Corresponding author: kanno@echem.titech.ac.jp

Ge0.25P0.75S4 are mixed by planetary ball milling to form composites that contain amorphous phases of the starting materials, which cause the deterioration of cyclability. The byproduct and the solid electrolyte itself during the battery reaction could contribute to the increase in resistance possibly because of the increased resistance of the composite. Structural and compositional changes of the byproduct and the solid electrolyte itself during the battery reaction could contribute to the increase in resistance that cause the deterioration of cyclability.

Composite sulfur electrodes are prepared by prolonged mechanical milling (≥300 min) for use in all-solid-state lithium-sulfur batteries, and their structure and electrochemical properties are investigated. These batteries exhibit a high initial discharge capacity (>1500 mAh g⁻¹). Sulfur, acetylene black, and the solid electrolyte Li₃.₂₅Ge₀.₂₅P₀.₇₅S₄ are mixed by planetary ball milling to form composites that contain amorphous phases of the starting materials, as well as a byproduct with a novel structural unit arising from the reaction between sulfur and the solid electrolyte. Batteries with a composite electrode/Li₃.₂₅Ge₀.₂₅P₀.₇₅S₄/Li-In anode configuration exhibit a high initial discharge capacity (>1100 mAh g⁻¹). However, the capacity fades during cycling (~500 mAh g⁻¹ at the 30th cycle), possibly because of the increased resistance of the composite. Structural and compositional changes of the byproduct and the solid electrolyte itself during the battery reaction could contribute to the increase in resistance that cause the deterioration of cyclability.

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Li$_2$S (Mitsuwa Chemical Co., Ltd., 99.9% purity), P$_2$S$_5$ (Aldrich, 99% purity), and GeS$_2$ (Kojundo Chemical Lab. Co., Ltd., 99.99% purity) powders were ground by hand in an agate mortar for 10 min. The powder was pressed into a pellet with a diameter of 13 mm at 575 MPa, and sealed in a Pyrex tube at 10 Pa. The pellet was sintered at 673 K for 8 h and then cooled to a temperature below 323 K. The product was ground again in an agate mortar, and the powder was sintered at 823 K for 8 h. The obtained powder was subjected to X-ray diffraction (XRD) measurements for phase identification, using a SmartLab (Rigaku) system with CuK$_{\alpha 1}$ radiation over a range of 2$\theta$ = 10–45$^\circ$ with a step width of 0.02$^\circ$ at 298 K. The ionic conductivity of the SE was measured by alternating current (AC)–impedance experiments with applied frequencies in the 1 Hz–8 MHz range using a frequency response analyzer (Model 1260A, Solartron) at 298 K. For impedance measurements, the SE powder was pressed into a pellet (ϕ = 10.2 mm) at 150 MPa. Both sides of the pellet were covered by Au powder to form the electrodes, followed by re-pressing at 380 MPa.

Sulfur (Kojundo Chemical Laboratory Co., Ltd., 99.99% purity), AB (HS-100, Denka Co., Ltd.), and the prepared SE were mixed in a ratio of 25:25:50 (wt%) and mechanically milled using a planetary ball mill (LP-M2H, Ito Seisakusho Co., Ltd.). The S–AB–SE mixture was placed in a zirconia ball-milling pot with zirconia balls (ϕ 3 mm × 90 and ϕ 5 mm × 45) in an Ar-filled glove box and milled at 480 rpm for various durations (10–600 min). The structure of the milled composite was investigated by scanning electron microscopy (SEM), XRD, and Raman spectroscopy. The electrochemical properties of all-solid-state batteries with the composite electrodes were evaluated by galvanostatic charge–discharge tests.

The morphology of the composite electrodes was observed by SEM (JSM-6610LV, JEOL) with an accelerating voltage of 5 kV. The composites were transferred from an Ar-filled glove box to the SEM observation room using an Ar-filled container to prevent side-reactions with air. Raman spectroscopy measurements were carried out on a confocal Raman microscope (Raman 11, Nanophoton Corp.) with an excitation wavelength of 532 nm and an accumulation of 1000 laser shots. The electrochemical properties of all-solid-state batteries with the composite electrodes were evaluated by galvanostatic charge–discharge tests.

