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, Li2S 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 Li2S positive and Si negative composite electrodes for oxide-type all-solid-state Li2S–Si batteries. These composite electrodes are prepared via a one-step mechanical milling process using Li2S 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 Li2S–Si full battery cell comprising Li2S 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.

Keywords: Oxide Electrolyte, All-solid-state Battery, Full Battery Cell, Li2S–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 Li10GeP2S12, Li2P2S11, and Li25SxSi47P41.4S11.1–Co3.1, exhibit relatively high performances because of the high ionic conductivity and softness of sulfide SEs. Conversely, the ionic conductivities of oxide SEs, such as Li1.35–Al3.35Ge2.5Ti1.45(PO4)3, Li10.35Li7P3S11, and Li10.35Li7P3S11, are also improving with time, exhibiting a relatively high ionic conductivity of ~10−3 S cm−1, which is more than one order of magnitude lower than those of organic electrolytes. Furthermore, since it is challenging to form Li-transfer paths between particles because crystalline oxide SEs exhibit low deformable property. Thus, oxide-type all-solid-state LIBs exhibit low battery performances. 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 Li1.35Sc2O3–Li2SO4–Li2CO3–Li2O–Li1.35Sc2O3 and Li1.35Sc2O3–Li2SO4–Li2CO3–Li2O–Li1.35Sc2O3 systems, demonstrated relatively high capacities at 45 and 25 °C, respectively. Furthermore, the full battery cell comprising Li2S 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 Li2SO4 (Sigma Aldrich, 99.99 %), Li2CO3 (Rare Metallic Corp., 99.99 %), LiBr (Sigma Aldrich, 99.999 %), LiI (Sigma Aldrich, 99.999 %), Li2O (Kojundo Chemical Lab. Co., Ltd., 99 %), Li2S (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, Li2SO4, Li2CO3, Si, and Li2O were vacuum dried for 12 h at 300 °C before the preparation of the composite electrode. The Li2S positive and Si negative composite electrodes were prepared via mechanical milling employing a ZrO2 pot and 40 g of 5 mm-diameter ZrO2 balls with a planetary ball-mill apparatus (Premium Line P-7, Fritsch Co.). The active materials (Li2S or Si), 

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were evaluated at a constant current density of 0.064 mA cm⁻². The SE layer comprised the Li₂S positive composite electrode and 80 mg of B (LiI powder) and 80 mg of B (Si negative composite electrode powder) and 80 mg of B–SE or Li₃PS₄–LiI systems were investigated. The half-battery cell structures comprised the Li₂S positive composite electrode/blended SE containing crystalline Li₄GeP₂S₁₂ 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/LiP₅Sₓ–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). 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 Li₃P₅Sₓ–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 Li₃PS₅–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-cell battery structure comprising Li₂S positive composite electrode/Li₃P₅Sₓ–LiI SE layer/Si negative composite electrode was obtained. Further, 10.0 mg of the Li₂S positive composite electrode powder, 80 mg of the Li₃P₅Sₓ–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-cell batteries 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 discipacity 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.

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

| Sample name     | Reagent ratio (weight) |
|-----------------|------------------------|
| Li₂S–LSCB–AC    | LiS : Li₂SO₄ : Li₂CO₃ : LiBr : AC = 30.0 : 31.8 : 14.2 : 14.0 : 10.0 |
| Si–LSCI–AC      | Si : Li₂SO₄ : Li₂CO₃ : LiI : AC = 30.0 : 25.9 : 11.6 : 22.5 : 10.0 |
| Li₂S–LOI–AC     | LiS : LiO : LiI : AC = 30.0 : 18.5 : 41.5 : 10.0 |
| Si–LOI–AC       | Si : LiO : LiI : AC = 30.0 : 18.5 : 41.5 : 10.0 |

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–LiBr 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 LiS–LiBr solid solution since the XRD patterns of Li₂S in Li₂S–LSCB–AC were lower than that of the starting material of Li₂S. 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.

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. 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 LiS–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 discharge 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. 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.

The next, 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 29 value corresponds to the Li₂S–LiI solid solution, and the Li₂O phases were detected in the XRD patterns of...
Li$_2$S–LOI–AC, indicating that the Li$_2$O phase remained because the ratio of LiI was reduced via the generation of the Li$_2$S–LiI solid solution and was out of the range of the Li$_2$O–LiI solid solution. Contrarily, the XRD patterns of Si–LOI–AC revealed only the Si crystalline phase without the Li$_2$O and LiI phases. Thus, it was assumed that it remained in the solid-solution range of the Li$_2$O–LiI systems in Si–LOI–AC.

