

## Review

# Toward Scalable Liquid-Phase Synthesis of Sulfide Solid Electrolytes for All-Solid-State Batteries

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**Abstract:** All-solid-state batteries (ASSBs) are promising to be next-generation battery that provides high energy density and intrinsic safety. Research in the field of ASSBs has so far focused on the development of highly conductive solid electrolytes (SEs). The commercialization of ASSBs requires well-established large-scale manufacturing for sulfide SEs with high ionic conductivity. However, the synthesis for sulfide SEs remains at the laboratory scale with limited scalability owing to their air sensitivity. The liquid-phase synthesis would be an economically viable manufacturing technology for sulfide SEs. Herein, we review a chemical perspective in liquid-phase synthesis that offers high scalability, low cost, and high reaction kinetics. This review provides a guideline for desirable solvent selection based on the solubility and polarity characterized by the donor number and dielectric permittivity of solvents. Additionally, we offer a deeper understanding of the recent works on scalable liquid-phase synthesis using solubilizers and reactant agents. We present an outlook on a universal liquid-phase synthesis of sulfide SEs toward the commercialization of sulfide-based ASSBs.

**Keywords:** all-solid-state batteries; sulfide solid electrolytes; liquid-phase synthesis; solution chemistry



**Citation:** Gamo, H.; Nagai, A.; Matsuda, A. Toward Scalable Liquid-Phase Synthesis of Sulfide Solid Electrolytes for All-Solid-State Batteries. *Batteries* **2023**, *9*, 355.  
<https://doi.org/10.3390/batteries9070355>

Academic Editors: Jae-won Lee

Received: 27 May 2023

Revised: 19 June 2023

Accepted: 30 June 2023

Published: 4 July 2023



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## 1. Introduction

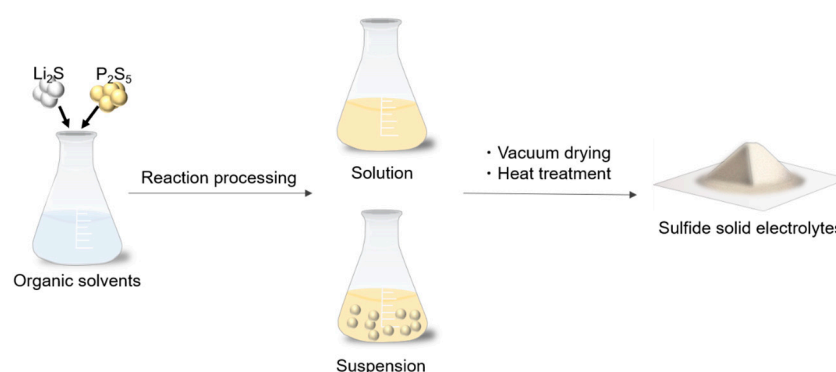
Lithium-ion batteries (LIBs) are attracting attention as a power source for electric vehicles (EVs) [1]. EV sales are expected to grow tenfold by the end of this decade, even though they were just 2–3% of total passenger vehicle sales in 2020 [2]. However, traditional LIBs with flammable organic liquid electrolytes have safety issues, such as leakage and ignition. These issues remain critical obstacles that hinder the market adoption of LIBs in the EV field [3]. All-solid-state lithium-ion batteries (ASLBs) with non-flammable inorganic solid electrolytes (SEs) offer inherently higher safety [3,4]. Inorganic SEs are crucial for the development of ASLBs that meet the demanding requirements of the EV sector for safer and greater batteries. Extensive material exploration to date has led to the discovery of highly conducting crystalline  $\text{Li}_7\text{P}_3\text{S}_{11}$  and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ , which exhibit an ionic conductivity in the order of  $10^{-2} \text{ S cm}^{-1}$  at room temperature, comparable with those of organic liquid electrolytes [5,6]. This discovery has largely advanced the application of sulfide-based ASLBs [7,8]. Recent research has focused on the material design of a family of argyrodite-type SEs with high ionic conductivity and moderate electrochemical stability. Sulfide SEs are generally synthesized by the solid-phase method using quartz ampoules or the mechanochemical method using ball-milling. These synthetic techniques are used on a laboratory scale for the discovery and design of novel materials. The synthesis is commonly performed in a glove box under an inert atmosphere because sulfide SEs and

their raw materials react with moisture in the air to release toxic  $\text{H}_2\text{S}$  gas. Given the low scalability of both synthetic methods, the scientific community developing sulfide-based ASLBs is currently interested in manufacturing technologies involving a level of practical application [9].

The liquid-phase method would be an economically viable technology for ASLB manufacturing [10,11]. However, the liquid-phase synthesis of sulfide SEs is not described by only the simple chemical reactions of raw materials [12]. The liquid-phase synthesis involves complex interactions influenced by a solvent coordination bond, competition between the solvent and chemical species, and other factors [13]. Such interactions are significantly influenced by raw materials and their compositions, which determine the solubility and reactivity in the liquid-phase synthesis of sulfide SEs. The reaction mechanism, solubility, and reactivity of  $\text{Li}_2\text{S}$ - $\text{P}_2\text{S}_5$  compounds (common sulfide SEs) in solvents are becoming evident, but there is sparse understanding of these chemical perspectives in the other family of sulfide SEs, which consists of  $\text{SiS}_2$  and  $\text{GeS}_2$  in solvents. In addition, the reaction mechanism of sulfide SEs doped with lithium halides, which are often introduced to improve ionic conductivity and electrochemical stability, in solvents is unclear because of the coordination structure altered by the presence of the halide ions. The liquid-phase synthesis involves several difficulties: estimation of increasing increments for the nucleophilic and electrophilic contributions, respectively; the choice of optimal empirical parameters for the nucleophilic and the electrophilic functions; and the understanding of the reaction mechanism [13–15]. Therefore, the liquid-phase synthesis of sulfide SEs has been advanced by an empirical approach so far [15–18]. This review aims to discuss the chemical perspective in the liquid-phase synthesis for sulfide SEs and provide a design guideline for the liquid-phase synthesis that realizes the high scalability, low cost, and short reaction processing time.

## 2. The Liquid-Phase Synthesis Method

In the liquid-phase synthesis, sulfide SEs are generally synthesized through a chemical reaction in solvents, solvent removal, and the crystallization process. This synthesis method is classified into suspension and solution synthesis, depending on the state of the solution in the reaction process, as shown in Figure 1. The state during the reaction process is determined by the properties of the solvent.