The morphology of the composite electrodes was observed by SEM (JSM-6610LV, JEOL) with an accelerating voltage of 5–20 kV. The composites were transferred from an Ar-filled glove box to the SEM observation room using an Ar-filled container to prevent side-reactions with air. Raman spectroscopy measurements were carried out on a confocal Raman microscope (Raman 11, Nanophoton Corp.) with an excitation wavelength of 532 nm. The composite was sealed in a glass capillary under Ar before the measurements.

The all-solid-state batteries were constructed in an Ar-filled glove box for charge–discharge measurements.4,20 The Li$_{2.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ powder (70 mg) was pressed into a pellet at 280 MPa, which served as the separator layer in the battery. Pressing was performed using a test cell consisting of a polyethylene terephthalate (PET) cylinder body with an inner diameter of approximately 10 mm. Subsequently, 5 mg of the composite electrode powder (as the cathode) with an Al current collector was pressed on one side of the solid electrolyte at 700 MPa. Two different anodes were used in this study: (i) Li–Al alloy (~0.3 V vs. Li/Li$^+$)21 and (ii) Li–In alloy (~0.6 V vs. Li/Li$^+$).22 For (i), lithium (thickness: 0.1 mm, diameter: 8 mm) and aluminum (thickness: 0.1 mm, diameter: 9 mm) foil with a Cu current collector were pressed on opposite sides at 17.6 MPa as the counter electrode. For (ii), lithium (thickness: 0.1 mm, diameter: 5 mm) and indium (thickness: 0.1 mm, diameter: 10 mm) foils with a Cu current collector were pressed on opposite sides at 17.6 MPa as the counter electrode.

The electrochemical properties of the cells were evaluated using a multichannel galvanostat (TOSCAT-3100, Toyo System Co., Ltd.). A constant current of 83.75 mA g$^{-1}$ (1/20 C) was applied for discharging and charging with a rest time of 1 h at the discharged and charged states. The current value was calculated based on the nominal sulfur content (25 wt% in the composite). The charge–discharge reaction was performed at 298 K.

3. Results and Discussion

SEM images of the S–AB–SE composites after 300 min of milling are shown in Fig. 1. Small primary particles (1–5 µm) and aggregated secondary particles (>10 µm) were observed. There were no significant differences in the particle size with respect to the milling time. Figures 2a and b show the 1st charge–discharge curves of all-solid-state batteries and the 1st discharge capacity as a function of milling time, respectively. Flat voltage regions were observed around 1.7 and 2.3 V (vs. Li–Al) during discharging and charging, respectively, indicative of the reversible reaction of sulfur with lithium in the composites.4,19 Additional reactions were confirmed at around 1.2 V for milling times of 300 and 600 min, indicative of a reaction of carbon and/or the solid electrolyte material with lithium. The composite milled for 10 min exhibited a low 1st discharge capacity of approximately 550 mAh g$^{-1}$, which is less than half of the theoretical capacity of sulfur. The discharge capacity increased with milling time from 10 to 300 min to reach 1580 mAh g$^{-1}$. This tendency is in good agreement with the previous reports that mechanical milling enhances the discharge performance of the all-solid-state Li–S battery.21,23 When the milling time is increased to longer than 300 min, very little change was observed in the discharge capacity, which remained at approximately 1500 mAh g$^{-1}$. 

