Room-temperature Operation of Lithium Sulfide Positive and Silicon Negative Composite Electrodes Employing Oxide Solid Electrolytes for All-solid-state Battery

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ABSTRACT

Oxide-type all-solid-state batteries are expected to be the next-generation batteries owing to their safety performance. Similarly, Li_2S and Si are also attracting attention as next-generation active materials owing to their high theoretical energy density. However, battery performances and manufacturing methods are associated with many challenges. Thus, this study focuses on an effective method for manufacturing Li_2S positive and Si negative composite electrodes for oxide-type all-solid-state Li_2S -Si batteries. These composite electrodes are prepared via a one-step mechanical milling process using Li_2S or Si as the active materials, carbon with a high specific surface area, and raw materials of oxide glass electrolyte. A solid electrolyte (SE), as well as composites of the active materials, SE, and carbon, are simultaneously generated via this process. Thereafter, the all-solid-state Li_2S -Si full battery cell comprising Li_2S positive and Si negative composite electrodes, respectively, as prepared via the cold press technology, exhibits a relatively high energy density of 283 Wh kg^{-1} (sum of the masses of the positive and negative composite electrodes) and an area capacity of 4.0 mAh cm^{-2} at 0.064 mA cm^{-2} and 25°C .

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 Keywords : Oxide Electrolyte, All-solid-state Battery, Full Battery Cell, Li_2S -Si Battery

1. Introduction

All-solid-state lithium-ion batteries (LIBs) utilizing inorganic solid electrolytes (SEs) are being actively researched, and they have demonstrated improved performances with time. Particularly, batteries employing sulfide SEs, such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$,¹ $\text{Li}_7\text{P}_3\text{S}_{11}$,² and $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$,³ exhibit relatively high performances because of the high ionic conductivity and softness of sulfide SEs. Conversely, the ionic conductivities of oxide SEs, such as $\text{Li}_{1.35}\text{Al}_{0.35}\text{Ge}_{0.2}\text{Ti}_{1.45}(\text{PO}_4)_3$,⁴ $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12}$,⁵ and $\text{Li}_{0.34}\text{La}_{0.56}\text{TiO}_3$,⁶ are also improving with time, exhibiting a relatively high ionic conductivity of $\sim 10^{-3} \text{ S cm}^{-1}$, which is more than one order of magnitude lower than those of organic electrolytes. Furthermore, since it is challenging to form a Li-transfer path between particles because crystalline oxide SEs exhibit low deformable property. Thus, oxide-type all-solid-state LIBs exhibit low battery performances.⁷ However, oxide-type all-solid-state LIBs would represent an ideal battery system if the battery performances can be improved because they do not generate toxic gases like sulfide SEs.

Recently, it was reported that Li_3BO_3 - Li_2SO_4 - Li_2CO_3 , Li_2CO_3 - Li_3BO_3 , and Li_2SO_4 - Li_2CO_3 systems with high deformability provided good inter particle contact between the active material, thereby demonstrating relatively high battery performance.^{8–10} Furthermore, we also reported the battery performances of a full battery cell in an oxide-type all-solid-state Li_2S -Si system with high energy density and area capacity employing Li_2SO_4 - Li_2CO_3 -LiX systems with excellent deformability and relatively high ionic conductivity at 45°C .¹¹ Here, Li_2S and Si are known for high-theoretical-capacity electrode active materials with specific capacities of 1166 and 4212 mAh g^{-1} , respectively.¹² Then, it reported relatively high deformability and high ionic conductivity of $> 3 \times 10^{-5} \text{ S cm}^{-1}$ for Li_2O -LiI systems.¹³ Based on the foregoing

reports, it was considered that highly deformable oxide SEs could effectively improve the battery performances of all-solid-state LIBs by forming good inter particle contact. Moreover, we also reported the preparation of high-battery-performance positive and negative composite electrodes for sulfide-type all-solid-state Li_2S -Si batteries via an effective one-step preparation method employing mechanical milling to accelerate the generation of SE employing activated carbon (AC) with a high specific area.¹³

