

**Designing solution chemistries for low-temperature
synthesis of sulfide-based solid electrolytes**

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Designing solution chemistries for low-temperature synthesis of sulfide-based solid electrolytes

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Developing synthesis methods for high quality solid electrolytes has been a key issue for enabling all-solid-state batteries. As compared to conventional methods using mechanical ball milling, liquid-phase synthesis methods would provide a facile way to produce solid electrolytes by reducing reaction time and heating temperature. The simplified process is also potentially applicable to scalable manufacturing. Here, we introduce a new solution-based synthesis method for an $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte by adding a nucleophilic agent, LiSC_2H_5 . The strong nucleophile can break the P-S bonds of P_2S_5 , fully dissolving the P_2S_5 in tetrahydrofuran (THF) and forming soluble intermediates. The modified synthesis protocol provides a kinetically favorable condition for P_2S_5 to react with the insoluble Li_2S , demonstrating the formation of high quality $\beta\text{-Li}_3\text{PS}_4$ solid electrolyte ($1.32 \times 10^{-4} \text{ S cm}^{-1}$) with a uniform particle shape.

Solid electrolytes (SEs) have been a key element to solving the prevailing safety issues of current lithium ion batteries using flammable organic electrolytes.¹⁻⁴ Among many candidates, sulfide-based SEs have attracted enormous attention due to their high conductivities.⁴⁻⁶ However, conventional synthesis methods for sulfide-based SEs are energy-intensive, requiring high temperature and pressure conditions and taking a long time to produce a final product. For example, $\text{Li}_2\text{S-P}_2\text{S}_5$ (*i.e.*, LPS) SEs have been mechanically synthesized by using high-energy ball milling followed by repeated sintering and pressurizing steps.⁷⁻⁹

Alternatively, liquid-phase synthesis (or solution-based synthesis) methods have been developed, providing a much faster and simpler way of synthesizing sulfide-based SEs compared to conventional methods.¹⁰⁻¹² Solvent medium helps promote a reaction between Li_2S and P_2S_5 and provides enough energy to form final products such as Li_3PS_4 and $\text{Li}_7\text{P}_3\text{S}_{11}$, which

greatly reduces both the sintering temperature and synthesis time. Various solvents such as THF,^{11, 12} acetonitrile (ACN),¹²⁻¹⁴ dimethyl carbonate (DMC),¹⁵ and 1,2-dimethoxyethane (DME)¹⁶ have been utilized for synthesizing LPS SEs. Normally, the insoluble precursors of Li_2S and P_2S_5 are dispersed in a solvent and stirred for a few days to react with each other. Then, the solution is filtered to collect a powder, which is compressed into an SE pellet. However, due to the insolubilities of precursors, unwanted residuals or by-products might precipitate together with the final product during the filtering or drying process.^{10, 14} In addition, the solution itself has rarely been applied as a direct coating on anode and cathode materials due to the precipitated particles. Although solvents with high dielectric constants (DC) such as N-methylformamide (NMF),¹⁷⁻¹⁹ and hydrazine²⁰ have succeeded in dissolving precursors or final products (*e.g.*, Li_3PS_4 and $\text{Li}_3\text{P}_7\text{S}_{11}$), their application is still limited due to the high reactivity of solvents, which can vigorously react with Li metal and cell components.

Here, we developed a new synthesis route for sulfide-based SEs by using the nucleophilic agent, LiSC_2H_5 (Lithium thioethoxide, LiSEt). It is first demonstrated that a chemical reaction between LiSEt and P_2S_5 forms the intermediate soluble compounds of $\text{LiSEt-P}_2\text{S}_5$ in the moderate DC solvent of THF. The dissolved P_2S_5 composite can then further react with Li_2S resulting in the formation of conductive $\beta\text{-Li}_3\text{PS}_4$ SEs. This modified method can produce homogenous and purified $\beta\text{-Li}_3\text{PS}_4$ SEs since soluble residuals or by-products can be completely removed during filtration. In addition, it provides a kinetically favorable condition (the reaction between two reactants of liquid and solid phases), which cannot be achieved by following the conventional methods.