![Figure 1](image1.png)

**Figure 1.** SEM images of the composite prepared with a milling time of 300 min.

![Figure 2](image2.png)

**Figure 2.** (a) Initial charge–discharge curves of composite electrodes prepared with milling times of 10, 300, and 600 min. (b) Milling time dependence of the 1st discharge capacity for the composite electrodes. The cut-off voltages for discharging and charging were 1.0 and 3.0 V, respectively, versus the Li–Al alloy anode.
Ionic conductivity (the sum of the bulk and grain boundary contributions) was evaluated before and after the milling process to assess the increase in discharge capacity by milling. The SE alone was subjected to mechanical milling for 300 min in the same manner as for the composite preparation. Before milling, the ionic conductivity was 1.8 mS cm\(^{-1}\), which is comparable to reported values.\(^{17}\) After milling for 300 min, the conductivity decreased to 0.7 mS cm\(^{-1}\), possibly due to deterioration of the crystallinity in the SE.\(^{24}\) Thus, mechanical milling can provide a well-mixed composite incorporating S, AB, and the SE. Increased conduction pathways for lithium ions and electrons were formed in the composite matrix, contributing to the high discharge capacity of the battery, even though the milling also reduced the ionic conductivity of the SE.\(^{25}\) The fact that prolonged milling (\(>300\) min) decreased the polarization for the charging and discharging reactions is clear evidence for this hypothesis.\(^{4}\)

XRD analysis was performed on the composite electrode, S, AB, and SE before and after milling individually for 300 min in the same manner as for the composite fabrication to elucidate the effect of mechanical milling on the crystal structure. The obtained XRD patterns are illustrated in Fig. 3. Diffraction peaks corresponding to S and AB disappeared after milling, indicative of material amorphization. Before milling, the SE exhibited sharp diffraction lines corresponding to the crystalline Li\(_{10}\)GeP\(_2\)S\(_{12}\)-type and \(β\)-Li\(_3\)PS\(_4\) phases.\(^{25}\) After milling, the diffraction peaks became broader, indicative of slight disorder in the long-range atomic arrangement of the crystal structure. Nevertheless, the crystal structure framework was maintained. On the other hand, the XRD pattern of the composite after milling was much broader than that of the individually milled SE. Hence, milling the mixture triggers additional reactions involving the SE.

Raman spectra were recorded for the composite electrode and for each material both before and after milling. As shown in Fig. 4, AB exhibited no Raman bands in the region of 200–700 cm\(^{-1}\) before or after milling. On the other hand, the Raman bands of S were almost unchanged after milling. Therefore, the S\(_8\) ring structure was maintained while the long-range atomic arrangement was distorted, as confirmed by XRD.

While the SE maintained its Raman bands, the intensities at around 290 and 380 cm\(^{-1}\) were slightly decreased. These intensities are attributable to PS\(_4\) and GeS\(_4\) units in the SE structure, respectively.\(^{26,27}\) The decrease in the intensity of the Raman bands indicates a distortion of the polyhedral units or decomposition of the materials incorporating the specific units\(^{28,29}\) indicating that the mechanical milling either reduced the symmetry of these local structures or decomposed the SE. On the other hand, the diffraction peaks in the XRD pattern result from long-range ordering of the crystal structure, which is composed of the ordered arrangements of polyhedral units. Therefore, the observed Raman results are in good agreement with the XRD characterization, which indicated a slight disorder in the long-range atomic arrangement.

For the composite, the Raman bands corresponding to the SE almost disappeared after milling, although a weak Raman band corresponding to sulfur was observed at around 480 cm\(^{-1}\). The SE clearly deteriorated more significantly after milling in the composite compared to that milled alone. These results also agree well with the XRD results.

An additional peak at around 350 cm\(^{-1}\) in the milled composite corresponds to the formation of a novel structural unit, namely a Ge–S-based material with non-crystalline characteristics and/or a sulfur-rich composition.\(^{30,31}\) This additional peak was not observed in the individually milled SE. Thus, the byproduct with a novel structural unit is likely formed by a reaction of the materials during milling. As the novel structure is possibly associated with Ge–S bonds, it could be generated by a reaction between the SE and S.
between sulfur and lithium in the composites.\textsuperscript{10} A high capacity of 300 mAh g\textsuperscript{-1} was observed around 1.2 V for the battery using a Li–In alloy anode.

