

STRUCTURE, PROPERTIES AND DEVELOPMENT PROSPECTS OF SULFIDE SOLID-STATE ELECTROLYTES

Ruize Jiang *

College of new energy, Harbin Institute of Technology (Weihai), Weihai 264209, Shandong Province, China

**jiangruize57@gmail.com*

Keywords: SULFIDE SOLID-STATE ELECTROLYTES; ALL-SOLID-STATE BATTERIES; IONIC CONDUCTIVITY; CHEMICAL STABILITY; ELECTRIC WINDOW

Abstract

As a key enabling technology for next-generation energy storage, all-solid-state batteries have gradually become a research hotspot in fields such as power batteries and consumer electronic batteries due to their higher energy density and better safety performance. Sulfide solid-state electrolytes have become one of the primary candidates for core electrolyte materials of all-solid-state batteries because of their advantages such as high room-temperature ionic conductivity, excellent mechanical flexibility and good interfacial contact. This paper systematically reviews the basic definition, composition classification of sulfide solid-state electrolytes, deeply analyzes their key performance parameters including ionic conductivity, mechanical properties, chemical stability and electrochemical window, and conducts an in-depth discussion on the core challenges faced by sulfide solid-state electrolytes in terms of environmental sensitivity, interfacial stability and production cost. Finally, combined with the current research progress, the future development direction of sulfide solid-state electrolytes are discussed from the perspectives of modification strategy, cost optimization, composite system design and artificial intelligence-assisted research and development, providing theoretical reference and technical support for their industrial application.

1 Introduction

With the acceleration of the global energy transition process, the demand for high-performance energy storage devices in fields such as new energy vehicles and large-scale energy storage is becoming increasingly urgent. Traditional lithium-ion batteries adopt liquid electrolytes, which have safety hazards such as flammability, explosion risk, and leakage, and their energy density has approached the theoretical limit, making it difficult to meet the future application requirements of high safety and high energy density. All-solid-state batteries replace traditional liquid electrolytes with solid-state electrolytes, fundamentally solving the safety problems of liquid batteries. At the same time, they can be compatible with lithium metal anodes and high-voltage cathode materials, with a theoretical energy density that can exceed $400 \text{ Wh} \cdot \text{kg}^{-1}$ [1], becoming a research focus in the energy storage field.

As the core component of all-solid-state batteries, the performance of solid-state electrolytes directly determines the energy density, cycle life, safety performance and production cost of batteries [2]. At present, the developed solid-state electrolytes are mainly divided into four types: oxides, sulfides, halides and polymers. Among them, oxide solid-state electrolytes (such as LLZO

A [3]) have good chemical stability and wide electrochemical window, but have problems such as low ionic conductivity, high mechanical brittleness and high interfacial contact resistance; polymer solid-state electrolytes have good

flexibility and excellent interfacial compatibility, but their room-temperature ionic conductivity is extremely low (usually lower than $10^{-4} \text{ S} \cdot \text{cm}^{-1}$)[4], which limits their practical application.

Since sulfide solid-state electrolytes were first reported in the 1980s[5], they have stood out due to their unique performance advantages. Their room-temperature ionic conductivity can reach the order of $10^{-3} \sim 10^{-2} \text{ S} \cdot \text{cm}^{-1}$, which is close to or even exceeds that of traditional liquid electrolytes ($10^{-2} \text{ S} \cdot \text{cm}^{-1}$). Moreover, they have a low Young's modulus (about 10 GPa)[6] and good mechanical flexibility, which can form tight contact with electrode materials through cold pressing, significantly reducing the interfacial contact resistance[7]. In addition, the preparation process of sulfide solid-state electrolytes is relatively simple, with potential for large-scale production. However, sulfide solid-state electrolytes also have prominent problems such as strong environmental sensitivity, narrow electrochemical window and poor interfacial stability, which restrict their industrialization process.

Compared with other solid-state electrolyte classes, sulfide electrolytes occupy a distinctive position. Oxide electrolytes (e.g., LLZO, LATP) offer wide electrochemical windows (4.0–6.0 V) and excellent thermal stability, but their high grain-boundary resistance and mechanical rigidity necessitate high-temperature sintering for adequate electrode contact. Polymer electrolytes (e.g., PEO-based) provide superior flexibility and interfacial compatibility, yet their room-temperature ionic conductivity ($<10^{-4} \text{ S} \cdot \text{cm}^{-1}$) is too low for most practical applications without heating. Halide

electrolytes (e.g., Li_3InCl_6) exhibit good oxidative stability but moderate conductivity and uncertain long-term stability against lithium metal. Sulfide electrolytes uniquely combine room-temperature conductivity approaching that of liquid electrolytes (10^{-3} – $10^{-2} \text{ S}\cdot\text{cm}^{-1}$) with sufficient mechanical ductility for cold-pressing assembly. Their principal shortcomings—a narrow electrochemical window, acute air sensitivity, and interfacial reactivity with high-voltage cathodes—constitute the core challenges that motivate this review. Based on the existing research results, this work systematically sorts out the basic theory, performance characteristics, system classification and preparation processes of sulfide solid-state electrolytes, deeply analyzes the core challenges they face, and looks forward to the future development direction, aiming to provide a comprehensive reference for the further research and industrial application of sulfide solid-state electrolytes (see Fig.1).

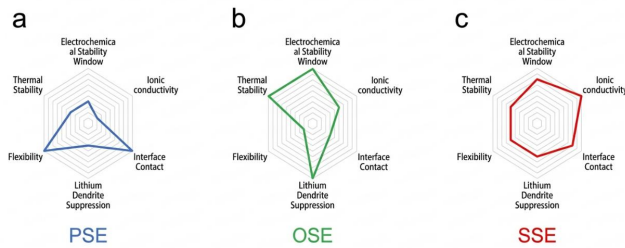


Fig. 1. Performance comparison of different solid-state electrolytes (SSEs). Radar chart comparing key performance metrics of polymer solid electrolytes (PSEs), oxide solid electrolytes (OSEs), and sulfide solid electrolytes (SSEs), including ionic conductivity, interfacial contact, lithium dendrite suppression, flexibility, thermal stability, and electrochemical window. Drawn by the author.

