The electrochemical window of solid electrolytes (SEs) plays a crucial role in designing active material–SE interfaces in high-energy-density all-solid-state batteries (ASSBs). However, the suitable electrochemical window for individual active materials is not yet investigated, as the electrochemical window of SEs is overestimated. In this study, the oxidation onset voltages (OOVs) of several SEs, namely those compatible with Li$_2$S as a high-capacity positive electrode material are determined. Results reveal that SEs with low OOVs decrease the capacity and increase the interfacial resistance of the corresponding ASSBs. The OOVs of SEs must exceed that of Li$_2$S by more than 0.2 V to achieve high capacity, which in turn depends on SE ionic conductivity. Therefore, an Li$_2$S positive electrode is combined with pseudobinary Li-oxyacid salts as SEs, exhibiting high OOVs and ionic conductivities, to afford a high-capacity (500 Wh kg$^{-1}$) ASSB with high Li$_2$S content.

1. Introduction

All-solid-state batteries (ASSBs) with solid electrolytes (SEs) have attracted considerable attention due to the advantages of their increased safety, high energy, and high power densities.[1–3] Although the use of high-energy-density active materials,[4,5] thick electrodes,[6] and thin SE layers[7] has allowed the realization of ASSBs with high gravimetric energy densities, these values are still lower than those of Li-ion batteries (maximum 300 Wh kg$^{-1}$).[8] This behavior can be partly ascribed to the high resistance of the sulfide SE–electrode material interfaces,[9,10] which is due to side reactions[11,12] and the loss of interfacial contacts.[13–15] Furthermore, electrochemical decomposition is typically not noted for SEs because they have wide electrochemical windows of 0–5 V versus Li (obtained by cyclic voltammetry).[16–18] However, the experimental electrochemical windows were different from those predicted by first-principles calculations.[19,20] This discrepancy is likely due to a limited area for the electrochemical reaction between the SE and a current collector.[21,22] Recently, working electrodes composed of SE–carbon (C) composite materials, in which carbon is used as a current collector and is dispersed in SEs, have been proposed to evaluate the intrinsic electrochemical windows of SEs.[23–25] The experimental electrochemical windows of sulfide SEs obtained using these electrodes corresponded to those predicted by first-principles calculations.[26,27] These results indicate that sulfide SEs were oxidized at potentials above 2 V versus Li, inducing high interfacial resistance between SEs and high-voltage active materials. In fact, the electrochemical oxidation of sulfide SEs on high-voltage transition-metal oxides results in high interfacial resistance on the positive electrode side.[28–30] The oxidative decomposition of sulfide SEs can be mitigated by the oxide coatings onto high-voltage active materials.[31–33] In addition, oxide and halide SEs with intrinsically high oxidation stabilities have been directly used in positive electrodes.[34–37]

ASSBs with an Li$_2$S based-positive electrode, an Li-metal negative electrode, and a thin SE layer demonstrate high energy densities of up to 370 Wh kg$^{-1}$[38] whereas ASSBs with an Li$_2$S-based positive electrode and realistic negative electrodes and SE layers can achieve energy densities of up to 500 Wh kg$^{-1}$.[1] In most related studies, triple-phase contacts among Li$_2$S, sulfide SEs, and C are formed using electronically and ionically conductive nanoscale networks to achieve high Li$_2$S capacities.[39,40] which is prepared by ball-milling between Li$_2$S, sulfide SEs, and C. In addition, the large contact area between sulfide SE and C enables that sulfide SEs not only provide ion-conduction paths but also act as active materials in Li$_2$S positive electrodes to increase their gravimetric capacities.[41,42] In our previous work, we developed Li$_2$S–LiI solid solutions and prepared composite of Li$_2$S–LiI and C (Li$_2$S–LiI–C) by ball-milling.[43] The characterization of the Li$_2$S–LiI solid solution as the active material needs to avoid the capacity contribution of sulfide SE as the active
material. In Li$_2$S–LiI–C composite itself as the positive electrode, the ionic conductive resistance across positive electrode would have the large impact on the capacity of Li$_2$S–LiI because the ionic conductivity of Li$_2$S–LiI was quite low (<5 × 10^{-6} S cm$^{-1}$).[44] For that reason, sulfide SE was necessary as the ionic conduction path across the positive electrode. Thus, we designed the electrode structure dividing ionically nanoscale (Li$_2$S–LiI–C) and microscale (sulfide SE) network, which was prepared by hand mixing with Li$_2$S–LiI–C and sulfide SEs (Li$_2$S–LiI–C + SE) to minimize the capacity contribution of sulfide SE. Surprisingly, the Li$_2$S–LiI–C + SE electrode have demonstrated a full utilization of Li$_2$S.[43] We have interpreted two points from the results. One is that SEs even with low ionic conductivity functions as the ionically nanoscale network, which is enabled by short ionic diffusion distance and Li chemical diffusion promoted by job-sharing mechanism in composite of SEs and C.[45,46] Another one is that sulfide SEs would be not enough as the ionically nanoscale conduction network due to the decline of ionic conductivity on the charging process; sulfide SE functions as the active material in the interface between sulphide SE and C from the charging process. Actually, the ion conductive resistance of ASSBs with Li$_4$PS$_5$Cl-C composite electrode have been investigated by impedance measurements.[47] During charging process, the oxidation of Li$_6$PS$_5$Cl slows down lithium ion transport and increases an overpotential of sulfur-based positive electrodes.[47]

Furthermore, the superior property of LiI to sulfide SE is only higher electrochemical oxidation stability.[20] The electrochemical oxidation of sulfide SEs lowering the lithium ion transport indicates that SEs should have the proper electrochemical oxidation stability even though 2 V-class sulfur-based electrodes.

In this study, we probed the relationship between the oxidation stability of SEs and the discharge capacity of ASSBs with Li$_2$S positive electrodes. Here, the oxidation stabilities of several Li salts were examined to verify their applicability as the SE, and the contribution of the capacity of sulfide Li$_3$PS$_4$ (LPS) was considered as negligible. In lithium ion batteries, the oxidation stability of liquid based electrolytes has been determined by the onset oxidation voltage (OOV) in linear sweep voltammetry (LSV) to discuss an initial electrolyte electrochemical decomposition reactions and factors controlling them.[48,49] In the same manner, the SE oxidation stability was characterized for SE–C nanocomposites by the OOV in LSV, while the ASSB discharge capacity was measured using a positive electrode comprising Li$_2$S and SE–C composites. The corresponding flow diagram is shown in Scheme 1.