Our strategy to synthesize SEs is to make a soluble intermediate reactant in THF in order to drive a reaction between liquid and solid phase reactants, rather than using the conventional solid-to-solid phase reaction. For a better understanding of the difference between the modified solution-based synthesis method and previous methods, a schematic illustration is provided in the Supporting Information (Fig. S1†).

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† Electronic Supplementary Information (ESI) available: Experimental methods, P-NMR and XRD analyses, SEM images, EDS elemental mapping results. See DOI: 10.1039/x0xx00000x

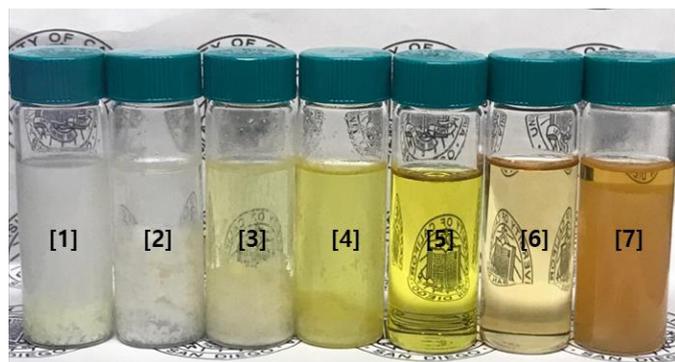


Fig. 1. Images of THF solutions dissolving P_2S_5 and $LiSC_2H_5$ with different molar ratios of 1:0, 1:0.1, 1:0.3, 1:0.5, 1:1, 1:3, and 1:6 from [1] to [7], respectively. 10 g of THF solvent is used in each solution.

We used LiSEt as an additive to make P_2S_5 soluble in THF because its strong nucleophilicity^{21, 22} is expected to break P-S bonds in P_2S_5 . To test the effect of LiSEt on the solubility of P_2S_5 , LiSEt with different molar ratios was mixed with P_2S_5 as shown in Fig. 1. Reference solution [1] (only P_2S_5 without $LiSC_2H_5$) precipitated most of the P_2S_5 as powders even after stirring for one day. As LiSEt is added into a solution, precipitates decreased as observed in solutions [1] to [4]. It should be noted that solution [5] (*i.e.*, 1:1 ratio of P_2S_5 and LiSEt) is transparent, suggesting that P_2S_5 can fully react with LiSEt and form certain soluble compounds. Although the solutions with high ratios of LiSEt ([6] and [7] with ratios of 1:3 and 1:6, respectively) can also dissolve P_2S_5 , focus is placed on solution [5] because it can fully dissolve P_2S_5 with a minimal amount of LiSEt.

Nuclear magnetic resonance (P-NMR), Fourier transform-infrared spectroscopy (FT-IR), and Raman spectroscopy were utilized to analyze solution [5] (Fig. 2). While the pristine P_2S_5 shows a sharp single characteristic peak at 57.3 ppm,²³ it is not dominant in solution [5]; instead, a small and broad bump is observed in the spectrum of solution state P^{31} NMR (Fig. 2a). It is also noted that new peaks at 118 and 88 ppm, which are attributed to $P(SR)_3$ and PS_4^{3-} , respectively,²⁴⁻²⁶ are detected, implying that P-S bonds in the pristine P_2S_5 are broken. Many of

the new peaks between 110-90 ppm, which are also undetectable in the pristine P_2S_5 , demonstrate the formation of various phosphorous bonding features in the solution. Phosphorous bonds with sulfur species which are either ionic with a negative charge (as in PS_4^{3-}) or covalently bonded to carbon (as in a P-S-Et configuration). It is reasonable to attribute the peaks between 110-90 ppm to thiophosphate species with a mixture of ionic and covalently bonded sulfur atoms. Additional results from NMR experiments on changing the molar ratio between LiSEt and P_2S_5 are provided in Fig. S2†. Therefore, it is concluded that the addition of LiSEt can trigger the bond breaking of P_2S_5 resulting in the formation of soluble composites (*i.e.*, $LiSEt \cdot P_2S_5$) with various phosphor bonding features.

