Solid Electrolyte



Solid Electrolyte Layers by Solution Deposition

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Solid state batteries hold the promise of enhanced safety and higher energy density over conventional lithium-ion batteries with flammable organic electrolytes. However, advancement of solid electrolyte materials has yet to translate into practical batteries due to the need to process the powders into thin sheets with high pressure compaction and high temperature sintering. Here, a new strategy is developed for synthesizing sulfide-based solid electrolyte using low-temperature solution processing, which is a simple and potentially cost-effective way to make a thin solid electrolyte layer. By controlling the stoichiometric ratio of Li₂S and S, soluble polysulfides are produced in diethylene glycol dimethyl ether, which are reacted with P2S5 to form a conductive Li₃PS₄ solid electrolyte. It is demonstrated that a dense solid electrolyte layer can be directly formed on Li metal with a high quality electrolyte/electrode interface, producing a solid electrolyte with promising electrochemical performance. Also, first-principles calculations are conducted to elucidate the formation mechanisms behind the soluble intermediates and the solid electrolyte layers.

1. Introduction

All-solid-state batteries have attracted great attention due to their potential to solve safety issues associated with current lithium ion batteries. Much effort has been devoted to search for new inorganic solid electrolyte (SE) materials because they are key components for advancing all-solid-state battery technology.^[1-3] Among them, sulfide-based SEs are considered the most promising due to their superior conductivities, some of which are comparable to liquid electrolytes.^[1,4-6] However, these materials have yet to see practical application for several reasons. SE materials are typically synthesized by solid-state reactions using mechanical milling and high temperature sintering.^[7–9] In order to fabricate a cell, the powder is mixed with a binder, cast into a sheet, and sintered at high temperatures.^[10–12] It is also common to fabricate a complete solid state battery by directly compressing two powder layers,

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one being the pure electrolyte and the other being a mixture of cathode active material and the solid electrolyte. Therefore, the electrolyte layers are normally thick (on the order of sub-millimeters), which results in low energy densities for solid state batteries. In addition, when lithium metal or cathode is attached to the electrolyte layer, the electrode/electrolyte interface suffers from voids and poor contacts which produce large resistances.^[13,14] These complexities are major hurdles for practical applications of SEs in all-solid-state batteries.

To address these challenges, a liquidbased synthesis and processing route to SEs is highly desirable because it can potentially achieve a thin electrolyte layer with good interface contact with electrode.^[15–17] In the case of sulfide electrolytes, precursor materials (e.g., Li₂S and P₂S₅) are dispersed in solvents, such as

tetrahydrofuran (THF),^[18,19] 1,2-dimethoxyethane (DME),^[20] acetonitrile,^[19] ethyl acetate,^[21] and dimethyl carbonate (DMC),^[22] and can react with each other to form SEs. However, these reported solution-processing methods have critical limitations. First, SEs solutions are limited to forming coatings on cathode materials and cannot be directly applied to Li metal because the reported processing solvents are highly reactive.^[15–17,23] Furthermore, the synthesized SEs usually require post processing at elevated temperatures of around 200–240 °C,^[19,20,22,24] which is over the Li melting point (180 °C). Second, none of these SEs have been fabricated as a thin film. Instead, they are precipitated as particles which need additional processing steps to be compatible with conventional battery fabrication.

In this work, we report a new strategy for synthesizing thin sulfide-based SEs using a solution-processing method. A conductive β -Li₃PS₄ that remains stable in a soluble form was successfully produced by inducing a chemical reaction between soluble polysulfides and P₂S₅ in diethylene glycol dimethyl ether (DEGDME) solvent. Due to the use of nonreactive solvent, it is possible to coat this solution directly on Li metal. Hence, the formation of a thin and dense SE layer (thickness of ~50 µm) with favorable interfacial contact was demonstrated. This solution-processing method does not require high temperature heat treatment or pressing steps. It is the simplest way to produce a thin SE layer directly on Li metal and will provide new insights to fabricating solid-state lithium batteries with high energy densities.