We have found that the experimentally determined OOVs, used as an indicator of SE oxidation stability, agree well with those previously predicted by first-principles calculations.[19,20] The capacities of ASSBs with Li$_2$S positive electrodes significantly increase up to 1000 mA h g$^{-1}$ when the employed SEs have OOVs of >2.6 V versus Li, which is 0.2 V higher than that

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**Scheme 1.** Experimental procedure used in the present study. Li$_2$S capacities were characterized for all-solid-state batteries (ASSBs) with positive electrodes comprising Li$_2$S–Li-salt–C composites and Li$_3$PS$_4$ (LPS). Oxidation stabilities were characterized by linear sweep voltammetry (LSV) of all-solid-state cells (ASSCs) with working electrodes comprising Li-salt–C composites and LPS. Li$_2$S capacity was correlated with the oxidation stability of the Li salts in the Li$_2$S–Li-salt–C composites.
of Li₂S. Furthermore, the discharge capacity of Li₂S using SEs with high OOVs depends on the ionic conductivity of the SEs. The developed, high-Li₂S-content positive electrodes using pseudobinary Li-oxyacid salts with critical OOVs and conductivities exhibit high capacities, which are comparable to the theoretical value of the Li₂S-based positive electrode (500 Wh kg⁻¹).

2. Results and Discussion

The commonly used Li₂S positive electrodes comprise Li₂S, carbon, and an SE prepared by ball-milling to form electronically and ionically conductive nanoscale networks, thus achieving high reversible capacity.⁵⁰–⁵² Therefore, the capacity per gram of Li₂S (mAh g⁻¹) is significantly affected by the electrochemical properties of SEs in the ionically conductive nanoscale networks of the positive electrodes. Most studies have employed sulfide SEs as nanoscale, ionically conductive networks, which are comparable to the theoretical value of the Li₂S-based positive electrode (500 Wh kg⁻¹). Of these, non-sulfide SEs were employed in the current study. As first-principles calculations of SE electrochemical windows suggest that SE oxidation voltage depends on the SE anion type,⁵⁹–⁶⁰ we used Li salts with different anions (LiF, LiCl, LiBr, LiI, Li₃BO₃, Li₂CO₃, Li₃PO₄, Li₂SO₄, LiBH₄, Li₃N, and Li₃P) as the nanoscale, ionically conductive networks of the positive electrodes. To prepare Li₂S–Li-salt–C composites, we mixed Li₂S with one of the Li salts and C by ball-milling. Since the ionic conductivities of the Li salts were much lower than that of the sulfide SE, the ionic conduction path across the positive electrode layers could significantly impact Li₂S capacity.⁶¹–⁶³ To mitigate this effect, we employed sulfide SEs to obtain an ion-conduction path across the electrode layer (i.e., the so-called microscale, ionically conductive network). To exclude the capacity contribution of sulfide SEs, their area of contact with C was minimized as much as possible.⁶⁴,⁶⁵ In SEM images and EDX mappings for mixture of sulfide SE and C prepared by hand mixing and ball-milling, sulfide SE was mixed with C in microscale and nanoscale, respectively.⁶⁶ Mixing method have an impact on their contact area. Figure 1c shows the charge–discharge curves of ASSBs that were fabricated from a mixture (LPS + C), prepared by the hand-mixing of LPS and C, and a composite (LPS–C), prepared by the ball-milling of LPS and C. In ASSBs (Li-In/LPS/LPS–C) with the LPS–C composite, LPS acted as an active material, whereas ASSBs (Li-In/LPS/LPS + C) with the LPS + C mixture exhibited...
and oxygen–phosphorus moieties are minor components and the most of peak were located at the lower binding energy compared to 130 eV. In the references, the binding energy of P 2p_{1/2} for Li_{2}P was located around from 126 to 130 eV. The P 2p spectrum of Li_{2}S–Li_{2}P–C featured peaks of P^5+ and P^6+, indicating the partial oxidation of Li_{2}P.

Figure 2a–c shows the charge–discharge curves of ASSBs (Li–In/LPS/Li_{2}S–Li-salt–C + LPS) with Li_{2}S–Li-salt–C composites, revealing the following capacities: 500 (Li_{2}S–LiF–C), 650 (Li_{2}S–LiCl–C), 800 (Li_{2}S–LiBr–C), 1000 (Li_{2}S–LiI–C), 500 (Li_{2}S–LiBO_{2}–C), 700 (Li_{2}S–Li_{2}CO_{3}–C), 650 (Li_{2}S–LiPO_{4}–C), 650 (Li_{2}S–Li_{2}SO_{4}–C), 150 (Li_{2}S–LiBH_{4}–C), 100 (Li_{2}S–Li_{2}N–C), and 400 mAh g\textsubscript{LPS}^{-1} (Li_{2}S–Li_{2}P–C). Notably, the last three values of those listed above were lower than the discharge capacities of ASSBs with Li_{2}S–Li-halide–C and Li_{2}S–Li-oxyacid–C composites. Furthermore, ASSBs with Li_{2}S–LiBH_{4}–C, Li_{2}S–Li_{2}N–C, and Li_{2}S–Li_{2}P–C had large irreversible capacities. In Li_{2}S–Li_{2}P–C, Li_{2}P acted as an active material (Figure S9, Supporting Information), and the Li_{2}S capacity in this case was calculated by subtracting the capacity of Li_{2}P from the overall capacity (for a more detailed discussion, see the Supporting Information).