Figures 2c and 2d show the charge–discharge curves of the half-battery cells employing Li$_2$S–LOI–AC and Si–LOI–AC at 0.064 mA cm$^{-2}$ and 45 °C, respectively. Li$_2$S–LOI–AC exhibited a lower overvoltage and a higher capacity than Li$_2$S–LSCB–AC, indicating that the resistance of the positive composite electrode was reduced by the high ionic conductivity of the Li$_2$O–LiI systems. However, an irreversible oxidation capacity of about 270 mAh g$^{-1}$ (Li$_2$S) 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$_2$S) 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...
Si–LSCI–AC, indicating that there were Li–Si alloys or other lithiated products owing to the reaction between Si and Li$_2$I 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 Li$_2$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 Li$_2$S–LOI–AC was much higher than that of Li$_2$S–LSCB–AC at 25 °C because of the high ionic conductivity of the Li$_2$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$_2$S, 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 Li$_2$S–LSCB–AC/Si–LSCI–AC and Li$_2$S–LOI–AC/Si–LOI–AC were demonstrated. Figures 3a and 3b show the charge–discharge curves of the full-battery cells of Li$_2$S–LSCB–AC/Si–LSCI–AC and Li$_2$S–LOI–AC/Si–LOI–AC at 0.064 mA cm$^{-2}$ and 45 °C, respectively. The capacities of Li$_2$S–LSCB–AC/Si–LSCI–AC increased gradually with the increasing cycles from the 1st to 5th cycles by increasing utilization of Li$_2$S. Thereafter, it exhibited a discharge capacity of 754 mAh g$^{-1}$ (Li$_2$S), which was similar to the half-battery cell of Li$_2$S–LSCB–AC in the 5th cycle. However, the first discharge capacity was smaller than that of the half battery cell of Li$_2$S–LSCB–AC because the delithiation potential of Si was limited to 0.5–1.0 V (vs. Li–Li$^+$) under discharge test conditions of the Li$_2$Si–Li full-battery cell. Conversely, Li$_2$S–LOI–AC/Si–LOI–AC exhibited similar first discharge capacity of half battery cell of Li$_2$S–LOI–AC because the potential of the negative electrode was low owing to the large irreversible charge capacity of Li$_2$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 Li$_2$S–LSCB–AC/Si–LSCI–AC and Li$_2$S–LOI–AC/Si–LOI–AC at 0.13 mA cm$^{-2}$ and 45 °C are shown in Fig. 3c. Li$_2$S–LSCB–AC/Si–LSCI–AC exhibited a discharge capacity of 753 mAh g$^{-1}$ (Li$_2$S) 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$_2$S. Dissimilarly, the cycling capacity of Li$_2$S–LOI–AC/Si–LOI–AC reduced with the increasing number of cycles to 638 mAh g$^{-1}$ (Li$_2$S) in the 15th cycle. The capacities of Li$_2$S–LOI–AC/Si–LOI–AC decreased because of a decrease in the Li$_2$O–LiI system, whereas the potential of the negative electrode was 1.0 V (vs. Li–Li$^+$) under discharge test conditions of the Li$_2$Si–Li full battery cell. Conversely, Li$_2$S–LOI–AC reduced with the increasing number of cycles because of the high ionic conductivity of the Li$_2$O–LiI system. Further, the cycling performances of Li$_2$S–LSCB–AC/Si–LSCI–AC at 0.13 mA cm$^{-2}$ and 45 °C were lower than those of Li$_2$S–LSCB–AC/Si–LSCI–AC at 0.064 mA cm$^{-2}$ and 45 °C because of the high ionic conductivity of the positive composite electrode decreased with the increasing temperature (Fig. 3d). Conversely, Li$_2$S–LOI–AC/Si–LOI–AC exhibited a first discharge capacity of 1043 mAh g$^{-1}$ (Li$_2$S) at 25 °C, which closed to that of 45 °C, because of the high ionic conductivity of Li$_2$O–Li$_2$I 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. Moreover, their cycling performances at
Li$_2$S–LOI–AC/Si–LOI–AC exhibited a higher capacity than Li$_2$S–LSCB–AC/Si–LSCB–AC until the 15th cycles, dissimilar to the test at 45 °C; this indicated that the ionic conductivity of Li$_2$S–LOI–AC was still high because the oxidation of LiI was slower at 25 °C than at 45 °C. Regarding Li$_2$S–LSCB–AC/Si–LSCB–AC, the capacity increased with the increasing cycles, indicating the improved utilization of Li$_2$S during the cycles.

The above results demonstrated the possibility of achieving a high-energy-density oxide-type all-solid-state Li$_2$S–Si battery and an effective method for preparing composite electrodes.

4. Conclusions

This paper reports a one-step method for preparing Li$_2$S-positive and Si-negative composite electrodes for an oxide-type all-solid-state Li$_2$S–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 Li$_2$S–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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