2. Results and Discussions

2.1. Solution-Processing Method

We first need to decide the preferred solvent that can facilitate the formation of a stable precursor solution and is readily removed during film deposition. A summary of the reported solution precursors for sulfide-based SEs (Li₂S-P₂S₅ system, i.e., LPS) synthesis is shown in Figure S1 of the Supporting Information. Strongly polar hosts such as NMF and hydrazine are very effective at dissolving SEs while their high dielectric constants enable them to dissolve ionic compounds composed of $PS_4^{3-,[25,26]}$ However, these solutions have high reactivity so they cannot be applied directly to Li metal surfaces. Conversely, less polar solvents such as THF, DMC, and DME cannot effectively dissolve synthesized SEs, which easily precipitate into particles.^[18,20,22]

To achieve SEs solution using solvents with moderate dielectric constants, we developed a new solution-processing method as schematically illustrated in Figure 1. Considering the physical properties of candidate solvents (Figure S2, Supporting Information), DEGDME was selected due to its relatively low boiling point, high stability, and appropriate dielectric property. To prepare a clear SE solution, Li₂S and S were premixed when they react to form fully soluble polysulfides. Subsequently, P_2S_5 was added into the solution to form the conductive β -Li₃PS₄ $(3Li_2S_3 + 1P_2S_5, i.e., L3PS)$. The prepared L3PS solution can be directly drop-cast on Li metal due to the high stability of DEGDME. The formation of an L3PS SE was achieved after slow evaporation of the solvent. The detailed procedures are described in the Experimental Section. As a reference case, the L1PS solution with the exact stoichiometry (i.e., $3Li_2S + 1P_2S_5$) for Li₃PS₄ was prepared following the same procedures. It is worth mentioning that the addition of sulfur can attribute to the formation of SEs solution in the medium dielectric solvent of DEGDME. The L3PS solution had no visible precipitations while rapid precipitation of white colored particles was observed in the L1PS solution (Figure S3, Supporting Information).



Our observation of the reference L1PS solution is consistent with previous reports showing that precursors are not fully dissolved and precipitated in the medium dielectric constant solvents.^[19,20] Liquid-phase synthesis using DME as the solvent, which has a similar dielectric constant as DEGDME, led to formation of powder precipitates.^[20] Enhanced solubility of Li₃PS₄ in the presence of additional sulfur was also previously observed.^[27] The reaction mechanisms and origin of the difference will be discussed later.

2.2. Material Characterizations

The different solution conditions between L1PS and L3PS SEs lead to a remarkable morphological difference as shown in Figure 2. For the L1PS SE, microscale particles are formed on Li surface (Figure 2a; Figure S4, Supporting Information). The formation of particle-type products is reasonable considering that L1PS SE was already precipitated in the solution and dried on Li metal. In that case, the interfacial contact between L1PS SE and Li metal is poor as demonstrated in the cross-sectional focused ion beam-scanning electron microscopy (FIB-SEM) image showing a gap between L1PS SE and the Li substrate (Figure S5, Supporting Information). Therefore, the previous solutionprocessed SEs need compression to form an effective interface with Li.^[19–22] By contrast, Figure 2b–d reveals that L3PS SE can form a dense film on Li metal. As observed in the SEM images (Figure 2b; Figure S6, Supporting Information), the entire surface of the Li substrate is uniformly covered with a layer of the L3PS SE. The corresponding energy dispersive X-ray spectroscopy (EDS) elemental mapping analyses (Figure S7, Supporting Information) proved that the film is a uniformly distributed mixture of S and P. To measure the thickness of the film, the SEM stage was tilted 30° and a crack point was imaged, as shown in Figure 2c,d. The L3PS SE layer is ≈40 µm thick and elemental line scan analyses (Figure S8, Supporting Information) confirm that Li metal lies underneath the L3PS SE layer, supporting the reliability of the thickness measurement in Figure 2d.