The OOVs of the SEs were determined by the LSV characterization of all-solid-state cells (ASSCs) containing Li_{2}S-free composites, which were prepared by the ball-milling of each Li salt and C. The working electrodes were then prepared by the hand-mixing of LPS and the Li-salt–C composites. A schematic illustration of these ASSCs (Li–In/LPS/Li-salt–C + LPS) with the working electrodes used to measure the OOVs of the Li salts is shown in Figure 2d, while the LSV curves of the ASSCs (Li–In/LPS/Li-salt–C + LPS) with the Li-salt–C composites are shown in Figure S10, Supporting Information. The intersection of the base line extrapolation with the curve showing the maximum peak current was defined as the OOV. ASSCs (Li–In/LPS/Li–salt–C + LPS) with Li-salt–C composites, except LiF–C, showed oxidation currents. The OOVs determined from the LSV curves and first-principles calculations are summarized in Table S1, Supporting Information and Figure 2e. In the case of the composites comprising Li halides, LiBH_{4}, and Li_{2}P, the measured OOVs were almost consistent with the calculated oxidation voltages. However, the measured OOVs for the Li-oxyacid- and Li_{2}N-containing composites were more than 1 V, lower and higher, respectively, than the calculated oxidation voltages. A more detailed discussion is presented in the Supporting Information.

Figure 3a shows the relationship between the discharge capacities of the ASSBs with Li_{2}S–Li-salt–C composites and the experimentally measured OOVs of the Li salts. The discharge capacity of ASSBs (Li–In/LPS/Li_{2}S–Li–F–C + LPS) with Li_{2}S–LiF–C was ruled out in the relationship because the OOV and ionic conductivity of LiF could not be measured. However, it should be noted the effect of LiF as an ionic conductive path on the capacity of Li_{2}S. LiF is capable of improving capacity and cycle life as SE interphase (SEI) for lithium metal and high voltage positive electrodes due to wide electrochemical stability. On the other hand, LiF accelerates an aggregation of organic SEI component and plays the role of glue in the SEI film. The interface between LiF and Li_{2}CO_{3} promotes Li\textsuperscript{+} ion defects and works as a high conductive SEI. Therefore, the
Ionic conduction of LiF only would not be enough in SEI. Actually, the capacity of ASSBs (Li–In/LPS/Li₂S–Li-salt–C + SE) with Li₂S–LiF–C is the lowest in the Li₂S-Li-halide–C and LiF only is not effective in the ion conduction path for Li₂S active material. The discharge capacities of the ASSBs (Li–In/LPS/Li₂S–Li₂S–Li-salt–C + LPS) with Li₂S–Li-salt–C composites were under 200 mAh g⁻¹ when the Li salts had OOVs under 2.5 V versus Li. Interestingly, LiBH₄ caused the low discharge capacity even though OOV of LiBH₄ was slightly higher than that of Li₂S. On the other hand, the discharge capacities of the same ASSBs exceeded 600 mAh g⁻¹ when the Li salts had OOVs under 2.5 V versus Li. Interestingly, LiBH₄ caused the low discharge capacity even though OOV of LiBH₄ was slightly higher than that of Li₂S. On the other hand, the discharge capacities of the same ASSBs exceeded 600 mAh g⁻¹ when the Li salts had OOVs under 2.5 V versus Li. Interestingly, LiBH₄ caused the low discharge capacity even though OOV of LiBH₄ was slightly higher than that of Li₂S. On the other hand, the discharge capacities of the same ASSBs exceeded 600 mAh g⁻¹ when the Li salts had OOVs under 2.5 V versus Li. Interestingly, LiBH₄ caused the low discharge capacity even though OOV of LiBH₄ was slightly higher than that of Li₂S.

Although the OOVs of LiBH₄ and LiI only differed by 0.1 V, the discharge capacities of the ASSBs (Li–In/LPS/Li₂S–Li-salt–C + LPS or Li₂S–LiI–C + LPS) with Li₂S–LiH₂BO₄–C and Li₂S–LiI–C were significantly different. To clarify the origin of this behavior, we compared the Nyquist plots of these two ASSBs (Li–In/LPS/Li₂S–Li-salt–C + LPS or Li₂S–LiI–C + LPS) after full charging (Figure 3b). In the case of the ASSB (Li–In/LPS/Li₂S–Li-salt–C + LPS or Li₂S–LiI–C + LPS) containing Li₂S–LiH₂BO₄, we observed a large semi-circle representing interfacial resistance. In the charging process, it is predicted that LiBH₄ is oxidized to an Li-poor oxidant Li₂BₓH₁₂, which would be formed at the interface between Li-salt and C. The formed Li-poor compounds did not act as nanoscale, ionically conductive networks. As the result, the interface area between Li₂S and LiBH₄ was decreased, which increases the interfacial resistance (Figure 3e). On the other hand, the ASSB (Li–In/LPS/Li₂S–LiI–C + LPS) with Li₂S–LiI–C had a smaller interfacial resistance than that of the ASSB (Li–In/LPS/Li₂S–LiBH₄–C + LPS) with Li₂S–LiBH₄–C. The cut off voltage of the charging process was 3.6 V versus Li and LiI (Li-salts with OOVs of >2.6 V vs Li) would be oxidized as well as LiBH₄. In coating materials for high voltage active materials, even though the oxidation voltage of coating materials (Li₂CO₃, Li₃BO₃, LiNbO₃, Li₁.₃Al₀.₃Ti₁.₇(PO₄)₃, Li₂ZrO₃, and LiZr₂(PO₄)₃) is lower than the cut off voltage of ASSBs with high voltage active materials, the coating materials have significantly decreased the interfacial resistance. Therefore, those coating materials would be also oxidized on the high voltage active materials but they still work as the Li ion conductive material. Based on the study about coating materials for high voltage electrode and the obtained Nyquist plots (Figure 3b), we speculate that the oxidation of LiI was limited and the interface area between Li₂S and LiI would be maintained (Figure 3e). Furthermore, when the Li salts exhibited OOVs of >2.6 V versus Li, the discharge capacities of ASSBs with Li₂S–Li-salt–C composites decreased with increasing OOV.
discharge capacities of ASSBs (Li–In/LPS/Li₂S–Li-halide–C + LPS) with Li₂S–Li-halide–C composites decreased depending on the halide in the order of LiI > LiBr > LiCl. However, the OOVs of these salts decreased in the opposite order. Figure 3c shows the impedance spectra of ASSBs (Li–In/LPS/Li₂S–Li-salt–C + SE) with Li₂S–LiCl–C, Li₂S–LiBr–C, and Li₂S–LiI–C after charging, to show the state-of-charge (SOC) value of 50%. The semi-circle in the plot attributed to the diffusion resistance of the Li flux in the Li₂S–Li-halide–C composite when the Li salts had OOVs over and under 2.6 V versus Li.