2 Basic Definition and Structural Classification of Sulfide Solid-State Electrolytes

2.1 Definition and Composition Classification

Sulfide solid-state electrolytes refer to solid compounds that take lithium sulfide (Li_2S) as the core component, form chemical bonds with other metal sulfides or non-metal sulfides, and have Li^+ conductivity. The core characteristic of their chemical composition is the inclusion of S^{2-} ions, and Li^+ migrate through the ion transport channels formed by the sulfide framework. According to the differences in composition, sulfide solid-state electrolytes can be divided into the following three categories[8].

2.1.1 Li_2S - Nonmetal Sulfide System (Binary System): This system uses Li_2S and nonmetal sulfides (mainly phosphorus-based sulfides) as raw materials, with the typical representative being the Li_2S - P_2S_5 system[9]. By adjusting the molar ratio of Li_2S to P_2S_5 , sulfide electrolytes with different compositions can be formed, such as Li_3PS_4 (LPS) and $\text{Li}_7\text{P}_3\text{S}_{11}$. Among them, P, as a nonmetal element, forms P-S tetrahedrons (PS_4^{3-}) with S, which constitute the basic structural units of the electrolyte, and Li^+ migrate through the vacancies between the tetrahedrons. The advantages of this

system are relatively low raw material cost and simple preparation process, making it one of the most widely studied sulfide electrolyte systems at present. However, its room-temperature ionic conductivity is usually lower than that of metal sulfide systems, and its stability needs to be improved.

2.1.2 Li_2S - Metal Sulfide System (Ternary System): This system uses Li_2S and transition metal or main group metal sulfides as raw materials to form composite sulfide electrolytes through chemical bonding. Common metal sulfides include GeS_2 , SnS_2 , ZnS , Sb_2S_3 , etc. For example, in the ternary system $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS)[10], Ge, as a metal element, forms Ge-S bonds with S to form the framework structure of the electrolyte, and Li^+ migrate rapidly in the gaps of the framework. The characteristic of this system is high ionic conductivity, and the room-temperature conductivity of some systems can reach the order of $10^{-2} \text{ S}\cdot\text{cm}^{-1}$. However, the high cost of metal elements (such as Ge) limits their large-scale application (see Fig.2).

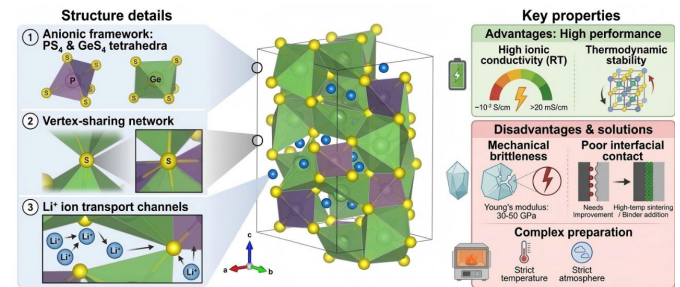


Fig. 2. Crystal structure and lithium-ion transport mechanisms in typical sulfide solid electrolytes. Three-dimensional framework of the LGPS-type electrolyte, illustrating the anionic lattice composed of PS_4 and MS_4 tetrahedra. Drawn by the author.

2.1.3 Composite System: To address the inherent drawbacks of single-component electrolytes, such as the chemical instability of sulfides and the low ionic conductivity of polymers, composite strategies integrating sulfides with oxides, polymers, or halides have been extensively explored. This synergistic approach effectively harnesses the unique merits of each component: sulfide electrolytes (e.g., $\text{Li}_6\text{PS}_5\text{Cl}$) ensure high room-temperature ionic conductivity and intimate interfacial contact; oxides (e.g., LATP, LLZ) enhance mechanical strength and thermal stability; polymers (e.g., PEO, PVDF) provide essential flexibility for processing; and halides (e.g., Li_3InCl_6) offer a wide electrochemical window and superior oxidative stability. Recent progress in multi-component systems has demonstrated significant leaps in electrochemical performance. For instance, by constructing a sulfide-polymer composite or employing a halide-sulfide bilayer architecture, the chemo-mechanical degradation at the cathode/electrolyte interface can be effectively suppressed. Experimental evidence reveals that all-solid-state batteries (ASSBs) utilizing these optimized composite electrolytes paired with high-nickel NCM cathodes can deliver excellent initial discharge capacity[11], significantly outperforming systems based on single-phase electrolytes. Moreover, such composite systems exhibit exceptional cycling durability, maintaining outstanding capacity retention during long-term

cycling, which is attributed to the stabilized interphase that inhibits continuous electrolyte decomposition and transition metal dissolution. A cross-system comparison reveals inherent trade-offs among the major sulfide electrolyte families. Binary Li_2S - P_2S_5 systems offer low raw material cost and simple processing, yet their room-temperature ionic conductivity (10^{-4} – $10^{-3} \text{ S}\cdot\text{cm}^{-1}$) and air stability (significant degradation within minutes of exposure) remain the weakest among all categories. Ternary LGPS-type electrolytes deliver the highest ionic conductivities (up to $12 \text{ mS}\cdot\text{cm}^{-1}$) but rely on expensive elements such as Ge and suffer from mechanical brittleness, limiting scalability. Glass-ceramic electrolytes such as $\text{Li}_7\text{P}_3\text{S}_{11}$ occupy an intermediate position, with moderate conductivity ($\sim 3 \text{ mS}\cdot\text{cm}^{-1}$), good flexibility, and acceptable cost—making them attractive for industrialization. Multi-element doped systems (e.g., LPSCI) improve both the electrochemical window (to $\sim 2.8 \text{ V}$ via Cl doping) and air tolerance ($>1 \text{ h}$ with $<30\%$ conductivity loss) through halogen incorporation, though at the expense of greater compositional complexity. In summary, no single sulfide electrolyte simultaneously optimizes all performance metrics; the choice of system must be guided by the target application, with glass-ceramic and doped systems currently offering the most balanced overall profiles.

3 Key Parameters of Sulfide Solid-State Electrolytes

3.1 Ionic conductivity

Ionic conductivity is the core indicator for evaluating the performance of solid-state electrolytes, which directly determines the rate performance and charge-discharge efficiency of all-solid-state batteries[1]. The ionic conductivity of sulfide solid-state electrolytes mainly depends on the Li^+ transference number, migration rate and structural characteristics of ion transport channels (see Fig.3).

