




Elucidation of the role of lithium iodide as an additive for the liquid-based synthesis of $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ solid electrolyte

His Muhammad Bintang^{1,2} | Seongsoo Lee^{1,3} | Jun Tae Kim^{1,4}  |
Hun-Gi Jung^{1,2} | Kyung Yoon Chung^{1,2}  | Dongmok Whang³ | Hee-Dae Lim^{1,2} 

¹Center for Energy Storage Research, Korea Institute of Science and Technology (KIST), Seoul, Republic of Korea

²Division of Energy & Environment Technology, KIST School, Korea University of Science and Technology (UST), Seoul, Republic of Korea

³SKKU Advanced Institute of Nanotechnology (SAINT) and School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Republic of Korea

⁴Department of Energy Engineering, Hanyang University, Seoul, Republic of Korea

Correspondence

Hee-Dae Lim, Center for Energy Storage Research, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea.
Email: hdlim@kist.re.kr

Funding information

Korea Institute of Science and Technology Institutional Program, Grant/Award Number: 2E30202; National Research Foundation (NRF), Grant/Award Number: 2017M1A2A2044482

Summary

Liquid-phase synthesis for a sulfide-based solid electrolyte has been widely studied due to its great advantage of being a simpler and more cost-effective method compared with the conventional solid-phase synthesis, even it could induce homogeneous reactions in the solution. However, the physically and chemically stable phosphorus pentasulfide (P_2S_5) is barely soluble in various solvents; this has been a major problem for achieving a pure solution-phase dissolving solid electrolyte. Therefore, exploring an effective additive for liquid-phase synthesis would be worthwhile and could potentially lead to the discovery of new chemicals to produce qualified solid electrolytes. In this paper, lithium iodide's (LiI) dual role as a strong nucleophile as well as a major reactant source for producing $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ is first investigated. The nucleophilic additive of LiI has been proven to break the P-S bonds of P_2S_5 , driving the insoluble P_2S_5 to become the soluble intermediate complex. Also, it is demonstrated that controlling the reaction times between the LiI and the P_2S_5 is key to achieving solution-based synthesis, and the role of LiI is investigated by conducting bonding analysis.

KEYWORDS

$\text{Li}_7\text{P}_2\text{S}_8\text{I}$, liquid-based synthesis, nucleophilic agent, solid-state electrolyte

1 | INTRODUCTION

The fast-growing markets for huge electrical devices such as energy storage systems and electric vehicles have naturally forced current portable batteries to progress to the next-generation battery systems.¹⁻⁴ Among many requirements, such as high-energy density, low cost, safety, and high efficiency, for next-generation battery systems, the first task would be to ensure a high level of safety,

considering that an explosion in a huge battery system could cause a large accident with significant financial losses. In this respect, much attention has been focused on all-solid-state batteries (ASSBs) with the hope of developing highly safe batteries.⁵⁻⁸ While the conventional liquid electrolytes suffer from fire hazards and have electrolyte leakage problems, a solid electrolyte (SE), as the key component of ASSBs, is highly safe and leakage-free due to the absence of a flammable organic solvent. Additionally, SEs could deliver high ionic conductivities comparable with those of the conventional organic electrolyte $\sim 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at room temperature.⁹⁻¹¹ In particular, sulfur-based SEs,

His Muhammad Bintang and Seongsoo Lee contributed equally to this work.

such as $\text{Li}_2\text{S}\cdot\text{P}_2\text{S}_5$ (LPS), $\text{Li}_7\text{P}_3\text{S}_{11}$, $\text{Li}_6\text{PS}_5\text{Cl}$, and $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ (LPSI), have been demonstrated to show high conductivities in the range of $10^{-3} \text{ S}\cdot\text{cm}^{-1}$.^{9,12-16}

Although the ionic conductivities of SEs already match those of conventional electrolytes, their practical applications have been limited due to costly and complex synthesis procedures.¹⁷⁻¹⁹ This is because most SEs are conventionally synthesized based on dried ball-milling methods, which require repeated pelleting steps under high pressure.^{20,21} Also, the conventional methods have critical limitations, including inevitable solid-to-solid contact, which induces serious interface problems that lead to decreased conductivity. However, a solution (or liquid)-based synthesis method is a simple and cost-effective way of synthesizing SEs. In particular, LPS and LPSI have been widely studied as major sources for solution-based syntheses and have been demonstrated to show high ionic conductivities under mild synthesis conditions.^{12,15,22-26} For solution-based synthesis, a key criterion that greatly affects the quality of products is whether the precursors are soluble or insoluble (ie, dispersed) in a solvent.²⁷ Although some toxic solvents such as N-methylformamide (NMF),^{28,29} hydrazine,³⁰ and hexane^{20,31} could help to dissolve the precursors of LPS or LPSI, the highly toxic solvents are hardly applicable to the current fabricating systems. Interestingly, it was reported that phosphorus pentasulfide (P_2S_5), which is insoluble in any kind of solvent, could be dissolved by the addition of a nucleophilic agent (lithium thioethoxide, LiSC_2H_5 , or LiSEt) in the less-toxic solvents of tetrahydrofuran (THF) and diethylene glycol diethyl ether.^{27,31} The nucleophilic agent has also been proven to significantly affect the synthesis kinetics, as well as change the morphologies of the final products. In this respect, exploring a nucleophilic additive for the liquid-phase synthesis method would be worthwhile and is anticipated to lead to the discovery of new chemicals of solution-based synthesis to produce qualified SEs.

