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# Research Progress of Inorganic Solid Electrolytes in All-Solid-State Lithium Metal Batteries

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**Abstract:** All-solid-state lithium metal batteries have become an important development direction for next-generation battery technologies due to their high energy density and high safety. As a core component, inorganic solid electrolytes demonstrate great potential in suppressing lithium dendrite growth and reducing the risk of internal short circuits because of their high ionic conductivity, wide electrochemical stability window, good thermal stability, and strong mechanical properties. This paper reviews recent research progress on inorganic solid electrolytes, especially oxide, sulfide, and halide solid electrolytes. The characteristics and interfacial issues of oxide solid electrolytes, including perovskite-type and LISICON-type materials, are discussed in detail, along with the advantages and challenges of sulfide and halide solid electrolytes in terms of high ionic conductivity and interfacial stability. Finally, the future prospects of inorganic solid electrolytes in all-solid-state lithium metal batteries are discussed.

**Keywords:** All-solid-state lithium metal batteries, inorganic solid electrolytes, oxides, sulfides, halides, ionic conductivity, interfacial stability.

## 1. Introduction

With the rapid development of electric vehicles and portable electronic devices, the demand for energy storage technologies with higher energy density and improved safety is continuously increasing. Traditional liquid lithium-ion batteries are limited in further development because of the flammability of organic liquid electrolytes and the risk of short circuits caused by lithium dendrite growth. All-solid-state lithium metal batteries (ASSLMBs), which replace liquid electrolytes with solid electrolytes, are considered ideal candidates for next-generation battery technologies due to their higher energy density, wider operating temperature range, and intrinsic safety [1]. As the core component of solid-state batteries, the performance of solid electrolytes directly determines the overall battery performance. Among them, inorganic solid electrolytes have attracted extensive attention because of their excellent overall properties [2]. This review aims to summarize the current research status of inorganic solid electrolytes, with emphasis on their structural characteristics, lithium-ion transport mechanisms, performance advantages, existing challenges, and future development directions.

## 2. Classification and Fundamental Characteristics of Inorganic Solid Electrolytes

Inorganic solid electrolytes are generally characterized by relatively high room-temperature lithium-ion conductivity, good thermal stability, nonflammability, and high mechanical strength. These characteristics make them highly attractive for use in solid-state lithium metal batteries. In contrast to liquid electrolytes, where ions migrate through liquid solvent media, lithium-ion transport in inorganic solid electrolytes occurs through vacancies, interstitial sites, or bottleneck pathways within the crystal lattice or amorphous framework. Therefore, the ion transport performance is highly dependent on crystal structure, defect chemistry, lattice dynamics, and grain boundary resistance.

Another important advantage of inorganic solid electrolytes is their ability to serve as a physical barrier against dendrite penetration. However, this function is often complicated by defects, pores, grain boundaries, and unstable interfaces, which can still provide pathways for dendrite propagation. As a result, the evaluation of inorganic solid electrolytes must consider not only bulk ionic conductivity but also interfacial resistance, mechanical integrity, and chemical compatibility with both the cathode and the anode.

From a broader perspective, the ideal inorganic solid electrolyte should satisfy several criteria simultaneously: high ionic conductivity close to that of liquid electrolytes, negligible electronic conductivity, wide electrochemical stability window, low interfacial resistance with electrodes, good air and moisture stability, low cost, and ease of processing into dense membranes. In reality, no single material currently satisfies all these requirements, which is why different families of inorganic solid electrolytes continue to be actively investigated.

According to chemical composition and structural characteristics, inorganic solid electrolytes can be mainly divided into oxide solid electrolytes, sulfide solid electrolytes, and halide solid electrolytes.

## 3. Classification and Characteristics of Inorganic Solid Electrolytes

Inorganic solid electrolytes generally possess high room-temperature ionic conductivity, a wide electrochemical stability window, good thermal stability, and strong mechanical strength, enabling them to effectively suppress lithium dendrite growth and reduce the risk of internal short circuits. Their ion conduction mechanism mainly depends on the migration of lithium ions within the crystal lattice and is closely related to the crystal structure, grain boundary characteristics, and lithium-ion concentration. According to their chemical composition and structural characteristics, inorganic solid electrolytes can mainly be divided into oxide solid electrolytes, sulfide solid electrolytes, and halide solid electrolytes.