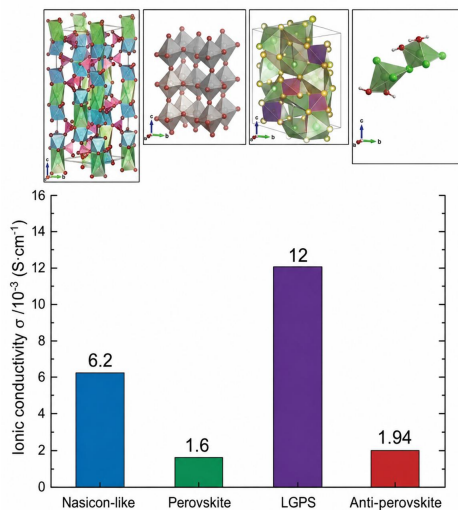


Fig. 3. Comparison of room-temperature ionic conductivities of representative solid-state electrolyte systems. Values shown: NASICON-type LATP ($6.2 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$)[12], perovskite-type LLTO ($1.60 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$)[13], LGPS-type $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ($12 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$), and anti-perovskite-type $\text{Li}_3\text{OCl}_{0.5}\text{Br}_{0.5}$ ($1.94 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$)[14]. Crystal

structure illustrations were obtained from the Materials Project (CC BY 4.0). Bar chart replotted by the author.

3.1.1 Ionic Conductivity in Room-Temperature: The room-temperature ionic conductivity of sulfide solid-state electrolytes exhibits significant system dependence, with notable differences among electrolytes of distinct structural types. Amorphous (glassy) systems typically display a room-temperature ionic conductivity in the range of 10^{-4} to $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ —for instance, the Li_3PS_4 glassy electrolyte has a conductivity of approximately $2 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, whereas the Li_2S - P_2S_5 glassy electrolyte (with a molar ratio of 7:3) exhibits a conductivity of around $8 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ [15]. In contrast, crystalline systems generally possess much higher room-temperature ionic conductivity, usually ranging from 10^{-3} to $10^{-2} \text{ S}\cdot\text{cm}^{-1}$, with some high-performance systems achieving even higher values. Representative examples include $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, which boasts a room-temperature conductivity of $12 \text{ mS}\cdot\text{cm}^{-1}$ [10], and $\text{Li}_{9.54}\text{Si}_{11.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$, whose room-temperature conductivity reaches $25 \text{ mS}\cdot\text{cm}^{-1}$ [16]. By comparison, glass-ceramic systems feature a room-temperature ionic conductivity that falls between those of amorphous and crystalline systems, typically spanning 10^{-3} to $10^{-2} \text{ S}\cdot\text{cm}^{-1}$. Typical examples are the $\text{Li}_7\text{P}_3\text{S}_{11}$ glass-ceramic electrolyte with a conductivity of about $3 \text{ mS}\cdot\text{cm}^{-1}$ and the Li_3PS_4 - LiCl glass-ceramic electrolyte with a conductivity of approximately $1 \text{ mS}\cdot\text{cm}^{-1}$ [17].

3.1.2 Li^+ Conduction Mechanism: The Li^+ conduction mechanism of sulfide solid-state electrolytes is mainly the vacancy migration mechanism, which is the most dominant ion transport mode in most sulfide electrolyte systems and differs from the interstitial migration mechanism commonly found in some oxide electrolytes[18]. Specifically, Li^+ realize long-range migration by continuously occupying the vacant lattice sites (vacancies) in the sulfide crystal framework, and this process relies on the dynamic balance between Li^+ detachment from original sites and occupation of new vacancies[19]. The conduction process can be broken down into three consecutive and closely linked steps: first, Li^+ gain sufficient energy under the action of an external electric field, which is enough to overcome the lattice binding energy, thereby being released from their original stable lattice positions and becoming free-moving ions; second, the detached free Li^+ quickly move to adjacent lattice vacancies or interstitial positions—these positions provide temporary stable sites for Li^+ and avoid the steric hindrance caused by direct movement between occupied lattice sites; third, after a short energy relaxation period at the new position, the Li^+ continue to migrate to farther vacant lattice sites under the continuous action of the electric field, forming a continuous and stable Li^+ transport path, which ultimately realizes efficient ion conduction in the electrolyte. The ion conduction rate, which directly determines the rate performance of all-solid-state batteries, is mainly influenced by three key factors: the structure of ion transport channels, Li^+ concentration, and activation energy. Specifically, continuous and wide-diameter transport channels are highly conducive to Li^+ migration, as they reduce the spatial resistance encountered during Li^+ movement—for example, a one-dimensional continuous Li^+

transport channel is formed in the crystal structure of LGPS ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$), with a channel diameter of about 0.3 nm, which matches well with the Li^+ radius (0.076 nm) and significantly reduces the spatial steric hindrance of Li^+ migration, thus enabling rapid Li^+ transport. Regarding Li^+ concentration, appropriately increasing the Li^+ concentration can effectively raise the number of charge carriers in the electrolyte, thereby improving ionic conductivity; however, excessive Li^+ will disrupt the ordered arrangement of the sulfide lattice, leading to lattice distortion and even blockage of ion transport channels, which in turn hinders Li^+ migration and reduces conductivity. As for activation energy, it is the minimum energy required for Li^+ to detach from their original lattice positions; the lower the activation energy, the easier it is for Li^+ to break free from lattice constraints and the faster the migration rate[20]. The activation energy of sulfide electrolytes is usually between 0.1~0.4 eV, which is significantly lower than that of oxide electrolytes (0.5~1.0 eV)—this fundamental difference is one of the core reasons why sulfide electrolytes exhibit higher room-temperature ionic conductivity than oxide electrolytes[21].