Figure 1. Schematic illustration of the solution-processing method for synthesizing sulfide solid electrolyte. The dissolved polysulfides are prepared by mixing Li_2S and S in DEGDME under a stirring condition at room temperature. The liquid phase of solid electrolyte is produced after the reaction with P_2S_5 in the solution. Then, it is casted on Li metal to form sulfide solid electrolyte layer and residual solvent is dried.





Figure 2. Morphologies of the synthesized L1PS and L3PS solid electrolytes. Top view SEM images of a) L1PS and b) L3PS solid electrolytes coated on Li metal. c) The SEM images of 30° tilted surface of L3PS solid electrolyte and d) the magnified SEM image in the region of white dotted box.

To closely investigate the interface between L3PS SE and Li metal, cross-sectional FIB-SEM and EDS elemental analyses were carried out as shown in Figure 3. The interface between Li metal and L3PS SE (Figure 3a,b) has no gaps or voids; an improvement over the Li/L1PS SE interface (Figure S5, Supporting Information). Corresponding EDS elemental mapping analyses further demonstrate the favorable interface contact (Figure 3c; Figure S9, Supporting Information). The vertical lines are an artifact generated by ion beam movement during the FIB cleaning; the original film is smooth and clean as observed in Figure 2d. To closely analyze elemental composition of L3PS SE, the elemental point scan is conducted by focusing on the inner film (Figure 3d). The L3PS SE is mainly composed of S and P, and the concentrations of other elements are negligible. There is a small loss of sulfur during the drying processes because the measured S/P ratio of the L3PS SE (5.5) is smaller than that of the L3PS solution (7). Furthermore, EDS elemental analyses using the line scan mode (Figure 3e) demonstrate that the ratio between S and P inside the film is constant, indicating the film is compositionally homogeneous. Based on the SEM and EDS analyses, we can conclude that a homogenous thin layer of L3PS SE is successfully formed on Li metal with the intimate interface contact.

2.3. Compositional Analysis

X-ray diffractometry (XRD), Fourier transform-infrared spectroscopy (FT-IR), Raman, and X-ray photoelectron spectroscopy (XPS) measurements were used to identify and analyze the composition of L3PS SE. In **Figure 4**a, XRD results prove that all the peaks of L3PS SE are well matched with β -Li₃PS₄, indicating that L3PS SE is mostly composed of the conductive β -Li₃PS₄ phase. On the contrary, L1PS SE has no relevant peaks while peaks from residual Li₂S are observed. This suggests that Li₂S and P₂S₅, which have negligible solubility in DEGDME, react very slowly with each other in L1PS solution without the addition of sulfur. The surface of L3PS SE coated on Li metal was analyzed using FT-IR spectroscopy in the attenuated total reflection (ATR) mode (Figure 4b). The measurements show a dominant peak at 580 cm⁻¹ consistent with the formation of Li₃PS₄ and no peaks associated with the solvent, confirming its complete removal. Other peaks in the 900–1300 cm⁻¹ region originated from surface contamination (Figure S10, Supporting Information). Formation of Li₃PS₄ is further confirmed by Raman analysis as shown in Figure 4c. The peak at 420 cm⁻¹ is attributed to the P–S vibration in the PS_4^{3-} tetrahedral unit, which is characteristic of Li3PS4.^[5,16,18,22] Weak signals are also observed that correspond to S-S vibrations in S⁰, implying the presence of elemental sulfur. Intuitively, L3PS SE should contain additional sulfur because the total amount of sulfur added to the solution is higher than the exact stoichiometry required for Li₃PS₄.

