Research Progress on Solid-State Electrolytes for Lithium-Ion Batteries

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Abstract: Lithium-ion batteries with high energy density are regarded as highly promising electrochemical energy storage systems. However, traditional liquid electrolytes present significant safety risks due to their propensity for leakage and flammability. In contrast, solid-state electrolytes have garnered extensive attention for their enhanced safety property, high energy density, and superior stability with lithium anodes. Consequently, research on solid-state electrolytes has become increasingly prominent. Despite this, the development of solid-state electrolytes remains in an exploratory phase, primarily hindered by issues such as high solid-state impedance and side reactions with electrodes. Moreover, the challenge lies in integrating the property advantages of various solid-state electrolytes. The primary obstacle is the poor compatibility between solid-state electrolytes and electrodes. Current strategies to address these issues include electrode modification, electrolyte recombination, and the introduction of interface layers. Nevertheless, solid-state electrolytes have not yet achieved the level of development necessary to fully replace liquid electrolytes. This article provides a comprehensive review of the status of organic polymer and inorganic solid-state electrolytes and discusses the future development trends of these materials.

1 INTRODUCTION

Human productivity increased significantly after the Industrial Revolution, and energy demand reached an unprecedented height. Industrial production mainly relies on fossil fuels such as coal, natural gas, and oil, which are non-renewable and lead to serious environmental pollution, such as global warming caused by greenhouse gas emissions. Therefore, the search for renewable new energy has become a huge challenge for human development at this stage. Currently, known renewable energy sources include wind, solar, geothermal, tidal, etc. However, these renewable energy sources are unstable and intermittent, and how to integrate these intermittent energy sources into a stable and efficient large-scale electric energy storage system is the key to solving the energy crisis today (Tao et al, 2022). Lithium-ion batteries stand out in many electrochemical energy storage systems because of their advantages of high working voltage, high energy density, low self-discharge rate, long cycle life, and no memory effect. However, the widely used traditional lithium-ion batteries have gradually exposed several problems due to using liquid electrolytes. The organic components in liquid electrolytes are prone to decomposition, combustion, and even explosion under high temperatures and currents. In addition, these organic components may decompose at high voltages, making liquid lithium-ion batteries used now difficult to match cathode materials with high electrode potentials. Therefore, one of the alternatives with the highest expectations is all-solid-state lithium-ion batteries prepared with solid-state electrolytes.

It is worth noting that the solid-state electrolyte currently is the main innovation which replaces the diaphragm and electrolyte in the liquid electrolyte. In this way, unnecessary chemical reactions between electrodes to dissolve active substances can be effectively inhibited, and the safety of batteries can be also improved (Janek and Zeier, 2023). Meanwhile, the solid electrolyte can be matched to the anode of lithium metal with a high theoretical specific capacity. Even better, this kind of anode can match the cathode material with a high specific capacity, thus comprehensively improving the energy density (400Wh/kg&1000Wh/L) (Aspinall et al., 2024). To pursue high energy density, the solid-state electrolyte

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layer needs to be thin enough, and the material needs to be thin and flexible, further broadening its application prospects. In addition, batteries with solid-state electrolytes also have the advantages of strong endurance, wide temperature range and fast charging speed.

Currently, the solid-state electrolyte is mainly divided into organic polymer solid-state electrolytes and inorganic solid-state electrolytes two categories. The inorganic solid-state electrolyte can be divided into oxide, halide and sulfide solid-state electrolyte. In this article, the current research progress of mainstream solid-state electrolytes is reviewed, and the future development direction of solid-state batteries is prospected.

2 SOLID-STATE ELECTROLYTE

2.1 Organic Polymer Solid-State Electrolyte

Organic polymer solid-state electrolyte is mainly composed of lithium salt with low dissociation energy and a polymer matrix with a high dielectric constant (Wang et al., 2023). According to the types of conductive particles, the organic polymer solid-state electrolyte can be divided into two categories: single-ion polymer solid-state electrolyte and double-ion polymer solid-state electrolyte. Single-ion polymer solid-state electrolyte is mainly composed of single-ion lithium salt and polymer matrix, in which anions are usually fixed on the polymeric main chain or provided to the polymer as an acceptor, so only cation migration in this kind of solid-state electrolyte. However, this causes anions to accumulate near the anode, which increases the resistance and affects the overall property of the battery. Double-ion polymer solid-state electrolyte is mainly composed of double-ion lithium salt and polymer matrix. The anions usually move faster than the cations. Therefore, double-ionic polymer solid-state electrolytes generally have higher ionic conductivity, while single-ionic polymer solid-state electrolytes have higher cation migration numbers.