To further elucidate the reaction between LiSEt and P_2S_5 , FT-IR and Raman analyses were performed (Fig. 2b and 2c). As observed in the blue lines of Fig. 2b and 2c, LiSEt fully dissolves in THF solvent without any side reactions, proving the high stability of LiSEt as an additive to the solvent molecules. After the addition of P_2S_5 in the solution, LiSEt loses its characteristic peaks and small unknown peaks are identified (red line in Fig. 2b). This result directly proves the chemical reaction between P_2S_5 and LiSEt, which is further supported in the Raman analysis (Fig. 2c). Any signal related to P_2S_5 is not detected in the mixture of P_2S_5 and LiSEt (red line in Fig. 2c), indicating the bond breaking of P_2S_5 is promoted by the LiSEt nucleophile. The disappearance of P_2S_5 signals after the formation of soluble composites is well matched to the previous report.²³ In this respect, it is identified that the strong nucleophile (*i.e.*, LiSEt) can break P-S bonding of P_2S_5 , which results in the formation of soluble intermediates in THF solvent.

Considering the results of the solubility test and bonding analyses above, we schematically describe the possible processes for the formation of Li_3PS_4 SEs (Fig. 3). Two moles of LiSEt are required to react with one mole of P_4S_{10} because the solution becomes fully transparent at a 1:1 molar ratio of P_2S_5 and LiSEt. In the transparent solution with $LiSEt \cdot P_2S_5$, we added Li_2S to investigate whether a conductive β - Li_3PS_4 forms. We

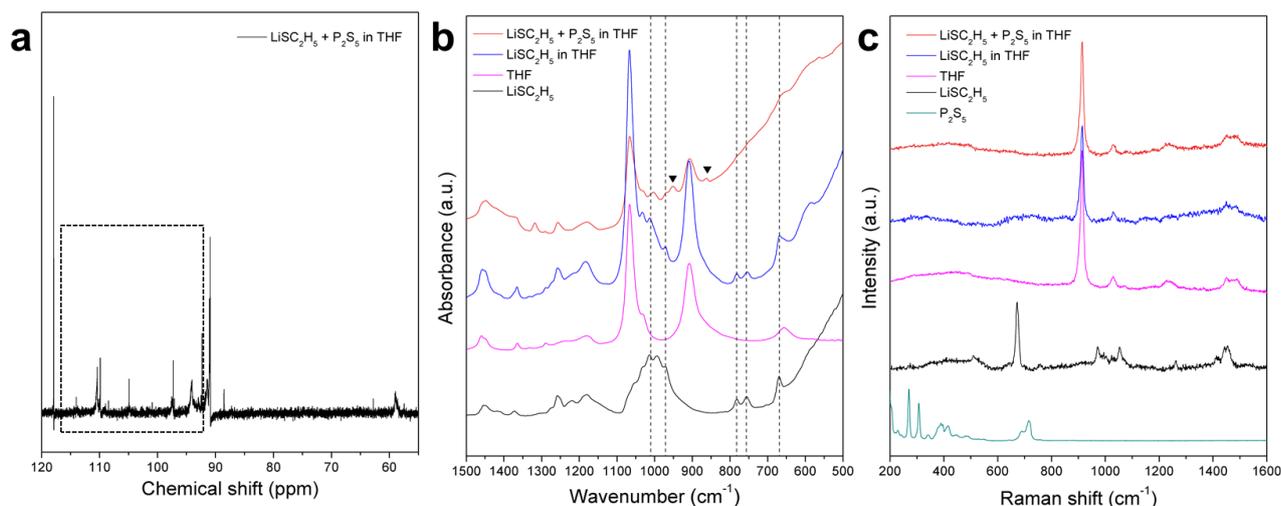


Fig. 2. (a) P-NMR, (b) FT-IR, and (c) Raman analyses of the THF solutions dissolving P_2S_5 and $LiSC_2H_5$ at a 1:1 molar ratio.