3.1.3 Breakthrough of Li^+ conductivity:

- $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS): Discovered by Kanno in 2011, it is the first sulfide electrolyte with room-temperature ionic conductivity exceeding $10 \text{ mS} \cdot \text{cm}^{-1}$. Its crystal structure contains a one-dimensional Li^+ transport channel, with an activation energy of only 0.2 eV and a room-temperature conductivity of $12 \text{ mS} \cdot \text{cm}^{-1}$. However, the cost of Ge is high (about $\$700 \cdot \text{kg}^{-1}$), and it is easily oxidized in air, which limits its large-scale application;
- $\text{Li}_7\text{P}_3\text{S}_{11}$: A typical representative of glass-ceramic electrolytes, prepared by melt quenching of Li_2S and P_2S_5 (molar ratio 7:3) followed by heat treatment. Its room-temperature conductivity is about $3 \text{ mS} \cdot \text{cm}^{-1}$ [22], activation energy is 0.3 eV, raw material cost is low, and mechanical flexibility is good, making it one of the key systems for industrialization exploration;
- Li_3PS_4 -LiCl composite system: By doping LiCl into Li_3PS_4 to form a glass-ceramic structure, the room-temperature conductivity is increased to $1 \text{ mS} \cdot \text{cm}^{-1}$, which is 5 times higher than that of pure Li_3PS_4 ($2 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$). The introduction of Cl^- optimizes the structure of ion transport channels, reduces the activation energy, and improves the stability of the electrolyte.

3.2 Chemical Stability

The chemical stability of sulfide solid-state electrolytes mainly includes air stability, water stability and compatibility with electrode materials, among which environmental sensitivity (air and water sensitivity) is one of the core bottlenecks in their industrialization process.

3.2.1 Air and Water Sensitivity: Sulfide solid-state electrolytes exhibit extremely high sensitivity to air and water, a critical bottleneck that severely hinders their practical application and industrialization[23]. When exposed to ambient air, they undergo a series of irreversible chemical reactions that damage their crystal structure and degrade their electrochemical performance, specifically involving three

main types of reactions. First, the reaction with water: the S^{2-} ions in sulfide electrolytes readily react with atmospheric moisture (H_2O) to generate toxic hydrogen sulfide (H_2S) gas. H_2S is a colorless gas with a pungent rotten-egg odor, which not only poses a serious hazard to human health (causing respiratory irritation and even poisoning at high concentrations) but also pollutes the environment and corrodes metal equipment used in electrolyte preparation and storage, thereby increasing overall production costs. Second, the oxidation reaction: oxygen (O_2) in the air oxidizes the S^{2-} ions in sulfide electrolytes to form SO_4^{2-} ions, which disrupt the ordered sulfide crystal framework and cause irreversible structural damage to the electrolyte. This structural impairment directly leads to a sharp decline in ionic conductivity, as the Li^+ transport channels are blocked or destroyed, impeding efficient Li^+ migration. Additionally, some sulfide electrolytes undergo deliquescence: a typical example is Li_3PS_4 , which has a strong tendency to absorb atmospheric moisture, resulting in deliquescence and the formation of liquid products. Once deliquescence occurs, the electrolyte loses its solid state and complete ionic conductivity, rendering it completely ineffective for use in all-solid-state batteries. Notably, significant differences in environmental sensitivity exist among sulfide electrolytes of different systems, which is closely associated with their crystal structure and chemical composition. Binary systems, such as Li_3PS_4 , are the most sensitive to air and water; obvious H_2S gas release can be observed within 10 minutes of exposure to ambient air, and their ionic conductivity decreases by more than 50%[24], making strict inert atmosphere protection essential for their storage and processing. In contrast, ternary systems, such as LGPS ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$), are slightly less sensitive due to the stabilizing effect of metal elements (e.g., Ge) in their structure, but significant oxidation still occurs after more than 30 minutes of air exposure, leading to gradual performance degradation. Multi-element doped systems, such as LPSCl (lithium phosphorus sulfide chloride), have significantly improved surface stability through halogen (Cl) doping—enhances the thermodynamic stability of the crystal lattice, and surface Cl^- preferentially reacts with water to form an inert LiCl passivation layer, effectively inhibiting hydrolysis and oxidation reactions. As a result, the decrease in their ionic conductivity can be controlled within 30% even after 1 hour of air exposure, demonstrating considerable potential for practical application[16, 25].

3.2.2 Compatibility with Electrode Materials: The compatibility between sulfide solid-state electrolytes and electrode materials is a critical factor that directly determines the cycle life and overall performance of all-solid-state batteries. For lithium metal anodes, which exhibit an extremely low standard electrode potential of -3.04 V vs SHE, sulfide electrolytes inevitably undergo reduction reactions upon direct contact with the lithium metal surface, producing products such as Li_2S and further forming an interfacial impedance layer with a typical thickness of 10–100 nm. Representative reduction reactions in such systems include the reaction between $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and Li and the reaction between Li_3PS_4 and Li. Notably, the reaction products (e.g.,

Li_2S , Li_3P) are electronic insulators but retain a certain degree of Li^+ conductivity, which inevitably increases the battery's interfacial resistance and consequently degrades its cycle performance. However, the interfacial reactions of some specific sulfide-lithium systems are self-limiting: once the generated impedance layer reaches a critical thickness, the reaction is effectively inhibited and eventually terminates, the interfacial resistance stabilizes, and its adverse effects on battery performance can be gradually mitigated through cycle activation[26]. For cathode materials, sulfide electrolytes feature a relatively narrow electrochemical window (1.7–2.5 V)[27], whereas most commonly used cathode materials in practical applications—such as NCM series, lithium-rich manganese-based materials, and lithium iron phosphate—operate at high voltages (2.5–4.8 V). As a result, oxidative decomposition reactions occur at the interface when sulfide electrolytes come into contact with high-voltage cathodes, generating transition metal sulfides (e.g., NiS , CoS) and by-products like Li_2SO_4 , which further form a high-impedance interfacial layer that impedes ion transport. For instance, the reaction between Li_3PS_4 and NCM811 cathodes yields products such as Ni_3S_2 and Co_3S_4 , with interfacial resistance exceeding $100\ \Omega \cdot \text{cm}^2$ [28], which severely impairs the battery's charge-discharge efficiency and long-term cycle life. In contrast, sulfide electrolytes demonstrate relatively better compatibility with low-voltage cathodes (e.g., lithium iron phosphate with an operating voltage of 3.4 V); however, slight interfacial side reactions still occur after prolonged cycling, gradually leading to the attenuation of battery capacity over time.