**Figure 1.** Schematic of the liquid-phase synthesis for sulfide-based solid electrolytes.

### 2.1. Suspension Synthesis

In suspension synthesis, precursor suspensions are obtained through the chemical reactions of raw materials in a solvent with moderate solubility [10]. The synthesis of sulfide SEs via suspension is summarized in Table 1.  $\text{Li}_2\text{S}$ - $\text{P}_2\text{S}_5$  systems are generally synthesized via the suspension because of their incomplete dissolution in most aprotic polar solvents. Liang et al. first synthesized nanoporous  $\beta\text{-Li}_3\text{PS}_4$  via the suspension process using tetrahydrofuran (THF) [19]. A mixture of  $\text{Li}_2\text{S}$  and  $\text{P}_4\text{S}_{10}$  (commonly referred to as  $\text{P}_2\text{S}_5$  in the literature) is reacted overnight in THF to generate an  $\text{Li}_3\text{PS}_4 \cdot 3\text{THF}$  complex. This

compound releases THF molecules under a vacuum at 80 °C, followed by heating at 140 °C under a vacuum to produce the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> with an ionic conductivity of  $7.4 \times 10^{-5} \text{ S cm}^{-1}$  at room temperature. Subsequent research found that 1,2-dimethoxyethane (DME) [20], acetonitrile (ACN) [15,16], ethyl acetate (EA) [21,22], ethyl propionate (EP) [23,24], pyridine [25,26], and anisole [27] are also used as an effective reaction solvent for the suspension synthesis owing to their moderate solubility and reactivity. Lithium sulfide and P<sub>2</sub>S<sub>5</sub> reactants are individually insoluble in most aprotic polar solvents, but form highly soluble solvate lithium thiophosphates at a 1:1 molar ratio of Li<sub>2</sub>S and P<sub>2</sub>S<sub>5</sub> [28]. The intermediate reacts with Li<sub>2</sub>S to generate Li<sub>3</sub>PS<sub>4</sub> precursors. The reaction from insoluble Li<sub>2</sub>S to insoluble Li<sub>3</sub>PS<sub>4</sub> involves a long processing time (1–3 days) because of the sluggish reaction kinetics. The suspension synthesis of Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and Li<sub>7</sub>P<sub>2</sub>S<sub>8</sub>I involves the rate-limiting process of the Li<sub>3</sub>PS<sub>4</sub> precursor formation [29–31]. This process involves the formation of heterogeneous precursors, which may increase the engineering cost of ASLB manufacturing, particularly for large-scale manufacturing. On the other hand, giving additional energy by mechanical [23], super sonication [32], and microwave [27] treatments allows us to boost the reaction kinetics and reduce the processing time. The liquid-phase synthesis assisted by the mechanical treatment provided the rapid synthesis of the Li<sub>3</sub>PS<sub>4</sub> SEs with an ionic conductivity over  $10^{-4} \text{ S cm}^{-1}$  at room temperature [33]. Amorphous Li<sub>3</sub>PS<sub>4</sub> prepared by the mechanochemical reaction shows higher ionic conductivity than the crystalline  $\beta$ -phase [34]. Thus, in the liquid-phase synthesis, the solvent removal process should be conducted at a lower temperature than the crystallization temperature of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> to achieve high ionic conductivity. The evaporation temperature of a coordinated solvent depends on the strength of the coordination bond between the solvent and intermediate molecular complex, which is determined by the polarity of the solvent. In the liquid-phase synthesis of Li<sub>3</sub>PS<sub>4</sub> via acetate solvent systems, solvents with lower polarity resulted in a lower temperature of the solvent removal [22]. Li<sub>3</sub>PS<sub>4</sub> synthesized using acetate solvents with lower polarity showed higher ionic conductivity because of the formation of low crystallinity Li<sub>3</sub>PS<sub>4</sub>, even after the solvent removal.

**Table 1.** Synthesis of sulfide SEs via suspension.

Product	Treatment	Solvent	Reaction Time (h)	Ionic Conductivity (mS cm <sup>-1</sup> )	Reference
Li <sub>3</sub> PS <sub>4</sub>	Stirring	THF	12	0.074	[19]
Li <sub>3</sub> PS <sub>4</sub>	Stirring	ACN	48	0.12	[14]
Li <sub>3</sub> PS <sub>4</sub>	Shaking	EP	6	0.20	[33]
Li <sub>7</sub> P <sub>3</sub> S <sub>11</sub>	Stirring	DME	72	0.27	[20]
Li <sub>7</sub> P <sub>3</sub> S <sub>11</sub>	Stirring	ACN	24	1.5	[35]
Li <sub>7</sub> P <sub>3</sub> S <sub>11</sub>	Sonication	ACN	0.5	1.0	[32]
Li <sub>7</sub> P <sub>3</sub> S <sub>11</sub>	Microwave	anisole	0.5	0.13	[27]
Li <sub>7</sub> P <sub>2</sub> S <sub>8</sub> I	Stirring	ACN	36	0.63	[31]
Li <sub>7</sub> P <sub>2</sub> S <sub>8</sub> I	Shaking	EP	6	0.34	[23]
Li <sub>7</sub> P <sub>2</sub> S <sub>8</sub> I	Shaking	EP	1	1.0	[36]
Li <sub>6</sub> PS <sub>5</sub> Cl	Stirring	THF+EtOH	36	2.4	[37]
Li <sub>6</sub> PS <sub>5</sub> Cl	Stirring	ACN+PTH	24	2.8	[38]

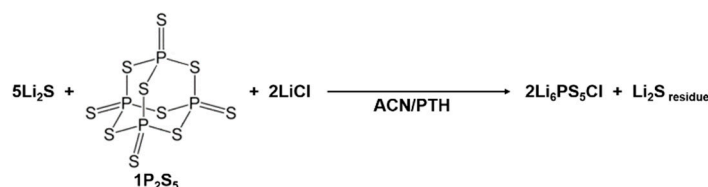
In the suspension synthesis of Li<sub>6</sub>PS<sub>5</sub>Cl, alcohol solvents are used as effective reaction mediators. For instance, ethanol (EtOH) solvent shows an extremely high solubility against Li<sub>2</sub>S and P<sub>2</sub>S<sub>5</sub>, but causes a substitution reaction between the O atom in the solvent and the S atom in the P<sub>2</sub>S<sub>5</sub> molecule. Despite this limitation, the Li<sub>6</sub>PS<sub>5</sub>Cl precursor was synthesized by the reaction of the Li<sub>3</sub>PS<sub>4</sub> THF complex precursor, Li<sub>2</sub>S, and LiCl in an alcohol solvent [37,39]. We believe that this is because the PS<sub>4</sub><sup>3−</sup> anion unit is protected from EtOH by steric hindrance from THF coordinated to 3Li<sup>+</sup>-PS<sub>4</sub><sup>3−</sup>. The Li<sub>6</sub>PS<sub>5</sub>Cl SEs did not return to their original argyrodite structure after dissolving in EtOH and heating again [40]. This should be derived from the severe decomposition of PS<sub>4</sub><sup>3−</sup> by EtOH. The decomposition of the Li<sub>6</sub>PS<sub>5</sub>Cl by EtOH can be minimized by decreasing the exposure time

to EtOH [41,42]. Considering the side reactions caused by EtOH, a synthesis method using an ACN/1-propanethiol (PTH) solvent was developed [38]. The  $\text{Li}_6\text{PS}_5\text{Cl}$  SEs synthesized using the THF/EtOH solvent contained an  $\text{Li}_3\text{PO}_4$  crystal phase as a secondary phase (see Figure 2a). Even  $\text{Li}_6\text{PS}_5\text{Cl}$  synthesized using THF/PTH formed oxides in the final product, which originated from the ring-opening reaction of THF solvent caused by the nucleophilic attack of the dissociated Cl ions and the  $\text{S}^-$  anion of PTH. On the other hand, highly pure  $\text{Li}_6\text{PS}_5\text{Cl}$  SEs without  $\text{Li}_3\text{PO}_4$  were successfully synthesized in an oxygen-free system using ACN/PTH solvent (Figure 2b). Additionally,  $\text{Li}_6\text{PS}_5\text{Cl}$  SEs with relatively high purity were synthesized using only the THF single solvent by employing a heat treatment to fully react the raw materials [43].