Further information on the chemical composition was gathered with XPS analysis and the Gaussian–Lorentzian line-shape function was applied to deconvolute the S 2p peaks (Figure 4d). The main signal is consistent with the P–S bond in the PS_4^{3-} tetrahedral units in β -Li₃PS₄ and the doublet originates from the spin–orbit splitting at a 1:2 ratio of $S_{2p3/2}$ and $S_{2p1/2}$.^[28] S–S bonds from sulfur bridging (S⁰) are also identified, which corroborates the results from Raman spectra as well as with previous reports.^[29,30] The S–S vibration can be more reliably identified by comparing to the spectra of a reference β -Li₃PS₄ material (Figure S11, Supporting Information), which does not show S–S vibrations. Based on these analyses, we conclude that L3PS SE







Figure 3. SEM and EDS characterizations for the L3PS solid electrolyte. a) Cross-sectional FIB-SEM image of L3PS solid electrolyte formed on Li metal. b) The magnified SEM image in the region of white dotted box and c) the corresponding EDS elemental mapping results. d) The point-scan EDS spectrum (inset table: atomic ratio) and e) changes of atomic ratios of P and S along the line scan. Each point is displayed in (a).

is primarily composed of $\beta\text{-}\text{Li}_3\text{PS}_4$ with small amounts of elemental sulfur.

2.4. Electrochemical Performances

The electrochemical properties of L1PS and L3PS SEs are analyzed and compared in Figure 5. To measure impedance properties, Li/electrolyte/Li symmetric cells were assembled and their Nyquist plots obtained at room temperature (RT) are shown in Figure 5a. The L1PS SE cell has an extremely high resistance of around 13 M Ω , whereas the L3PS SE cell shows a much lower resistance. Also, the measured conductivity of L3PS SE is 4.18×10^{-7} S cm⁻¹ at RT, which is three orders of magnitude higher than that of L1PS SE. The low conductivity of L1PS SE is likely due to the existence of nonconductive Li₂S and poor interfacial contact with Li metal. Contrarily, the L3PS SE cell forms conductive β -Li₃PS₄ and improves contact, which enhances ion conduction both in the bulk and at the interface, resulting in enhanced ionic conductivity. Although the measured conductivity of L3PS SE film ($\approx 10^{-7}$ S cm⁻¹) is much lower than that of commercial β -Li₃PS₄ powder ($\approx 10^{-4}$ S cm⁻¹), this finding is still significant because the conductivity is measured without any compression process and directly on lithium metal. As a result, the contribution from the Li/electrolyte interface is also included in the conductivity data. To measure the bulk ionic conductivity of L3PS SE without the influence of the Li metal substrate, L3PS SE powders were prepared and compressed into a pellet (Figure S12, Supporting Information). The ionic conductivity of L3PS SE powder is 2.76×10^{-5} S cm⁻¹, which is significantly higher than that of the L3PS SE film on Li metal. Research to understand the source of the differences in conductivities is ongoing. Although the bulk conductivity of L3PS SE is still one order of magnitude lower than that of commercial β -Li₃PS₄ (2.12×10^{-4} S cm⁻¹), the value is competitive and the decrease is attributed to the residual sulfur.

Comparing Bode plots in Figure 5b reveals additional contrasting conduction behavior for the two samples. The different slopes for L1PS and L3PS SEs in the high frequency region indicate that they have different ionic conduction behaviors due to their differing compositions (i.e., Li₂S and Li₃PS₄, respectively, as demonstrated in the XRD results). Also, the impedance value of L3PS SE saturates at a higher frequency range than L1PS SE meaning that the electrochemical impedance







Figure 4. Material characterizations for the L3PS solid electrolyte. a) XRD patterns of L1PS and L3PS solid electrolytes. b) FT-IR spectra of L3PS solid electrolyte and DEGDME solvent. c) Raman and d) XPS analyses of L3PS solid electrolyte.

spectroscopy (EIS) resistance of L3PS SE presented in Figure 5a is mainly bulk resistance, while that of L1PS SE includes both charge transfer resistance and bulk resistance. Therefore, charge transfer at interface would be the rate-determining step for ionic conduction for L1PS SE. This may be due to the poor interfacial contact of L1PS SE to Li metal. Most importantly, the impedance of L3PS SE is lower than that of L1PS SE over all frequency ranges, confirming the enhanced conductivity of L3PS SE over L1PS SE.