This study focuses on improving the battery performances of Li_2S positive and Si negative composite electrodes for oxide-type all-solid-state Li_2S -Si batteries. A one-step preparation method involving mechanical milling employing oxide SE raw materials was employed for the procedure. The half-battery cell comprising Li_2S positive and Si negative composite electrodes, which were prepared from raw materials of Li_2SO_4 - Li_2CO_3 -LiX and Li_2O -LiI systems, demonstrated relatively high capacities at 45 and 25°C , respectively. Furthermore, the full battery cell comprising Li_2S positive and Si negative composite electrodes is demonstrated at 25°C operation and exhibited an energy density of 283 Wh kg^{-1} (sum of the masses of the positive and negative composite electrodes) and an area capacity of 4.0 mAh cm^{-2} at 0.064 mA cm^{-2} .

2. Experimental

Reagent-grade Li_2SO_4 (Sigma Aldrich, 99.99 %), Li_2CO_3 (Rare Metallic Corp., 99.99 %), LiBr (Sigma Aldrich, 99.999 %), LiI (Sigma Aldrich, 99.999 %), Li_2O (Kojundo Chemical Lab. Co., Ltd., 99 %), Li_2S (Mitsuiwa Chem., 99.9 %), Si (Niraco Co., 99.999 %), and AC (MSC-30, Kansai Coke and Chemicals Co., Ltd.) were used as starting materials for the positive and negative composite electrodes. Here, Li_2SO_4 , Li_2CO_3 , Si, and Li_2O were vacuum dried for 12 h at 300°C before the preparation of the composite electrode. The Li_2S positive and Si negative composite electrodes were prepared via mechanical milling employing a ZrO_2 pot and 40 g of 5 mm-diameter ZrO_2 balls with a planetary ball-mill apparatus (Premium Line P-7, Fritsch Co.). The active materials (Li_2S or Si),

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Table 1. Weight ratios of the Li₂S and Si composite electrodes.

Sample name	Reagent ratio (weight)
Li ₂ S–LSCB–AC	Li ₂ S : Li ₂ SO ₄ : Li ₂ CO ₃ : LiBr : AC = 30.0 : 31.8 : 14.2 : 14.0 : 10.0
Si–LSCI–AC	Si : Li ₂ SO ₄ : Li ₂ CO ₃ : LiI : AC = 30.0 : 25.9 : 11.6 : 22.5 : 10.0
Li ₂ S–LOI–AC	Li ₂ S : Li ₂ O : LiI : AC = 30.0 : 18.5 : 41.5 : 10.0
Si–LOI–AC	Si : Li ₂ O : LiI : AC = 30.0 : 18.5 : 41.5 : 10.0

AC, and SE raw materials were composited in an Ar atmosphere at a rotational speed of 370 rpm for 8 h.^{11,14} The weight ratios of the active material for all the positive and negative composite electrodes were set to 30 wt%, and those of the other components are displayed in Table 1. Here, composition formulae of LSCB, LSCI, and LOI were 0.45Li₂SO₄–0.30Li₂CO₃–0.25LiBr, 0.42Li₂SO₄–0.28Li₂CO₃–0.30LiI, and 0.67Li₂O–0.33LiI, respectively. Additionally, the ionic conductivities of LSCB, LSCI, and LOI prepared by mechanical milling following previous reports were 3.7, 5.9, and 16 × 10^{−6} S cm^{−1}, respectively.^{11,13}

X-ray diffraction (XRD, CuKα1, SmartLab II, Rigaku Co.) was employed to identify the residual crystalline phases in the Li₂S positive and Si negative composite electrodes. XRD was performed in a sealed cell that was assembled in an Ar-filled glove box for the evaluation in an Ar atmosphere, following our previous studies.¹¹