For the first time, we focused on the effect of Lithium Iodide (LiI) for synthesizing the high ionic conductive LPSI SEs. Similar to the role of LiSEt , it has been proven that the strong nucleophilic agent of LiI could form soluble $\text{P}_2\text{S}_5\cdot\text{LiI}$ complexes in a THF solvent. LiI could perform a dual role in this system. It would be an additive that helps dissolve the insoluble P_2S_5 in the THF, and it is used as a major reactant source to produce LPSI by reacting with P_2S_5 and Li_2S . It is found that the insoluble P_2S_5 could chemically react with LiI to become a soluble $\text{LiI}\cdot\text{P}_2\text{S}_5$ complex in the THF solvent. The effect of this soluble complex is investigated by comparing the conventional liquid-based synthesis method with the modified two-step (TS) process. The conventional method is processed by adding precursors of Li_2S , P_2S_5 , and LiI at a molar ratio of 3:1:1 at the same time, while the effect of

the $\text{LiI}\cdot\text{P}_2\text{S}_5$ complex is investigated using the TS process; a pre-solution of $\text{LiI}\cdot\text{P}_2\text{S}_5$ in the THF was prepared and then reacted with Li_2S to synthesize LPSI SEs. By comparing the two different reaction procedures, we carefully elucidated the effect of LiI as an additive and described the reaction mechanism based on the chemical bonding analyses.

2 | RESULTS AND DISCUSSION

As illustrated in schematic images in Figure 1, we designed two different synthesis procedures. One-step (OS) synthesis is processed by mixing Li_2S , P_2S_5 , and LiI at a molar ratio of 3:1:1 in THF solvent. Then, the reaction kinetics among the precursors are investigated by controlling the stirring times during which they react with each other. In this instance, LiI is mainly used as one of the precursors to produce LPSI SEs instead of as an additive. By contrast, the two-step (TS) synthesis is designed to demonstrate the effect of LiI in driving solid P_2S_5 into the soluble species. In the first step of the TS synthesis, P_2S_5 and LiI are mixed in THF with varying reaction times; we then investigate the effect of LiI as a nucleophilic agent, that is, whether or not it reacts with P_2S_5 . If there is a reaction, that is, if LiI partially breaks the P-S bonds of P_2S_5 , the intermediate $\text{LiI}\cdot\text{P}_2\text{S}_5$ complex is expected to be soluble in the THF, which would appear as a transparent solution. Subsequently, the homogeneous reaction between the intermediates and the additional $3\text{Li}_2\text{S}$ precursors is anticipated, thus producing the stoichiometric of LPSI SEs. By differing the reaction times and analyzing the powders produced, the effects of the LiI as an additive, as well as a precursor, are investigated.

Figure 2A shows the synthesis procedures for the OS method, which is carried out by simply mixing Li_2S , P_2S_5 , and LiI simultaneously. To alter the reaction conditions, the stirring times were controlled by 10 minutes, 1 hour, and 1 day (referred to as OS-1, OS-2, and OS-3, respectively). The mixed solutions were pre-dried at 90°C to evaporate the THF solvents and then heat treated at 280°C to produce the final products. Interestingly, different stirring times resulted in different states of the mixtures, as shown in Figure 2B. The color of each solution appears different, and most of the reactants in all the solutions appear insoluble and easily precipitated. It has already been demonstrated that both P_2S_5 and Li_2S have negligible solubility in THF³²⁻³⁴; therefore, it is reasonable to assume that the mixtures of the three precursors are also insoluble regardless of the stirring times. This phenomenon has similarly been observed in the previous reports, demonstrating the formations of the precipitated