Ionic conductivities of L1PS and L3PS SEs were also measured by analyzing the DC response under a constant voltage of 1 V at RT as shown in Figure 5c. Devices with nonblocking electrodes (Li) of L1PS and L3PS SEs show DC resistances of ~15.2 MΩ and ~11.7 kΩ, respectively, which are consistent with the EIS results. When blocking electrodes are used, i.e., In/L3PS/In, the steady current is three orders of magnitude lower than that of nonblocking electrodes. This confirms that the synthesized L3PS SE is a single ionic conductor with negligible electronic conductivity, which is consistent with previously reported SEs synthesized using a solution method.^[17,21] In addition, activation energy (E_a) is estimated from ionic conductivities obtained under different temperatures (Figure 5d). The activation energy of L3PS electrodes (40.21 kJ mol⁻¹) is much lower than that of L1PS electrode (71.17 kJ mol⁻¹), and the value of L3PS is comparable to the previous reports as shown in Figure S1 of the Supporting Information.

To evaluate the electrochemical stability of the L3PS SE, cyclic voltammetry (CV) was conducted as shown in Figure 5e. Reversible lithium deposition and removal peaks at around 0 V are the only redox processes observed in the region from -0.5 to 5.0 V, which guarantees high stability of the L3PS SE. The electrochemical stability is further demonstrated by a cycling test of an Li/L3PS/Li symmetric cell (Figure 5f). Constant voltage plateaus were obtained during discharge and charge processes, and long-term reversible cycling is demonstrated (Figure S13, Supporting Information). The stable CV and reversible cycling performance demonstrate that the L3PS SE film derived from the solution-processing method can be utilized as a solid electrolyte layer directly in a practical Li cell with a high ionic conductivity as well as favorable interface with Li metal. However, testing at higher discharge and charge rates results in apparent internal short circuits (Figure S14, Supporting Information). Although we successfully formed a thin film of SE on an Li metal, the thin film would be relatively vulnerable to the ADVANCED SCIENCE NEWS ______





Figure 5. Evaluation of the electrochemical properties for the L3PS solid electrolyte. a) Nyquist and b) Bode plots of L1PS and L3PS solid electrolytes at room temperature. c) Responses of DC current for the blocking and nonblocking electrodes at a constant voltage of 1 V (vs Li/Li⁺) at room temperature. c) Temperature dependence of ionic conductivities (Arrhenius plots) of L1PS and L3PS solid electrolytes. e) Cyclic voltammetry of L3PS cell (Li/L3PS/stainless steel foil) at a constant scan rate of 10 mV s^{-1} from -0.5 to 5.0 V (vs Li/Li⁺). f) Cycling performance of the symmetry cell (Li/L3PS/Li) at a current density of 0.01 mA cm⁻² with 0.5 h time interval at 60 °C.

dendritic growth of lithium compared to the conventional SE film densified under a high pressure. The internal short could be prevented by using a porous Li metal anode, and also, formation of thicker solid electrolyte film would help to enhance rate capability and cyclability of the symmetry cell. Additionally, a possibility for using the L3PS electrolyte in half-cell and full-cell was examined (Figure S15, Supporting Information).

2.5. Discussions

The different properties of L1PS and L3PS SEs originate from the different solution conditions. For L1PS, both of Li_2S and P_2S_5 have negligible solubilities in moderately polar solvents, i.e., DEGDME, so reaction between them is expected to be difficult and slow. Thus, residual nonconductive Li_2S particles



are observed in L1PS SE which leads to a high resistance and poor electrochemical property. On the contrary, the addition of sulfur to Li_2S in the L3PS SE solution triggers the formation of soluble polysulfides, which can more efficiently react with $P_2\text{S}_5$ to form Li_3PS_4 . Furthermore, the solution containing Li_3PS_4 is stable without forming any precipitates, which results in the favorable interfacial contacts with the Li substrate and the formation of a thin film that appears to be free of grain boundaries.