The organic polymer electrolyte matrix material is usually a polymer with polar functional groups to promote the dissociation and ion transfer of lithium salts so that it can have a relatively lower interface impedance (Wang et al., 2023). Simultaneously, polymer solid-state electrolytes are more suitable for large-scale production because of their good flexibility and elasticity, easy processing and low cost. However, its organic composition results in limited thermal stability and a low electrochemical window (<4V). At the cathode interface, there are many factors contributing to the instability of the interface, such as the oxidation decomposition of the polymer, the side reaction between the polymer and the cathode, and the ageing of the battery interface in the long cycle. At the anode interface, because of the high reducibility of lithium metal, the polymer is reduced, and structural changes occur, thereby reducing the overall property of the solid-state battery.

To solve the above problems of organic polymer solid-state electrolyte, the researchers proposed the following solutions: 1) Improve the cathode material: By combining the cathode material with the organic polymer, the interface impedance can be effectively reduced, the ion transfers much faster, and the interface instability of the cathode can be solved effectively. 2) Introduction of the interface layer: reduce the physical contact between the polymer solid-state electrolyte and the electrode, reduce the interface impedance from the source and restrain the side reaction between the cathode and the electrolyte. The interfacial layer between the electrolyte and the anode can also restrain the reduction reaction and the growth of lithium dendrites.

2.2 Inorganic Solid-State Electrolyte

2.2.1 Oxide Solid-State Electrolyte

Oxide solid-state electrolytes are composed of metal oxides containing lithium, which are mainly divided into calcareous, garnet and NASICON types according to their different structural forms (Yao et al., 2023). The calcareous type has the structural formula ABO_3, where A is the larger cation (usually rare earth ions), and B is the smaller cation (usually transition metal ions). However, the calcareous type of oxide solid-state electrolyte has large grain boundary impedance and small ionic conductivity, especially at low potential, thereby reducing the conductivity of lithium ions (Luo et al., 2024).

Garnet-type (LLZO) oxide solid-state electrolytes (such as $Li_5La_3M_2O_{12}$, M = Ta and Nb) are composed of lithium, lanthanum, and transition metal elements, as shown in Figure 1. This kind of oxide solid-state electrolyte has high electrochemical stability to the metal lithium anode and has a higher electrochemical window, which can match the high voltage cathodes.

However, the main challenge is the interface compatibility between the electrolyte and cathodes and anodes.

NASICON-type oxide solid-state electrolyte, also known as sodium superionic conductor, its structural formula is $AM_2(PO_4)_3$. Where A represents alkali metal ions (Li^+\Na^+), M represents Ti, Ge, Zr and other elements. By substituting lithium for sodium, lithium-ion conductors with higher ionic conductivity can be obtained. The typical NASICON-type oxide solid-state electrolyte is $LiTi_2 (PO_4)_3$ (LTP). This kind of electrolyte is stable in air and water and is not easy to react to. However, its cost is high, and it is difficult for large-scale production. In addition, due to the presence of Ti4+ ions, like calcareous oxide solid-state electrolytes, these electrolytes are also easy to be reduced by lithium metal anode at low potential, thereby reducing the overall property of the battery.

To solve the problem of an oxide-solid-state electrolyte, the researchers proposed the following solutions: 1) the introduction of a buffer layer: for the interface impedance problem between the solid-state electrolyte and the cathode, a layer of aluminium oxide can be deposited to reduce the interface impedance; for the reduction reaction between several particular solid-state electrolytes and the lithium metal anode, the lithium-ion conductor can be used as the buffer layer between the solid-state electrolyte and the electrode to inhibit the reduction reaction. 2) Improve the electrode: on the one hand, lithium alloy electrodes can be manufactured to reduce adverse reactions. On the other hand, the electrolyte component can be compounded with the cathode active component by heating and other methods to achieve a good electrolyte-electrode contact interface, thereby reducing the interface impedance. 3) Ion doping: The skeleton of sodium superionic conductors can be modified by intercalating cations of different valence states and ionic radii, thereby causing lattice distortion and improving ionic conductivity (Luo et al., 2024).

