

Sulfide solid electrolytes for all-solid-state lithium batteries: Structure, conductivity, stability and application



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ABSTRACT

This review focuses on the research progress of sulfide solid electrolytes. Two systems of $(100-x)\text{Li}_2\text{S}-x\text{P}_2\text{S}_5$ and $\text{Li}_2\text{S}-\text{M}_x\text{S}_y-\text{P}_2\text{S}_5$ are systematically reviewed from four aspects, the crystal structure, conductivity, stability and application. The methods for preparing sulfide solid electrolytes are summarized, and their advantages and disadvantages are compared and analysed. Sulfide solid electrolytes with high conductivities are closely related to their crystal structures, and they can be improved via doping, such as substitution doping, interstitial doping, dual-doping, etc. The conductivities are introduced and summarized according to their classifications. Experimental studies and theoretical results are discussed in parallel to illustrate the relationship between the conductivity and crystal structure. Furthermore, the stabilities of sulfide electrolytes with lithium metal, active materials, organic solvents and humid air are reviewed separately, and corresponding methods for improvement are proposed. Finally, according to the different functions of sulfide electrolytes in all-solid-state lithium batteries (ASSLBs), they are categorized and generalized scientifically in terms of composite electrolyte, buffer material and electrolyte. Additionally, the techniques proposed in the recent works to achieve sufficient contact between the sulfide solid electrolyte and the electrode in the ASSLBs are summarized. The present review aims to provide a thorough understanding of the properties of sulfide solid electrolytes, including conductivity, structure, and stability, to allow for more efficient and target-oriented research to improve the performance of sulfides-based ASSLBs.

1. Introduction

The rapidly growing domination of lithium ion batteries in daily life has raised concerns regarding both safety and durability issues of state-of-the-art lithium ion batteries with liquid electrolytes. The replacement of organic liquid electrolytes with inorganic solid electrolytes has attracted enormous attention, because they not only offer a wide electrochemical stability window, but also make the batteries safer and more durable, with a higher energy density and simple battery design as well [1–3].

In particular, among solid electrolytes, sulfide solid electrolytes are attracting much consideration, owing to their high conductivity, which is comparable to that of liquid electrolytes. Sulfide solid electrolytes originate from oxide solid electrolytes, and are formed by replacing oxygen ions with sulfur ions. Due to the lower electro-negativity, the bonding strength between the sulfur and lithium ions is smaller than that of oxygen and lithium ions, which could lead to more free-moving

lithium ions. Additionally, the radius of a sulfur ion is larger than that of an oxygen ion. Therefore, the sulfide solid electrolytes could process a larger migration tunnel for lithium ions, which is beneficial for the migration of lithium ions. As a result, sulfide solid electrolytes exhibit higher ionic conductivities approximately 10^{-3} – 10^{-4} S cm^{-1} at room temperature. Recently, it was reported that the sulfide solid electrolytes exhibited high Li-ionic conductivities close to those of conventional liquid electrolytes [4,5]. Especially, thio-Lithium Super Ionic CONductor (thio-LISICON) $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ presents a high ionic conductivity of 1.2×10^{-2} S cm^{-1} , an electrochemical window of up to 5 V vs. Li/Li^+ and an activation energy of 0.24 eV [5]. Argrodite-type crystals $\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br or I) [6–8] also exhibit high ionic conductivities ($> 10^{-3}$ S cm^{-1}). Additionally, some glasses, such as $67(75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5)-33\text{LiBH}_4$ [9] and $30\text{Li}_2\text{S}-26\text{B}_2\text{S}_3-44\text{LiI}$ [10], show high ionic conductivities of approximately 2×10^{-3} S cm^{-1} with doped lithium salts [11].

Known as fast ionic conductors, sulfide solid electrolytes can be categorized into the following three types based on their structural

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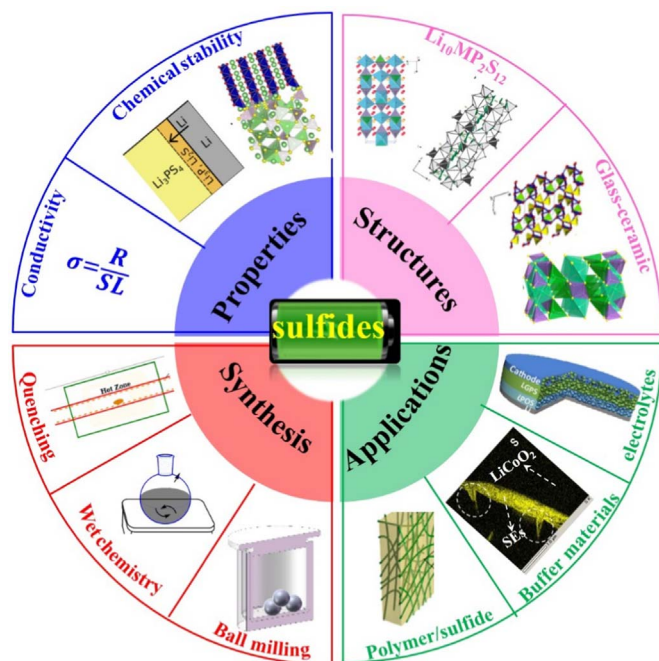
characteristics: glass-ceramics, crystalline and amorphous (glass) [3]. The crystallization of sulfide glasses occurred easily during the cooling process, which led to the difficulties in preparation of sulfide glasses with high Li ionic concentrations. Therefore, the twin-roller rapid-quenching method or the mechanical milling method have been demonstrated effective ways to prepare sulfide glasses [12,13]. Glass-ceramics could be prepared by mechanically heating milled glass to a moderately high temperature [14]. This method can also be used to prepare crystalline electrolytes.