For the Li fluxes in the Li₂S–Li-halide–C composites, the Li halides would work as the nanoscale, ionically conductive network rather than Li₂S during charging. We focused on the ionic conductivities of the Li salts themselves, which were measured from the alternating current (AC) impedance measurements of their compressed powder pellets (Table S1, Figure S12, Supporting Information). Figure 3d shows that the discharge capacities of the ASSBs (Li–In/LPS/Li₂S–Li-salt–C + LPS) with Li₂S–Li-halide–C composites increased with decreasing diffusion resistance of the Li flux in the Li₂S–Li-halide–C composite. Therefore, the capacities of these ASSBs likely originate from the varying Li fluxes in the Li₂S–Li-halide–C composites (Figure 3e).

The impedance ($Z$) of finite diffusion in an electrode composed of spherical particles is defined in Equation (1), wherein variables $C$ and $R_d$ are calculated using Equations (2) and (3), respectively. 

$$Z = \left( R_o + \frac{1}{S} R_d \right) \frac{j}{\omega C} \quad (1)$$

$$C = \frac{r}{3} \left( \frac{F}{\partial E/\partial c} \right) \quad (2)$$

$$R_d = \left( \frac{-\partial E/\partial c}{FD} \right) \frac{r}{FD} \quad (3)$$

where $R_o$ is the charge transfer resistance, $\omega$ is the angular frequency, $E$ is the open-circuit voltage (OCV), $c_i$ is the concentration of the electroactive species in the active electrode material, $r$ is the diffusion length, $D$ is the diffusion coefficient of the electroactive species, and $F$ is the faraday constant. Additionally, $R_d$ in Equation (3) is the ratio of applied voltage to the flux of an electroactive species in the active electrode material; thus, we assumed that $R_d$ in our study represents the diffusion resistance of the Li flux in the Li₂S–Li-halide–C composite ($R_d$ Li₂S–Li-halide–C). The semi-circle in the plot attributable to $R_d$ was not observed. Therefore, the capacities of the ASSBs with Li₂S–Li-salt–C depend on the diffusion resistance of the Li flux in the Li₂S–Li-salt–C composite when the Li salts had OOVs over and under 2.6 V versus Li. The intersection points of the tangent of the slope with the phase angles of 45° and 90° are defined as transitions from semi-infinite diffusion to finite diffusion in active materials. Furthermore, the real axis of the intersection was determined to be represented by $\frac{1}{2} R_d$ (Figure S11, Supporting Information) in Equation (1). The values of $R_d$ Li₂S–LiCl–C, $R_d$ Li₂S–LiBr–C, and $R_d$ Li₂S–LiI–C were 2250, 1670, and 675 Ω cm², respectively. Figure 3d shows that the discharge capacities of the ASSBs (Li–In/LPS/Li₂S–Li-halide–C + LPS) with Li₂S–Li-halide–C composites increased with decreasing diffusion resistance of the Li flux in the composites. Therefore, the different capacities of these ASSBs likely originate from the varying Li fluxes in the Li₂S–Li-halide–C composites (Figure 3e).
increased with increasing ionic conductivities of the Li halides, indicating that the conductivities of Li salts have a greater effect on the Li$_2$S positive electrodes when the SEs have OOVs of >2.6 V versus Li. Thus, SEs should preferably have OOVs of >2.6 V versus Li and high ionic conductivities (Figure 3e).

The development of broadly applicable energy storage devices with energy densities of ≈500 Wh kg$^{-1}$ is an important research target. In particular, calculations assuming a 20-µm-thick Li negative electrode, 20-µm-thick SE layer, and 10-µm-thick current collectors (Equation (S12), Table S2, Figure S13, Supporting Information) suggest that ASSBs with an energy density of 500 Wh kg$^{-1}$ require a Li$_2$S content of >40 wt% and a capacity of >1000 mAh g$_{Li2S}$$^{-1}$; however, the Li$_2$S content reported in most papers is 30–40 wt% (Table S3, Supporting Information). Herein, positive electrodes with an Li$_2$S content of 40 wt% were prepared using Li$_2$S as a nanoscale, ionically conductive network (Li$_2$S:Li$_2$C:LiPS = 40:10:10:40, w/w/w/w) to exhibit the highest capacity (Figure 3a). Figure S14, Supporting Information presents the charge-discharge curves of the ASSBs (Li–In/LPS/Li$_2$S–LiliC + LPS, 30 and 40 wt% Li$_2$S) with 30 and 40 wt% Li$_2$S. The battery capacity in latter case was much lower than that in the former case. The volume ratio of Li$_2$S:Li$_2$C + C in Li$_2$S–LiliC–C was then decreased from 18 vol% (Li$_2$S:Li$_2$C = 30:20:10, w/w/w) to 8 vol% (Li$_2$S:Li$_2$C = 40:10:10, w/w/w) based on the densities of Li$_2$S (1.66 g cm$^{-3}$), Li$_2$C (4 g cm$^{-3}$), and carbon (2 g cm$^{-3}$). As ionically conductive Li$_2$S has a relatively high density, this decrease in its volume within the composite decreased the capacity of the ASSB (Li–In/LPS/Li$_2$S–LiliC + LPS, 40 wt% Li$_2$S) with 30 wt% Li$_2$S. Therefore, we concluded that SEs must have a low density as well as critical OOV and ionic conductivity values.

