

Review

Advances in All-Solid-State Batteries Based on Chloride Solid Electrolytes

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Abstract

Driven by the imperative for enhanced battery safety, solid electrolytes have emerged as a leading strategy in next-generation energy storage technologies. Beyond conventional polymer, oxide, and sulfide systems, chloride-based inorganic solid electrolytes have recently garnered significant attention due to their unique combination of high ionic conductivity, favorable electrochemical stability, and processability. This work presents a comprehensive review of chloride solid electrolytes, examining their crystal structures, synthesis approaches, ionic transport mechanisms, and physicochemical stability under operational conditions. Furthermore, we discuss critical considerations for integrating these materials into practical all-solid-state batteries (ASSBs), including performance across wide temperature ranges, scalable cell fabrication methods, and cost-effectiveness. By bridging fundamental material properties with device-level engineering challenges, this review aims to provide a roadmap for future research and development, highlighting the substantial promise of chloride electrolytes in enabling safe, high-performance solid-state batteries.

Keywords: all-solid-state batteries; solid electrolytes; chloride; crystalline; amorphous; synthesis; performance; theoretical prediction

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1. Introduction

The evolution of electrochemical energy storage technologies has been profoundly shaped by the development of secondary batteries, particularly Li-ion batteries (LIBs) and Na-ion batteries (NIBs). These systems now underpin applications ranging from portable electronics to electric vehicles and grid-scale storage [1,2]. However, conventional liquid electrolytes remain a critical bottleneck due to their flammability, volatility, and limited electrochemical stability. This has catalyzed intense interest in ASSBs, which promise enhanced safety, higher energy density, and improved thermal resilience [3,4]. At the heart of ASSB performance lies the solid electrolyte, a material that must simultaneously deliver high room-temperature ionic conductivity ($>1 \text{ mS}\cdot\text{cm}^{-1}$) [5], a wide electrochemical stability window (2–4.5 V vs. Li^+/Li or Na^+/Na) [6], chemical and mechanical compatibility with

electrodes to ensure good interfaces and suppress parasitic side reactions, and suitability for scalable manufacturing [7–13]. Historically, SE research has primarily focused on sulfides [14–16], oxides [17–19], and polymers [20–22]. Sulfide electrolytes boast exceptional ionic conductivities ($>10 \text{ mS}\cdot\text{cm}^{-1}$) but suffer from narrow electrochemical windows and poor air stability, necessitating stringent handling protocols. Oxide-based electrolytes are renowned for their chemical and thermal stability but require high-temperature sintering ($>1000^\circ\text{C}$), complicating interfacial contact and large-scale processing. Polymer electrolytes offer mechanical flexibility and ease of fabrication yet are limited by low ambient-temperature conductivity and insufficient oxidative stability for high-voltage cathodes [23–25]. Composite strategies aim to synergize these advantages but often face challenges with inhomogeneous ion transport and complex integration. Borohydride SEs feature a good electrochemical window, enabling direct matching with both cathode and anode materials. Furthermore, they exhibit a low Young's modulus that allows for cold pressing forming and hold considerable development potential. However, their commercialization is hindered by the high cost of raw materials and the complexity of preparation processes [26–28]. In contrast, halide-based SEs, particularly chlorides, have recently attracted renewed attention due to their unique combination of ionic transport properties, electrochemical resilience, and processability. As highlighted by X. Sun et al. [29], T. Asano et al. [30], and S. Wang et al. [31], halides exhibit intrinsically fast lithium-ion transport kinetics, attributed to their relatively long ionic bond lengths, which lower migration barriers and enhance ion mobility. This structural feature also imparts notable deformability, facilitating better interfacial contact without requiring high external pressure. Furthermore, halide anions (especially F^- and Cl^-) possess high electronegativity and strong bonding with metal cations, resulting in elevated oxidation potentials and wider electrochemical stability windows compared to sulfides. Notably, certain chloride electrolytes can be synthesized via scalable wet-chemical routes, offering practical pathways toward industrial deployment [32,33]. Recent advances have demonstrated improved tolerance to ambient air and moisture, addressing longstanding concerns for SEs [34]. Most significantly, several chloride systems now enable stable cycling in ASSBs using bare lithium metal anodes and uncoated high-voltage cathodes, eliminating the need for interfacial coating or protective layers [35]. Halide SEs encompass fluorides [36,37], chlorides [38,39], bromides [40,41], and iodides [42,43], corresponding to the four halogen anions (F^- , Cl^- , Br^- , and I^-). However, not all are equally viable for battery applications. Their suitability is governed by anion-dependent trade-offs: oxidation stability decreases in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ [29,44]. Fluorides exhibit the highest oxidative stability, often exceeding 6 V versus Li^+/Li , but typically suffer from low room-temperature ionic conductivity due to strong ionic bonding and rigid lattices. Bromides and iodides, while more conductive, display limited oxidative stability ($<3 \text{ V}$), restricting their use with conventional high-voltage cathodes. Chlorides strike a compelling balance: they offer moderate-to-high ionic conductivity (ranging from 1 to $>10 \text{ mS}\cdot\text{cm}^{-1}$), an electrochemical window extending up to $\sim 4 \text{ V}$ [31,45], good mechanical compliance, and emerging compatibility with scalable synthesis. These attributes position chlorides as the most promising subclass among halide SEs for next-generation ASSBs [46–48].