Notably, most sulfide solid electrolytes are not stable in conventional environments [15]. Therefore, the atmosphere in which sulfide solid electrolytes are handled requires special consideration because most of them can easily react with H₂O, releasing a highly toxic gas, H₂S [16]. As a result, their preparations must be conducted under an inert atmosphere. Furthermore, when synthesizing these sulfide solid electrolytes, controlling the stoichiometry is difficult due to the high volatility of sulfur [17]. In addition to the development of sulfide solid electrolytes with high Li⁺ ion conductivities, another important criterion for all-solid-state lithium batteries (ASSLBs) application, is to make suitable solid-solid interfaces between electrolyte and electrode materials. Thus, the compatibility of sulfide solid electrolytes with the electrode materials, and the interface design of a sulfide solid electrolyte with an electrode should be taken into consideration. The charge transfer in ASSLBs occurs only at the contact interfaces. Consequently, favourable contacts at electrode/electrolyte solid-solid interfaces should be formed by minimizing the large resistance at the electrode/solid-electrolyte interface to improve the electrochemical performance of ASSLBs. Moreover, for the ASSLBs, the volume change of the electrode during the charging/discharging process results in fragmentation of the electrolyte particles and capacity loss. This fragmentation is mainly affected by the elastic modulus of the solid electrolytes. Therefore, to improve the performance of ASSLBs, electrolytes should have a moderate elastic modulus, and normally, sulfide electrolyte particles present softer mechanical strength than oxide electrolyte ones.

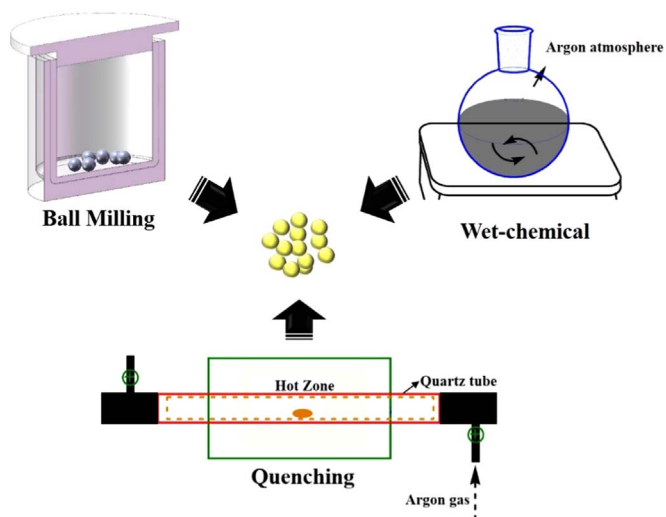
In this review, sulfide solid electrolytes, mainly including the (100-x)Li₂S-xP₂S₅ and Li₂S-M_xS_y-P₂S₅ systems, are reviewed in terms of their crystal structures, conductivities, stabilities and applications, as displayed in Scheme 1. This review is structured as follows: Firstly, the advantages and disadvantages of their preparation methods, including melt quenching, mechanical ball-milling, and the wet-chemical method, are compared systematically. Secondly, the relationships between the crystal structures and conductivities from the experimental studies and theoretical results are discussed in parallel, and various conductivity improving methods are proposed and analysed. Thirdly, their potential stability with lithium metal, a variety of active materials, solvents and humid air is also explored. Finally, the applications of sulfide solid electrolyte in the ASSLBs that act as composite electrolytes, buffer materials and solid electrolytes are described in sequence. Additionally, the recent development of sulfide solid electrolytes and the proposed techniques to achieve favourable contact between the solid electrolyte and electrode in the ASSLBs are summarized. This review aims to provide not only a detailed or comprehensive description in developments of the sulfides and sulfides-based batteries, but also a panorama that covers the recent research frontiers in crystal structures, conductivities, stabilities and applications of sulfide solid electrolytes. Particularly, the future research directions will be pointed out in this review, and deliver a resourceful starting point for researchers new to the field.

2. Preparation methods

The preparation methods of sulfide solid electrolytes mainly belong to three categories including melt quenching, mechanical ball-milling with high energy and the wet-chemical method, as presented in Scheme 2.



Scheme 1. Research progress on sulfide solid electrolytes*. * All the figures cited in Scheme 1 were authorized from the publishers.



Scheme 2. Preparation methods of sulfide solid electrolytes.

2.1. Melt quenching method

The melt quenching method is one of the most conventional techniques to obtain glassy sulfides. A mixture of raw materials was sealed in a carbon-coated quartz tube and then heated at a high temperature in a furnace. Then, the molten sample was rapidly quenched in ice water. Tatsumisago et al. [18] investigated the local structures and lithium conductivities of 70Li₂S-30P₂S₅ (Li₇P₃S₁₁, mol %) glasses, which were prepared by quenching melts from different temperatures and crystallization of these glasses. Their results showed that an increase in the melting temperature from 750 to 900 °C resulted in the formation of P₂S₆⁴⁻ ions. Seino et al. [19] developed a hot-press method in the crystallization process to further improve the lithium conductivities of sulfide solid electrolytes by reducing the grain boundary resistance, and the obtained electrolyte exhibited the extremely high ionic conductivity of 1.7 × 10⁻² S cm⁻¹, with the lowest conduction activation energy (17 kJ mol⁻¹), as shown in Fig. 1. Moreover, Kanno et al. [20] prepared the vacancy-doped sulfide

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