(a) Synthesis using THF/EtOH or THF/PTH solvent



(b) Synthesis using ACN/PTH solvent



**Figure 2.** Schematics of the wet-chemical synthesis of  $\text{Li}_6\text{PS}_5\text{Cl}$  SEs in (a) THF/EtOH or THF/PTH and (b) ACN/PTH solvents.

## 2.2. Solution Synthesis

The solution synthesis involves the formation of a homogeneous precursor solution in an organic solvent with high solubility. Hence, the solution synthesis method provides faster reaction kinetics in comparison with suspension synthesis. Table 2 summarizes the synthesis of sulfide SEs via the solution. Recent works reported that ethylene diamine (EDA) and EA dissolve  $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$  [44,45] and  $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$  (mol%) [21], respectively. It should be noted that the solubility of the solvent may be influenced by the presence of slight moisture in the solvent. In addition, polar hydrophilic protonic solvents, such as dimethylformamide (DMF) and 1-methyl-2-pyrrolidone (NMP), exhibit high solubility against  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$  [46]. However, their use is limited because of their high basicity, which leads to the decomposition of anion units in intermediate molecular complexes [17,46,47]. Thiol solvents were found to be effective solvents for the solution synthesis of sulfide SEs [48,49]. Thiol solvents exhibit desirable properties, such as high polarity, high solubility, moderately low boiling point, and no side reactions with the raw materials and intermediates. A mixed solvent containing thiol solvent and EDA is a useful reaction solvent for a broad range of sulfide SEs, including  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_{10}\text{Ge}_2\text{PS}_{12}$  [49]. With the use of ethanedithiol (EDT) solvent, carbonized solvent molecules remained in the sulfide SEs after heat treatment. This should be ascribed to the strong coordination bonds between the solvent molecules and solutes. The presence of residual solvent molecules led to high electronic conductivity of the SEs, which negatively affected their performance as an electrolyte for ASLBs. Generally, there is a relationship between the strength of the coordination bonds with solvent molecules and the evaporation temperature of the coordinated solvent. The use of the highly polar solvent may increase the industrial cost due to the large energy consumption in the solvent removal process. Taking this into consideration, an ideal manufacturing process would involve the complete dissolution of the precursor and precipitation of the

final product, thereby improving yield, reducing production costs, and minimizing waste and solvent removal.

**Table 2.** Synthesis of sulfide SEs via solution.

Product	Treatment	Solvent	Reaction Time (h)	Ionic Conductivity (mS cm <sup>−1</sup> )	Reference
Li <sub>3</sub> PS <sub>4</sub>	Stirring	EDA	3	$2.3 \times 10^{-3}$	[44]
Li <sub>7</sub> P <sub>3</sub> S <sub>11</sub>	Stirring	EA	2	0.12	[21]
Li <sub>6−x</sub> P <sub>5</sub> S <sub>5−x</sub> Cl <sub>1+x</sub> (0 ≤ x ≤ 0.5)	Stirring	EDA	—	2.9	[25]
Li <sub>10</sub> Ge <sub>2</sub> PS <sub>12</sub>	Stirring	EDA+ET	3	1.2	[49]

### 3. Solvent Selection

The solvent selection in the liquid-phase synthesis is a critical consideration, taking into account factors such as solvent polarity, solubility of reactants, products, and intermediates, solvent removal processes, and industrial concerns [12]. This review focuses on the topics of polarity and solubility. The polarity of organic solvents varies the bond properties in the intermediate molecular complexes. The extent of polarization induced by a given bond relies on the strength of the coordination bonds with the nucleophile and/or electrophile. The stronger the coordination interaction, the greater the induced polarization. The reaction between Li<sub>2</sub>S and P<sub>2</sub>S<sub>5</sub> is initiated by the dissociation reaction of the P<sub>2</sub>S<sub>5</sub> through nucleophilic attack by the electron donor [50]. Therefore, the introduction of empirical functional parameters related to nucleophilic property is important for the effective synthesis of sulfide SEs via the liquid phase. Donor number (DN) and dielectric permittivity are commonly used as empirical parameters to quantify polarity. Table 3 summarizes the DN, dielectric permittivity, and boiling point of various solvents.

**Table 3.** Functional parameter and physical properties of various solvents [13,51].

Solvent	Donor Number [kcal·mol <sup>−1</sup> ]	Dielectric Permittivity	Boiling Point [°C]
1,4-dioxan	15	2.2	101
Carbon sulfide	2	2.63	46
Anisole	9	4	154
Tetrahydropyran	22	5.5	88
Ethyl acetate	17	6	77
1,2-Dimethoxyethane	24	7.2	83
Tetrahydrofuran	20	7.6	66
Pyridine	33	12	115
Ethylene diamine	55	14	116
Ethanol	32	19	78
Dimethylformamide	27	36	153
Acetonitrile	14	38	82

#### 3.1. Donor Number

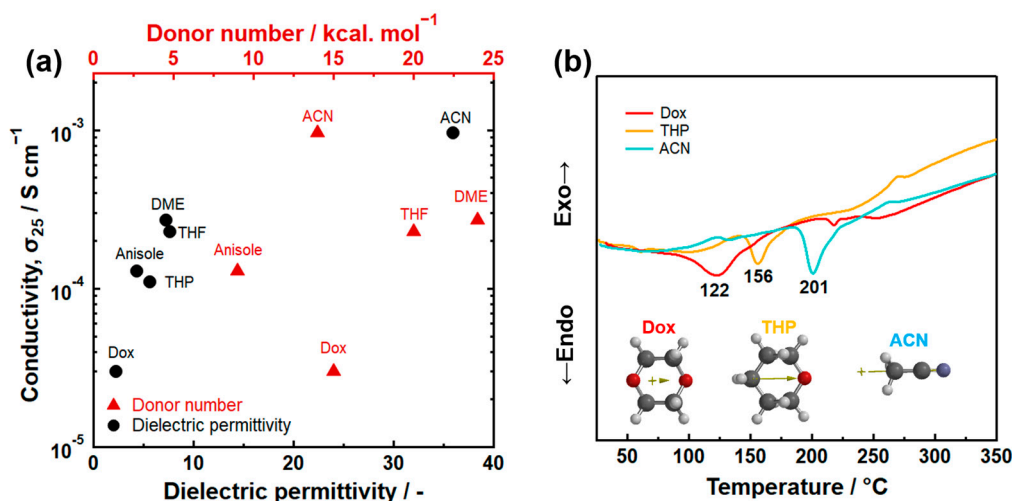
The DN is defined as the negative enthalpy for the reaction of complexation with SbCl<sub>5</sub> in a highly diluted solution of dichloroethane. The concept of DN was proposed to express quantitatively the Lewis basicity of solvents. Aprotic solvents, in general, exhibit poor acceptor properties, and their DN values are related to the extent of charge transfer associated with ion solvation [13]. Hence, the DN of a solvent serves as an indicator of its reactivity in liquid-phase synthesis. Previous studies reported that organic solvents with DN higher than 14 kcal mol<sup>−1</sup> were unsuitable for solution processing of Li<sub>3</sub>PS<sub>4</sub> SEs because of their decomposition caused by nucleophilic attacks [18]. While THF has 20 kcal mol<sup>−1</sup> of DN, it is often used for the solution processing of sulfide SEs [40,43]. However, the guideline for solvent selection is not contingent on DN indicators only. EDA