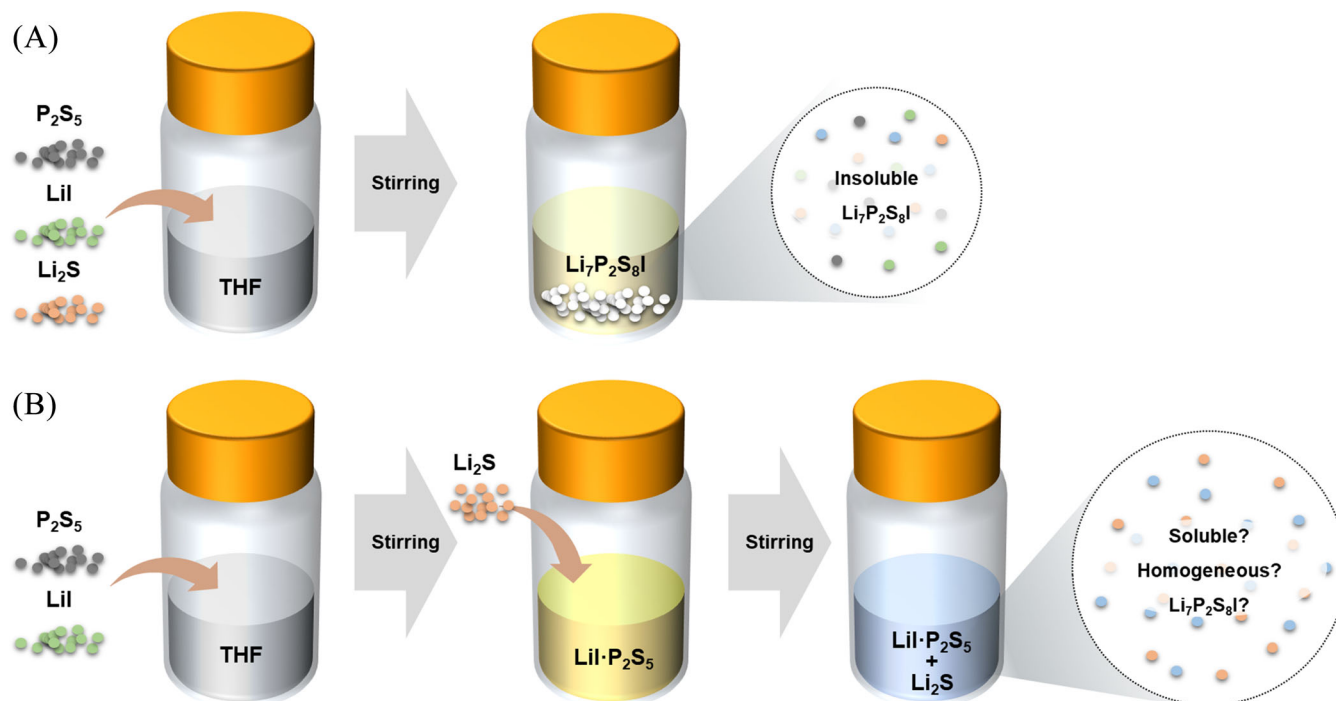


FIGURE 1 Schematic image of the liquid-phase synthesis processes of $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ solid electrolytes. (A) One-step synthetic method; all precursors (P_2S_5 , LiI , and $3\text{Li}_2\text{S}$) are mixed and reacted at the same time in the tetrahydrofuran to produce $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ SE. (B) Two-step synthetic method; the insoluble P_2S_5 is first reacted with LiI until the formation of the soluble $\text{LiI}\cdot\text{P}_2\text{S}_5$ complex, then $3\text{Li}_2\text{S}$ is added to form stoichiometric $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ SE [Colour figure can be viewed at wileyonlinelibrary.com]

products when producing LPS-based SEs through liquid-phase synthesis.^{15,35}

The produced powders with different reaction times are analyzed using X-ray diffraction (XRD) without exposure to air. It should be mentioned that all the synthesis, as well as the analysis, processes are carefully controlled in a glovebox to perfectly exclude the effect of moisture or other gases. The stirred solutions are dried and heat treated under different conditions; vacuum drying at 90°C for 4 hours and heat treating at 280°C for 9 hours. After the vacuum drying (Figure 2C), there is no detectable crystalline phase of the LPSI, and the precursors of Li_2S , P_2S_5 , and LiI are not identified, implying the formation of amorphous complexes in the THF. Afterwards, the formation of the LPSI crystal phase is clearly determined after the heat treatment at 280°C , as shown in Figure 2D. While OS-1 and OS-2 have some residual precursors and unknown by-products, OS-3 can produce a LPSI phase without any impurities. This means that the reactions times applied for OS-1 and OS-2 are insufficient, while a day of stirring (OS-3) is sufficient for the precursors in the solutions to be fully reacted. Additionally, stirring is continued in OS-3 for 1 week (Figure S1), and it is found that the crystallinity is somewhat improved and is without impurities. Therefore, the successful synthesis of LPSI SE is identified, and we believe

that the wet-chemical synthesis would be advantageous for mass production with high-quality reaction products.