By using first-principles density functional theory (DFT) calculations (**Figure 6**; Figure S16, Supporting Information), we fundamentally investigated the different reaction mechanisms and arrived at two main conclusions. First, formation of soluble polysulfides is favored over the dissolution of Li₂S in DEGDME. There is a large thermodynamic barrier to dissolve Li₂S solids into solutions to form $2Li^+$ and S^{2-} (step #0 to #1), which

explains the presence of residual Li2S in L1PS SE. However, this barrier can be greatly reduced by introducing S with Li₂S to form polysulfides (the L3PS case). Once dissolved in DEGDME, polysulfides form a variety of species including S42-, S62-, S82-, S₃⁻⁻ (Figure S17, Supporting Information). Among them, S₃⁻⁻ generated from the S_6^{2-} dissociation is the most probable and stable species (step #1 to #1') to react with P_2S_5 . This hypothesis is consistent with other studies^[31,32] and S₃⁻⁻ is also the dominant species according to UV-vis absorption spectra of the solution (Figure S17, Supporting Information). In this case, the dissolved polysulfide anions have higher collision probability to react with P₂S₅, which is kinetically far more favorable compared to the insoluble Li2S. Second, polysulfides are thermodynamically favored to react with P2S5 to form Li3PS4. All the polysulfide anions dissolved in solution should transfer sulfur atoms and electrons to $1/2P_4S_{10}$ molecule to finally make $2PS_4^{3-}$ anions (step #1 to #2). Because the P–S bond easily breaks when the P_4S_{10} molecule uptakes one electron (Figure S18, Supporting Information), this reaction will readily proceed with the sequential transfer of sulfur atoms and electrons supplied from the various polysulfide anions. After generating PS_4^{3-} anions, all subsequent steps (step #2 to #4) to the formation of Li₃PS₄ are thermodynamically favorable. Consequently, introduction of intermediate polysulfides could greatly enhance the reaction kinetics while reducing the thermodynamic barrier for the formation of Li₃PS₄. We also expect that the sluggish transport property of DEGDME could help Li₃PS₄ molecular moiety stay dissolved (step #2 to #3) rather than precipitating out as crystalline Li_3PS_4 (step #3 to #4). Another possibility is that the addition of sulfur could enhance the solubility of Li₃PS₄ by attaching sulfur to the sulfur chain of the PS43- tetrahedral unit.[27] Further study is required to better understand and explain the state of Li₃PS₄ in the solution.

This is the report where a thin SE layer was formed directly onto Li metal without relying on compression, high temperature sintering or high-energy ball milling. Even though the conductivity value of L3PS SE is lower than that of commercial Li₃PS₄ powders synthesized using high-energy ball milling, we





Figure 6. Overall reaction thermodynamics for formation of $2Li_3PS_4(s)$. Chemical states and relative energies for formation of $2Li_3PS_4(s)$ from $3Li_2S(s)$ and $1/2P_4S_{10}(s)$. The overall energy change from step #0 to #4 (-1.78 eV/2Li_3PS_4) indicates formation enthalpy of $Li_3PS_4(s)$ from $Li_2S(s)$ and $P_4S_{10}(s)$.

anticipate that higher conductivity is possible by reducing the amount of sulfur and/or identifying more suitable solvents. In addition, the ability to form solid electrolyte layers from a lowtemperature solution process is an important advancement in solid state batteries. We envision forming electrolyte layers on electrodes with complex geometries where the layer thickness of SEs can be readily controlled by adjusting amount of coating solution. The solution precursor is also ideal for forming intimate composites with active materials to serve as solid state electrodes. By eliminating the need for forming free standing sheets of solid electrolytes, the solution-based electrolyte deposition process has the potential to enable all-solid-state batteries with thinner solid electrolytes and higher energy densities.