solvent shows the highest DN among the solvents listed in Table 3. The EDA with high DN acts as a strong nucleophilic agent, breaking the P-S bond in  $P_2S_5$  and facilitating the complete dissolution of  $P_2S_5$  [44]. The  $75Li_2S$   $25P_2S_5$  solution in EDA contains various units such as  $PS_4^{3-}$ ,  $P_2S_6^{4-}$ ,  $P_2S_6^{2-}$ , and  $PS_3^-$ , which convert into  $\beta$ - $Li_3PS_4$  consisting exclusively of  $PS_4^{3-}$  units after heat-treatment at  $200^\circ C$  under vacuum.

### 3.2. Dielectric Permittivity

Dielectric permittivity is an important indicator for evaluating the polarity of solvents and determining their reactivity in wet-chemical synthesis. It was found that the dielectric permittivity of solvents used in the synthesis relates to the ionic conductivity of  $Li_7P_3S_{11}$  prepared by the suspension synthesis [15]. Figure 3a illustrates the correlation between the ionic conductivity of  $Li_7P_3S_{11}$  at room temperature and the dielectric permittivity of the used organic solvents. Higher dielectric permittivity of the solvents leads to increased ionic conductivity in the  $Li_7P_3S_{11}$ . There is no relationship between the DN of the solvent and the ionic conductivity of  $Li_7P_3S_{11}$  SEs. Figure 3b displays differential thermal curves of  $Li_7P_3S_{11}$  precursors prepared using ACN, THP, and Dox solvents. An endothermic peak was observed between  $100$  and  $200^\circ C$ , which is attributed to the evaporation of the solvent coordinated with lithium thiophosphates. Differential thermal analysis showed that the strength of the chemical interaction between the  $Li_2S$ - $P_2S_5$  system and solvent molecules increased with an increasing dielectric permittivity of the coordinated solvent. Therefore, the correlation between the conductivity and dielectric permittivity can be described using the argument that the use of an organic solvent with high dielectric permittivity increases the reactivity of the precursor, resulting in the formation of the highly pure  $Li_7P_3S_{11}$ . Besides dielectric permittivity, other selection criteria for the suspension synthesis of  $Li_2S$ - $P_2S_5$  systems include the absence of side reactions with raw materials, intermediates, and products, as well as a reasonably low boiling point. Given these requirements, ACN solvent is the optimal choice for the suspension synthesis of  $Li_7P_3S_{11}$  at present.



**Figure 3.** (a) The relationship between the dielectric permittivity of organic solvents and ionic conductivity at room temperature of  $Li_7P_3S_{11}$  prepared by the suspension synthesis method. Dox represents 1,4-dioxane and THP represents tetrahydropyran. (b) Differential thermal curves of  $Li_7P_3S_{11}$  precursors prepared using ACN, THP, and Dox solvents [15]. The arrows within the molecular structure represent dipole moment.

### 3.3. Solubility

The formation of soluble precursors is preferred for the reaction to proceed quickly. EA solvent completely dissolves the intermediate resulting from  $70Li_2S$   $30P_2S_5$ , enabling the rapid synthesis of  $Li_7P_3S_{11}$  SEs [21]. Individual  $Li_2S$  and  $P_2S_5$  are insoluble in EA solvent during solution synthesis. This indicates that a rapid synthesis for sulfide SEs does

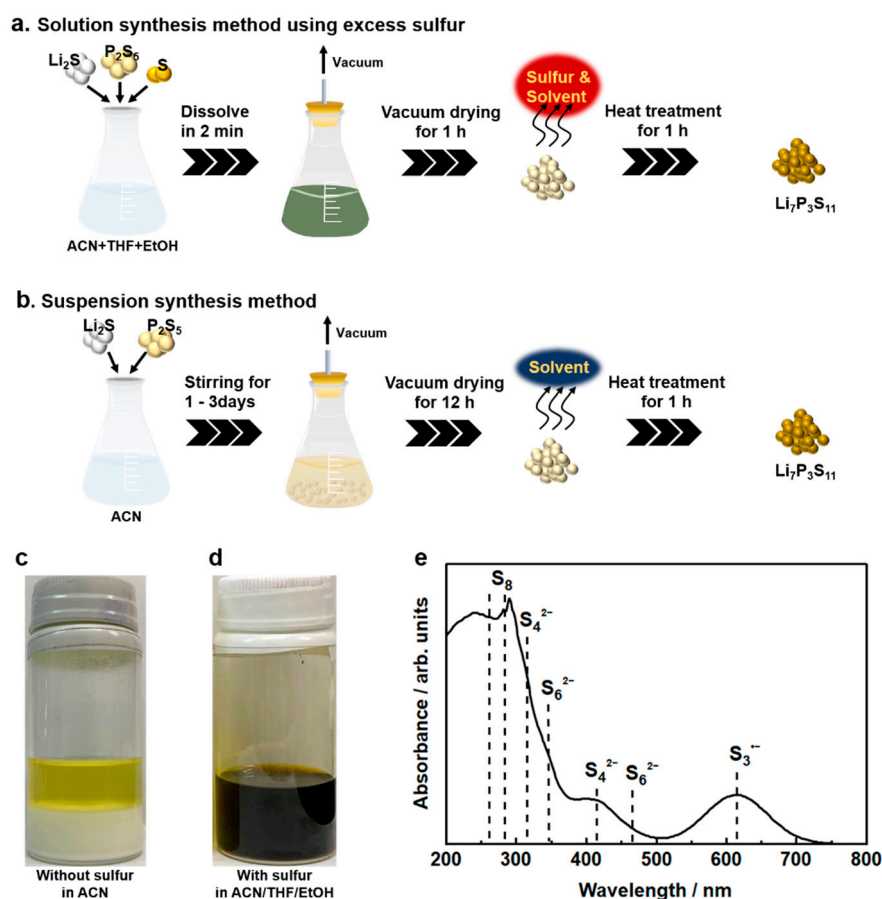
not necessarily require the solubilization of  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$  raw material. In other words, the overall reaction rate in the synthesis process depends on the solubility of solvents for intermediate complexes, as follows: ACN and EP dissolve  $1\text{Li}_2\text{S} \cdot 1\text{P}_2\text{S}_5$  (molar ratio) [24,28]; THF dissolves  $1.5\text{Li}_2\text{S} \cdot 1\text{P}_2\text{S}_5$  [52]; and a mixed solvent of ACN and THF at a volume ratio of 1:1 dissolves  $2\text{Li}_2\text{S} \cdot 1\text{P}_2\text{S}_5$  [53]. Of course, the solubility of the solvent depends on a given compound. The solubility of  $\text{Li}_2\text{S}$ - $\text{GeS}_2$  and  $\text{Li}_2\text{S}$ - $\text{SnS}_2$  in organic solvents remains poorly understood. The strong covalent bonding between the metal and chalcogen atoms typically brings a challenge for the direct dissolution of these compounds. In 2009, it was reported that a bulk chalcogenide semiconductor and chalcogen in hydrazine solvent form a highly soluble hydrazinium-based salt of the chalcogenide semiconductor through a redox reaction [54]. Hydrazine is an effective solvent for the solution processing of metal chalcogenide, but its highly toxic, explosive, and carcinogenic properties make it less attractive for scale-up. A binary thiol/amine mixture was developed as an ideal alkali solvent system for the solution processing of chalcogenide semiconductors [55]. A mixed solvent of EDA and EDT fully dissolves  $\text{SnS}_2$  and  $\text{GeS}_2$  [49,56]. EDA solvents do not cause a nucleophilic attack to the germanium moiety on  $\text{GeS}_2$ , even though EDA solvent with high DN shows a strong nucleophilic attacker capable of breaking P-S bonds. In contrast, the thiolate anion in thiol solvents dissociates Ge-S bonds in the  $\text{GeS}_2$  through the nucleophilic attack. The high solubility of the mixed solvent of EDA and EDT for sulfides was first demonstrated in studies on the dissolution of bulk semiconductors, such as  $\text{As}_2\text{Ch}_3$ ,  $\text{Sb}_2\text{Ch}_3$ , and  $\text{Bi}_2\text{Ch}_3$  ( $\text{Ch} = \text{S}, \text{Se}, \text{Te}$ ) which are insoluble in common organic solvents [57]. As mentioned above, depending on the solvent combination, mixed solvents may show higher solubility than a single solvent. Recent work reported that the mixtures of  $\text{Li}_2\text{S}$  and  $\text{SiS}_2$  with a molar ratio of 2:1 are soluble in ACN solvent [58]. However, no comprehensive guidelines for gaining high solubility in starting materials for sulfide SEs have been proposed.