Li$_3$PO$_4$ exhibits a suitable OOV (2.6 V vs Li) and a relatively low mass density (2.5 g cm$^{-3}$) but features a suboptimal ionic conductivity (Table S1, Supporting Information). Therefore, if the ionic conductivity of this salt is improved, it can be used as a nanoscale, ionically conductive network to increase the Li$_2$S content, while maintaining its high reversible capacity. To improve the ionic conductivity of Li$_3$PO$_4$, there are several strategies such as solid solution with aliovalent element substitution/doping at both cationic and anionic sites, interface engineering due to the addition of insulating fine particles, and composite ceramic/polymer electrolytes. Here, we focused on the use of the mixed anion effect to improve the conductivity of Li-ion-conducting glasses in pseudobinary systems, because the XRD pattern of Li$_2$S–Li$_3$PO$_4$–C revealed the amorphous nature of its Li$_3$PO$_4$ component (Figure S1b, Supporting Information). There are possible combinations and compositions of the pseudobinary systems. For the present study, an Li$_3$PO$_4$–Li$_2$SO$_4$ pseudobinary system, prepared by the ball-milling of Li$_3$PO$_4$ and Li$_2$SO$_4$, was investigated because Li$_2$SO$_4$ has higher conductivity and OOV values than those of Li$_3$PO$_4$. Furthermore, Li$_3$PO$_4$–Li$_2$SO$_4$ glass (50:50 mol%) could be prepared by rapid quenching. The conductivity of this system was obtained from the AC impedance of the corresponding compressed powder pellet. Figure 4a shows the Nyquist plots of Li$_3$PO$_4$–Li$_2$SO$_4$ pure Li$_3$PO$_4$, and pure Li$_2$SO$_4$. The semi-circle and spike observed in the Nyquist plot of Li$_3$PO$_4$–Li$_2$SO$_4$ indicated that this system exhibited an ionic conductivity of 10$^{-8}$ S cm$^{-1}$, a value greater than those of pure Li$_3$PO$_4$ and Li$_2$SO$_4$. The improved ionic conductivity has been seen in many mixed glass former glasses although the mechanism has not been fully explained due to a nonlinear and non-additive change in the ionic conductivity. In Li$_3$BO$_4$–Li$_2$SO$_4$ glass system, the elastic moduli are decreased with increasing the Li$_2$SO$_4$ content, which enables the densification of the pellet by cold pressing. Thus, one of the reasons in the improved ionic conductivity would be a reduced grain boundary resistance in Li$_3$PO$_4$–Li$_2$SO$_4$.

An Li$_3$PO$_4$–Li$_2$SO$_4$–C composite was then prepared by ball-milling to measure the OOV of Li$_3$PO$_4$–Li$_2$SO$_4$. Figure 4b presents the LSV curve of an ASSC (Li–In/LPS/Li$_3$PO$_4$–Li$_2$SO$_4$–C + LPS) with Li$_3$PO$_4$–Li$_2$SO$_4$–C, as well as those of ASSCs with Li$_3$PO$_4$–C and Li$_2$SO$_4$–C. The OOV of Li$_3$PO$_4$–Li$_2$SO$_4$ was found to be ≈2.1 V versus Li–In, which corresponds to 2.7 V versus Li, and was not significantly different from that of Li$_3$PO$_4$. Thus, the prepared Li$_3$PO$_4$–Li$_2$SO$_4$ had a relatively high conductivity and an OOV of 2.7 V versus Li, making it a suitable, ionically conductive, nanoscale network for the Li$_2$S–Li-salt–C composite. An Li$_3$S–Li$_2$PO$_4$–Li$_2$SO$_4$–C composite was prepared by ball-milling in the same way as the Li$_2$S–Li-salt–C composites were, with the corresponding XRD pattern shown in Figure 4c. This pattern featured no peaks of Li$_3$PO$_4$, Li$_2$SO$_4$, or C, suggesting that Li$_3$PO$_4$ and Li$_2$SO$_4$ were present in an amorphous state. Figure 4d presents the SEM images and EDX mappings of the Li$_3$S–Li$_2$PO$_4$–Li$_2$SO$_4$–C composite, demonstrating the homogeneous mixing of its constituents. The XPS spectra of this composite (Figure 4e) featured the P 2p and S 2p signals of Li$_3$PO$_4$ and Li$_2$SO$_4$, indicating that no side reactions occurred between Li$_3$S, Li$_3$PO$_4$, Li$_2$SO$_4$, and C.