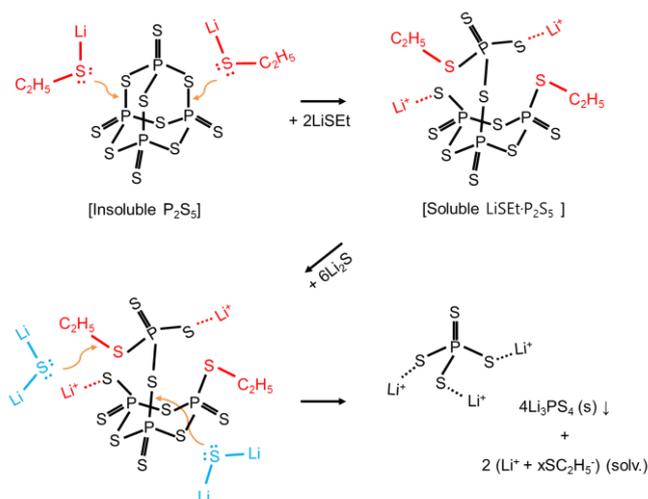


Fig. 3. Schematic illustration of the processes for the formation of Li_3PS_4 solid electrolyte promoted by a nucleophile of LiSC_2H_5 .

expected a chemical reaction between $\text{LiSET}\cdot\text{P}_2\text{S}_5$ and Li_2S because once P-S bonds in P_2S_5 are opened, the asymmetric structure of the complex can easily engage in successive reactions. The precipitation of white powders was observed after the addition of Li_2S into the $\text{LiSET}\cdot\text{P}_2\text{S}_5$ solution, and we determined that the precipitate ($\text{LiSET@Li}_3\text{PS}_4$) is composed of $\beta\text{-Li}_3\text{PS}_4$, as discussed later.

By following this synthesis process, reaction kinetics can be improved because the $\text{LiSET}\cdot\text{P}_2\text{S}_5$ (solv.) complex has greatly enhanced the chances of reacting with Li_2S (s) in the solution while the conventional solution-based synthesis methods utilized two insoluble P_2S_5 (s) and Li_2S (s) particles. In addition, the asymmetrically opened P_2S_5 will have a lower activation barrier to react with Li_2S compared to the pristine P_2S_5 . Even if there are un-reacted residuals (e.g., SC_2H_5^- or $\text{P}_x\text{S}_y\text{-C}_2\text{H}_5$), they can be easily removed during filtration and are distinguishable from the precipitates. This method provides an easy way to produce a high purity solid electrolyte, which is challenging to

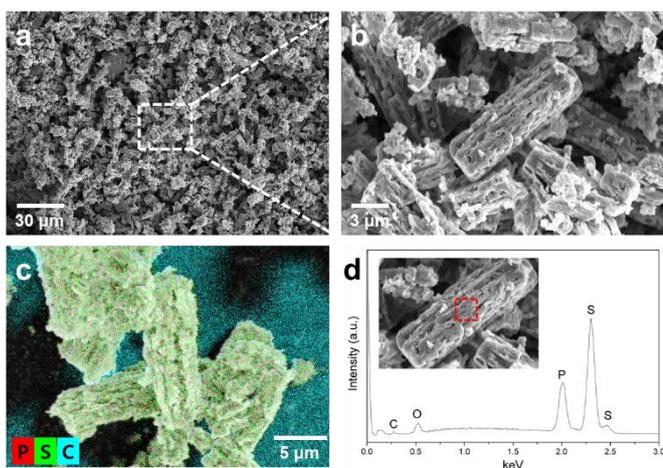


Fig. 4. (a,b) SEM images, (c) EDS elemental mapping result, and (d) EDS elemental analysis of the synthesized $\text{LiSET@Li}_3\text{PS}_4$ solid electrolytes.

achieve by following the conventional solution-based synthesis methods.