#### 4. Strategies for Rapid Synthesis

##### 4.1. Solubilizer

Solution synthesis is a desirable manufacturing technology for sulfide SEs. However, there are restrictions on the selection of solvents that dissolve raw materials and intermediates, e.g.,  $\text{Li}_2\text{S}$  and  $\text{Li}_3\text{PS}_4$ , and no leading guidelines for solvent selection have been established. The introduction of a solubilizer has been examined as one of the strategies to dissolve  $\text{Li}_2\text{S}$  and  $\text{Li}_3\text{PS}_4$ . Excess elemental sulfur reacts with these insoluble materials to form intermediate molecular complexes that are soluble in specific solvents, such as THF and diethylene glycol diethyl ether (DEGDME) [59,60]. Lim et al. first proposed solution processing using excess elemental sulfur as the manufacturing technology for sulfide-based ASLBs [59]. In the sulfide SE solution processing,  $\text{Li}_2\text{S}$  and S reacted in DEGDME solvent to form fully soluble lithium polysulfides. Subsequently,  $\text{P}_2\text{S}_5$  was added to the obtained solution to generate the  $\beta\text{-Li}_3\text{PS}_4$  precursor. The  $\beta\text{-Li}_3\text{PS}_4$  after drying treatment exhibited an ionic conductivity of  $2.8 \times 10^{-5} \text{ S cm}^{-1}$  at room temperature. The low conductivity might be attributed to residual sulfur due to an insufficient drying process at  $140^\circ\text{C}$ . The synthesis method using excess sulfur requires a heat-treatment process over  $250^\circ\text{C}$  for the removal of excess sulfur, and is therefore unsuitable for synthesizing SEs that exhibit high ionic conductivity in the low-temperature phase, for example, amorphous  $\text{Li}_3\text{PS}_4$  and  $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ . Subsequent work successfully synthesized  $\text{Li}_6\text{PS}_5\text{Cl}$  SEs via soluble lithium thiophosphates with excess sulfur, which showed a high ionic conductivity of  $1.8 \text{ mS cm}^{-1}$  at room temperature [61]. However, the reported solution processing via polysulfide involved a long reaction time of 24 h or more. To achieve rapid solution synthesis of  $\text{Li}_7\text{P}_3\text{S}_{11}$ , a synthesis method based on polysulfide chemistry was introduced (Figure 4a) [53]. Conventional suspension synthesis of highly conductive  $\text{Li}_7\text{P}_3\text{S}_{11}$  requires a long reaction process to ensure sufficient reaction completion (Figure 4b). As shown in Figure 4c, the  $7\text{Li}_2\text{S} \cdot 3\text{P}_2\text{S}_5$  system in ACN solvent formed a white suspension and a yellowish solution after stirring for 3 days; they correspond to the  $\text{Li}_3\text{PS}_4$  complex and soluble

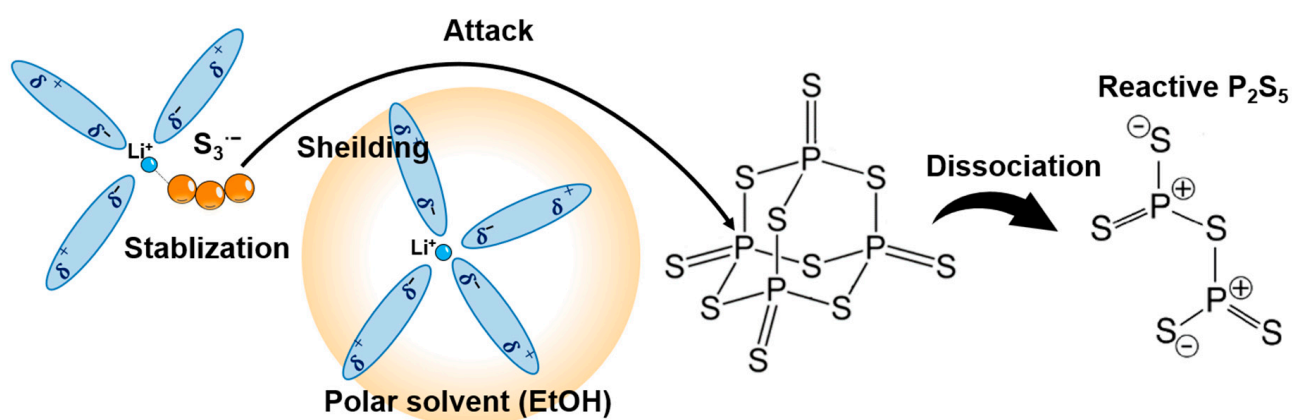
$1\text{Li}_2\text{S} \cdot 1\text{P}_2\text{S}_5$ , respectively. According to the reaction mechanism proposed in the previous reports,  $\text{Li}_7\text{P}_3\text{S}_{11}$  SEs are formed through a solid-state reaction of the  $\text{Li}_3\text{PS}_4$  complex and  $\text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5$  (a molar ratio of 1:1) intermediate during heat treatment above  $200^\circ\text{C}$  [29]. On the other hand,  $7\text{Li}_2\text{S} \cdot 3\text{P}_2\text{S}_5 \cdot 5\text{S}$  in a mixed solvent of ACN, THF, and a trace amount of EtOH formed a black colored solution without additional energy in an extremely short time of 2 min (Figure 4d). The formation of the black solution suggests the presence of polysulfide ions. In the UV-Vis absorption spectra of  $7\text{Li}_2\text{S} \cdot 3\text{P}_2\text{S}_5 \cdot 5\text{S}$  in the mixed solvent,  $\text{S}_8$ ,  $\text{S}_6^{2-}$ ,  $\text{S}_4^{2-}$ , and  $\text{S}_3^{\cdot-}$  were detected at 265, 350, 410, and 610 nm, respectively (see Figure 4e). Research in the field of lithium sulfur batteries reported that lithium polysulfides with different chain lengths are stabilized in specific organic solvents through disproportionate and dissociation reactions [62,63]. Tri-sulfur radical anions with high reactivity are the dominant chemical species in the complex system of equilibria. The reaction kinetics in the synthesis method with excess sulfur is significantly influenced by the chemical stability of the  $\text{S}_3^{\cdot-}$  radical anions. Intrinsically unstable  $\text{S}_3^{\cdot-}$  radical anions are stabilized in highly polar organic solvents because of the competition for Li ions between strong coordinated bonds of highly polar solvents and electrostatic interactions of polysulfide anions. The rapid solution synthesis shown in Figure 4a can be achieved by the existence of highly polar EtOH, which enhances the chemical stability of the  $\text{S}_3^{\cdot-}$  radical anion in the precursor solution.



