

Cation and Anion Doping in Sulfide Solid Electrolytes for All-Solid-State Lithium Batteries

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Abstract. Compared with traditional liquid lithium-ion batteries, all-solid-state lithium batteries (ASSLBs) show great application potential. They possess better safety performance, higher energy density and adaptability to a wider range of working temperatures. Among multiple types of solid electrolytes, sulfide solid electrolytes have attracted extensive research attention. Their outstanding room-temperature ionic conductivity and great compatibility with battery electrodes make them one of the most competitive candidates. However, several inherent shortcomings still limit the practical use of sulfide solid electrolytes in high-performance batteries. Unstable interfacial chemical properties, a narrow electrochemical window, and structural damage during repeated charging and discharging cycles are the main obstacles. This review mainly focuses on the latest research progress of cation and anion doping modification strategies for sulfide solid electrolytes. By collecting and analyzing recent relevant studies, this paper summarizes the working mechanisms of different cation and anion dopants. It also compares and discusses how these doping methods affect the ionic conductivity, structural stability and interfacial compatibility of sulfide electrolytes. And in summary, the results demonstrate that rational dual doping or single doping can effectively optimize crystal lattice structure, reduce grain boundary resistance, and suppress interfacial side reactions. Appropriate doping modification significantly improves the electrochemical performance and cycling durability of sulfide electrolytes.

Keywords: sulfide solid electrolytes, all-solid-state lithium batteries, ion doping, interfacial stability, air stability

1. Introduction

All-solid-state lithium batteries (ASSLBs) are considered as next generation energy storage systems that could overcome many intrinsic disadvantages of the conventional liquid lithium-ion batteries (LIBs), such as the low energy density, flammable organic electrolytes and inadequate operation safety. And it possesses non-flammable solid electrolytes that enable safe use of the high capacity lithium metal anode and high voltage cathode materials, significantly enhancing the energy density of battery systems. More significantly, common safety issues of traditional liquid batteries (electrolyte leakage, combustion and explosion) can be completely avoided with solid-state battery

structures. Therefore, all-solid-state lithium batteries (ASSLBs) have great application potential in electric vehicles, wearable electronic devices and large-scale energy storage systems. Sulfide solid electrolytes (SSEs) are among the solid electrolytes which have attracted a lot of interest in recent research because of their overall good performance. The conductivity of lithium ions in SSEs is higher than that in oxide and polymer solid electrolytes at room temperature, and is nearly the same as that of commercial liquid electrolytes. They also possess a low grain boundary resistance and a good mechanical ductility. Such ductile properties enable the electrolytes to be in closer contact with the battery electrodes, thus reducing the interfacial resistance and accelerating the migration of lithium ions. The above advantages make the SSEs one of the most promising materials for high performance ASSLB and can be used for future commercial applications.

Even pure sulfide solid electrolytes, however, still have some intrinsic problems that should be overcome before they can be used practically and industrialized. First, pristine SSEs have a narrow electrochemical stability window, which easily causes severe side reactions with lithium metal anodes and high-voltage cathodes [1]. In addition, they are sensitive to moisture. When exposed to the air, their internal structure may collapse and produce harmful gas. These problems will lead to continuous capacity decay, increasing interfacial resistance and shorter cycle life, which seriously reduce the overall electrochemical performance of ASSLBs [2].

Doping modification is regarded as a simple and effective method to improve the above shortcomings of SSEs. By introducing heteroatoms or functional groups into the sulfide crystal lattice, the lithium ion transport paths can be optimized, thus improving ionic conductivity and broadening the electrochemical stability window. Appropriate doping can also restrain undesirable interfacial reactions, maintain structural stability and improve moisture resistance. It can also keep stable contact between electrodes and electrolytes during long-term battery cycles. For these reasons, this study mainly focuses on the doping modification of sulfide electrolytes. The purpose is to prepare electrolyte materials with high ionic conductivity and high stability, and provide effective references for the future application and industrial development of high-performance all-solid-state lithium batteries.

2. Main problems of sulfide solid electrolytes

Undoped sulfide solid electrolytes have several built-in defects that prevent the practical use of high performance all-solid-state lithium batteries. Firstly, they have low intrinsic ionic conductivity, leading to poor lithium-ion migration and are not able to meet the high rate charge–discharge requirements of commercial batteries. Then, the poor air stability is a key limitation: pristine sulfide materials are susceptible to reacting with moisture and oxygen in ambient air leading to structural degradation, performance loss and poor environmental adaptability. Third, the interfacial stability is very poor, which seriously affects the battery performance; during the cycle, the undoped sulfide electrolyte has interfacial side-reactions with the electrode material, and the interfacial impedance increases, the cycle life of the battery decreases. While doping with both anions and cations can be used to remedy the above drawbacks, optimizing the lattice structure to enhance lithium ion transport pathways and suppress side reactions on the interface and in the atmosphere, this doping modification strategy cannot fully compensate the intrinsic drawbacks of sulfide electrolytes. Beyond a limit, if the doping level is increased, it will cause serious distortion of lattice and create a huge amount of defects, which act as scattering centers for ions and will inhibit the continuous ionic conduction process. However, the conductivity of the doped sulfide electrolyte systems has not yet approached that of conventional liquid electrolyte systems at room temperature and serious

problems of stability and interface reaction still exist in the large-scale use of these systems in practice [3].