Further electrochemical characterization was conducted for the composite prepared by milling for 300 min. To evaluate the cyclability of the battery, the low-voltage Li–Al anode was replaced with a Li–In anode to eliminate unexpected reactions (e.g., that between carbon and lithium) and to prevent the decomposition of SE in the low voltage region.\textsuperscript{4,20,23} In addition to this change, cut-off voltage of discharge process was slightly increased. The cut-off voltage of 0.73 V (vs. Li–In; 1.33 V vs. Li) was selected instead of 1.0 V (vs. Li–Al; 1.30 V vs. Li). This difference of 0.03 V also could contribute to suppressing the additional capacity from the side reactions. Figure\textsuperscript{5(a)} shows the charge–discharge curves of the battery using the composite electrode. Flat voltage regions were observed around 1.3 and 1.7 V (vs. Li–In), indicating a reaction between sulfur and lithium in the composites.\textsuperscript{10} A high capacity of over 1100 mAh g\textsuperscript{-1} was observed at the initial discharge. The specific capacity is smaller than that of the battery using a Li–Al anode. However, no additional plateau region in the discharge curve was observed in the low voltage region, which was confirmed around 1.2 V for the battery using a Li–Al anode (Fig. 2). The electrochemical capacity from this region is approximately 300 mAh g\textsuperscript{-1} for the battery using a Li–Al anode. The difference in the capacity due to the changes of the anode electrode and cut-off voltage is approximately 450 mAh g\textsuperscript{-1}. Thus it can be concluded that dominant contribution for the difference could be raised from the decomposition of the solid electrolyte and reaction between carbon and lithium. Consequently, the battery using the Li–In anode showed smaller discharge capacity than that of the battery with Li–Al anode.

Figure\textsuperscript{5(b)} shows that the discharge capacity decreased with cycling, and a low value of 500 mAh g\textsuperscript{-1} was observed at the 30th cycle. While the Coulombic efficiency increased with cycling, it did not exceed 97\%, indicating some irreversibility of the battery reaction. Although prolonged milling possibly contributes to the high electrochemical activity of the composite electrode with the SE (Li\textsubscript{1.25}Ge\textsubscript{0.25}P\textsubscript{0.75}S\textsubscript{4}), the resulting cycle capability is not sufficient for practical use. The low capacity retention is partly caused by the 3\% irreversible capacity loss. Hence, a small fraction of the lithium inserted during discharging is not extracted from sulfur in the following charging process. In addition, an increase in charge-discharge polarization is confirmed in the charge-discharge curves. On the other hand, significantly better performance has been reported for a composite of sulfur, AB, and 80Li\textsubscript{2}S·20P\textsubscript{2}S\textsubscript{5} (mol\%) glass–ceramic that was prepared by mechanical milling for 300 min at 370 rpm. The other composite exhibited a discharge capacity of >1000 mAh g\textsuperscript{-1} in the 50th cycle with 100\% efficiency.\textsuperscript{10} These differences clearly show that the composition of SEs employed in the composite affects the battery performance.

The charge-discharge curves were analyzed to identify additional contributions to the insufficient cycle capability of the composite prepared in this study. Figure\textsuperscript{6} shows the differential capacity plots of the charge-discharge curves. With cycling, the peak positions shifted to high and low potentials during charging and discharging, respectively. In particular, the peak associated with charging shifted and became broader. The charging and discharging peaks in the differential capacity plots were analyzed by Gaussian fitting to evaluate inner resistance quantitatively. Charging and discharging peak voltages are plotted in Fig. 7(a). The charging peak was shifted from 1.75 to 1.95 V during cycling while the discharging peak showed a relatively small shift to a lower voltage (1.23 to 1.18 V). Since the charge-discharge measurements correspond to the DC