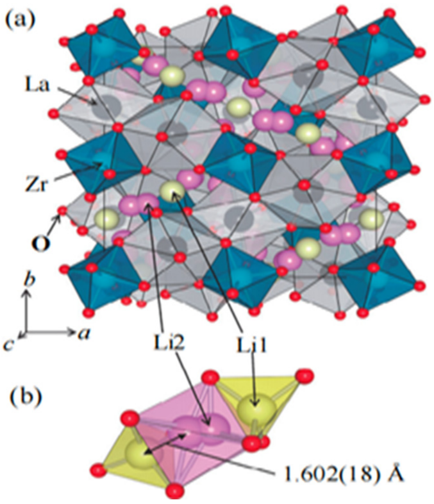

Figure 1: (a)Cubic Li7La3Zr2O12 crystal structure(b) Coordination polyhedral around Li1 and Li2 sites (Yao et al., 2023).

2.2.2 Halide Solid-State Electrolyte

Halide solid-state electrolyte is mainly composed of lithium, transition metal elements and halogen elements, and its structure is determined by the coordination number determined by the atomic radius ratio of metal elements and halogen atoms. According to the coordination number, halide solid-state electrolytes can be divided into three categories: 1) Li_a-M-Cl_6; 2) Li_a-M-Cl_4, 3) Li_a-M-Cl_8. Among them, Li_a-M-Cl_8 is unstable at room temperature, and its conductivity is lower than Li_a-M-Cl_6 and Li_a-M-Cl_4. Therefore, Li_a-M-Cl_6 electrolytes and some Li_a-M-Cl_4 electrolytes have been studied more at present (Chen et al., 2023).

Li_a-M-Cl_6 halide solid-state electrolytes are mainly composed of group IIIB metal ions. The common crystal structures of this kind of solid-state electrolyte include the tripartite crystal system of the P3m1 space group (hcp-T), the orthogonal crystal system of the pnma space group (hcp-O) and the cubic crystal system of C2/m space group (ccp). Among them, the Li_a-M-Cl_6 halide solid-state electrolyte has better conductivity in the C2/m structure. Lia-M-Cl_4 halide solid-state electrolytes are mainly composed of trivalent and other valence metal ions, as shown in Figure 2. The defect anti-spinel structure has the highest electrical conductivity. Due to the introduction of higher-priced cations, more vacancies are created to maintain electrical neutrality, and this structure is beneficial to the transport of lithium ions.

Currently, halide solid-state electrolytes generally have low phase transition temperatures, and a high crystallinity phase can be obtained by the low reaction temperature. In addition, fluoride and chloride_electrolytes have special advantages like electrochemical windows (Yu et al., 2023). However, halide-solid-state electrolytes have poor humidity and air stability. This is because halogen salts are easy to form into crystalline hydrates, and the more obvious the polarization of the metal cation of halogen salts in water, the easier it is to form a crystalline hydrate. These crystalline hydrates will undergo a hydrolysis reaction after heating, which makes it easy to form metal oxide double salts that hinder the migration of lithium ions. However, some studies have shown that halides show good stability in dry air, and after a strictly controlled dehydration process, the hydrate can be reversely converted to return to its structure and electrochemical properties before water absorption.

In addition, the instability of halide solid-state electrolytes and lithium metal mainly depends on the type of transition metal element in the halide composition. For example, the Li_3HoCl_6 electrolyte can realize the stable cycle of assembled Lin-symmetric batteries, but it is easy to short-circuit when assembled with Li metal symmetric batteries. In contrast, Li_3HoCl_6 has better stability against Li metal, which may be because the products formed by fluoride contact with lithium metal can better fill the vacancies and defects located in the solid-state electrolyte and related interfaces, forming a denser intermediate layer, thereby preventing the development of further reactions.

