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Recent progress in sulfide-based solid electrolytes for Li-ion batteries

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ABSTRACT

Sulfide-based ionic conductors are one of most attractive solid electrolyte candidates for all-solid-state batteries. In this review, recent progress of sulfide-based solid electrolytes is described from point of view of structure. In particular, lithium thio-phosphates such as $Li_7P_3S_{11}$, $Li_{10}GeP_2S_{12}$ and $Li_{11}Si_2PS_{12}$ etc. exhibit extremely high ionic conductivity of over 10^{-2} S cm^{-1} at room temperature, even higher than those of commercial organic carbonate electrolytes. The relationship between structure and unprecedented high ionic conductivity is delineated; some potential drawbacks of these electrolytes are also outlined.

1. Introduction

Power/energy densities are critical parameters for developing next generation Li-ion batteries for hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) applications. High energy density can be achieved either by high voltage or high capacity [1,2]. Currently, state-of-the-art Li-ion batteries utilize organic liquid electrolytes consisting of $LiPF_6$ dissolved in flammable alkyl carbonates. The operating voltages of some high-voltage cathode electrodes, such as $LiMn_{1.5}Ni_{0.5}O_4$ and $LiCoPO_4$, are beyond the voltage stability window of the aforementioned electrolyte [3]. Thus, the electrolyte undergoes continuous oxidative decomposition during cycling. In addition, overcharging of the battery may lead to a decomposition of the solid electrolyte interface (SEI) and to chemical reactions between electrolyte and electrode materials. The resulting temperature increase may then cause melting of the separator and finally burning of the battery [4]. Therefore, safety issues become immense concern in developing advanced energy storage technologies, especially for Li-ion batteries. In the past two decades, all-solid-state rechargeable lithium batteries have attracted more and more attention because the replacement of an organic liquid electrolyte with a safer and more reliable inorganic solid electrolyte simplifies the battery design and improves safety and durability of the battery [5,6].

Solid electrolytes need to have high ionic conductivity at room temperature and low activation energy (E_a) for use over a broad range of operating temperatures. Lithium nitride (Li_3N) was firstly discovered in the 1970s [7] with high ionic conductivity of 6×10^{-3} S cm^{-1} at room temperature as a potential solid electrolyte [8]. Unfortunately, its low electrochemical decomposition potential prevents it being used in practical applications. In addition, other properties such as electrochemical stability against the anode and cathode, and environmental stability are also preferred for solid electrolytes as they reduce the complexity of the battery. Studies in the past decades have mainly focused on ionically conducting oxides and sulfides such as NASICON (*Na Super Ionic Conductor*)-type $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ [9], LISICON (*Lithium Super Ionic Conductor*)-type $Li_{14}ZnGe_4O_{16}$ [10], perovskite $La_{0.5}Li_{0.5}TiO_3$ [11], garnet $Li_7La_3Zr_2O_{12}$ [12] and glass-ceramic Li_2S-P_2S_5 [13,14]. These conductors exhibit ionic conductivities at room temperature of the order of 10^{-3} S cm^{-1} with E_a ranging from 0.3 to 0.6 eV [15]. Another system currently being investigated as solid electrolyte is amorphous Lipon (*Lithium Phosphorus Oxynitride*). Although has a relatively lower ionic conductivity of 2×10^{-6} S cm^{-1} at 25 °C, a very thin layer (1 μm) of Lipon can be used as electrolyte in solid-state batteries to compensate for its low conductivity [16,17]. And it has been reported to show excellent cell performance over thousands of cycles at room temperature [18]. However, the limited cell capacity due to low loading of active material and high cost of fabrication are disadvantages of thin-film batteries.