**Figure 4.** Schematics of (a) the solution synthesis method using excess sulfur and (b) the suspension synthesis method for  $\text{Li}_7\text{P}_3\text{S}_{11}$  SEs. Solubility of (c)  $7\text{Li}_2\text{S} \cdot 3\text{P}_2\text{S}_5$  mixtures in ACN solvent after stirring at  $50^\circ\text{C}$  for 72 h and (d)  $7\text{Li}_2\text{S} \cdot 3\text{P}_2\text{S}_5 \cdot 5\text{S}$  in ACN/THF/EtOH solvent after stirring at room temperature for 2 min. (e) UV-Vis spectrum of  $7\text{Li}_2\text{S} \cdot 3\text{P}_2\text{S}_5 \cdot 5\text{S}$  at  $1.0 \text{ mmol L}^{-1}$  in ACN/THF/EtOH solvent [53].



Figure 5 outlines the proposed reaction of lithium phosphates with excess elemental sulfur in the precursor solution [53]. First, lithium ions form strong coordination bonds with highly polar EtOH and ACN solvents (step 1). Next, the polysulfides generated by the reaction of  $\text{Li}_2\text{S}$  and excess sulfur are shielded from Li ions (Step 2). Tri-sulfur radical anions are stabilized owing to the competition between the polysulfide dianions and salt anions for the Li cation (Step 3). Then, the  $\text{S}_3^{\cdot-}$  radical anions with unpaired electrons attack the phosphorus moiety on  $\text{P}_4\text{S}_{10}$  (step 4). The  $\text{P}_4\text{S}_{10}$  with an adamantane-like cage structure dissociates to reactive  $\text{P}_2\text{S}_5$  (step 5). The reactive  $\text{P}_2\text{S}_5$  reacts with lithium polysulfides to form a soluble lithium thiophosphate. The added excess elemental sulfur is removed without deteriorating influence on the formation of the final products during the heat treatment for crystallization. Recent works demonstrated that  $\text{Li}_6\text{PS}_5\text{Cl}$  and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  are rapidly synthesized via the precursor solution with excess elemental sulfur in the ACN/THF/EtOH solvent [64,65]. A mixture of  $\text{Li}_2\text{S}$ ,  $\text{P}_2\text{S}_5$ ,  $\text{LiX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ), and  $\text{S}$  at a molar ratio of 5:1:2:15, which represents the raw materials of  $\text{Li}_6\text{PS}_5\text{X}$  SEs, formed a black solution in the ACN/THF/EtOH solvent, as shown in Figure 6a. This black coloration arises from the formation of polysulfide ions (see Figure 6b–d). The existence of a trace EtOH enhanced the solubility of the precursor solution and the chemical stability of polysulfides, which is explained by the coordination chemistry shown in Figure 5.



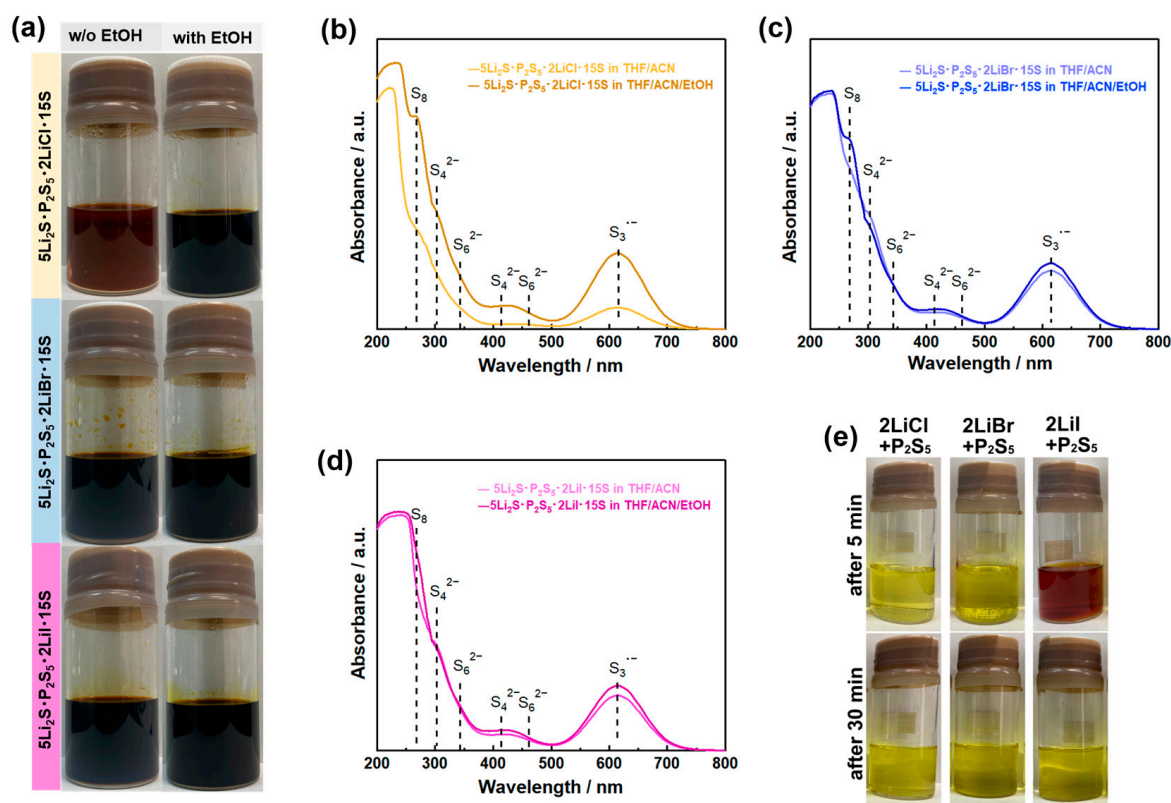
**Figure 5.** Schematics of the reaction mechanism for  $\text{Li}_2\text{S}\cdot\text{P}_2\text{S}_5$  systems in ACN/THF/EtOH solvent [53]. Step 1: Lithium ions are strongly coordinated with highly polar EtOH molecules. Step 2: Polysulfides are shielded from Li ions. Step 3:  $\text{S}_3^{\cdot-}$  radical anions are stabilized. Step 4: The  $\text{S}_3^{\cdot-}$  radical anions attack the phosphorus moiety on  $\text{P}_4\text{S}_{10}$ . Step 5:  $\text{P}_4\text{S}_{10}$  with cage structure breaks and converts to reactive  $\text{P}_2\text{S}_5$ .

