 (MM-20). (e) SEM and (f) TEM images of MM-5 particles.

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