Recently, a series of overviews on inorganic Li-ion conductors have been published by Quartarone and Mustarelli [19], Knauth [15], Goodenough and Singh [20] and Kim et al. [21]. Moreover, Anantharamulu et al. [22] summarized the comprehensive information of NASICON-type compositions; the recent developments in garnet solid electrolytes were reviewed by Teng et al. [23]; meanwhile, Thangadurai et al. [24] also compared the garnet-type solid-state Li-ion conductors for lithium batteries; the development of sulfide solid electrolytes was reported from the viewpoint of processing and fabrication of all-solid-state lithium batteries

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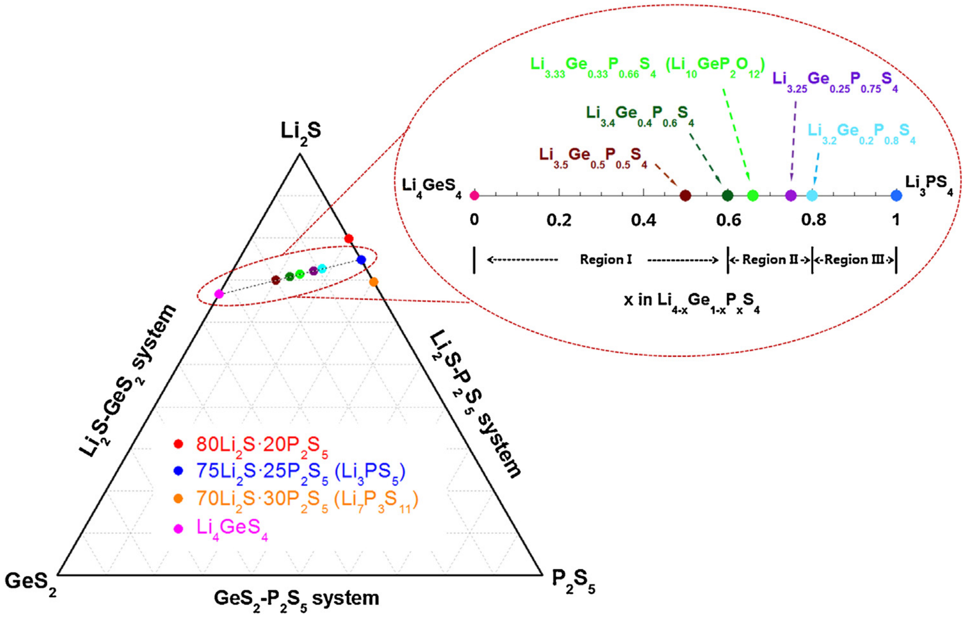

Fig. 1. Li_2S-GeS_2-P_2S_5 ternary diagram showing various sulphide compounds as solid electrolytes for Li-ion batteries.

by Berbano et al. [25] and Tatsumisago et al. [26], respectively. In present work, we review the recent progress of the sulfide-based solid electrolytes for lithium batteries. But unlike ref. [25] and [26], we mainly focus on the sulfide-based solid electrolytes from a structural point of view. Especially, the structural developments of Li_2S-P_2S_5 glass and glass-ceramic are firstly reviewed. Meanwhile, many additives such as M_xS_y (M = Sn, Ge, Si, Bi, etc.) and Li_aX_b (X = Cl, Br, I, O, etc.) have been used to increase the ionic conductivity of sulfide-based solid-state electrolyte. Therefore, the structural change and ionic conductivity of Li_2S-M_xS_y-P_2S_5 solid solution and Li_2S-P_2S_5-Li_aX_b system are also discussed separately in this work.

2. Development of sulfide-based solid electrolytes

Material design of crystalline ionic conductors is based on certain structural criteria [5,27,28]: (1) mobile ions should have a suitable size for conduction pathways in the lattice, (2) there should be disorder in a mobile ion sublattice, and (3) highly polarizable mobile ions and anion sublattices are preferable. Since the radius of S^{2-} is larger than O^{2-}, substitution of O^{2-} by S^{2-} can significantly enlarge the size of Li^+ transport bottlenecks. In addition, S^{2-} has better polarization capability than O^{2-}, thus weakens the interaction between skeleton and Li^+ ions. Therefore, a series of sulfide compounds have been explored and exhibited high ionic conductivity (over 10^{-5} S cm^{-1}) at room temperature. For example, Fig. 1 shows the different Li_2S-GeS-P_2S_5 ternary system compounds as Li-ion conductors and the corresponding conductivities are summarized in Table 1.