Secondly, doped sulfide electrolytes are not air stable and this fact is one of the main challenges to their large scale fabrication and industrialization [4]. By their nature, sulfide materials are vulnerable to moisture and oxygen in the environment and will erode. Although extensive doping modification is made, there are still spontaneous hydrolysis reactions taking place on the surface of the electrolyte, forming toxic hydrogen sulfide gas and insulating by-products. These interfacial residuals block ion transport channels and also reduce the electrochemical conductivity of electrolytes. At the same time, they require very strict anhydrous and oxygen-free conditions for the manufacture of batteries, making the production very difficult, resulting in high production costs.

Third, the weak stability at the interface between the doped sulfide electrolyte and electrode materials seriously reduces the long-term cycling performance of the battery. In the cycling process, continuous side reactions take place at the interfaces due to the electrochemical window mismatch between the electrolytes and electrodes. Additionally, the solid–solid contact structure is not flexible and tends to result in poor interfacial adhesion and non-uniform stress distribution. The progressive interfacial degradation leads to rising interfacial impedances, fast capacity decay and shortening of the cycle life, and, ultimately, limited operational stability and lifetime of all-solid-state lithium battery systems.

3. Ion-doping-induced improvements

3.1. Effects of cation doping

The addition of cations to sulfide solid electrolytes (SSEs) is a simple and effective method to overcome the intrinsic shortcomings of the sulfide solid electrolytes, such as low lithium ion mobility, poor crystal structure stability and low electrochemical activity during long cycling, directly improving the electrochemical performance and long-term stability of all-solid-state lithium batteries. Doping with metal cations is simple and successful way to modify sulfide solid electrolytes. It mainly enhances the battery performance from two aspects: firstly, improve the transport of lithium ions; secondly, stabilize the original crystal structure of sulfide electrolytes [5]. The lattice parameters and the lithium migration channels can be adjusted by the introduction of appropriate doped foreign cations. By this change, the migration energy barrier of Li ions is lowered and the ionic conductivity of solid-state electrolytes is successfully improved. Moreover, cation doping has the effect of enhancing the lattice stiffness [6]. It is able to prevent lattice distortion and phase transition during continuous Li insertion and extraction of battery cycling. Thus, the structural degradation and interface failure after long-term electrochemical reactions can be sufficiently alleviated.

Aluminium doping is a trivalent doping which primarily achieves charge compensation and lattice modulation in sulphide electrolytes. When low valence Al ions are substituted, the formation of additional lithium carriers to maintain lattice charge balance is stimulated. This process enhances the lithium concentration and further enhances the ionic conductivity. The stable Al–S bonding network in the meantime, enhances the structure robustness of sulfide electrolytes. It suppresses the volume changes which are evident when the battery is used during cycling and enhances the mechanical stability and electrochemical stability of electrolyte bulk and of electrolyte-electrode interface [7].

Overall, the aforementioned metal cation doping approaches are effective in enhancing the conductivity and stability of sulfide solid electrolytes. The modification strategies offer feasible

solutions to the future development and application of high performance all-solid-state batteries.

3.2. Effects of anion doping

Anion doping is one of the potential methods to optimize the lattice structure and Li^+ transport properties in sulfide solid electrolytes (SSEs) to develop all-solid-state lithium batteries. This approach is mostly achieved by partial replacement of S^{2-} with halogen anions (Cl^- , Br^- , I^-). In contrast, doping with heteroatoms, such as oxygen and nitrogen, is rarely investigated and is mainly used as an additional modification method.

Aliovalent substitution between S^{2-} and halogen ion creates lithium vacancies which aid the migration of Li^+ but the three halogens provide three different modification effects.

The ionic radius of Cl^- is similar to that of S^{2-} and Cl^- can induce a considerable disorder in the anionic sublattice when doping. The disordered structure reduces the activation barrier for the hopping motion of Li^+ and also stabilize the cubic phase that has good ionic conductivity, which explains the excellent ionic conductivity of Cl^- doped SSEs at room temperature. Despite this, poor air stability is a characteristic of Cl^- doped materials. An excess amount of Cl^- generally leads to the formation of insoluble secondary phase of LiCl which clogs ion conducting pathways and affects the overall electrochemical properties.