The scientific journey of crystalline chloride SSEs spans nearly a century in Figure 1. Early studies by T.E. Phipps [49,50] and colleagues in the 1920s investigated molten NaCl and LiCl , noting ionic conductivities as low as $10^{-7} \text{ S}\cdot\text{cm}^{-1}$ [51], insufficient for practical use but foundational in understanding ion mobility. A pivotal leap came in the 1950s when Y. Haven demonstrated that doping LiCl with MgCl_2 could enhance Li^+ conduction via vacancy creation, establishing defect engineering as a core design principle [52]. Progress accelerated in the late 1970s and 1980s, when W. Weppner reported LiAlCl_4 with a conductivity of $\sim 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ [53,54], and Ryoji Kanno introduced the spinel-type family, Li_2

$2x\text{M}_{1+x}\text{Cl}_4$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Cd}$) [55]. Among these, $\text{Li}_{1.52}\text{Mn}_{1.24}\text{Cl}_4$ exhibited a conductivity of $\sim 1.5 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ but suffered from a low decomposition voltage (1.1–1.3 V vs. Li^+/Li). D. L. Heinz's work revealed that tetrahedrally coordinated Li^+ ions exhibit higher mobility than octahedrally coordinated ones, a key insight into structure–conductivity relationships [56]. The 1990s brought deeper structural understanding through B. Andreas's systematic study of Li_3MCl_6 compounds ($\text{M} = \text{Y}, \text{Sc}$, and lanthanides), uncovering distinct crystal symmetries (e.g., trigonal $\text{P}\bar{3}\text{m1}$ and orthorhombic Pnma) linked to varying Li^+ mobility. Despite these advances, limited stability and modest conductivity stalled progress until a transformative resurgence began in 2018. T. Asano reported Li_3YCl_6 and Li_3YBr_6 , achieving ionic conductivities of $5.1 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ and $1.7 \text{ mS}\cdot\text{cm}^{-1}$, respectively, and demonstrated their ability to support cycling with uncoated LiCoO_2 cathodes [30]. This breakthrough reignited global interest in chloride SEs, and a diverse family of chlorides rapidly emerged, including Li_3ErCl_6 [39], Li_3HoCl_6 [57], Li_3InCl_6 [32], Li_2ZrCl_6 [34], $\text{Li}_{3-x}\text{M}_{1-x}\text{Zr}_x\text{Cl}_6$ ($\text{M} = \text{Y}, \text{Er}$) [58], $\text{Li}_{1.9}\text{OHCl}_{0.9}$ [59], $\text{LiNbOCl}_4/\text{LiTaOCl}_4$ (LNOC/LTOC) [60], $\text{Li}_x\text{ScCl}_{3+x}$ [38], and even sodium analogues like $\text{Na}_{2.25}\text{Y}_{0.25}\text{Zr}_{0.75}\text{Cl}_6$ [61].

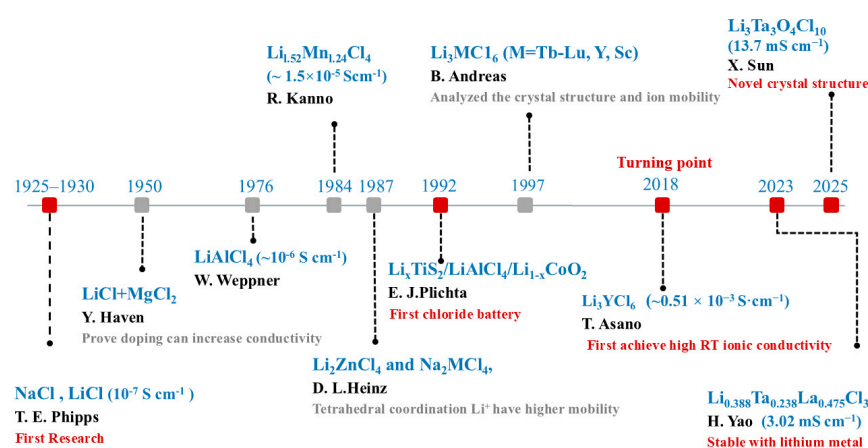


Figure 1. Timeline of crystalline chloride solid electrolyte development [30,35,49–56,62–66].