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(a) Charge-discharge curves of the composite prepared with a milling time of 300 min. (b) Cycle dependence of discharge capacity (black circle) and Coulombic efficiency (red triangle: [charge capacity–discharge capacity]). The cut-off voltages for discharging and charging were 0.73 and 2.4 V, respectively, versus the Li–In alloy anode.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Differential charge-discharge capacity plots for the composite prepared with a milling time of 300 min.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Charging/discharging peak voltage estimated from the differential capacity plots (a), and overpotentials of the charging/discharging reaction (b).}
\end{figure}
polarization of the cell, this asymmetric peak shift is attributable to not the separator electrolyte but to the electrode reaction. As the Li-In anode is generally used as a counter or reference electrode in all-solid-state batteries, its asymmetric reaction is assumed to be negligible. Thus, the asymmetric peak shift may be caused by the composite electrode. These results also indicate the increased inner resistance of the composite electrode, and the slow reaction kinetics of the charging reaction, i.e., lithium extraction. The overpotentials of the charging/discharging reaction were estimated from the differential capacity plots using the average reaction voltage of 1.49 V, which was determined from the average voltage of the 1st charge/discharge peaks (Fig. 7(b)). The charging and discharging overpotentials increased from 0.26 to 0.46 V and 0.26 to 0.32 V, respectively. From these values and the applied current (83.75 mA g\(^{-1}\)), the inner resistances were estimated to be 4920 and 7371 \(\Omega\) at the 1st and 30th cycle, respectively. This significant increase in the inner resistance of the battery could be a dominant factor in its poor cyclability.

According to the structural characterizations by XRD and Raman measurements, the composites predominantly contain the byproduct with the novel structural unit. Therefore, the poor reversibility and high resistance are attributed to this byproduct from the reaction between the \(\text{Li}_2\text{S–GeS}_2–\text{P}_2\text{S}_5\)-based SE and sulfur. This reaction may be due to the lower electrochemical stability of the \(\text{Li}_2\text{S–GeS}_2–\text{P}_2\text{S}_5\)-based SE than the Li–P–S–based system. \(^{23}\)

Although the slow kinetics of the charging reaction in this system remain under investigation, the contribution of the SE to the inner resistance was analyzed. Charge-discharge experiments were performed using a composite of SE and AB prepared by mechanical milling for 300 min, and Fig. 8 shows the charge-discharge curves. The composite exhibited electrochemical activity with reversible capacities at around 60 mAh g\(^{-1}\). The solid electrolyte was possibly activated by prolonged milling, and relatively high reaction potentials were observed at around 1.3 and 1.7 V (vs. Li–In) for discharging and charging, respectively, which are also indicative of SE contributing to the battery reaction. \(^{14,15}\) During battery reactions, the composition, crystal structure, and lattice parameters of the SE are expected to be modified. \(^{13}\) Therefore, the activation of the SE (\(\text{Li}_2\text{GeS}_2\text{P}_2\text{S}_5\)) itself not only contributes to the capacity but also increases the resistance of the composite.

4. Conclusion

Composite electrodes incorporating sulfur, acetylene black, and a thio–LISICON solid electrolyte \(\text{Li}_2\text{GeS}_2\text{P}_2\text{S}_5\) were prepared by mechanical milling for use in an all-solid-state lithium-sulfur battery. The discharge capacity of the battery with a Li–Al alloy anode and the as-prepared composite electrode depends on the milling time. A long milling time of 300 min afforded a high initial charge-discharge capacity (>1500 mAh g\(^{-1}\)) for the composite, possibly associated with the formation of ionic and/or electronic conduction pathway during prolonged milling.

Structural and electrochemical analysis of the composite prepared by milling for 300 min led to the following conclusions:

(i) A long milling time deteriorates the crystal structure of the materials and triggers side reactions between S and the SE.

(ii) The composite exhibits a high discharge capacity (\(>1100\) mAh g\(^{-1}\)) with the Li–In alloy anode but with insufficient cycle capability.

(iii) Capacity fading of the battery is attributed to the irreversible reaction and increased the inner resistance of the composite.

(iv) The SE (\(\text{Li}_2\text{GeS}_2\text{P}_2\text{S}_5\)) itself can contribute to the battery reaction as well as the resistance, due to the compositional changes associated with the insertion or extraction of lithium.

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