(1) Oxide Solid Electrolytes

Oxide solid electrolytes are among the most extensively studied inorganic solid electrolyte systems. They exhibit high chemical stability and electrochemical stability and can remain stable in air, making them convenient for processing. Their main types include:

Garnet-type oxide solid electrolytes: Represented by $Li_7La_3Zr_2O_{12}$(LLZO), which has both cubic and tetragonal phases. Cubic LLZO exhibits relatively high room-temperature ionic conductivity, typically around $10^{-4}$-$10^{-3}$ S $cm^{-1}$, and a wide electrochemical stability window [3]. However, LLZO is brittle, difficult to machine, prone to reacting with $CO_2$ and $H_2O$ to form passivation layers, and shows poor interfacial wettability with lithium metal anodes, leading to high interfacial resistance.

NASICON-type oxide solid electrolytes: Represented by $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$(LATP) and $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$(LAGP). These materials possess open three-dimensional ion transport channels and relatively high room-temperature ionic conductivity [4]. LATP has the advantages of low raw-material cost, simple preparation process, and good chemical stability in air. However, $Ti^{4+}$ in LATP is easily reduced to $Ti^{3+}$ when in contact with a lithium metal anode, resulting in interfacial instability. Researchers have improved its interfacial stability by introducing strategies such as Al-LiF dual inorganic interlayers, PEO adhesive interlayers, and composite interfacial layers [5].

Perovskite-type oxide solid electrolytes: With the general formula $ABO_3$, a typical representative is $Li_{3x}La_{2/3-x}TiO_3$ (LLTO) [6]. The bulk ionic conductivity is high and can reach $10^{-3}$ S $cm^{-1}$, but severe grain boundary resistance remains a major issue. In addition, $Ti^{4+}$ in LLTO can also be reduced to $Ti^{3+}$ by lithium metal, causing poor interfacial stability.

LISICON-type oxide solid electrolytes: With the general formula $Li_{2+2x}Zn_{1-x}XO_4$, a typical example is $Li_{14}ZnGe_4O_{16}$ [7]. Their room-temperature ionic conductivity is relatively low, approximately $10^{-7}$ S $cm^{-1}$, and they tend to react with lithium metal at high temperatures. Their chemical stability is poor, and they can also react with $CO_2$ and $H_2O$ in air.

(2) Sulfide Solid Electrolytes

Compared with oxide solid electrolytes, sulfide solid electrolytes contain sulfur atoms with lower electronegativity and larger ionic radii, which are beneficial for the rapid migration of lithium ions. They usually exhibit high room-temperature ionic conductivity, typically in the range of $10^{-3}$-$10^{-2}$ S $cm^{-1}$, along with good ductility and plasticity, making them easy to densify by cold pressing and helpful for improving interfacial contact with electrode materials [8]. Sulfide solid electrolytes can generally be classified into glassy, glass-ceramic, and crystalline types. Crystalline sulfide solid electrolytes such as $Li_{10}GeP_2S_{12}$(LGPS) and $Li_6PS_5Cl$ exhibit extremely high ionic conductivity. However, sulfide solid electrolytes have poor chemical stability in air and easily react with moisture to generate H2S gas, which imposes strict environmental requirements during preparation. In addition, their electrochemical stability window is relatively narrow, and interfacial side reactions may occur with high-voltage cathode materials and lithium metal anodes.