The all-solid-state half- and full-battery cells were fabricated according to our previous reports.¹¹ The half-battery cell structures comprised the Li₂S positive composite electrode/blended SE containing crystalline Li₁₀GeP₂S₁₂ and 80Li₂S–20P₂S₅ glass (B–SE) (4.5 mS cm^{−1}) as the SE layer/Li–In alloy counter electrode and Si negative composite electrode/Li₃PS₄–LiI (1.5 mS cm^{−1}) as the SE layer/Li–In alloys. Here, the molar ratio of Li/In in the counter electrode was 0.64, and the potential of the Li–In alloys was a constant value (0.62 V vs. Li).¹⁵ Next, 10.0 mg of the Li₂S positive composite electrode powder (or 5.0 mg of the Si negative composite electrode powder) and 80 mg of B–SE or Li₃PS₄–LiI powder were placed in a 10-mm-inner-diameter ceramic tube and pressed by stainless steel at 720 MPa to form a two-layered pellet. Next, the Li–In alloy counter electrode was formed by pressing a stack of Li and In foil on the surface of the two-layered pellet, which was in contact with B–SE or Li₃PS₄–LiI at 80 MPa. The resulting three-layered pellet was subsequently sandwiched in two stainless-steel rods, which acted as current collectors. Afterward, the full-battery cell structure comprising Li₂S positive composite electrode/Li₃PS₄–LiI SE layer/Si negative composite electrode was obtained. Further, 10.0 mg of the Li₂S positive composite electrode powder, 80 mg of the Li₃PS₄–LiI powder, and 5.0 mg of the Si negative composite electrode powder were placed in a 10-mm-inner-diameter ceramic tube and pressed by the stainless steel at 720 MPa to form a three-layered pellet. The resulting three-layered pellet was subsequently sandwiched in two stainless-steel rods, which acted as the current collectors. Here, the half- and full-battery cells were assembled in an Ar-filled glove box and placed in a sealed vessel. The battery performances of the Li₂S and Si half-battery cells and Li₂S–Si full-battery cells between 0.5–2.5, −0.6 to 2.0, and 0–3.0 V, respectively, were evaluated at a constant current density of 0.064–0.13 mA cm^{−2} at 45 and 25 °C employing a charge–discharge measuring device (ACD-01, Asuka Electronics Co. Ltd.). Here, the discapacity of the Si half-battery cells was limited to 2500 mAh g^{−1} (Si) to prevent Li dendrite growth and reduce cycle deterioration due to the volume change of Si.

3. Results and Discussion

The XRD patterns revealed that no crystalline phase was

observed in Li₂S–LSCB–AC and Si–LSCI–AC that were prepared from the raw materials of the Li₂SO₄–Li₂CO₃–LiX systems other than crystalline active materials (Figs. 1a and 1b), and this indicated that the particles of the active materials were miniaturized during the process since their peaks were much broader than those of their starting materials. Furthermore, the result indicated that Li₂S was changed into an Li₂S–LiBr solid solution since the XRD patterns of Li₂S in Li₂S–LSCB–AC were lower 2θ than that of the starting material of Li₂S.¹⁶ Thus, it was assumed that both electrodes were prepared via the one-step process employing the active materials, AC, and SE raw materials to simultaneously generate oxide SE and their composite, as observed in the one-step preparation of Li₂S and Si composite electrodes for sulfide systems.¹⁴