3.3 Mechanical Properties

The mechanical properties of sulfide solid-state electrolytes are mainly characterized by parameters such as Young's modulus and fracture toughness, which directly influence their interfacial contact with electrode materials and the cycling stability of batteries. Among these core mechanical performance indicators, Young's modulus is particularly crucial, as it determines the mechanical flexibility and interfacial adaptability of the electrolytes. Its value varies significantly with the crystal structure of sulfide solid-state electrolytes, which in turn induces differences in fracture toughness and interfacial contact performance. Specifically, the Young's modulus of sulfide solid-state electrolytes typically ranges from 10 to 50 GPa, much lower than that of oxide solid-state electrolytes (100–200 GPa)[6], thereby endowing them with excellent overall mechanical flexibility. For amorphous (glassy) electrolytes, the Young's modulus is approximately 10–20 GPa, along with high fracture toughness and good plasticity; this allows them to form tight contact with electrode materials via cold pressing, with the interfacial contact resistance as low as less than $10\ \Omega \cdot \text{cm}^2$. In contrast, crystalline electrolytes exhibit a higher Young's modulus of about 30–50 GPa[6], which gives rise to high mechanical brittleness, low fracture toughness, and poor interfacial contact with electrode materials. Therefore, it is necessary to improve interfacial contact by adding binders or

employing high-temperature sintering methods. Glass-ceramic electrolytes have a Young's modulus of around 15–30 GPa, integrating the flexibility of amorphous electrolytes and the structural stability of crystalline electrolytes. Their fracture toughness lies between that of amorphous and crystalline electrolytes, making them the type with the optimal comprehensive mechanical properties among sulfide solid-state electrolytes.

3.4 Electrochemical Window:

refers to the range between the maximum voltage an electrolyte can withstand prior to oxidative decomposition and the minimum voltage it can endure before reductive decomposition, serving as a key indicator to evaluate the electrolyte's compatibility with electrode materials. The electrochemical window of sulfide solid-state electrolytes is narrow, typically ranging from 1.7 to 2.5 V, which is significantly lower than that of oxide (4.0–6.0 V) and halide (2.0–6.0 V) solid-state electrolytes. The electrochemical window of sulfide electrolytes is commonly determined by Linear Sweep Voltammetry (LSV), using stainless steel as the working electrode, lithium metal as both the counter and reference electrodes, and a scan rate of $1\text{--}10\ \text{mV} \cdot \text{s}^{-1}$; an obvious current surge in the scan curve indicates the corresponding oxidative decomposition voltage (upper limit) and reductive decomposition voltage (lower limit) of the electrolyte. For instance, Li_3PS_4 has an oxidative decomposition voltage of approximately 2.6 V and a reductive decomposition voltage of about 2.1 V, resulting in an electrochemical window of 2.1–2.6 V[29]; LGPS exhibits an oxidative decomposition voltage of around 2.5 V and a reductive decomposition voltage of about 1.8 V, with an electrochemical window of 1.8–2.5 V[16]. Notably, the electrochemical window of multi-element doped systems can be appropriately widened through modification—for example, the oxidative decomposition voltage of LPSCI is increased to 2.8 V, expanding its electrochemical window to 1.8 – 2.8 V. However, the narrow electrochemical window of sulfide electrolytes hinders their compatibility with high-voltage cathode materials (operating voltage > 3 V): among current commercial cathode materials, NCM523 operates at 3.0–4.3 V, NCM811 at 3.0–4.5 V, and lithium-rich manganese-based cathodes at up to 3.0–4.8 V, all exceeding the oxidative decomposition voltage of sulfide electrolytes. When the battery is charged to high voltages, the sulfide electrolyte undergoes oxidative decomposition, leading to rapid capacity fading, shortened cycle life, and even potential safety risks. To address this issue, researchers typically adopt methods such as cathode coating, interface modification, and composite electrolytes to form a protective layer between sulfide electrolytes and high-voltage cathodes, inhibiting oxidative decomposition reactions. For example, coating NCM cathodes with oxides like Al_2O_3 and LiNbO_3 [30] can reduce the interfacial resistance to less than $30\ \Omega \cdot \text{cm}^2$, increasing the battery's capacity retention rate from 58% to 82% after 50 cycles(see Fig.4).

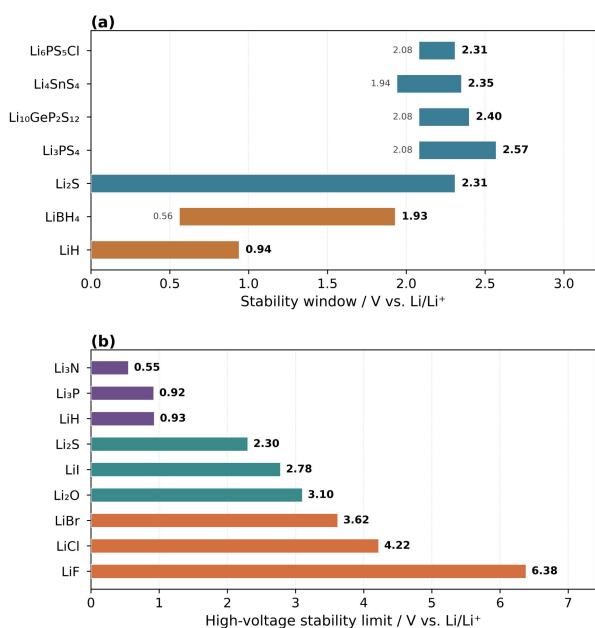


Fig. 4. Electrochemical stability windows of representative solid electrolytes and lithium-containing binary compounds. (a) Stability windows of selected sulfide and hydride solid electrolytes. (b) High-voltage stability limits of lithium binary compounds relevant to interphase formation. The values were estimated from Figures 1(c) and 2 of Richards et al. and replotted by the author[31].

4. Challenges and Development Prospects of Sulfide Solid-State Electrolytes

4.1 Challenges

Although sulfide solid-state electrolytes have excellent performance advantages, they still face many core challenges in the industrialization process, mainly including chemical stability, interfacial stability, production cost and other aspects: First, chemical stability. The strong sensitivity of sulfide electrolytes to air and water is the biggest bottleneck for their industrialization. During production, storage, transportation and battery assembly, it is necessary to maintain an inert atmosphere (such as Ar, N₂) throughout the process, which will significantly increase production equipment costs and operating costs. Secondly, the interfacial reaction between sulfide electrolytes and cathode and anode materials leads to increased interfacial impedance, which is a key factor affecting the cycle life of all-solid-state batteries. For example, the interface impedance layer formed by products such as Li₂S and Li₃P generated by the reaction with lithium metal anodes will increase the Li⁺ migration resistance; the transition metal sulfides and Li₂SO₄ and other products generated by the reaction with high-voltage cathodes will significantly reduce the charge and discharge efficiency and cycle stability of the battery. Finally, the price of core raw material Li₂S is much higher than that of traditional electrolyte raw materials, and the cost of raw materials such as Ge and P is also relatively high; processes such as inert atmosphere production and high-temperature sintering increase energy consumption and equipment

investment; the packaging and transportation of inert atmosphere further increase storage and transportation costs and reduce market competitiveness(see Fig.5).