Interestingly,  $5\text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5 \cdot 2\text{LiCl} \cdot 15\text{S}$  precursor in ACN/THF solvent formed a reddish-brown solution, indicating lower chemical stability of the polysulfides than other precursor solutions. A Raman study showed that this observation may be caused by the strong competitive interaction between  $\text{Cl}^-$  ions and ACN molecules in the precursor solution [64]. In this solution synthesis method using excess elemental sulfur as a solubilizer, the coordination environment of solvent molecules, Li-ions, and polysulfides determines the chemical stability and reactivity of each chemical species. The coordination chemistry is also of interest in the research field of lithium-sulfur batteries [63,66,67]. Thus, this method can promise further advances by integrating the insight gained from coordination chemistry studies in the field of lithium-sulfur batteries.

#### 4.2. Reactant Agent

As mentioned above, the wet-chemical synthesis of lithium thiophosphates initiates the dissociation reaction of  $\text{P}_4\text{S}_{10}$ . The dissociation reaction is driven by nucleophilic attack from lone-pair electrons of  $\text{Li}_2\text{S}$  and/or donor solvents [26,29]. The introduction of reactant agents for activating  $\text{P}_4\text{S}_{10}$  is a useful strategy for the rapid synthesis of sulfide SEs. The

addition of lithium thioethoxide and lithium halide facilitates the formation of soluble chemical species [64,68,69]. Halide ions are nucleophilic, and quickly dissociate  $P_2S_5$  in organic solvents, as shown in Figure 6e [64]. Lithium ions are strongly solvated by donor solvents owing to their strong Lewis acid. Therefore, the bond of Li ions with counter ions is strongly polarized and more easily dissociated. In the coordination environment, where the cation is highly stabilized, the anion species would be available as reactive chemical species in the system. Taking this into consideration, the reaction mechanism in the wet-chemical synthesis of  $Li_7P_2S_8I$  SEs may intrinsically differ from that of  $Li_3PS_4$  [23,24].



**Figure 6.** (a) Optical images of  $5Li_2S \cdot P_2S_5 \cdot 15S$  (molar ratio) and  $5Li_2S \cdot P_2S_5 \cdot 2LiX \cdot 15S$  ( $X = Cl, Br,$  and  $I$ ) at  $0.1 \text{ mol L}^{-1}$  in ACN/THF and ACN/THF/EtOH solvents. UV-Vis spectra of (b)  $5Li_2S \cdot P_2S_5 \cdot 2LiCl \cdot 15S$ , (c)  $5Li_2S \cdot P_2S_5 \cdot 2LiBr \cdot 15S$ , and (d)  $5Li_2S \cdot P_2S_5 \cdot 2LiI \cdot 15S$  solutions at  $0.5 \text{ mmol L}^{-1}$  in ACN/THF and ACN/THF/EtOH solvents. (e) Optical images of  $2LiCl \cdot P_2S_5$ ,  $2LiBr \cdot P_2S_5$ , and  $2LiI \cdot P_2S_5$  in THF/ACN solvent ( $0.1 \text{ mol L}^{-1}$ ) from the standing samples for 5 and 30 min. Reprint with permission [63]: Copyright 2023, American Chemical Society.

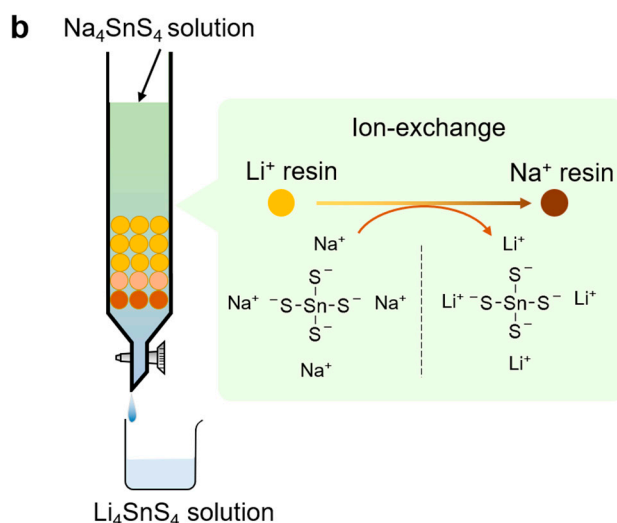
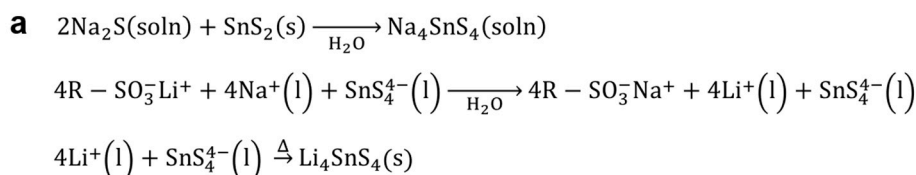
## 5. Low-Cost Synthesis

The price of ASLBs per energy density is one order of magnitude higher than that of conventional LIBs, and is dominated by the cost of raw materials for SEs [61]. Among these raw materials,  $Li_2S$ , an essential raw material, is one to two orders of magnitude more cost-expensive per gram than  $P_2S_5$  [12]. Hence, it is necessary to develop a synthetic method using inexpensive starting materials instead of  $Li_2S$ . A liquid-phase synthesis of Li-ion SEs using inexpensive  $Na_2S$  raw material was recently developed: the synthesis of  $Li_4SnS_4$  from  $Na_4SnS_4$  using the ion-exchange method [70]; and the synthesis of  $Li_6PS_5Cl$  using  $Na_2S$  as a sulfurizing agent [71–73].