Figures 1c and 1d show the charge–discharge curves of the half-battery cells employing Li₂S–LSCB–AC and Si–LSCI–AC at 0.064 mA cm^{−2} and 45 °C, respectively. Li₂S–LSCB–AC underwent reversible charge–discharge reactions with capacities that gradually increased with the increasing cycles from the 1st to 5th cycles, after which it exhibited a discharge capacity of 848 mAh g^{−1} (Li₂S) at the 5th cycle. This improved capacity might be due to the improvement of the utilized Li₂S with the increasing cycles, as observed with the Li₂S positive composite electrode that was prepared from 0.45Li₂SO₄–0.30Li₂CO₃–0.25LiBr via a two-step process.¹¹ However, the capacity was lower than those of the Li₂S positive composite electrodes that were prepared via the two-step process. The low ionic conductivity of SE in Li₂S–LSCB–AC might be due to the decreasing ratio of LiBr in SE since the reaction for generating SE competes with the generation of the Li₂S–LiBr solid solution. Conversely, the capacities of Si–LSCI–AC gradually increased with the increasing cycles from the 1st to 5th cycles and exhibited a charge capacity of 2490 mAh g^{−1} (Si), which was an almost controlled capacity, in the 5th cycle. This performance was much similar to that of the two-step-prepared electrode.¹¹ It was assumed that 0.42Li₂SO₄–0.28Li₂CO₃–0.30LiI was generated via the one-step process since Si, dissimilar to Li₂S, did not compete with the generation of the solid solution. Further, Figs. 1e and 1f show the charge–discharge curves of the half-battery cells employing Li₂S–LSCB–AC and Si–LSCI–AC at 0.064 mA cm^{−2} and 25 °C, respectively. The capacities of Li₂S–LSCB–AC increased with the increasing cycles from the 1st to 5th cycles, exhibiting a discharge capacity of 547 mAh g^{−1} (Li₂S) in the 5th cycle. However, the capacity was much lower because of the lower ionic conductivity of SE and the reactivity of Li₂S at 25 °C than at 45 °C. Contrarily, the performances of Si–LSCI–AC were similar at 25 °C and 45 °C where the overvoltage is slightly large. These differences between the Li₂S and Si composite electrodes were caused by the different conductivities of Li₂S and Si. Therefore, it is important to improve the performance of the positive composite electrode since it would strongly influence the performance of the Li₂S–Si full-battery cell.

Next, the raw materials of Li₂O–LiI systems were investigated as the starting materials to improve the ionic conductivities of the positive and negative composite electrodes. Figures 2a and 2b show the XRD patterns of Li₂S–LOI–AC and Si–LOI–AC, respectively. Li₂S with the low 2θ value corresponds to the Li₂S–LiI solid solution, and the Li₂O phases were detected in the XRD patterns of

Figure 1. XRD patterns of (a) $\text{Li}_2\text{S-LSCB-AC}$ and (b) Si-LSCI-AC . Charge-discharge curves of the (c, e) $\text{Li}_2\text{S-LSCB-AC}$ and (d, f) Si-LSCI-AC half-battery cells at 0.064 mA cm^{-2} at 45 and 25 °C.

Figure 2. XRD patterns of (a) $\text{Li}_2\text{S-LOI-AC}$ and (b) Si-LOI-AC . Charge-discharge curves of the (c, e) $\text{Li}_2\text{S-LOI-AC}$ and (d, f) Si-LOI-AC half-battery cells at 0.064 mA cm^{-2} at 45 and 25 °C.

$\text{Li}_2\text{S-LOI-AC}$, indicating that the Li_2O phase remained because the ratio of LiI was reduced via the generation of the $\text{Li}_2\text{S-LiI}$ solid solution and was out of the range of the $\text{Li}_2\text{O-LiI}$ solid solution. Contrarily, the XRD patterns of Si-LOI-AC revealed only the Si crystalline phase without the Li_2O and LiI phases. Thus, it was assumed that it remained in the solid-solution range of the $\text{Li}_2\text{O-LiI}$ systems in Si-LOI-AC .

Figures 2c and 2d show the charge-discharge curves of the half-battery cells employing $\text{Li}_2\text{S-LOI-AC}$ and Si-LOI-AC at 0.064 mA cm^{-2} and 45 °C, respectively. $\text{Li}_2\text{S-LOI-AC}$ exhibited a lower overvoltage and a higher capacity than $\text{Li}_2\text{S-LSCB-AC}$, indicating that the resistance of the positive composite electrode was

reduced by the high ionic conductivity of the $\text{Li}_2\text{O-LiI}$ systems. However, an irreversible oxidation capacity of about 270 mAh g^{-1} (Li_2S) was observed in the 1st cycle, and it corresponds to the oxidation of LiI in the solid-solution component. Thereafter, the charge and discharge capacities were about 950 mAh g^{-1} (Li_2S) with coulombic efficiencies of $>97\%$ from the 2nd to 5th cycles. Thus, it was assumed that the oxidation of SE in the positive composite electrode proceeded mainly during the 1st charge cycle. Conversely, the discharge and charge capacities of Si-LOI-AC in the 1st cycle were 2500 and 3150 mAh g^{-1} (Si), respectively, indicating a higher charge capacity than the discharge one. Furthermore, the 1st discharge potential of Si-LOI-AC was much lower than that of