To investigate the effect of LiI as a nucleophilic agent that is expected to dissolve P_2S_5 in THF, we designed the TS synthesis method. As illustrated in Figure 3A, P_2S_5 and LiI are mixed in THF in the absence of Li_2S by changing their ratios at 1:0, 1:0.5, 1:1, and 1:3 to prepare the pre-solution of P_2S_5 and the LiI mixture (ie, PS). The strong bonds between the phosphorus and sulfur make the P_2S_5 insoluble in the THF, and its insolubility can be directly observed in the 1:0 solution vial (Figure 3B). That is, before the addition of LiI , most of the P_2S_5 powders are dispersed in the THF after 2 hours of stirring, even after 3 days of stirring as shown in Figure 3B. It is worth noting that by adding LiI into the P_2S_5 -dispersed THF, the solution turns transparent when forming the soluble $\text{LiI}\cdot\text{P}_2\text{S}_5$ complex. The mixture of P_2S_5 and LiI at a 1:1 ratio seems sufficient to be fully dissolved in the THF after 2 hours of stirring (PS-2 hours). The formation of a transparent solution is quite interesting, and the formation of a soluble P_2S_5 -complex, with the aid of LiI , is initially demonstrated. The dissolution of P_2S_5 with the help of the LiI additive in other solvents is additionally determined (Figure S2 and Table S1). This phenomenon had been observed in the previous report, using a nucleophilic agent of LiSEt ; however, the residual functionals,