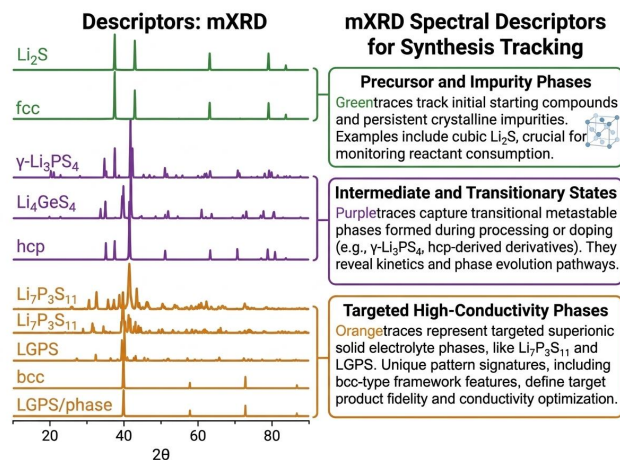


Fig. 5. Classification of mXRD spectral descriptors for synthesis process monitoring of sulfide solid-state electrolytes. Green traces: precursor and impurity phases (e.g., Li₂S); purple traces: intermediate and metastable transition states (e.g., γ-Li₃PS₄); orange traces: targeted high-conductivity superionic phases (e.g., Li₇P₃S₁₁ and LGPS). Reproduced under a Creative Commons Attribution 4.0 International License (CC BY 4.0).

4.2 Prospects

In response to the core challenges confronting sulfide solid-state electrolytes—including their high environmental sensitivity (susceptibility to hydrolysis and oxidation in air), poor interfacial compatibility with electrode materials (tendency to form high-impedance interfacial layers), and high production costs that impede large-scale industrialization. To address these challenges, future development directions focus primarily on four key areas: modification strategy optimization, cost reduction, composite system design, and artificial intelligence (AI)-assisted research and development. All these initiatives aim to comprehensively enhance the stability and interfacial compatibility of sulfide electrolytes, break through the technical bottlenecks restricting their practical application, and ultimately advance their industrialization in the field of all-solid-state batteries. Among these directions, modification optimization strategies serve as the most direct and effective approach to improving electrolyte performance, encompassing specific methods such as doping modification, surface coating modification, and composite structure design. Doping modification involves introducing heteroatoms (e.g., Cl, Br, F) or metal elements (e.g., Sn, Zn) into the sulfide framework to optimize the structure of Li⁺ transport channels, reduce the activation energy for Li⁺ migration, and concurrently enhance the electrolyte's environmental stability. For instance, doping Cl into Li₃PS₄ not only increases the room-temperature ionic conductivity from 2×10⁻⁴ S·cm⁻¹ to 1×10⁻³ S·cm⁻¹ but also significantly diminishes its air sensitivity. Surface coating modification entails depositing a thin protective layer (e.g., Al₂O₃, LiNbO₃, or polymer films) on the surface of sulfide electrolytes, which isolates the

electrolyte from air and moisture while inhibiting interfacial reactions between the electrolyte and electrodes—thereby improving both environmental stability and interfacial compatibility. In terms of cost optimization, key efforts focus on three aspects: reducing raw material costs, optimizing preparation processes, and lowering storage and transportation costs. To cut raw material costs, researchers are actively developing Ge/Sn-free sulfide electrolyte systems to replace high-cost metal elements and optimizing the production process of core raw materials such as Li_2S . For preparation process optimization, the emphasis is on simplifying inert atmosphere operations, developing continuous and low-energy-consumption technologies (e.g., advanced mechanical ball milling and low-temperature sintering), and reducing energy consumption and equipment investment. Regarding storage and transportation costs, improvements in packaging materials and methods, alongside the development of low-cost inert atmosphere storage and transportation technologies, are crucial to minimizing losses caused by electrolyte oxidation or hydrolysis during storage and transportation. The rationale behind composite system design stems from the inherent trade-offs of single-type solid-state electrolytes (whether sulfide, oxide, polymer, or halide). For example, sulfide electrolytes exhibit high ionic conductivity but poor stability, while oxide electrolytes offer

good stability but low conductivity. By constructing sulfide-based composite electrolytes, the goal is to integrate the advantages of different solid-state electrolyte types, compensate for their respective shortcomings, and ultimately achieve both high power density and high energy density in all-solid-state batteries. Common composite forms include sulfide-oxide, sulfide-polymer, and sulfide-halide composites, all of which can significantly enhance the comprehensive performance of electrolytes. Finally, in the realm of AI, machine learning algorithms (e.g., neural networks, random forests, and support vector machines) are employed to systematically analyze the vast volume of experimental data accumulated in sulfide electrolyte research, including data on electrolyte composition, microstructure, preparation process parameters, and electrochemical performance. Through in-depth learning and training, these algorithms can accurately predict the quantitative relationships between electrolyte composition, structure, process, and performance, thereby guiding the design of new high-performance sulfide electrolyte systems, reducing the number of blind experiments, saving research and development (R&D) costs, and greatly shortening the R&D cycle. This cross-integration of AI and materials science has emerged as a new trend in sulfide solid-state electrolyte research[32], providing fresh momentum for their rapid advancement.