### 5.1. Ion-Exchange Method

$Li_4SnS_4$  was synthesized from  $Na_4SnS_4$  using the ion-exchange method via water [70]. Firstly, an  $Na_4SnS_4$  solution was prepared through the reaction between  $Na_2S$  and  $SnS_2$  in water. The obtained  $Na_4SnS_4$  solution flowed through a column packed with Li-type ion

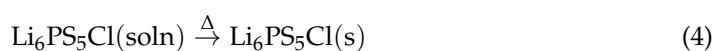
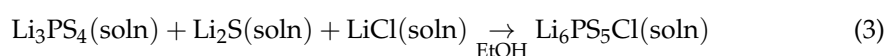
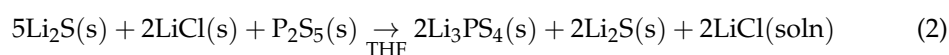
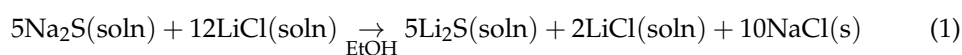
exchange resin to exchange from  $\text{Na}^+$  to  $\text{Li}^+$  ions in  $\text{Na}_4\text{SnS}_4$ . The resultant  $\text{Li}_4\text{SnS}_4$  aqueous solution was dried and heated to obtain  $\text{Li}_4\text{SnS}_4$  SEs (see Figure 7). The  $\text{Li}_4\text{SnS}_4$  obtained from this method showed an ionic conductivity of approximately  $1 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature, which is the same value as  $\text{Li}_4\text{SnS}_4$  prepared by the solid-phase method and mechanochemical reaction. Unlike  $\text{Li}_2\text{S}$ ,  $\text{Na}_2\text{S}$  can be handled in air, and it is easy to process the reaction in an aqueous solution. This method using inexpensive  $\text{Na}_2\text{S}$  and  $\text{H}_2\text{O}$  as reaction solvents resolves environmental loads owing to the use of organic solvents and economic concerns.



**Figure 7.** (a) Reactions and (b) schematic for the synthesis of  $\text{Li}_4\text{SnS}_4$  solid electrolytes via aqueous solution ion-exchange. The circles in the schematic represent ion exchange resin.

### 5.2. Sulfurizing Agent

Lithium chloride reacts with  $\text{Na}_2\text{S}$  in EtOH solvent to generate precipitated  $\text{Na}_2\text{S}$  and  $\text{Li}_2\text{S}/\text{LiCl}$  EtOH solution [71–74]. The  $\text{Li}_2\text{S}/\text{LiCl}$  mixture powder, separated by the distillation of the product, and  $\text{P}_2\text{S}_5$  are added into THF solvent to form  $\text{Li}_3\text{PS}_4$  intermediate molecular complexes. The  $\text{Li}_3\text{PS}_4$ ,  $\text{Li}_2\text{S}$ , and  $\text{LiCl}$  mixture powder, prepared by the drying treatment of the precursor suspension, dissolves in EtOH solvent, followed by drying and heat treatment to obtain  $\text{Li}_6\text{PS}_5\text{Cl}$  SEs.



This method allows us to synthesize  $\text{Li}_2\text{S}$  from  $\text{Na}_2\text{S}$  and  $\text{LiCl}$  on the basis of the difference in the solubility of EtOH for  $\text{Li}_2\text{S}$  and  $\text{NaCl}$ . A further examination of the

sulfurizing agent such as  $\text{Na}_2\text{S}$  can contribute to the development of the liquid-phase synthesis for sulfide SEs from inexpensive Li salts other than  $\text{Li}_2\text{S}$ .

## 6. Environmental Aspects

The industrial adaption of the liquid-phase synthesis for sulfide SEs to the electric vehicle fields requires consideration of environmental aspects, such as the toxicity of sulfide SEs and organic solvents, yield rate, energy-saving route, recycling of sulfide SEs. Sulfide SEs consisting of P or Si element release toxic gas, that is,  $\text{H}_2\text{S}$  gas, in contact with atmospheric moisture [75–77]. The air-stability of these materials is based on the classical hard-soft acid-base theory (HSAB) [76–81]. According to HSAB theory, the sulfur anion is a softer base than the oxygen anion and thus metal cations classified as softer acids form stronger bonds with sulfur than oxygen. Using softer acids, such as  $\text{Sn}^{4+}$  and  $\text{Sb}^{5+}$ , as central cations has been an effective strategy to improve the air stability of sulfide SEs. Importantly,  $\text{Li}_4\text{SnS}_4$  can be processed in a solution using water, which is the most environmentally friendly solvent [78]. This stability is desirable for recycling technology of sulfide SEs through energy-saving routes. Indeed, the  $\text{Li}_4\text{SnS}_4$  subjected to exposure to water, followed by vacuum drying and heat treatment, showed almost the same ionic conductivity as the as-synthesized  $\text{Li}_4\text{SnS}_4$  [78]. However, a family of  $\text{Li}_4\text{SnS}_4$  SEs showed an ionic conductivity in the order of  $10^{-4} \text{ S cm}^{-1}$  at room temperature, which is insufficient for practical application in ASLBs [70,78–80]. On the other hand, the solution processing of a family of  $\text{Li}_2\text{S-P}_2\text{S}_5$  with high ionic conductivity in water is unable to avoid detrimental effects on the electrochemical and structural properties of the  $\text{Li}_2\text{S-P}_2\text{S}_5$  SEs [75]. The use of green solvent EtOH in solution processing may potentially contribute to the environmentally friendly synthesis of sulfide SEs [39,42,71,72]. In some cases, the introduction of protective agents may be necessary. The influence of green solvents on the nature of sulfide SEs still requires further exploration [82,83]. Such a chemical perspective would offer significant insights into SE recycling.

## 7. Summary

In this review, we have highlighted a chemical perspective on the liquid-phase synthesis of sulfide SEs for ASLBs. This article has discussed the role of an additive (e.g., reactant, solubilizer, and sulfurizing agent) and organic solvent for realizing rapid and low-cost synthesis of sulfide SEs.

The liquid-phase synthesis method of sulfide solid electrolytes for all-solid-state batteries offers many advantages: low cost, high scalability, and short processing time. The liquid-phase synthesis method is classified into the suspension method and solution method. The chemical reaction in these methods is determined by the nature of the solvent. We summarized a guideline for solvent selection based on the donor number, dielectric permittivity, and solubility. The suspension method leads to low energy consumption during solvent removal; however, it involves a long processing time owing to the poor reaction kinetics in the precursor suspension. In contrast, the solution method provides higher scalability and a shorter processing time than the suspension method. Studies on the solvent effect induced by various solvent combinations have the potential to greatly advance large-scale solution synthesis technologies. Moreover, the addition of the solubilizer and reactant is an effective strategy for achieving enhanced reaction kinetics in wet-chemical synthesis. The addition of excess elemental sulfur plays a role as the solubilizer and reactant, offering the rapid solution synthesis of a variety of SEs. Given that the cost of ASLBs is still higher than conventional LIBs, the development of a synthesis method using inexpensive raw materials instead of  $\text{Li}_2\text{S}$  reduces barriers to the commercialization of ASLBs. Additionally, minimizing solvent removal in the synthesis process will increase the feasibility of its application into all-solid-state battery manufacturing. The chemical perspective in the liquid-phase synthesis gives significant insight into recycling SEs. The recent progress in the community of ASLBs has focused on their demonstration in lab-scale



cells. There is a demand for the development of a large-scale manufacturing technology that takes into account environmental load owing to the use of organic solvent and cost.

**Author Contributions:** Conceptualization, H.G.; writing—original draft preparation, H.G.; writing—review and editing, A.N. and A.M.; visualization, H.G. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no funding.

**Data Availability Statement:** No new data were created or analyzed in this study. Data sharing is not applicable to this article.

**Conflicts of Interest:** The authors declare no conflict of interest.

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