Figure 5 shows the electrochemical properties of ASSBs (Li–In/LPS/Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C + LPS) with Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C. Figure 5a shows the charge-discharge curves of ASSBs (Li–In/LPS/Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C + LPS, Li$_2$S–LiliC + LPS, Li$_2$S–LPS–C + LPS, 40 wt% Li$_2$S, 1 mg cm$^{-2}$) with Li$_3$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C, Li$_3$S–LiliC, and Li$_2$S–LPS–C. The Li$_2$S content in the positive electrode was fixed at 40 wt%. For the electronically and ionically conductive nanoscale network, the contents of C, Li salt, and LPS were all fixed at 10 wt%. For the ionically conductive microscale network, the LPS content was fixed at 40 wt%. Thus, the positive electrodes differed only in the Li salt used as the nanoscale, ionically conductive network. ASSBs (Li–In/LPS/Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C + LPS, Li$_2$S–LiliC + LPS, Li$_2$S–LPS–C + LPS, 40 wt% Li$_2$S, 1 mg cm$^{-2}$) with Li$_2$S–LiliC, Li$_2$S–LPS–C, and Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C exhibited capacities of 400, 650, and 1000 mAh g$_{Li2S}$$^{-1}$, respectively. Notably, ASSBs with Li$_3$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C exhibited high capacity even at a high Li$_2$S content. Li$_3$PO$_4$–Li$_2$SO$_4$ functions as the nanoscale, ionically conductive network even though the ionic conductivity of Li$_3$PO$_4$–Li$_2$SO$_4$ was 10$^{-8}$ S cm$^{-1}$, which was much lower than that of LPS. Chen et al., have found the ultrafast Ag diffusion in the composite of RbAg$_4$I$_5$ and graphite. At an interface of RbAg$_4$I$_5$ and graphite, Ag$^+$ ions and electrons conduct in RbAg$_4$I$_5$ and graphite, which increases the diffusion coefficient by about 10 000 times of RbAg$_4$I$_5$; job-sharing chemical diffusion. In our study, the Li chemical diffusion in Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C would be enabled by the job-sharing chemical diffusion, in which Li$^+$ ions and electrons conduct in Li$_3$PO$_4$–Li$_2$SO$_4$ and C.
For an ASSB (Li–In/LPS/Li₂S–Li₃PO₄–Li₂SO₄–C + LPS) with an Li₂S-based positive electrode to achieve an energy density of 500 Wh kg⁻¹, it should exhibit a reversible capacity of 1167 mAh g⁻¹ Li₂S with an Li₂S content of 40 wt% or a reversible capacity of 1000 mAh g⁻¹ Li₂S with an Li₂S content of 50 wt% (Figure S13, Supporting Information). These values are based on calculations assuming a certain anode, SE layer, and current collector (Equation (S12), Table S2, Supporting Information). Figure S15, Supporting Information shows the effects of Li₂S loading and operating temperature on the electrochemical performance of ASSBs (Li–In/LPS/Li₂S–Li₃PO₄–Li₂SO₄–C + LPS) containing Li₂S–Li₃PO₄–Li₂SO₄–C. To prepare a positive electrode with an Li₂S content of 50 wt%, the content of LPS as the microscale, ionically conductive network was reduced while maintaining the mass ratio of Li₂S:Li₃PO₄:Li₂SO₄:C in the Li₂S–Li₃PO₄–Li₂SO₄–C composite. Accordingly, the weight ratio of Li₂S:Li₃PO₄:Li₂SO₄:C:LPS equaled 50:6.25:6.25:12.5:25. Figure S15a, Supporting Information shows the charge–discharge curves of the ASSBs (Li–In/LPS/Li₂S–Li₃PO₄–Li₂SO₄–C + LPS, 50 wt% Li₂S, 2, 5, or 10 mg cm⁻², 60 °C) containing Li₂S–Li₃PO₄–Li₂SO₄–C with 50 wt% of Li₂S at Li₂S loadings of 2, 5, and 10 mg cm⁻², revealing that the respective discharge capacities equaled 750, 800, and 500 mAh g⁻¹ Li₂S, respectively, that is, they increased with increasing temperature because of the concomitant decrease in internal resistance. Figure S15b, Supporting Information shows the charge–discharge curves of the ASSBs (Li–In/LPS/Li₂S–Li₃PO₄–Li₂SO₄–C + LPS, 50 wt% Li₂S, 2, 5, or 10 mg cm⁻², 60 °C) containing Li₂S–Li₃PO₄–Li₂SO₄–C with an Li₂S content of 40 wt% and a loading of 2 mg cm⁻² that were recorded at operating temperatures of 25 and 60 °C. At 25 and 60 °C, the discharge capacities equaled 400 and 800 mAh g⁻¹ Li₂S, respectively, that is, they increased with increasing temperature because of the concomitant decrease in internal resistance. Figure S15b, Supporting Information shows the charge–discharge curves of the ASSBs (Li–In/LPS/Li₂S–Li₃PO₄–Li₂SO₄–C + LPS, 50 wt% Li₂S, 2, 5, or 10 mg cm⁻², 60 °C) containing Li₂S–Li₃PO₄–Li₂SO₄–C with 50 wt% of Li₂S at Li₂S loadings of 2, 5, and 10 mg cm⁻², revealing that the respective discharge capacities equaled 750, 800, and 500 mAh g⁻¹ Li₂S, respectively, that is, they increased with increasing temperature because of the concomitant decrease in internal resistance. Figure S15b, Supporting Information shows the charge–discharge curves of the ASSBs (Li–In/LPS/Li₂S–Li₃PO₄–Li₂SO₄–C + LPS, 50 wt% Li₂S, 2, 5, or 10 mg cm⁻², 60 °C) containing Li₂S–Li₃PO₄–Li₂SO₄–C with 50 wt% of Li₂S at Li₂S loadings of 2, 5, and 10 mg cm⁻², revealing that the respective discharge capacities equaled 750, 800, and 500 mAh g⁻¹ Li₂S, respectively, that is, they increased with increasing temperature because of the concomitant decrease in internal resistance. Figure S15b, Supporting Information shows the charge–discharge curves of the ASSBs (Li–In/LPS/Li₂S–Li₃PO₄–Li₂SO₄–C + LPS, 50 wt% Li₂S, 2, 5, or 10 mg cm⁻², 60 °C) containing Li₂S–Li₃PO₄–Li₂SO₄–C with 50 wt% of Li₂S at Li₂S loadings of 2, 5, and 10 mg cm⁻², revealing that the respective discharge capacities equaled 750, 800, and 500 mAh g⁻¹ Li₂S, respectively, that is, they increased with increasing temperature because of the concomitant decrease in internal resistance.
Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C electrodes with an Li$_2$S content of 40 wt%.

b) Charge–discharge curves of ASSBs (Li–In/SE/Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C) and 0.05 C (Figure 5b) and 0.1 C (Figure S17, Supporting Information) show the results obtained for ASSBs (Li–In/SE/Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C) with Li$_2$S loading of 10 mg cm$^{-2}$ at 0.02, 0.03, 0.05, and 0.1 C. d) Charge–discharge curves of ASSBs (Li–In/SE/Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C) recorded at 60 °C and 25 °C containing Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C electrodes with Li$_2$S content of 40 wt% and Li$_2$S loading of 10 mg cm$^{-2}$ at 0.1 C and 60 °C for 50 cycles. 

e) Cycle performance of ASSBs (Li–In/SE/Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C) in fine SE, 40 and 50 wt% Li$_2$S, 10 mg cm$^{-2}$ recorded at 60 °C and 1000 mAh g Li$_2$S$^{-1}$, corresponding to an areal capacity of 900 mAh g cm$^{-2}$. The ASSB (Li–In/LPS/Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C + fine SE, 50 wt% Li$_2$S, 10 mg cm$^{-2}$, 60 °C) containing Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C electrodes with Li$_2$S at a loading of 10 mg cm$^{-2}$. The ASSB (Li–In/LPS/Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C + fine SE, 50 wt% Li$_2$S, 10 mg cm$^{-2}$, 60 °C) containing Li$_2$S–Li$_3$PO$_4$–Li$_2$SO$_4$–C with an Li$_2$S content of 40 wt% and an Li$_2$S loading of 10 mg cm$^{-2}$ recorded at 0.1 C and 0.2 C (Figure S17, Supporting Information) respectively, for 50 to 60 cycles run at 60 °C. The areal and gravimetric capacities of the positive electrode are summarized in Table S4, Supporting Information and presented in Figure 5f. For ease of comparison, the previously obtained capacities of the Li$_2$S-based positive electrode were standardized with respect to positive electrode mass, and the capacities of ASSBs with Li$_2$S-based positive electrodes (both areal and per gram of positive electrode) were also included (Table S3, Supporting Information). Figure 5f displays the predicted energy densities of ASSBs based on the capacity per gram of positive electrode and the areal capacity calculated by Equation (4) (assuming an SE layer and current collectors) (Table S2, Supporting Information). The ASSBs with Li$_2$S and Li$_2$S–LiI nanocomposites exhibited high gravimetric and areal capacities, reaching the predicted energy density of 300–400 Wh kg$^{-1}$. However, these gravimetric and areal capacities were still insufficient to reach an energy density of 400–500 Wh kg$^{-1}$. On the other hand, the Li$_2$S positive electrode containing Li$_3$PO$_4$–Li$_2$SO$_4$ could potentially be used to fabricate ASSBs with an energy density of 400–500 Wh kg$^{-1}$. Thus, SEs with critical OOVs, high ionic conductivities, and low mass densities were...
found to be suitable for the construction of high-Li$_2$S-content positive electrodes with high reversible capacity.