Figure 3. Charge–discharge curves of the (a, d) $\text{Li}_2\text{S-LSCB-AC/Si-LSCI-AC}$ and (b, e) $\text{Li}_2\text{S-LOI-AC/Si-LOI-AC}$ full-battery cells at 0.064 mA cm^{-2} at 45 and 25°C . Cycling performances of the (c) $\text{Li}_2\text{S-LSCB-AC/Si-LSCI-AC}$ and (f) $\text{Li}_2\text{S-LOI-AC/Si-LOI-AC}$ full-battery cells at 0.13 mA cm^{-2} at 45 and 25°C .

Si-LSCI-AC , indicating that there were Li-Si alloys or other lithiated products owing to the reaction between Si and Li_2O during the mechanical milling of Si-LOI-AC . Subsequently, the discharge and charge capacities were stable at about 2500 mAh g^{-1} (Si) (controlled value) with coulombic efficiencies of $>99\%$ at the 2nd–5th cycles. Furthermore, Figs. 2e and 2f show the charge–discharge curves of the half-battery cells employing $\text{Li}_2\text{S-LOI-AC}$ and Si-LOI-AC at 0.064 mA cm^{-2} and 25°C , respectively. These capacities are slightly lower than those at 45°C . However, the capacity of $\text{Li}_2\text{S-LOI-AC}$ was much higher than that of $\text{Li}_2\text{S-LSCB-AC}$ at 25°C because of the high ionic conductivity of the $\text{Li}_2\text{O-LiI}$ system. Next, Si-LOI-AC and Si-LSCI-AC exhibited similar reversible capacities from the 2nd to the 5th cycles. Thus, it was assumed that the electrodes employing low-reactive active materials, such as Li_2S , were more sensitive for the ionic conductivity of SE than high electroconductive active materials, such as Si .

Finally, the charge–discharge performances of the full-battery cells for $\text{Li}_2\text{S-LSCB-AC/Si-LSCI-AC}$ and $\text{Li}_2\text{S-LOI-AC/Si-LOI-AC}$ were demonstrated. Figures 3a and 3b show the charge–discharge curves of the full-battery cells of $\text{Li}_2\text{S-LSCB-AC/Si-LSCI-AC}$ and $\text{Li}_2\text{S-LOI-AC/Si-LOI-AC}$ at 0.064 mA cm^{-2} and 45°C , respectively. The capacities of $\text{Li}_2\text{S-LSCB-AC/Si-LSCI-AC}$ increased gradually with the increasing cycles from the 1st to 5th cycles by increasing utilization of Li_2S . Thereafter, it exhibited a discharge capacity of 754 mAh g^{-1} (Li_2S), which was similar to the half-battery cell of $\text{Li}_2\text{S-LSCB-AC}$ in the 5th cycle. However, the first discharge capacity was smaller than that of the half battery cell of $\text{Li}_2\text{S-LSCB-AC}$ because the delithiation potential of Si was limited to $0.5\text{--}1.0 \text{ V}$ (vs. Li-In) under discharge test conditions of the $\text{Li}_2\text{S-Si}$ full-battery cell. Conversely, $\text{Li}_2\text{S-LOI-AC/Si-LOI-AC}$ exhibited similar first discharge capacity of half battery cell of $\text{Li}_2\text{S-LOI-AC}$ because the potential of the negative electrode was low owing to the large irreversible charge capacity of $\text{Li}_2\text{S-LOI-AC}$ and the existence of the Li-Si alloy in Si-LOI-AC . However, the capacities were reduced with the increasing number of cycles probably because the oxidation of LiI in Si-LOI-AC proceeded

