An all-solid-state lithium–sulfur battery using two solid electrolytes having different functions

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HIGHLIGHTS

- Ionic conductivity of $Li_{1.5}PS_{3.3}$ is increased by addition of LiI.
- The positive electrode included two SEs that have different functions.
- Improving sulfur reactivity and ionic conductivity using two kinds of SEs.
- The cell using the positive electrode was estimated to be 540 W h kg^{-1} at cell level.

ARTICLE INFO

ABSTRACT

All-solid-state lithium–sulfur batteries are expected to be valuable next generation batteries. To improve the performance of all-solid-state lithium–sulfur batteries, it is essential to raise both the reactivity of sulfur and the ionic conductivity of the positive composite electrode. For achieving this, we investigate a positive composite electrode prepared using P_2S_5 and a solid electrolyte with a high ionic conductivity. As a result, we have found that the lithium–sulfur cell exhibits a relatively low activation energy together with high ionic conductivity. The positive composite electrode exhibits an extremely high capacity of 1550 mA h g^{-1} (sulfur) at 1.3 mA cm^{-2} and 25 °C. Moreover, when using the positive electrode, the energy densities at the cell level (18650) are 540 W h kg^{-1} and 990 W h L^{-1}, estimated from the equivalent structure of a current lithium-ion battery.

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1. Introduction

Energy storage technology is becoming increasingly important as a consequence of the increased global usage of portable devices and the diversification of energy sources. Rechargeable batteries are one of the key energy storage technologies available. The development of high-performance batteries is therefore of great interest. Lithium–sulfur (Li–S) batteries are one of the next generation of batteries that are capable of meeting the demands of future electronic devices because elemental sulfur has an extremely high theoretical specific capacity of 1672 mA h g^{-1} [1]. However, there are several challenges in the development and use of lithium–sulfur batteries. The first problem is poor cycle stability resulting from the dissolution of lithium polysulfide [2]. The second

problem arises low reactivity of sulfur because that insulating characteristics [3].

Using an ionic liquid or solid electrolyte (SE) can alleviate the first problem because both electrolyte types do not dissolve lithium polysulfide and greatly improve cycle performance [4]. Using an SE, in particular, facilitates the simple incorporation of a bipolar structure in the cell because it can be limited to pass way of lithium ion transfer [5]. Furthermore, some SEs such as $Li_2S–P_2S_5$, $Li_2S–P_2S_5–LiI$, $Li_2S–P_2S_5–LiBH_4$, and $Li_2S–GeS_2–P_2S_5$ systems possess extremely high ionic conductivities and have shown lithium-ion conductivities exceeding 10^{-3} S cm^{-1} at 25 °C [6–9]. Here the SEs have lithium-ion transference numbers of almost 1 [10]. These compounds clearly exhibit high conductivities that are same as or greater than those of organic liquid electrolytes.

To address the second problem, we have previously reported that the reactivity of sulfur is improved by an SE with a high P/S ratio (i.e., the number of P atoms/number of S atoms) and carbon having a high specific surface area [11,12]. Moreover, we reported

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that battery performance is improved by the inclusion of activated carbon, which raised the electronic conductivity of the conductive polymer [13]. The performance of all-solid-state lithium−sulfur batteries has been greatly improved by the above solutions. Therefore, it was considered that all-solid-state Li−S batteries are one of the most likely batteries to successfully fulfill future technological demands.

Phosphorus pentasulfide, which has a high P/S ratio and an extremely low ionic conductivity, has been reported to improve the reactivity of sulfur and produce an extremely high-capacity all-solid-state cell following the transformation of P_2S_5 into a lithium phosphorus sulfide solid electrolyte during the first charge−discharge process of the battery [14].

In this report, we investigate a positive composite electrode that uses P_2S_5 in combination with an SE that exhibits a high ionic conductivity to raise both the reactivity of sulfur and the ionic conductivity of the positive composite electrode. As a result, we found that the all-solid-state Li−S cell has a relatively low activation energy and a high ionic conductivity. This positive composite electrode exhibits an extremely high capacity, i.e., 1550 mA h g^{-1} (sulfur) at 1.3 mA cm^{-2} and 25 °C. Furthermore, when using this positive electrode, the energy and power densities at the cell level (in an 18650 cell) are 540 W h kg^{-1} (990 W h L^{-1}), estimated from the equivalent structure of a current lithium-ion battery. This value is twice that of the current lithium ion-battery; therefore, we believe that the all-solid-state lithium−sulfur battery has practical applications.