Br^- is doped in a similar way to Cl^- . A significant lattice disorder is maintained with the appropriate Br^- substitution, which leads to an expansion of lattice channels and hence to a higher rate of diffusion of Li^+ . Br^- modified SSEs show slightly better electrochemical stability with lithium metal compared to the Cl^- ones. However, the greater size of the Br^- leads to a smaller range of validity for doping and over-doping with Br^- causes significant lattice distortion, which results in a rapid decrease in bulk ionic conductivity.

I^- has much larger ionic radius than S^{2-} , Cl^- and Br^- . In usual synthesis conditions, the random anion mixing is greatly suppressed and ordered anion lattices are formed, which hinders the efficient Li^+ transport. The oxidation stability of I^- substituted sulfides is slightly improved by I^- doping, but the ionic conductivity is much lower than that of the Cl^- and Br^- doped sulfides. Furthermore, I^- containing phases exhibit poor thermal stability and thermal decomposition is likely to occur during the sintering process, which limits their use to a great extent.

Complementary minor modification with the introduction of O and N is gaining more and more attention to overcome the intrinsic drawbacks of halogenated sulfide. A typical approach of improving bonding between anions and cations in sulfide matrices is by adding oxygen [8]. Adding oxygen to the material properly can effectively enhance the electrochemical stability window of the material and moisture resistance, so as to reduce the occurrence of unnecessary side reactions at the interface between the cathode and electrolyte. The formation of strong P–O bonds, however, will cause the original structure of PS_4^{3-} polyanion frameworks to be altered. Especially for the sulfide electrolytes, a too high oxygen doping results in phosphate impurities of low conductivity, which reduces the ionic conductivity of the sulfide electrolyte.

In contrast to oxygen doping, the primary effect of nitrogen modification is to modify the local electronic structure, and increase the structural stability of sulfide materials. Low-concentration nitrogen doping is able to increase the critical current density and inhibit the growth of lithium dendrites. However, there is an obvious drawback with this method: the solubility of N in sulfide lattices is very low [9]. After a threshold doping concentration, a small concentration, the amorphous nitride byproducts are formed, which will increase the grain boundary impedance.

Generally speaking the primary doping species for optimizing ionic conductivity are halogen anions and the secondary doping species are trace amounts of oxygen and nitrogen for optimizing

the interfacial performance and chemical stability [10]. The precise control of the doping concentration should be studied in the future. It is important to be able to balance the ionic transport capability, structural integrity and electrode compatibility without putting it at a disadvantage with excessive element substitution, which results in a performance trade-off between conductivity and stability [11].

Table 1. Comparison between cation doping and anion doping

Comparison aspect	Cation Doping	Anion Doping
Doping site	Substitute framework cations (e.g., Ge^{4+} , Sn^{4+} , P^{5+} , Sb^{5+}) or lithium sites	Substitute S^{2-} anion sites
Typical dopants	Sn, Si, Ge, Sb, As, Al, Zn, Zr, etc.	Halogens (Cl, Br, I); minor O and N
Core mechanism	Tune lattice dimension, framework flexibility and anion polarization environment; stabilize high-conductivity phases	Generate Li vacancies via aliovalent substitution, introduce anionic disorder and reduce migration energy barrier
Primary optimization targets	Phase stability, mechanical properties and interfacial compatibility	Room-temperature ionic conductivity, stabilization of cubic conductive phases
Effect on ionic conductivity	Indirect regulation via structural modification; limited enhancement magnitude	Direct and remarkable improvement, often achieving 10^{-3} – 10^{-2} S/cm
Effect on stability	Several cations (Sn, Sb, etc.) improve electrochemical and chemical stability	Halogen doping offers limited stability enhancement; O/N modification improves moisture resistance and stability window
Common limitations	Narrow doping window; heavy doping easily induces impurity phases or reduces Li carrier concentration	Excessive halogen doping forms insulating Li_x precipitates; I^- with large radius suffers poor miscibility; low solid solubility of O and N
Synthetic difficulty	Relatively facile; high structural tolerance of cation framework	Halogens tend to volatilize; iodine-containing phases exhibit poor thermal stability; precise dosage control is required

4. Conclusion

Overall, cation doping serves as a simple and effective way to improve ion transport in solid-state materials. The introduced foreign cations can slightly change the local crystal structure, which creates more paths for ion movement and lowers the energy required for ions to jump between lattice sites. Even a relatively low doping amount can successfully increase ionic conductivity, so

this method is widely used when faster ion transportation is needed. However, inappropriate doping conditions may negatively affect the structural stability of the material.

To sum up, single-type doping has obvious drawbacks. Methods that promote ion conduction tend to weaken structural stability, while adjustments for better stability usually reduce ionic transport ability. Therefore, future material research should focus on balancing these two key properties. Cation-anion co-doping is considered a promising strategy to develop practical solid materials with both good ionic conductivity and stable long-term performance.

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