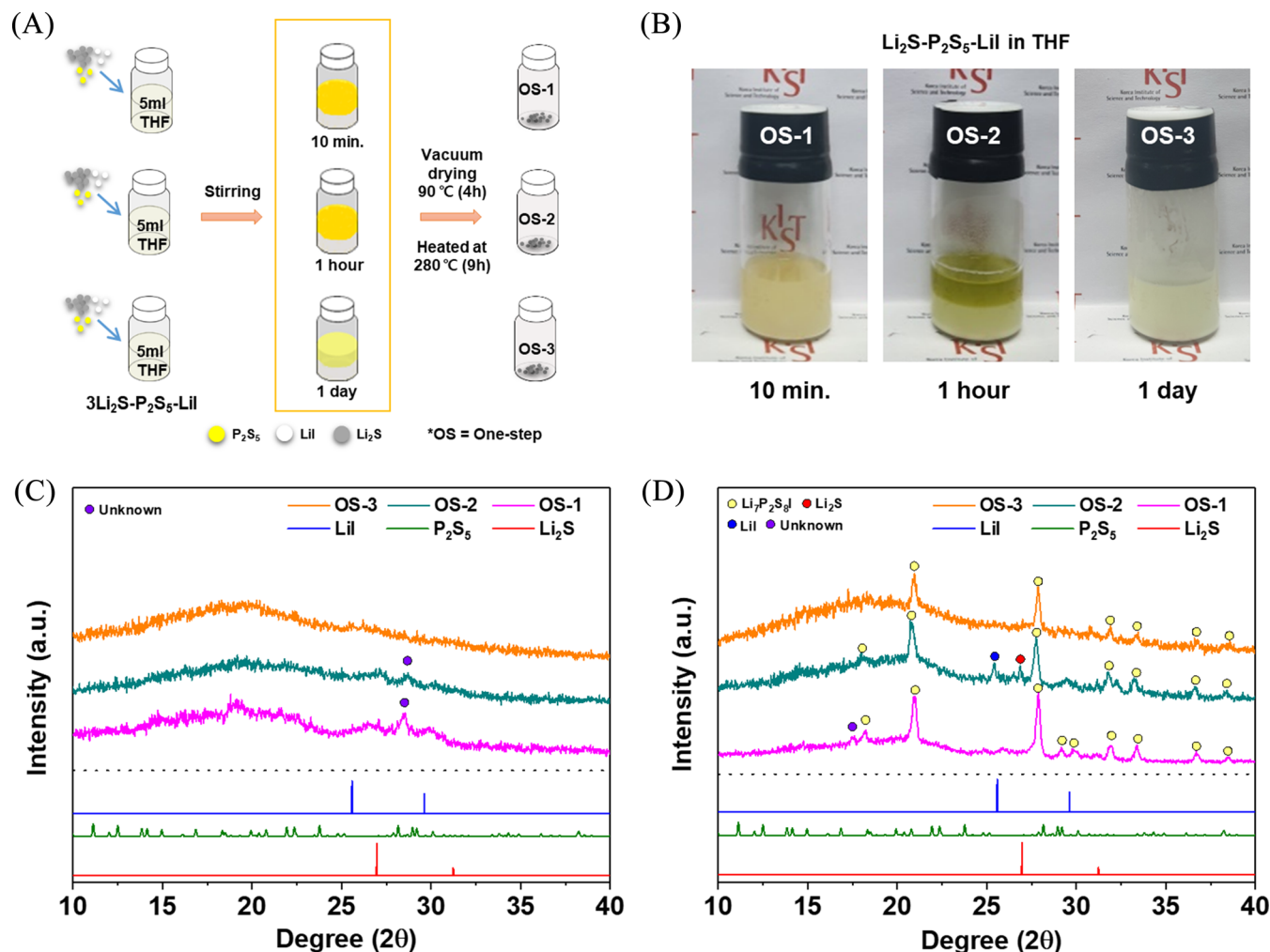


FIGURE 2 (A) Synthesis procedures for the one-step method for synthesizing $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ solid electrolytes. (B) Photographs of the mixed $\text{Li}_2\text{S}\cdot\text{P}_2\text{S}_5\text{-LiI}$ solutions depending on different reaction times; they are marked by the yellow box in Figure 2A. X-ray diffraction patterns of the $\text{Li}_2\text{S}\cdot\text{P}_2\text{S}_5\text{-LiI}$ mixtures prepared with different stirring times, and (C) dried at 90°C for 4 hours and (D) heat treated at 280°C for 9 hours [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

such as $-\text{S}$ and C_2H_4 from LiSEt , could contribute to the decreased ionic conductivity.^{32,33} Indeed, LiI could be a promising nucleophilic agent, considering that the condition of a 1:1 ratio between the P_2S_5 and the LiI is a perfect stoichiometric to produce LPSI SEs (ie, $\text{Li}_2\text{S}:\text{P}_2\text{S}_5:\text{LiI} = 3:1:1$) if they could react with the additional $3\text{Li}_2\text{S}$.

To investigate whether it forms LPSI with the addition of Li_2S , the solutions of PS with a 1:1 ratio between P_2S_5 and LiI were prepared. As the smaller ratio of LiI ($\text{P}_2\text{S}_5:\text{LiI} = 1:0.5$) could not fully dissolve the P_2S_5 , the excess LiI ($\text{P}_2\text{S}_5:\text{LiI} = 1:3$) must contain many residuals of LiI in the solutions. Additionally, the two solutions of PS-2 hours and PS-3d are chosen because the colors of the solutions gradually become colorless on stirring; a yellowish solution of PS-2 hours (green box in Figure 3) and a colorless solution of PS-3d (orange box in Figure 3) were separately prepared.

For synthesizing LPSI SEs, additional $3\text{Li}_2\text{S}$ is needed to add to the solutions with the $\text{LiI}\cdot\text{P}_2\text{S}_5$ complex (PS-2 hours and PS-3d), and the procedures are schematically shown in Figure 4A. After the addition of Li_2S , the stirring times are controlled according to the reaction by 10 minutes (TS-1), 1 hour (TS-2), and 1 day (TS-3), similar to the tests used in the OS approach in Figure 2. While the OS methods reveal different solution states and colors according to the stirring times (Figure 2B), the state of each solution after the addition of Li_2S does not seem to be sensitive to the reaction times. Even after 1 day of stirring, the cloudy solutions of TS-1, TS-2, and TS-3 show similar conditions, merely dispersing the Li_2S particles in the THF.

To investigate whether or not the LPSI phase was produced, XRDs were measured for each of the solutions dried at 90°C (Figure 4C) and heat treated at 280°C