Scanning electron microscopy (SEM) images of the precipitated particles after heat treatment from the reaction between $\text{LiSET}\cdot\text{P}_2\text{S}_5$ and Li_2S are shown in Fig. 4. The solution was centrifuged and filtered to collect the precipitates, which were further heat treated to remove the residual solvent. Most of the particles show a consistent cylinder-like shape (Fig. 4a and 4b). While the overall shape of the particle looks similar to that of a previous report using a THF solvent,¹¹ the average particle size is smaller and the aspect ratio is higher. This is because the different solvent-reactant interactions can affect particle shape and size.^{10, 12, 13}

Elemental composition of the resultant product (designated as $\text{LiSET@Li}_3\text{PS}_4$) was analyzed using EDS analyses as shown in Fig. 4c, 4d and Fig. S3†. $\text{LiSET@Li}_3\text{PS}_4$ is composed of a sulfur and phosphorus mixture, which is homogeneously detected in most of the precipitated particles. Additional SEM images at low magnification are provided in the Supporting Information (Fig. S4†). The high homogeneity of the final products can be attributed to the use of liquid-phase mobile reactant (i.e., $\text{LiSET}\cdot\text{P}_2\text{S}_5$). Moreover, it should be noted that carbon and oxygen elements are negligible in the particles. This proves that LiSET does not remain in the particle after the reaction, and any residuals related to LiSET are clearly filtered out.

To investigate the properties of $\text{LiSET@Li}_3\text{PS}_4$ SE, Raman and X-ray diffraction (XRD) measurements were taken as shown in Fig. 5a and 5b, respectively. In the Raman analyses (Fig. 5a), the dominant peak around 420 cm^{-1} is observed in the $\text{LiSET@Li}_3\text{PS}_4$ (red line, after heat treatment), and its peak position is identical to the reference $\beta\text{-Li}_3\text{PS}_4$ demonstrating the formation of tetrahedral units of PS_4^{3-} .^{11, 12, 27} Therefore, it is concluded the final product is mostly composed of a conductive $\beta\text{-Li}_3\text{PS}_4$. The same characteristic peak is also observed in the sample before a heat treatment, which implies that the $\text{LiSET}\cdot\text{P}_2\text{S}_5$ chemically

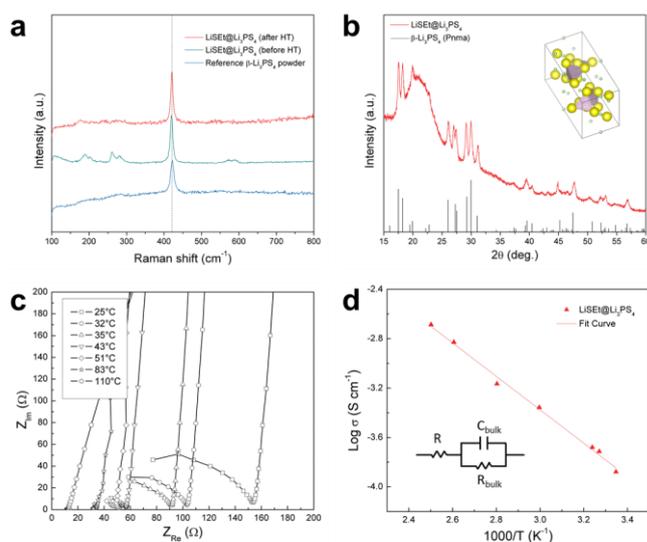


Fig. 5. (a) Raman and (b) XRD spectra of the synthesized $\text{LiSET@Li}_3\text{PS}_4$ solid electrolytes. (c) Nyquist plots and (d) Arrhenius plots of $\text{LiSET@Li}_3\text{PS}_4$ solid electrolytes at different temperatures using a blocking electrode cell (inset: equivalent circuit model).

reacted with Li_2S and formed the tetrahedral units of PS_4^{3-} in THF solvent. Peaks around $200\sim 300\text{ cm}^{-1}$ are attributed to solvent molecules bonded to lithium ions, which decreased after heat treatment in accordance with previous reports.¹¹ It is worth noting that any signal related to LiSEt was not detected, which corresponds well with the results of EDS analysis (Fig. 4d), supporting that LiSEt was fully removed.