3. Conclusion

We successfully demonstrated the use of SEs with critical oxidation stability to increase the capacity of Li$_2$S as the active material of ASSBs (Li–In/LPS/Li$_2$S–Li–salt–C + SE). The capacities of ASSBs with an Li$_2$S positive electrode significantly increased when the employed SEs had OOVs of >2.6 V versus Li, in which case the capacities were limited by the ionic conductivities of these SEs. Therefore, it was concluded that proper SEs should exhibit an OOV of >2.6 V versus Li and have the maximum possible ionic conductivity to act as nanoscale, ionically conductive networks in Li$_2$S positive electrodes. This obtained insight was used to fabricate a pseudo-binary Li-oxycide SE with the critical OOV (> 2.6 V vs Li) and ionic conductivity of 10$^{-8}$ S cm$^{-1}$, which allowed us to achieve a high capacity of >1000 mAh g$^{-1}$Li$_2$S with a high Li$_2$S content (40 to 50 wt%) in the positive electrode. In addition, the corresponding positive electrode could enable the design of ASSBs with an energy density of 400–500 Wh kg$^{-1}$. The adopted strategy will be also suitable for the development of both 2-V-class, sulfur-based positive electrode materials and high-voltage positive electrode materials. Furthermore, these results are expected to aid the design of artificial SE interfaces on electrode active materials and deepen our understanding of the role of these interfaces in Li-ion batteries.

4. Experimental Section

Preparation of Li$_2$S–Li–salt–C Composites: Li$_2$S (Mitsuwa Chemicals Co., Ltd.) was hand-mixed with LiF (Aldrich, 99.9%), LiCl (Aldrich, 99.9%), LiBr (Aldrich, 99.9%), LiI (Aldrich, 99.9%), Li$_3$BO$_3$, Li$_2$CO$_3$, Li$_3$PO$_4$, Li$_2$SO$_4$, LiBH$_4$ (Aldrich, 90%), Li$_3$N, or Li$_3$P in a 30:20 weight ratio. The mixture of Li$_3$PO$_4$–Li$_2$SO$_4$ and LiF, LiCl, LiBr, LiI, Li$_3$BO$_3$, Li$_2$CO$_3$, Li$_3$N, LiBH$_4$, Li$_3$P, or Li$_3$P with C in a weight ratio of 50:10. The mixture was placed into a ZrO$_2$ pot (45 mL) with 160 ZrO$_2$ balls (diameter = 4 mm) and was mechanically milled using a planetary ball mill (Fritsch Pulverisette 7) for 10 h at 510 rpm under Ar. To obtain Li$_3$BO$_3$, a mixture of Li$_2$S–Li salt composites was prepared by hand-milling mixtures of the Li$_2$S–Li salt composites. The sample mass was about 0.2 g.

Preparation of Li$_2$S–Li–salt–C Composites: Li$_2$S (Mitsuwa Chemicals Co., Ltd.) was hand-mixed with LiF (Aldrich, 99.9%), LiCl (Aldrich, 99.9%), LiBr (Aldrich, 99.9%), LiI (Aldrich, 99.9%), Li$_3$BO$_3$, Li$_2$CO$_3$, Li$_3$PO$_4$, Li$_2$SO$_4$, LiBH$_4$ (Aldrich, 90%), Li$_3$N, or Li$_3$P in a weight ratio of 50:10. The mixture of Li$_3$PO$_4$–Li$_2$SO$_4$ and C in a 5:1 weight ratio using a planetary ball mill (Fritsch Pulverisette 7) for 10 h at 510 rpm under Ar. To obtain Li$_3$BO$_3$, a mixture of Li$_2$S–Li salt composites was prepared by hand-milling mixtures of the Li$_2$S–Li salt composites. The sample mass was about 0.2 g.

Preparation of Li$_2$S Positive Electrodes: The LPS glass SE prepared by mechanical milling and used as the microscale, ionically conductive network in the positive electrode and SE layers for ASSBs featured an ionic conductivity of >10$^{-4}$ S cm$^{-1}$ at 25 °C. The Li$_2$S positive electrodes comprised Li$_2$S–Li–salt–C and LPS in a weight ratio of 60:40. Accordingly, the weight ratio of Li$_2$S, Li salt, C, and LPS in the positive electrode equaled 30:20:10:40. The prepared Li$_2$S–Li–salt–C and LPS were hand-mixed in a dry, Ar-filled glove box to decrease the capacity contribution of LPS.

ASSBs with Li$_2$S Positive Electrodes: Fabrication and Electrochemical Characterization: ASSBs with a Li–In/Li$_2$S–Li–salt/LPS electrode were fabricated as follows: The prepared Li$_2$S positive electrodes (~3 mg cm$^{-2}$) with an Li$_2$S loading of 0.9−1.0 mg cm$^{-2}$ and an SE layer (80 mg) were set in a polycarbonate tube (diameter = 10 mm) and pressed at 360 MPa. A 300-μm-thick In foil and a 250-μm-thick Li foil were then placed on the surface of the SE side of the bilayer pellet as a counter-reference electrode. The three-layered pellet was then sandwiched between two stainless-steel disks as current collectors. Finally, ASSBs were obtained by pressing at 72 MPa. Charge–discharge tests of the constantly tightened cells were conducted at a constant current density of 64 μA cm$^{-2}$ (0.5 C, 1 C = 1167 mA g$^{-1}$) and 25 °C under Ar using a charge–discharge device (BTS-2004, Nagano Co.). The voltage ranged from 0 to 3.0 V versus Li–In. The interfacial and diffusion properties of the positive electrode were probed by AC impedance measurements, which were carried out at voltages and frequencies of 10 mV versus OCV and 10$^{-2}$−10$^{2}$ Hz, respectively.