In response to the above halide solid-state electrolyte problems, the researchers proposed the following improvement methods: 1) solid-phase reaction synthesis: through ball milling to improve the uniformity of raw material mixing and refine the electrolyte particles, to improve the point contact problem, reduce the interface impedance. 2) Liquid phase synthesis: This method can save time and improve efficiency, the halide is uniformly distributed in the solid-state electrolyte, and it is easier to obtain samples with uniform grain size after crystallization.

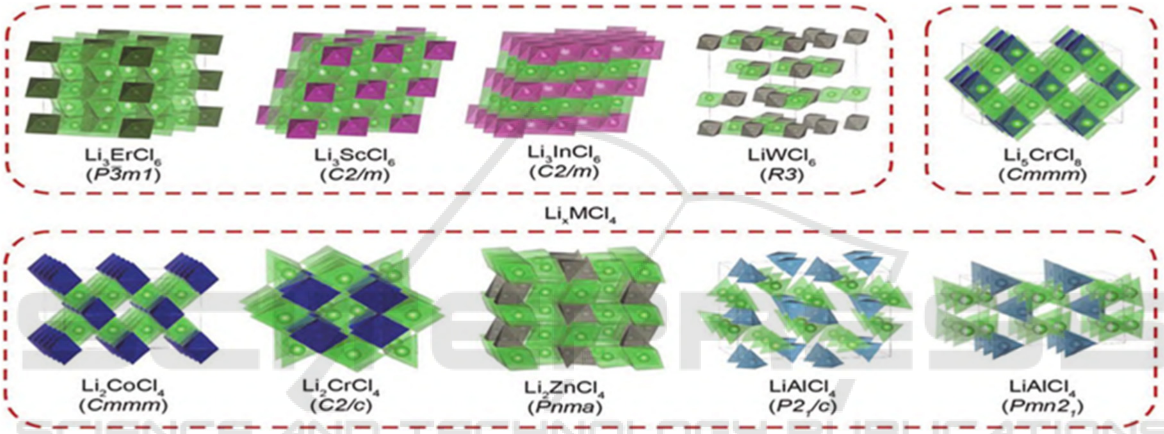

Figure 2: Structure diagram of the third-class halide solid-state electrolyte (Chen et al., 2023)

2.2.3 Sulfide Solid-State Electrolyte

Sulfide solid-state electrolyte is mainly composed of lithium, sulfur, phosphorus and other elements. According to its crystal structure, it can be divided into glass phase, glass ceramic phase and crystal phase (Chen, 2021). Compared with the glass phase and glass ceramic phase, crystalline sulfide solid-state electrolyte has higher ion transport efficiency due to its unique structure, and thus exhibits higher ionic conductivity at indoor temperature (Qin and Gu, 2021). However, this kind of sulfide solid-state electrolyte is prone to reduction and oxidation reactions with lithium metal anode, which leads to the instability of the interface between anode and electrolytes. The sulfide solid-state electrolyte has good mechanical strength, mechanical flexibility, and high ionic conductivity, and its overall property is greater than other types of solid-state electrolytes. For example, the relatively low hardness of sulfide makes it easy to deform during extrusion, thereby improving the contact problem with the cathode through deformation, which also makes it easier to process. However, the material also has many shortcomings. At the cathode interface, 1) insufficient ion and electron penetration leads to a low utilization rate of the cathode material; 2) There is a space charge effect. Due to the large gap between the chemical potential of lithium ions in the cathode and the electrolyte, lithium ions tend to diffuse from the sulfide electrode to the cathode, and an area with a low concentration of lithium ions is easily formed on the sulfide side of the interface, thereby reducing the ionic conductivity and improving the interface impedance; 3) The volume change of the cathode material leads to poor contact and increased impedance. At the anode interface, 1) the growth of lithium dendrites is a problem, and 2) the interface is unstable, which makes it easy to form a conductive phase layer mixed with ions and electrons. In addition, due to the sensitivity of sulfide to water vapour, it is easy to react with water to produce toxic hydrogen sulfide gas, resulting in a decrease in ionic conductivity (Yu et al., 2023).