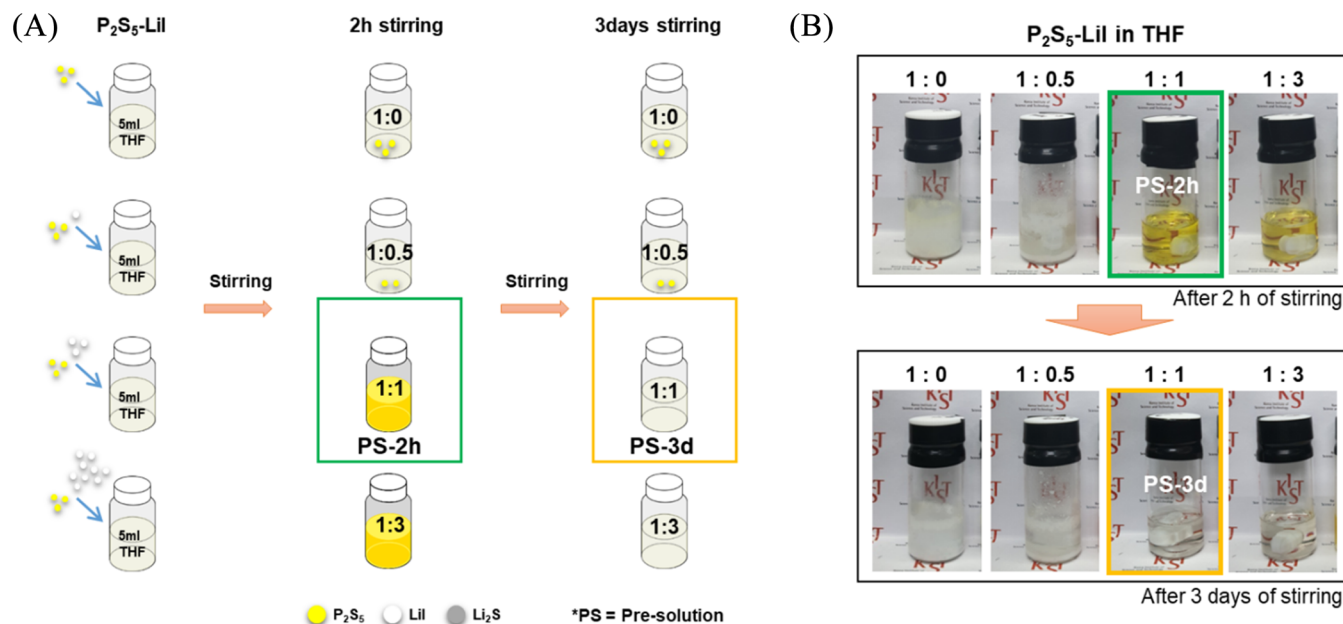


FIGURE 3 (A) Schematic illustrations for the reaction test between Li₂S and LiI in the THF. (B) Photographs of the P₂S₅-LiI mixture solutions in the THF depending on the different reaction ratios between of P₂S₅ and LiI, and the different reaction times [Colour figure can be viewed at wileyonlinelibrary.com]

(Figure 4D). Most of the powders dried at 90°C are demonstrated to be Li₂S, suggesting that the dissolved LiI·P₂S₅ complex could not react with the Li₂S. Even after the heat treatment at 280°C, they have not reacted each other and the LiI is re-crystallized at the high temperature as shown in Figure 4D. No sign relating to LPSI is detectable, which implies that the soluble P₂S₅-LiI complex is not reactive to the Li₂S. On the other hand, the mixture of P₂S₅, LiI, and Li₂S produced using the OS method (Figure 2) is shown to be amorphous and becomes the LPSI crystal phase after the heat treatment at 280°C. In the case of the PS-3d, which appears as a transparent PS solution, there are also no characteristic peaks of LPSI (Figure S3). The formation of LPSI phase was also demonstrated by electrochemical impedance spectroscopy (Figure S4). The Li₂S·P₂S₅-LiI mixtures prepared by the OS method showed a relatively high ionic conductivity of 0.0158 mS cm⁻¹ (OS-90) even in the amorphous phase, indicating it potentially developed an ion-conducting channel. The amorphous phase turned into the crystalline phase with a heat-treatment, and thus the ion-conducting channel became more ordered and the ionic conductivity was notably increased to 0.1392 mS cm⁻¹ (OS-280). Although the TS method also produced the amorphous Li₂S·P₂S₅-LiI mixtures from the reaction between the precursors, it showed no ionic conductivities (TS-90), which reveals that the product generated by the TS method does not form the ion-conducting phase (ie, LPSI).

It is important to understand why the LiI·P₂S₅ complex shows less reactivity, while the complex of LiSEt·P₂S₅ is sufficiently active with Li₂S to form the LPS phase under similar conditions.³³ This is due to the high affinity of P to the soft base I⁻, which contributes to the strong binding energy of P-I.³⁶ Therefore, it seems that the subsequent reaction with Li₂S would be difficult to trigger, while it is relatively easy in LiSEt·P₂S₅ complex. To analyze details of the different behaviors and reaction mechanisms of LiI, Fourier transform-infrared spectroscopy (FT-IR) was performed for each solution (Figure 4E). As indicated by the red line, LiI is stably dissolved in THF without side reactions, verifying the high chemical compatibility of LiI as an additive in the THF solvents. After forming the intermediate LiI·P₂S₅ complex solution (PS-2 hours), characteristic peaks corresponding to P—S—P stretching (dashed green line, 663 and 640 cm⁻¹) are identified.³⁷ These peaks are not detectable before the addition of LiI, indicating that the chemical reaction between P₂S₅ and LiI had taken place. Notably, the signal related to P—S—P is the result of the P=S bond breaking into the P—S bond when attacked by the LiI nucleophile (described in the inset of Figure 4F), which suggests the formation of an intermediate LiI·P₂S₅ complex. This is further determined by analyzing the chemical state of each element, including S, P, and I (Figure S5). These results explain well how the insoluble P₂S₅ becomes soluble in the THF solvent. Meanwhile, no significant changes were seen in the spectra after the addition of the 3Li₂S to the PS-2 hours (ie, TS-3), supporting