2. Experimental

2.1. Solid electrolyte

The lithium phosphorus sulfide SEs, $(1 − x)(Li_{1.5}PS_{3.3})\cdot x(LiI)$ (mol%) ($0 \leq x \leq 0.25$), used in the batteries were obtained by mechanical milling [15]. Here, reagent grade lithium iodide (Aldrich, 99.999%) and $Li_{1.5}PS_{3.3}$, prepared according to a previous report [11], were used as starting materials. The SEs were prepared using a mechanochemical method from a mixture of $(1 − x)$ $Li_{1.5}PS_{3.3}$ and $xLiI$ ($x = 0, 0.11, 0.18,$ and 0.25) in a planetary ball mill apparatus (FRITSCH PULVERISETTE 7) using a ZrO_2 pot (90 mL) containing approximately 180 g of 4-mm diameter ZrO_2 balls under an Ar atmosphere [6] and a rotation speed of 500 rpm for 10 h. The ionic conductivities of the SEs at 25 °C were measured with an impedance analyzer (Cell Test System 1400, Solartron Analytical)
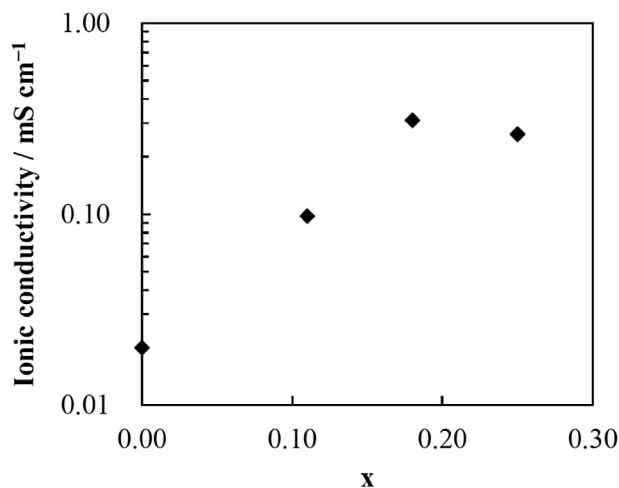

Fig. 1. Ionic conductivity of $(1 − x)(Li_{1.5}PS_{3.3})\cdot x(LiI)$.

using 1-mm diameter pellet samples previously pressed under 200 MPa pressure. The results of these measurements are shown in Fig. 1.

Any peaks were not observed by X-ray diffraction (XRD; measured by Ultima 4, Rigaku Co.) (Fig. S1). Therefore, it can be assumed that all SEs were nearly amorphous.

2.2. Positive composite electrodes

Several positive composite electrodes containing elemental sulfur as the active material were prepared by ball milling using a planetary ball mill apparatus under an Ar atmosphere [4]. The mechanochemical treatment using a ZrO_2 pot (45 mL) containing approximately 40 g of 4-mm diameter ZrO_2 balls was performed for the following mixtures of sulfur active material, P_2S_5, activated carbon (AC; Kansai Coke and Chemicals Co., Ltd.), and SE to yield four different positive composite electrode materials, as follows: (a) {S-SE(0)}, (b) {S-SE(I)}, (c) {S+10PS-SE(I)}, and (d) {S+20PS-SE(1)}.

(a) The {S-SE(0)} electrode was obtained by milling a mixture of sulfur, AC, and $Li_{1.5}PS_{3.3}$ (weight ratio 50:10:40) using a planetary ball mill apparatus [12].
(b) The {S-SE(1)} electrode was obtained by milling a mixture of sulfur, AC, and $0.82(Li_{1.5}PS_{3.3})\cdot0.18(LiI)$ (weight ratio 50:10:40) using a planetary ball mill apparatus.
(c) The {S + 10PS-SE(1)} electrode was obtained by milling a mixture of sulfur and P_2S_5 (weight ratio 50:10) using a planetary ball mill apparatus to yield S + 10PS, followed by milling of a mixture of the S + 10PS composite, AC, and $0.82(Li_{1.5}PS_{3.3})\cdot0.18(LiI)$ (weight ratio 60:10:30) using a ball mill apparatus.
(d) The {S + 20PS-SE(1)} electrode was obtained by milling a mixture of sulfur and P_2S_5 (weight ratio 50:20) using a planetary ball mill apparatus to yield S+20PS, followed by milling of a mixture of the S+20PS composite, AC, and $0.82(Li_{1.5}PS_{3.3})\cdot0.18(LiI)$ (weight ratio 70:10:20) using a ball mill apparatus.

Entire mechanical milling was undertaken using a rotation speed of 370 rpm for 4 h.

2.3. Electrochemical measurement

The electrochemical properties of the positive composite electrodes were investigated in an all-solid-state cell [16]. The two-electrode cells were assembled in an Ar-filled glove box using several composite electrodes as the positive electrode, Li−In alloys as the negative electrode, and $Li_{10}GeP_2S_{12}$ [9] as the solid electrolyte layer.

The positive electrode powder (7.5 mg) and $Li_{10}GeP_2S_{12}$ powder (70 mg) were placed in a 10-mm diameter polycarbonate tube and pressed under 200 MPa of pressure to form a two-layered pellet. The negative electrode formed by the superimposition of lithium foil onto indium foil was placed on the surface of the two-layered pellet such that the superimposed foils were in contact with the solid electrolyte. In this process, the Li and In foils formed a Li−In alloy layer. The resulting three-layered pellet was then sandwiched between two stainless steel rods, which acted as current collectors. The molar ratio of Li/In in the negative electrode was 0.79. When the molar ratio is less than 1, the potential of Li−In alloys has been reported to be constant at approximately 0.6 V vs. Li [17]. Here, a value of 0.6 was adopted for the potential difference between Li−In and Li.

Electrochemical tests were conducted at several constant current densities from 0.64 to 6.4 mA cm^{-2} at 25 °C under an Ar