In response to the above sulfide solid-state electrolyte problem, the researchers proposed the following solutions: 1) Add a small amount of electrolyte: Add a small amount of electrolyte between the solid-state electrolyte and the electrode or inside the solid-state electrolyte, so that it cannot flow freely in the battery, choose the electrolyte that does not react with the sulfide solid-state electrolyte but can dissolve lithium salt. Alternatively, a glass fibre diaphragm containing electrolyte can be introduced into the cathode and the sulfide solid-state electrolyte to improve the ionic conductivity and solve the contact problem, thereby reducing the interface impedance. 2) Composite with polymer electrolyte: the polymer can act as a binder, conductive network or skeleton material in the composite to effectively inhibit the space charge effect. 3) oxide-doped sulfide: can effectively absorb H_2S and inhibit the formation of H_2S.

3 PROSPECTS FOR SOLID-STATE ELECTROLYTES

The main factors contributing to the properties of solid-state electrolytes are contact failure and instability between electrodes and electrolytes. First, the contact failure problem is that the electrolyte and the electrode are both solid and the contact between the two is point contact. The liquid electrolyte used before like ethylene carbonate and diethyl carbonate can fill all the pores caused by the charge and discharge of the electrode. Additionally, the periodic volume change of the electrode is unable to affect it. Lithium tends to deposit in pores and rough edges of grain boundaries, resulting in uneven deposition. Therefore, the problem of the lithium dendrites occurs. This non-uniformity of deposition will further cause the contact between the solid-state electrolyte and the cathode to decrease, thus the more lithium depositing, the lithium dendrites will puncture the electrolyte and connect the two electrodes, causing the battery to short-circuit. Second, the presence of a large solid interface impedance contributes to the instability between the solid-state electrolyte and the electrode. To improve the power density of solid-state batteries, reducing the impedance can effectively improve the transform efficiency of lithium ions. Sufficient power density can achieve the requirements of commercial mass-produced production of power storage systems. The causes of solid impedance at the interface include reduction side reaction between electrolyte and electrode, formation of space charge layer and periodic volume change of electrode. When the solid-state electrolyte matches the cathode, the mismatch of the electrochemical windows results in the oxidation decomposition of the solid-state electrolyte itself and the anion replacement between the electrolyte and the electrode. Those two kinds of reactions generally occur simultaneously. When the solid-state electrolyte matches the metal lithium anode, due to the strong reduction of lithium itself, some cations with high valency in the electrolyte are easy to have reduction reactions, forming a new high-impedance interface, which hinders the transmission of lithium ions and makes the overall property of the battery decline.

All kinds of solid-state electrolytes have their property advantages, but there is no solid-state electrolyte that can have all the property advantages simultaneously and achieve inexpensive expenditure and easy production, as shown in Figure 3. The real problem facing solid-state electrolytes is that if it is to replace traditional liquid lithium batteries in large-scale commercial production, simply having high ionic conductivity (such as the high cost of high-property sulphide solid-state electrolyte) is not enough to support its position in the industrial application of all-solid-state batteries. Therefore, researchers have developed composite solid-state electrolytes, aiming to get a kind of comprehensive one with various advantages to form an electrolyte system with high ionic conductivity, good processability, cycle stability and low cost (Zhan et al., 2023). For example, in the oxide/sulphide complex electrolyte, increasing the oxide content is conducive to achieving uniform dispersion of the oxide solid-state electrolyte, and improving the interface bond between the oxide and the sulphide, thereby increasing the migration rate of lithium ions. In addition, organic polymers can also be combined with sulphide solid-state electrolytes. The organic polymer can be used as a binder to disperse the sulphide in the composite film, to improve the interface impedance. At the same time, the polymer can also act as a skeleton, improve the flexibility of the sulphide, and due to its low-cost characteristics, large-scale preparation can be achieved. Through these composite methods, the advantages of different solid-state electrolytes can be effectively integrated, and the limitations of a single material can be overcome, to promote the industrial application of all-solid-state batteries.