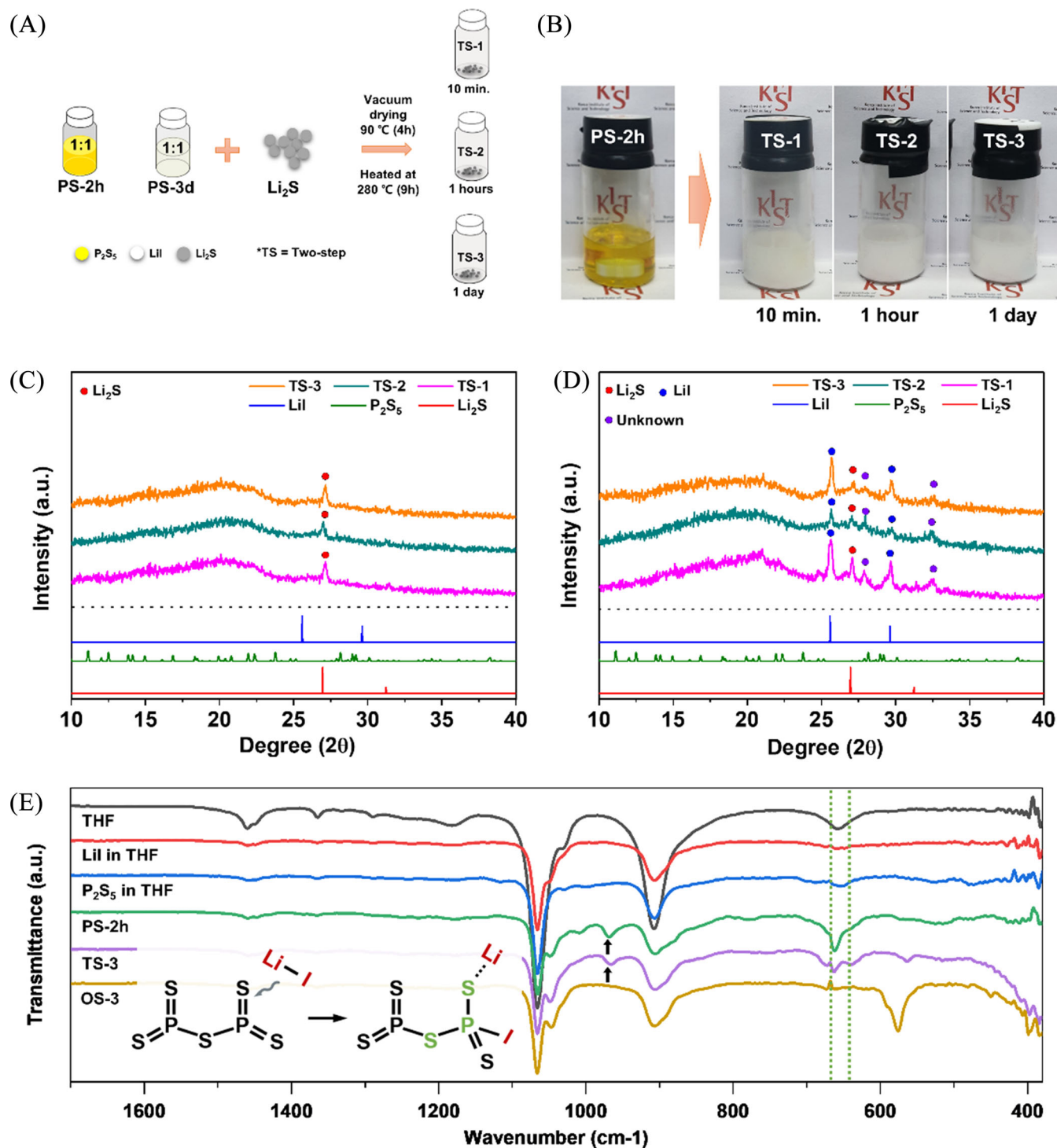


FIGURE 4 (A) Synthesis procedures for the two-step method for synthesizing $Li_7P_2S_8I$ solid electrolytes. (B) Photographs of Li_2S - P_2S_5 -LiI mixture solutions in THF depending on different reaction times. (C) XRD patterns of Li_2S - P_2S_5 -LiI mixtures prepared with PS-2 hours intermediate solution, and (C) dried at 90°C for 4 hours and (D) heat treated at 280°C for 9 hours. (E) FT-IR analysis of the THF solutions. Inset shows the schematic illustration of the nucleophilic attack of LiI to the P-S bonds of P_2S_5 . FT-IR, Fourier transform-infrared spectroscopy; THF, tetrahydrofuran; XRD, X-ray diffraction [Colour figure can be viewed at wileyonlinelibrary.com]