The structural property of $\text{LiSEt@Li}_3\text{PS}_4$ is analyzed as shown in Fig. 5b. All the peaks matched well with $\beta\text{-Li}_3\text{PS}_4$ (Pnma space group) without any by-product. Also, the crystallinity of $\text{LiSEt@Li}_3\text{PS}_4$ is higher than that of the reference Li_3PS_4 SE prepared without the addition of LiSEt (Fig. S5[†]). Considering impurities can precipitate in grain boundaries and greatly decrease conductivity,^{12, 16} making a soluble intermediate and producing high purity SE will be essential for synthesizing high quality LPS SEs. To measure the conductivity of $\text{LiSEt@Li}_3\text{PS}_4$, electrochemical impedance spectroscopy (EIS) was analyzed using a blocking electrode cell as shown in Fig. 5c and 5d. $\text{LiSEt@Li}_3\text{PS}_4$ shows a high conductivity of $1.32 \times 10^{-4}\text{ S cm}^{-1}$ at room temperature (RT) and $1.48 \times 10^{-3}\text{ S cm}^{-1}$ at $110\text{ }^\circ\text{C}$ with an activation energy (E_a) of 25.93 kJ mol^{-1} . This value is comparable to one of the highest recorded conductivities achieved by the nanoporous Li_3PS_4 SE ($1.64 \times 10^{-4}\text{ S cm}^{-1}$ at RT) synthesized by using solution-based method,¹¹ and slightly higher than that of a commercial $\beta\text{-Li}_3\text{PS}_4$ powder (Fig. S6[†]). The high conductivity of $\text{LiSEt@Li}_3\text{PS}_4$ is expected considering the soluble intermediate helps to enhance particle homogeneity and prevent a co-precipitation of residuals resulting in the formation of purified $\beta\text{-Li}_3\text{PS}_4$ SEs. Additionally, electrochemical performance for $\text{LiSEt@Li}_3\text{PS}_4$ solid electrolyte is evaluated by cyclic voltammetry and galvanostatic cycling tests (Fig. S7[†]). A stable electrochemical window of -0.5 to 6 V is observed in cycle voltammetry while stable cycling of lithium metal is demonstrated during cycling tests.

Conclusions

We developed a solution-based method to synthesize $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte by adding a nucleophilic agent of LiSEt (*i.e.*, LiSC_2H_5). We demonstrated that the nucleophile can react with P_2S_5 , forming soluble intermediates ($\text{LiSEt}\cdot\text{P}_2\text{S}_5$) in THF solvent. The intermediates can further react with Li_2S , resulting in the formation of $\beta\text{-Li}_3\text{PS}_4$. By tuning the reaction protocol, a kinetically and thermodynamically favorable reaction (the reaction between $\text{LiSEt}\cdot\text{P}_2\text{S}_5(\text{solv.})$ and $\text{Li}_2\text{S}(\text{s})$) can be realized, which is difficult to achieve using the conventional solid-to-solid reactions. Because residuals or additives of LiSEt can be readily removed during filtration, high purity $\beta\text{-Li}_3\text{PS}_4$ solid electrolyte can be produced with a high conductivity ($1.32 \times 10^{-4}\text{ S cm}^{-1}$ at RT). This approach will provide insights for investigating new synthesis methods for high quality solid electrolytes.

Conflicts of interest

There are no conflicts to declare.

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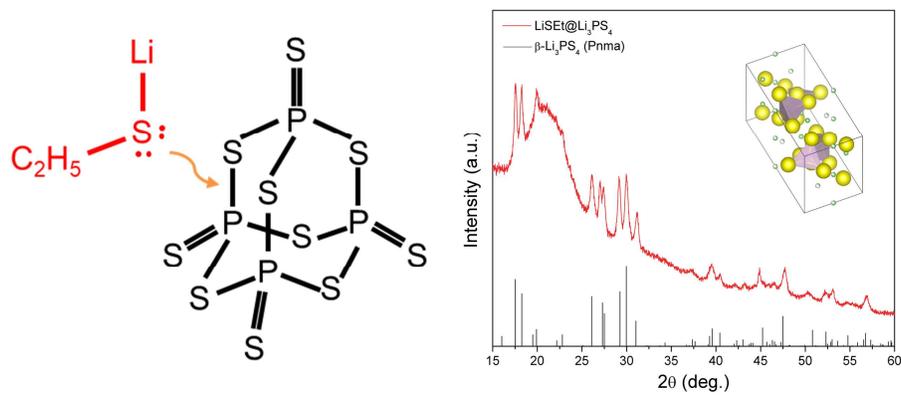
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