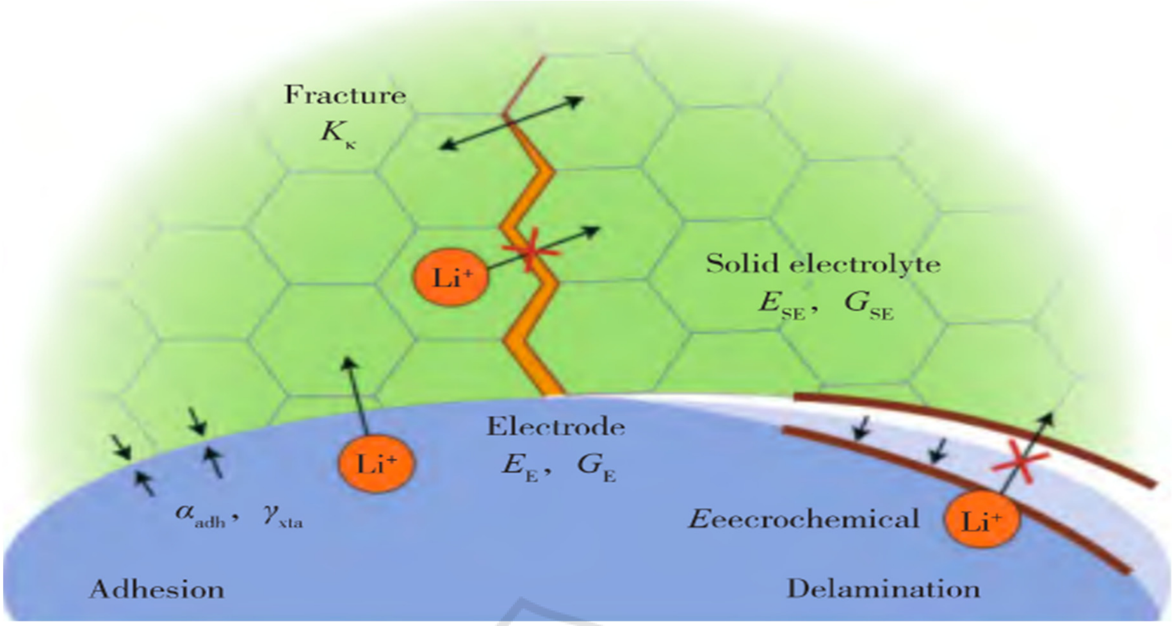

Figure 3: Contact diagram at the interface between the solid-state electrolyte and the electrode (FAMPRIKIST et al., 2019)

4 CONCLUSION

This study reviews the various types of solid-state electrolytes, including oxide, halide, sulfide, and organic polymer solid-state electrolytes, and analyses their application potential and challenges. Each type of solid-state electrolyte has its unique property advantages, but there is no solid-state electrolyte that can have comprehensive property advantages and meet the requirements of low cost and easy production. Although sulfide-solid-state electrolyte has high ionic conductivity and good mechanical properties, it is expensive and sensitive to water vapour. Although oxide-solid-state electrolyte is stable in air and water, it has the problem of large interface impedance and insufficient ionic conductivity. Halide-solid-state electrolytes have advantages in terms of electrochemical windows, but their humidity stability is poor and unstable with lithium metal. Although the polymer solid-state electrolyte has excellent machining properties and low cost, its electrochemical window is narrow, and its thermal stability is insufficient. The development of a composite solid-state electrolyte has become an effective solution to single limitations. Using combination and doping, the advantages of various solid-state electrolytes can be combined to form an electrolyte system with high ionic conductivity, low cost, good machining properties, and cycle stability. For example, the oxide/sulfide composite electrolyte can improve the interface bonding by increasing the oxide content, thus increasing the migration rate of lithium ions. The combination of organic polymer and sulfide can improve the interface impedance and flexibility by using the bonding and skeleton action of the polymer and achieve low-cost, large-scale preparation. In summary, the research on composite solid-state electrolytes provides a new path for the commercial application of all-solid lithium-ion batteries. Future research should continue to explore the combination strategy of different solid-state electrolytes to optimize property, reduce production costs, and promote the commercialization of all-solid-state battery technology.

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