the fact that the intermediate $LiI \cdot P_2S_5$ complex remained inactive for the chemical reaction with the Li_2S . The unknown peak at 969 cm^{-1} is expected from the vibration related to the P-I, also suggesting the formation of the

soluble $LiI \cdot P_2S_5$ complex. Interestingly, this peak is not observed in OS-3, which indicates that the high nucleophilic LiI might produce an alternative complex, rather than directly form the $LiI \cdot P_2S_5$ complex where LiI, P_2S_5 ,

and Li_2S are mixed at the same time. In short, LiI is demonstrated to be an effective nucleophilic additive that helps to dissolve P_2S_5 in the THF; however, once the soluble complex is generated in the solution, it is difficult for it to further react with the Li_2S . The addition of LiI is meaningful only when it is used as a reactant by mixing it with P_2S_5 and Li_2S at the same time, and these should be mixed together while vigorously stirring for at least 1 day.

3 | CONCLUSION

In this study, we investigated the effect of lithium iodide as an additive for synthesizing LPSI SEs. The formation of soluble $\text{P}_2\text{S}_5\text{-LiI}$ in the THF with the aid of an additive is initially demonstrated, and this would have potential for LiI to be widely applicable for driving the solution phase of SEs under the facile synthesis route. It has been demonstrated that a key to producing LPSI SE is controlling the reaction time, which determines the purity of the synthesized SEs. When sufficient reaction times were applied, bond breaking of P-S could be triggered, resulting in the formation of the soluble $\text{LiI-P}_2\text{S}_5$ complex in the THF. On the other hand, the strong binding energy of P-I would hinder further reaction with the Li_2S , contributing to undesirable side reactions. We believe that the discovery of this trade-off will contribute to progress for the practical applications of the solution-based synthesis method. Also, it will generate a broad interest in finding other effective additives for synthesizing sulfide-based electrolytes, which might solve many of the challenges currently faced in the field of ASSBs.

4 | EXPERIMENTAL

4.1 | Preparation of liquid-phase synthesis of $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ solid electrolyte

The precursors of Li_2S (Aldrich, 99.98%), P_2S_5 (Aldrich, 99%), and anhydrous LiI (Aldrich, 99.99%) were used as received. All the synthesis processes were conducted in an argon-filled glovebox or vacuum condition. The OS synthesis method was performed by mixing the three precursors altogether into 5 mL of anhydrous THF (Aldrich, 99.9%) with the water content less than 60 ppm. A stoichiometric ratio of 3:1:1 ($\text{Li}_2\text{S}:\text{P}_2\text{S}_5:\text{LiI}$) was used to form the LPSI SE. The stirring time was varied from 10 minutes to 1 h to 1 day at 300 rpm in an ambient temperature. The modified TS method was started by mixing P_2S_5 and LiI for 2 hours or 3 days, denoted as PS-2 hours and PS-3d respectively. Subsequently, Li_2S was added in the intermediate solutions and stirred with the same time variation as

in the OS method. All the prepared solutions were dried in a vacuum using a Büchi glass oven B-585 at 90°C for 4 hours. The obtained powders were heat treated at 280°C for 9 hours at a heating rate of $2^\circ\text{C}\cdot\text{min}^{-1}$ inside the glovebox.

XRD was performed using with the Miniflex II monochromatic $\text{Cu K}\alpha$ radiation (Rigaku, Japan) at a scan speed of $4^\circ\cdot\text{min}^{-1}$ in the 2θ range 10° to 70° . The powders were prepared in the argon-filled glovebox and sealed with Kapton film to avoid exposure to air when transferred. To examine the nucleophilic effects of LiI , the bonding analyses were performed using FT-IR (FT-IR, Perkin Elmer, Spectrum 100 FT-IR).

ACKNOWLEDGEMENTS

This research was supported by the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science & ICT (grant number: 2017M1A2A2044482), and also supported by the Korea Institute of Science and Technology Institutional Program (Project No. 2E30202).

ORCID

Jun Tae Kim  <https://orcid.org/0000-0002-7725-3861>

Kyung Yoon Chung  <https://orcid.org/0000-0002-1273-746X>

Hee-Dae Lim  <https://orcid.org/0000-0002-1379-6832>

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Bintang HM, Lee S, Kim JT, et al. Elucidation of the role of lithium iodide as an additive for the liquid-based synthesis of $\text{Li}_7\text{P}_3\text{S}_8\text{I}$ solid electrolyte. *Int J Energy Res.* 2020; 44:11542-11549. <https://doi.org/10.1002/er.5775>