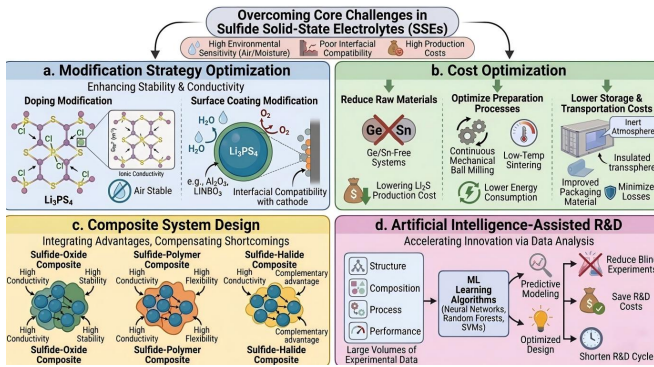


Fig. 6. Comprehensive optimization strategy and future development directions of high-performance sulfide solid-state electrolytes. The diagram summarizes four core research directions: modification strategy optimization (doping/coating), cost reduction (Ge/Sn-free design/low-energy preparation), composite system design (sulfide-oxide/sulfide-polymer), and artificial intelligence (AI)-assisted R&D, with key performance targets and industrialization requirements indicated for each direction. Drawn by the author.

The diagram summarizes four core research directions: modification strategy optimization (doping/coating), cost reduction (Ge/Sn-free design/low-energy preparation), composite system design (sulfide-oxide/sulfide-polymer) and artificial intelligence (AI)-assisted R&D; the key performance improvement targets (ionic conductivity, air stability, cycle life) and industrialization requirements are marked for each direction(see Fig.6).

5. Conclusion

As a core candidate material for next-generation all-solid-state batteries (ASSBs), sulfide solid-state electrolytes (SSEs) hold broad application prospects in the field of high-power-density ASSBs, owing to their distinctive advantages: high room-temperature ionic conductivity (typically ranging from 10^{-3} to $10^{-2} \text{ S}\cdot\text{cm}^{-1}$, which is comparable to that of conventional liquid electrolytes), excellent mechanical flexibility that can effectively accommodate the volume variation of electrodes during charge-discharge cycles, and superior cold-pressing formability that simplifies the battery assembly process. This paper systematically reviews the fundamental definition, structural classification, core performance parameters (including ionic conductivity, electrochemical window, mechanical strength, and chemical stability), mainstream material systems, and potential application scenarios of SSEs. It also deeply analyzes the core challenges encountered in their practical application, such as strong environmental sensitivity (they tend to react with moisture and oxygen in the air, generating toxic gases and deteriorating performance), poor interfacial stability with electrode materials (prone to forming high-impedance interfacial layers that impede ion transport), and high production costs (attributed to the high purity requirements of raw materials and the complexity of preparation processes), while looking forward to their future development directions. Notably, the structural types of SSEs—including amorphous, crystalline, and glass-ceramic phases—directly determine their comprehensive performance characteristics. Among these, glass-ceramic electrolytes, which integrate the high ionic conductivity of crystalline electrolytes and the excellent mechanical processability of amorphous glass electrolytes, are currently the most promising type for practical

application. Meanwhile, the mainstream material systems of SSEs have continuously evolved from early binary (e.g., $\text{Li}_2\text{S-P}_2\text{S}_5$) and ternary systems to multi-component doped systems, with their comprehensive performance being steadily optimized. Among these systems, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, $\text{Li}_7\text{P}_3\text{S}_{11}$, and LPSCl (lithium phosphorus sulfide chloride) stand out due to their exceptional room-temperature ionic conductivity and relatively good stability. In terms of preparation processes, the solid-state method (including mechanical ball milling and high-temperature sintering) is currently the dominant industrial preparation approach, benefiting from its mature technology and high production efficiency. In contrast, the liquid-phase method (such as solution casting and sol-gel method) and other special preparation techniques are gradually moving towards low-cost, green, and large-scale directions to meet the demands of industrial mass production. Although SSEs still face prominent challenges, including strong environmental sensitivity, poor interfacial stability with electrodes, and high production costs, these issues are being gradually mitigated through various technical means. These include element doping modification to enhance ionic conductivity and stability, surface coating technology to isolate the electrolyte from the external environment and electrodes, and composite system design to integrate the advantages of different materials. In the future, with the continuous optimization of material modification strategies, the steady reduction of production costs through process improvement, the in-depth application of AI-assisted research and development (which can accelerate the screening of high-performance materials and the optimization of preparation processes), and the advancement of multi-functional integrated materials, SSEs are expected to achieve large-scale industrial application in fields such as automotive power batteries, consumer electronic batteries, and energy storage batteries. This will thereby promote the rapid development of ASSB technology and lay a solid foundation for the popularization of new energy equipment.

5 Acknowledgements

The figures in this paper were created and refined using Google Gemini, Adobe Photoshop, and GIMP. All figure content and data have been manually verified by the authors, who take full responsibility for their scientific accuracy, copyright compliance, and overall integrity.