3. Li_2S-P_2S_5 glass and glass-ceramic

Sulfite glasses in the systems Li_2S-P_2S_5 and Li_2S-SiS_2, prepared by the melt-quenching method, are known to be Li-ion conductors with conductivities over 10^{-4} S cm^{-1} at room temperature [29,31]. For instance, in the binary system of Li_2S-P_2S_5, perfect amorphous with no crystalline structure were obtained up to the Li_2S contents of 75 mol%, and the maximum conductivity of the glassy powders was about 2×10^{-4} S cm^{-1} at 25 °C in the case of $75Li_2S{\cdot}25P_2S_5$ [32]. In order to improve the conductivity of glassy electrolytes, several approaches have been proposed. One effective way is to simply crystallize the glass precursors. Precipitation of thermodynamically stable Li_2S-P_2S_5 glass electrolytes produces glass-ceramic (crystallized glass) electrolytes. However, different results have been reported for the correlation between conductivity and crystallization. For instance, Minami and Machida [37] suggested that the Cu^+ ion conducting glasses exhibited higher ionic conductivity than crystals since glasses have larger free volume than crystals because of their random and open structure. Whereas Pietrzak et al. [38] showed significant increase in electronic conductivity of nanocrystallized V_2O_5-P_2O_5 glasses. While in the Li_2S-P_2S_5 system, ionic conductivity was reported to depend on the temperature range [14,32]. Fig. 2 shows the X-ray diffraction (XRD) patterns of the pristine $80Li_2S{\cdot}20P_2S_5$ glass and the samples after heating at different temperatures. As can be seen from Fig. 2, several new diffraction peaks were observed after heat treatment up to 500 °C. And the highest conductivity of 7.4×10^{-4} S cm^{-1} was obtained when the temperature was around 210–230 °C. Tatsumisago [32] assumed that the Li-richer $Li_{3+5y}P_{1-y}S_4$ phases,

Table 1
Conductivities of different sulfide compounds at 25 °C.

Composition	Conductivity at 25 °C (S cm^{-1})	Classification	Reference
$2Li_2S{\cdot}P_2S_5$	1.0×10^{-4}	Glass	[29]
$70Li_2S{\cdot}30P_2S_5$	5.4×10^{-5}	Glass	[14]
$75Li_2S{\cdot}25P_2S_5$	2.0×10^{-4}	Glass	[32]
$70Li_2S{\cdot}30P_2S_5$	3.2×10^{-3}	Glass-ceramic	[14]
$80Li_2S{\cdot}20P_2S_5$	7.4×10^{-4}	Glass-ceramic	[32]
$Li_7P_3S_{11-z}$	5.4×10^{-3}	Glass-ceramic	[30]
$Li_7P_3S_{11}$	1.7×10^{-2}	Glass-ceramic	[33]
$Li_{3.25}P_{0.95}S_4$	1.3×10^{-3}	Glass-ceramic	[34]
γ-Li_3PS_4	3.0×10^{-7}	Crystalline	[35]
β-Li_3PS_4	1.6×10^{-4}	Crystalline	[36]
$Li_{3.25}Ge_{0.25}P_{0.75}S_4$	2.2×10^{-3}	Crystalline	[27]
$Li_{10}GeP_2S_{12}$	1.2×10^{-2}	Crystalline	[40]
$Li_{10}SnP_2S_{12}$	4.0×10^{-3}	Crystalline	[43]
$Li_{11}Si_2PS_{12}$	$>1.2 \times 10^{-2}$	Crystalline	[44]
$80(0.7Li_2S{\cdot}0.3P_2S_5){\cdot}20LiI$	5.6×10^{-4}	Glass	[48]
$95(0.8Li_2S{\cdot}0.2P_2S_5){\cdot}5LiI$	2.7×10^{-3}	Glass	[49]
$Li_7P_2S_8I$	6.3×10^{-4}	Crystalline	[50]
$56Li_2S{\cdot}24P_2S_5{\cdot}20Li_2O$	$>1.0 \times 10^{-4}$	Glass	[52]
$75Li_2S{\cdot}21P_2S_5{\cdot}4P_2O_5$	$>1.0 \times 10^{-4}$	Glass	[53]
$67.5Li_2S{\cdot}7.5Li_2O{\cdot}25P_2S_5$	1.1×10^{-4}	Glass	[54]
$0.33(0.7B_2S_3{\cdot}0.3P_2S_5)$-$0.67L_2S$	1.4×10^{-4}	Glass	[57]
$67(0.75Li_2S{\cdot}0.25P_2S_5){\cdot}33LiBH_4$	1.6×10^{-3}	Glass	[58]

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