Preparation of Li salt–C Electrode for the Determination of Li Salt Oxidation Onset Voltage: Li salt–C composites were prepared by hand-mixing LiF, LiCl, LiBr, LiI, Li$_3$BO$_3$, Li$_2$CO$_3$, Li$_3$N, LiBH$_4$, Li$_3$P, or Li$_3$P with C in a weight ratio of 50:10. The mixture was placed into a ZrO$_2$ pot (45 mL) with 160 ZrO$_2$ balls (diameter = 4 mm) and mechanically milled using a planetary ball mill (Fritsch Pulverisette 7) for 10 h at 510 rpm under Ar. The sample mass equaled 0.3 g. The Li salt–C electrodes comprised an Li salt–C composite and LPS in a weight ratio of 60:40. Accordingly, the weight ratio of Li salt, C, and LPS in the electrodes equaled 50:10:40. Li salt–C and LPS were hand-mixed in a dry Ar-filled glove box, and the obtained Li salt–C electrodes were used as the ASSC working electrodes. ASSCs with Li–In/Li salt–C electrodes were fabricated as follows: The prepared Li salt–C electrode (~3 mg cm$^{-2}$) and the SE layer (80 mg) were set in a polycarbonate tube (diameter = 10 mm) and pressed at 360 MPa. A 300-μm-thick indium foil and a 250-μm-thick lithium foil were then placed on the surface of the SE side of the bilayer pellet as a counter-reference electrode. The three-layered pellet was then sandwiched between two stainless-steel disks as current collectors. Finally, ASSCs were obtained by pressing at 72 MPa. LSV analysis of the constantly tightened cells was conducted at a sweep rate of 1 mV s$^{-1}$ and room temperature under Ar using a potentiostat (VersaSTAT 3, AMETEK, Inc.). The voltage ranged from the OCV to 5.0 V (vs Li–In).

Preparation of Li$_2$PO$_4$–Li$_2$SO$_4$ and Li$_2$PO$_4$–Li$_3$SO$_4$–C Composites: To prepare Li$_2$PO$_4$–Li$_2$SO$_4$–C, hand-mixed Li$_2$PO$_4$ and Li$_2$SO$_4$ (25:25, w/w) were mechanically milled under the aforementioned conditions. The Li$_2$PO$_4$–Li$_3$SO$_4$–C composite was prepared by mechanically milling a mixture of Li$_2$PO$_4$–Li$_2$SO$_4$ and C in a 5:1 weight ratio using a planetary ball mill under the aforementioned conditions. The Li$_2$PO$_4$–Li$_3$SO$_4$–C electrode, composed of Li$_2$PO$_4$–Li$_3$SO$_4$–C and LPS, was prepared by hand-mixing Li$_2$PO$_4$, Li$_3$SO$_4$, and C, and LPS in a weight ratio of 25:25:10:40. ASSCs with Li–In/Li$_2$PO$_4$–Li$_3$SO$_4$–C electrodes were fabricated using the procedure employed for ASSCs with Li–In/Li salt–C electrodes to determine the OOV, as shown above. The LSV analysis of constantly tightened cells was conducted under the previously mentioned conditions.

Preparation of Li$_2$S–Li$_2$PO$_4$–Li$_3$SO$_4$–C Positive Electrode for Li$_2$S Capacity Characterization: To fabricate Li$_2$S–Li$_2$PO$_4$–Li$_3$SO$_4$–C, a mixture of Li$_2$S, Li$_2$PO$_4$, and Li$_3$SO$_4$ was prepared by hand-milling a mixture in a weight ratio of 40:5:5. The mixture was mechanically milled using a planetary ball mill under the conditions used to prepare the Li$_2$S–Li salt composites. Li$_2$S–Li$_2$PO$_4$–Li$_3$SO$_4$–C was prepared by the ball-milling of the
corresponding constituents in a weight ratio of 40:5:5:10. The Li$_2$S positive electrodes comprised Li$_2$S-Li$_2$PO$_4$-Li$_2$SO$_4$-C and LPS in a weight ratio of 60:40 and were prepared by hand-mixing. The Li$_2$S:Li$_2$PO$_4$:Li$_2$SO$_4$:C:LPS weight ratio in these positive electrodes equaled 40:5:5:10:40.

ASSBs with High-Energy Li$_2$S Positive Electrodes: Fabrication and Electrochemical Characterization: Li$_2$S-Li$_2$PO$_4$-Li$_2$SO$_4$-C positive electrodes with high Li$_2$S contents were prepared as shown above using Li$_2$S-Li$_2$PO$_4$:Li$_2$SO$_4$:C:SE weight ratios of 40:5:5:10:40 and 50:6.25:6.25:12.5:25. In Li$_2$S-Li$_2$PO$_4$-Li$_2$SO$_4$-C positive electrodes with 50 wt% Li$_2$S, the tested Li$_2$S loadings equaled 2, 5, and 10 mg cm$^{-2}$ (corresponding to electrode loadings of 4, 10, and 20 mg cm$^{-2}$, respectively). For an Li$_2$S loading of 10 mg cm$^{-2}$, a fine sulfide SE powder was used to mitigate the ion conductivity resistance in the positive electrodes. ASSBs with an Li-In/Li$_2$S positive electrode were fabricated as described above. Charge–discharge tests of constantly fabricated as described above. Charge–discharge tests of constantly fabricated as described above.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

T.H. conceived the study concept, designed the experiments, and synthesized the Li$_2$S-based positive electrode. T.H. and Y.F. performed material characterization. M.D. carried out XPS measurements. T.H. and Y.K. carried out AC impedance measurements. T.H. and M.O. summarized the reported capacity of ASSBs with the Li$_2$S-based positive electrode. T.H. calculated the predicted energy density of ASSBs. A.S., A.H., and M.T. supervised the project. T.H. and A.S. wrote the draft. All authors discussed the results and reviewed the manuscript.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

active material, all-solid-state batteries, electrochemical window, ionic conductivity, lithium sulfide, solid electrolytes

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