with the increasing number of cycles, thereby reducing the ionic conductivity of SE. Further, the cycling performances of $\text{Li}_2\text{S-LSCB-AC/Si-LSCB-AC}$ and $\text{Li}_2\text{S-LOI-AC/Si-LOI-AC}$ at 0.13 mA cm^{-2} and 45°C are shown in Fig. 3c. $\text{Li}_2\text{S-LSCB-AC/Si-LSCI-AC}$ exhibited a discharge capacity of 753 mAh g^{-1} (Li_2S) in the 15th cycle, and this value corresponds to the result of the low current density test since it continued to improve the utilization of Li_2S . Dissimilarly, the cycling capacity of $\text{Li}_2\text{S-LOI-AC/Si-LOI-AC}$ reduced with the increasing number of cycles to 638 mAh g^{-1} (Li_2S) in the 15th cycle. The capacities of $\text{Li}_2\text{S-LOI-AC/Si-LOI-AC}$ were lower than those of $\text{Li}_2\text{S-LSCB-AC/Si-LSCI-AC}$ despite its higher initial capacity at 0.064 mA cm^{-2} at 45°C . This is probably because the oxidation of LiI in $\text{Li}_2\text{S-LOI-AC}$ proceeded further and reduced the ionic conductivity. Figures 3d and 3e show their charge–discharge curves at 0.064 mA cm^{-2} and 25°C . Regarding $\text{Li}_2\text{S-LSCB-AC/Si-LSCI-AC}$, the capacities increased with the increasing number of cycles, although it was much lower than that at 45°C because the ionic conductivity of the positive composite electrode decreased with the decreasing temperature (Fig. 3d). Conversely, $\text{Li}_2\text{S-LOI-AC/Si-LOI-AC}$ exhibited a first discharge capacity of 1043 mAh g^{-1} (Li_2S) at 25°C , which close to that of 45°C , because of the high ionic conductivity of $\text{Li}_2\text{O-LiI}$ systems. From the average voltage (1.36 V) and capacity at the first discharge at 0.064 mA cm^{-2} and 25°C , it was calculated a relatively high energy density of 283 Wh kg^{-1} (the sum of the masses of the positive and negative composite electrodes) and an area capacity of 4.0 mAh cm^{-2} . Incidentally, the energy density of the test cell including weight of SE layer was 45 Wh kg^{-1} (the sum of the masses of the positive, negative composite electrodes, and SE layer) that dramatically changes by preparation of full-battery cell construction, such as thickness of SE layer. Thus, it is possible to consider the quality of performance by considering based on the weight of the positive and negative electrodes and electrode area when discussing the energy density and area capacity of a full-battery cells. The performance was higher than those of recently researched sulfide-type Li-S batteries.¹⁷ Moreover, their cycling performances at

0.13 mA cm⁻² and 25 °C are shown in Fig. 3f. Li₂S–LOI–AC/Si–LOI–AC exhibited a higher capacity than Li₂S–LSCB–AC/Si–LSCB–AC until the 15th cycles, dissimilar to the test at 45 °C; this indicated that the ionic conductivity of Li₂S–LOI–AC was still high because the oxidation of LiI was slower at 25 °C than at 45 °C. Regarding Li₂S–LSCB–AC/Si–LSCB–AC, the capacity increased with the increasing cycles, indicating the improved utilization of Li₂S during the cycles.

The above results demonstrated the possibility of achieving a high-energy-density oxide-type all-solid-state Li₂S–Si battery and an effective method for preparing composite electrodes.

4. Conclusions

This paper reports a one-step method for preparing Li₂S-positive and Si-negative composite electrodes for an oxide-type all-solid-state Li₂S–Si battery and the battery performances of the full battery cells employing these positive and negative composite electrodes at 25 °C. The battery performances were greatly improved by improving the potential profile gap between positive and negative electrodes, which was due to the partially lithiated Si negative composite electrode. Further, the oxide-type all-solid-state Li₂S–Si full battery cell exhibited a relatively high energy density of 283 Wh kg⁻¹ (sum of the masses of the positive and negative composite electrodes) and an area capacity of 4.0 mAh cm⁻² at 0.064 mA cm⁻² and 25 °C.

CRediT Authorship Contribution Statement

Hiroshi Nagata: Conceptualization (Lead)
Junji Akimoto: Supervision (Supporting)

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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