6 References

- [1] Janek, J.; Zeier, W. G.: 'A solid future for battery development'. *Nat. Energy* 2016, 1, (9), pp 16141
- [2] Chen, S.; Xie, D.; Liu, G.; et al.: 'Sulfide solid electrolytes for all-solid-state lithium batteries: Structure, conductivity, stability and application'. *Energy Storage Mater.* 2018, 14, pp 58-74
- [3] Murugan, R.; Thangadurai, V.; Weppner, W.: 'Fast Lithium Ion Conduction in Garnet-Type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ '. *Angew. Chem., Int. Ed.* 2007, 46, (41), pp 7778-7781
- [4] Mindemark, J.; Lacey, M. J.; Bowden, T.; et al.: 'Beyond PEO—Alternative host materials for Li^+ -conducting solid polymer electrolytes'. *Prog. Polym. Sci.* 2018, 81, pp 114-143
- [5] Mercier, R.; Malugani, J.-P.; Fahys, B.; et al.: 'Superionic conduction in $\text{Li}_2\text{S} - \text{P}_2\text{S}_5 - \text{LiI}$ - glasses'. *Solid State Ion.* 1981, 5, pp 663-666
- [6] Sakuda, A.; Hayashi, A.; Tatsumisago, M.: 'Sulfide Solid Electrolyte with Favorable Mechanical Property for All-Solid-State Lithium Battery'. *Sci. Rep.* 2013, 3, (1), pp 2261
- [7] Xu, R.; Han, F.; Ji, X.; et al.: 'Interface engineering of sulfide electrolytes for all-solid-state lithium batteries'. *Nano Energy* 2018, 53, pp 958-966
- [8] Famprikis, T.; Canepa, P.; Dawson, J. A.; et al.: 'Fundamentals of inorganic solid-state electrolytes for batteries'. *Nat. Mater.* 2019, 18, (12), pp 1278-1291
- [9] Man, B.; Zeng, Y.; Liu, Q.; et al.: A Comprehensive Review of Sulfide Solid-State Electrolytes: Properties, Synthesis, Applications, and Challenges. In *Crystals*, 2025; Vol. 15, p 492.
- [10] Kamaya, N.; Homma, K.; Yamakawa, Y.; et al.: 'A lithium superionic conductor'. *Nat. Mater.* 2011, 10, (9), pp 682-686
- [11] Cheng, F.; Zhang, X.; Qiu, Y.; et al.: 'Tailoring electrolyte to enable high-rate and super-stable Ni-rich NCM cathode materials for Li-ion batteries'. *Nano Energy* 2021, 88, pp 106301
- [12] Monchak, M.; Hupfer, T.; Senyshyn, A.; et al.: 'Lithium Diffusion Pathway in $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) Superionic Conductor'. *Inorganic Chemistry* 2016, 55, (6), pp 2941-2945
- [13] Inaguma, Y.; Nakashima, M.: 'A rechargeable lithium-air battery using a lithium ion-conducting lanthanum lithium titanate ceramics as an electrolyte separator'. *Journal of Power Sources* 2013, 228, pp 250-255
- [14] Zhao, Y.; Daemen, L. L.: 'Superionic Conductivity in Lithium-Rich Anti-Perovskites'. *Journal of the American Chemical Society* 2012, 134, (36), pp 15042-15047
- [15] Hayashi, A.; Hama, S.; Morimoto, H.; Tatsumisago, M.; Minami, T.: "Preparation of $\text{Li}_2\text{S-P}_2\text{S}_5$ Amorphous Solid Electrolytes by Mechanical Milling". *Journal of the American Ceramic Society* 2001, 84, (2), pp. 477-479
- [16] Kato, Y.; Hori, S.; Saito, T.; et al.: 'High-power all-solid-state batteries using sulfide superionic conductors'. *Nat. Energy* 2016, 1, (4), pp 16030
- [17] Minami, K.; Hayashi, A.; Tatsumisago, M.: 'Preparation and characterization of superionic conducting $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal from glassy liquids'. *J. Ceram. Soc. Jpn.* 2010, 118, (1376), pp 305-308
- [18] Lian, P.-J.; Zhao, B.-S.; Zhang, L.-Q.; et al.: 'Inorganic sulfide solid electrolytes for all-solid-state lithium secondary batteries'. *J. Mater. Chem. A* 2019, 7, (36), pp 20540-20557
- [19] Weber, D. A.; Senyshyn, A.; Weldert, K. S.; et al.: 'Structural insights and 3D diffusion pathways within the lithium superionic conductor $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ '. *Chem. Mater.* 2016, 28, (16), pp 5905-5915

- [20] Richards, W. D.; Miara, L. J.; Wang, Y.; et al.: 'Interface stability in solid-state batteries'. *Chem. Mater.* 2016, 28, (1), pp 266-273
- [21] Bachman, J. C.; Muy, S.; Grimaud, A.; Chang, H.-H.; Pour, N.; Lux, S. F.; Paschos, O.; Maglia, F.; Lupart, S.; Lamp, P.; Giordano, L.; Shao-Horn, Y.: "Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction". *Chemical Reviews* 2016, 116, (1), pp. 140–162.
- [22] Seino, Y.; Ota, T.; Takada, K.; et al.: 'A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries'. *Energy Environ. Sci.* 2014, 7, (2), pp 627-631
- [23] Zhang, Q.; Cao, D.; Ma, Y.; et al.: 'Sulfide-Based Solid-State Electrolytes: Synthesis, Stability, and Potential for All-Solid-State Batteries'. *Adv. Mater.* 2019, 31, (44), pp 1901131
- [24] Ahmad, N.; Zhou, L.; Faheem, M.; et al.: 'Enhanced air stability and high Li-ion conductivity of $\text{Li}_{6.988}\text{P}_{2.994}\text{Nb}_{0.2}\text{S}_{10.934}\text{O}_{0.6}$ glass–ceramic electrolyte for all-solid-state lithium–sulfur batteries'. *ACS Appl. Mater. Interfaces* 2020, 12, (19), pp 21548-21558
- [25] Liu, B.; Fang, C.: 'From Mechanism to Metrics: Quantitative Insights into Moisture Stability of Solid-State Electrolytes'. *ACS Energy Lett.* 2026, pp
- [26] Li, J.; Li, Y.; Liu, T.; et al.: 'Self-Limiting Reaction of Solid Electrolyte Empowering Ultralong Lifespan All-Solid-State Lithium Metal Batteries with $\text{Li}_6\text{PS}_5\text{Cl}$ -Based Electrolyte Membrane'. *Adv. Funct. Mater.* 2025, pp 2504546
- [27] Xiao, Y.; Wang, Y.; Bo, S.H. et al.: "Understanding interface stability in solid-state batteries". *Nat Rev Mater* 2020, 5, pp. 105–126.
- [28] Koerver, R.; Aygün, I.; Leichtweiß, T.; et al.: 'Capacity Fade in Solid-State Batteries: Interphase Formation and Chemomechanical Processes in Nickel-Rich Layered Oxide Cathodes and Lithium Thiophosphate Solid Electrolytes'. *Chem. Mater.* 2017, 29, (13), pp 5574-5582
- [29] Han, F.; Westover, A. S.; Yue, J.; et al.: 'High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes'. *Nat. Energy* 2019, 4, (3), pp 187-196
- [30] Ohta, N.; Takada, K.; Sakaguchi, I.; et al.: 'LiNbO₃-coated LiCoO₂ as cathode material for all solid-state lithium secondary batteries'. *Electrochem. Commun.* 2007, 9, (7), pp 1486-1490
- [31] Richards, W. D.; Miara, L. J.; Wang, Y.; et al.: 'Interface Stability in Solid-State Batteries'. *Chemistry of Materials* 2016, 28, (1), pp 266-273
- [32] Sendek, A. D.; Yang, Q.; Cubuk, E. D.; et al.: 'Holistic computational structure screening of more than 12 000 candidates for solid lithium-ion conductor materials'. *Energy Environ. Sci.* 2017, 10, (1), pp 306-320