3. Conclusion

The synthesis of a conductive β -Li₃PS₄ film on Li metal was achieved through a solution deposition method. Using DEGDME as the solvent, we induced polysulfide anions by reacting sulfur with Li₂S to derive kinetically and thermodynamically favorable routes for the formation of an Li₃PS₄ solution. The prepared solution was successfully coated on Li metal without compression or any other post processing, which results in the formation of an Li₃PS₄ film with a high quality interface with Li metal. Moreover, the solution-deposited SEs have a stable electrochemical window from -0.5 to 5 V (vs Li/Li⁺) and enable stable cycling of a symmetric Li/electrolyte/Li cell. This solution deposition process is facile and cost-effective to synthesize SE at ambient temperatures and can enable practical all-solid-state batteries.

4. Experimental Section

Synthesis of Solution-Processing Solid Electrolyte: Solution of solid electrolyte was prepared by mixing precursors in DEGDME electrolyte.





All the precursors were finely grinded and the solvent was dehydrated with molecular sieves before use. All experiments were conducted in a glove box with Ar atmosphere and carefully controlled without exposure to air. Li₂S (0.244 g) and S (0.341 g) powders were mixed in DEGDME under a stirring for 1 d and P₂S₅ powder (0.394 g) was added. Then, the solution was additionally stirred for 3 d. The prepared solution was coated on Li chip (15 mm diameter) to form a solid electrolyte layer, which was predried in a vacuum for 2 h and further dried in a vacuum furnace at 140 °C for 12 h.

Characterization and Electrochemical Analyses: For the characterization of solid electrolytes, FIB-SEM (FEI Scios, Scios DualBeam), FT-IR (Perkin Elmer, Spectrum 100 FT-IR) with ATR mode, Raman spectroscopy (Raman, Perkin Elmer, Raman Station 400F), and XRD (Bruker, D2 Phaser 2nd generation) with Cu-K α radiation at 30 kV and 10 mA were used. XPS (Kratos Analytical, Kratos AXIS Supra) was carried out using Al anode source at 15 kV was used and all the peaks were fitted based on the reference C-C bond at 284.7 eV. Samples were carefully prepared in the Ar glove box and transferred in the XRD, XPS, and Raman instruments without air exposure. Electrochemical performances were measured using a potentio-galvanostat (Wuhan LAND electronics, CT2001A) and electrochemical impedance was analyzed using EIS (BioLogic, VMP-300t). Li/electrolyte/Li symmetric cell was prepared by stacking two L(n)PS SE electrodes that were made separately on each Li metal and conductivities were calculated by assuming a layer thickness of 40 um.

Computational Details: DFT calculations were performed using the Jaguar 8.9 software^[33] for molecular reaction energies under the Poisson-Boltzmann implicit solvation condition. The exchangecorrelation function of B3LYP,^[34,35] along with the 6-31G** basis set was used. After acquiring gas-phase ground state geometries and electronic structures of each reaction intermediates, solution-phase calculations were performed. For solvation condition of DEGDME, 7.23 was adopted for dielectric constant and 3.04 for probe radius considering molecular weight and liquid density. The Vienna ab initio simulation package^[36] was also used for the calculations of the cohesive energy of crystal structures with the exchange-correlation function of PBE-D2^[37] to properly describe the van der Waals interactions. The electron-ion interaction was considered in the form of the projector augmented wave method with a plane wave up to an energy of 450 eV. Gamma-centered automatic k-point grids of $5 \times 5 \times 5$ for Li₂S, $3 \times 3 \times 3$ for P₄S₁₀, $1 \times 1 \times 1$ for S₈, and $3 \times 4 \times 5$ for Li₃PS₄ crystals were used.

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.

Keywords

electrolyte layer, ${\rm Li}_3{\sf PS}_4,$ solid electrolyte, solid state batteries, soluble polysulfides

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