(3) Halide Solid Electrolytes

Halide solid electrolytes generally have the formula $Li_3MX_6$, where M is a metal cation and X is a halide ion such as Cl, Br, or I. They possess various crystal structures and can achieve room-temperature ionic conductivity up to $10^{-3}$ S $cm^{-1}$[9]. The relatively large ionic radius and low electronegativity of halide ions facilitate the fast migration of lithium ions, contributing to their high ionic conductivity at room temperature. At the same time, they exhibit a wide electrochemical stability window, good chemical compatibility with high-voltage cathode materials, and better stability toward moisture and oxygen in air than sulfide solid electrolytes. However, halide solid electrolytes generally show poor chemical stability against lithium metal anodes, because halide ions are easily reduced when in direct contact with lithium metal. Researchers have improved interfacial stability through strategies such as introducing buffer layers, combining them with oxide or sulfide electrolytes, and applying anion doping modifications. For example, replacing part of $Cl^-$ with $O^{2-}$ to construct $UCl_3$-type oxychloride solid electrolytes (LLTCO) can significantly enhance interfacial stability. In addition, the metal elements commonly used in halide solid electrolytes are often scarce, and the raw-material cost is relatively high, which limits their large-scale application [10].

## 4. Sulfide Solid Electrolytes

Sulfide solid electrolytes have attracted enormous attention because of their exceptionally high ionic conductivity, which can approach or even match that of liquid electrolytes. Compared with oxygen, sulfur has lower electronegativity and higher polarizability, which weakens the interaction between lithium ions and the anion framework and facilitates fast ion migration. As a result, many sulfide electrolytes exhibit room-temperature ionic conductivity in the range of $10^{-3}$ to $10^{-2}$ S $cm^{-1}$.

Another major advantage of sulfide electrolytes is their relatively soft mechanical nature. Unlike rigid oxide ceramics, sulfide materials can often be densified by cold pressing, enabling better interfacial contact with electrode particles. This feature is particularly beneficial for reducing interfacial voids and lowering contact resistance in composite electrodes.

Typical sulfide solid electrolytes include glassy, glass-ceramic, and crystalline materials. Among them, crystalline compounds such as $Li_{10}GeP_2S_{12}$(LGPS) and argyrodite-type $Li_6PS_5Cl$ are widely known for their outstanding ionic transport properties.

However, sulfide electrolytes also face significant challenges. Their chemical stability in air is poor, and they can react with moisture to generate toxic $H_2S$ gas. In addition, many sulfide electrolytes exhibit limited electrochemical stability windows, leading to side reactions at both the cathode and anode interfaces. These reactions can form decomposition products that increase resistance and degrade cycling performance.

In recent years, considerable efforts have been devoted to improving the practicality of sulfide electrolytes through coating technologies, compositional tuning, and protective interphase design. Surface coatings on cathode active materials can reduce oxidative decomposition, while artificial interlayers on lithium metal can mitigate reductive instability. Moreover, partial substitution of sulfur with other elements and the development of sulfide-based composite electrolytes have shown promise in balancing conductivity, stability, and processability. These advances suggest that sulfide electrolytes remain among the strongest candidates for near-term application in high-performance solid-state batteries, provided that their air sensitivity and interfacial instability can be effectively controlled.

## 5. Halide Solid Electrolytes

Halide solid electrolytes are an emerging class of inorganic electrolytes that have gained increasing attention in recent years. They are generally described by the formula $Li_3MX_6$, where M is a metal cation and X is a halogen anion such as Cl, Br, or I. These materials combine several attractive features, including relatively high ionic conductivity, broad electrochemical stability windows, and good compatibility with high-voltage cathode materials.

Compared with sulfide electrolytes, halide electrolytes often exhibit better oxidative stability and improved tolerance to air and moisture. Their large and polarizable halide anions can create favorable lithium-ion migration environments, allowing room-temperature ionic conductivity to reach approximately $10^{-3}$ S $cm^{-1}$ in optimized systems. This makes halide materials especially promising for pairing with high-energy cathodes in solid-state battery configurations.

Despite these advantages, halide electrolytes are not without limitations. Their compatibility with lithium metal is often poor because halide ions may be reduced at low potentials. In addition, some halide systems rely on relatively scarce or expensive metal elements, which may impede large-scale commercialization.

Current research on halide electrolytes is expanding rapidly, particularly in the areas of aliovalent doping, anion substitution, crystal-structure regulation, and hybrid electrolyte design. For instance, partial substitution of halide ions with oxygen-containing species has been explored to improve interfacial stability and mechanical strength. Researchers are also investigating combinations of halide electrolytes with polymers, oxides, or sulfides to achieve synergistic improvements in flexibility, conductivity, and electrochemical stability. Because of their attractive balance between conductivity and cathode compatibility, halide electrolytes are increasingly seen as a promising platform for next-generation solid-state battery development.

## 6. Key Challenges in Practical Application

Although inorganic solid electrolytes have shown great promise, their practical application in all-solid-state lithium metal batteries still faces several major obstacles.

Inorganic solid electrolytes still face several key challenges that hinder their practical application in all-solid-state batteries. First, interfacial resistance remains a major issue. Unlike liquid electrolytes, which can readily wet electrode surfaces, solid electrolytes rely on intimate solid-solid contact with the electrodes. However, surface roughness, electrode volume variation during cycling, chemical incompatibility, and mechanical mismatch often lead to insufficient interfacial contact and thus high resistance. Second, poor chemical and electrochemical stability at the electrode-electrolyte interface may induce side reactions and generate resistive decomposition products. These interfacial reactions consume active lithium, aggravate polarization, and ultimately shorten battery lifespan. Third, mechanical degradation, including cracking, interfacial delamination, and lithium dendrite penetration, cannot be neglected. Even solid electrolytes with high intrinsic mechanical strength may undergo local failure in the presence of structural defects or stress concentration. Fourth, large-scale manufacturing remains challenging, since many inorganic solid electrolytes require high-temperature sintering, strictly moisture-free processing conditions, or costly raw materials, all of which increase fabrication complexity and cost. In addition, translating promising laboratory-scale results into commercially viable battery technologies requires addressing practical cell-level factors, including areal capacity, stack pressure, electrode thickness, processing efficiency, and long-term operational reliability. Although many studies have reported excellent intrinsic properties at the material level, only a limited number of systems have achieved stable cycling in practical full-cell configurations with high cathode loading and limited excess lithium. Therefore, future efforts should place greater emphasis on integrated cell engineering rather than solely on the optimization of individual electrolyte materials.

## 7. Future Perspectives

Future research on inorganic solid electrolytes should focus on several interrelated priorities. Foremost is interface engineering: designing interphases that are chemically stable, highly lithium-ion conductive, and mechanically compliant will be crucial to lower interfacial resistance, prevent unwanted side reactions, and enable long-term cycling with lithium metal anodes.

Equally important is the discovery and optimization of new electrolyte chemistries that simultaneously deliver higher ionic conductivity, wider electrochemical stability windows, improved resistance to moisture and $CO_2$, and cost-effective raw materials and synthesis routes. Hybrid and composite approaches that merge the complementary strengths of oxides, sulfides, halides, and polymers can offer practical pathways to reconcile trade-offs that single-component systems cannot resolve.

Scaling laboratory advances to industrial practice demands the development of manufacturable processes — from low-cost powder synthesis and densification to thin-film fabrication and robust cell assembly — that preserve material performance at large scale. Finally, accelerating progress will require tight integration of computational materials design, machine learning-guided screening, and advanced in situ characterization to reveal ion-transport mechanisms and degradation pathways. Coupling these scientific tools with engineering considerations such as areal capacity, stack pressure, processing compatibility, and end-of-life recycling will be essential to translate promising materials into commercially viable all-solid-state lithium metal batteries.

## 8. Conclusion

Inorganic solid electrolytes have become one of the most important research directions in the development of all-solid-state lithium metal batteries. Oxide electrolytes offer excellent chemical stability and mechanical strength, but often suffer from poor interfacial contact and limited compatibility with lithium metal. Sulfide electrolytes provide ultrahigh ionic conductivity and good processability, yet their air sensitivity and interfacial side reactions remain major obstacles. Halide electrolytes present a promising balance of ionic conductivity, oxidative stability, and cathode compatibility, although their compatibility with lithium metal and material cost still require further improvement.

Overall, the progress of inorganic solid electrolytes demonstrates that no single material system is perfect, and the future of solid-state batteries will likely depend on the coordinated optimization of material design, interface engineering, microstructure control, and manufacturing technology. With continued advances in both fundamental understanding and practical cell design, inorganic solid electrolytes are expected to play a decisive role in enabling safer, higher-energy, and longer-lasting energy storage systems in the future.

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