These studies explored chlorides from multiple angles: scalable synthesis, humidity tolerance (e.g., water-mediated route to Li_3InCl_6 , achieving $2.04 \text{ mS}\cdot\text{cm}^{-1}$) [32], and structural innovation [65]. In 2023 H. Yao's discovery of $\text{Li}_{0.388}\text{Ta}_{0.238}\text{La}_{0.475}\text{Cl}_3$ reached $3.02 \text{ mS}\cdot\text{cm}^{-1}$ at 25°C and enabling stable cycling with bare lithium metal for over 5000 h, marking the first chloride SSE to operate without interfacial modification against both Li metal and high-voltage cathodes (e.g., NCM523 up to 4.35 V) [35]. Most recently, X. Sun's group reported $\text{Li}_3\text{Ta}_3\text{O}_4\text{Cl}_{10}$, achieving an extraordinary $13.7 \text{ mS}\cdot\text{cm}^{-1}$ and functioning down to -50°C with a 4.9 V stability window, demonstrating how strategic oxygen incorporation can simultaneously boost conductivity and robustness [66]. Collectively, crystalline chlorides have evolved from simple binary salts into sophisticated multi-cation architectures engineered for high performance and interfacial harmony. Parallel to advances in crystalline halides, amorphous chloride SEs have emerged as a revolutionary frontier, particularly for Na-ion systems, where crystalline chlorides have long suffered from intrinsically low ionic conductivity ($\sim 10^{-5} \text{ S}\cdot\text{cm}^{-1}$) due to the large ionic radius of Na^+ and mismatched diffusion pathways in rigid lattices [67]. In contrast, the absence of long-range order in amorphous networks eliminates directional bottlenecks, enabling isotropic ion diffusion, lower migration barriers, and exceptional compositional flexibility, all critically advantageous for accommodating sluggish Na^+ transport. This paradigm shift began in earnest only recently, as early glass science focused almost exclusively on oxides and sulfides [68,69]; chlorides were historically dismissed as poor glass formers due to chlorine's low electronegativity and inability to sustain a continuous random network alone. Initial

studies treated Cl^- merely as a dopant in oxide or sulfide glasses, while fluoride-based halide glasses remained the sole focus among true halide glasses [70–72]. The first breakthrough in inorganic amorphous chloride electrolytes came not with sodium, but with lithium. In a landmark study, Yoshitaka's team [73] demonstrated that TaCl_5 could be readily vitrified when combined with common lithium salts, including LiF , LiCl , LiBr , LiI , Li_2O , LiOH , Li_2O_2 and Li_2S . The resulting materials showed no discernible crystalline peaks in X-ray diffraction (XRD), confirming their fully amorphous nature, and delivered remarkably high room-temperature ionic conductivities of $4\text{--}10\text{ mS}\cdot\text{cm}^{-1}$. Full cells assembled with these glassy chlorides operated stably at 4.3 V and sustained high-rate cycling at 2C, providing the first compelling proof of concept for inorganic glassy chloride SEs. Building on this foundation, the field rapidly expanded in the same year through nearly simultaneous reports from Sun, Yao and Ma on novel lithium-ion amorphous chloride systems [74–76]. Ma's group introduced LiZrClO , which existed predominantly in a highly amorphous state with only trace crystallinity, while Sun's team achieved a completely amorphous structure by using Li_2O as a network modifier, where bridging oxygen atoms linked Ta-Cl polyhedra, creating a percolating framework rich in mobile Li^+ sites. Both systems exhibited ionic conductivities well above $1\text{ mS}\cdot\text{cm}^{-1}$, igniting widespread interest in amorphous chlorides as viable SSEs [77]. This momentum soon extended to sodium systems.

A pivotal breakthrough came in 2023 when Y. Hu's team unveiled viscoelastic inorganic glass (VIGLAS), the first amorphous sodium ion chloride-based solid electrolyte to simultaneously combine high ionic conductivity (up to $1.33\text{ mS}\cdot\text{cm}^{-1}$ at room temperature) with polymer-like viscoelasticity [78]. This unique duality bridges the gap between rigid ceramic SSEs and soft polymers: VIGLAS enables pressure-free cell assembly and features intrinsic self-healing, enabling performance recovery through mild thermal annealing. By demonstrating stable, high-voltage operation without interfacial engineering, VIGLAS shattered the long-standing assumption that sodium ion chlorides are inherently unsuitable for practical ASSBs, marking the dawn of a new era in halide-based amorphous electrolyte design. The field rapidly accelerated thereafter.

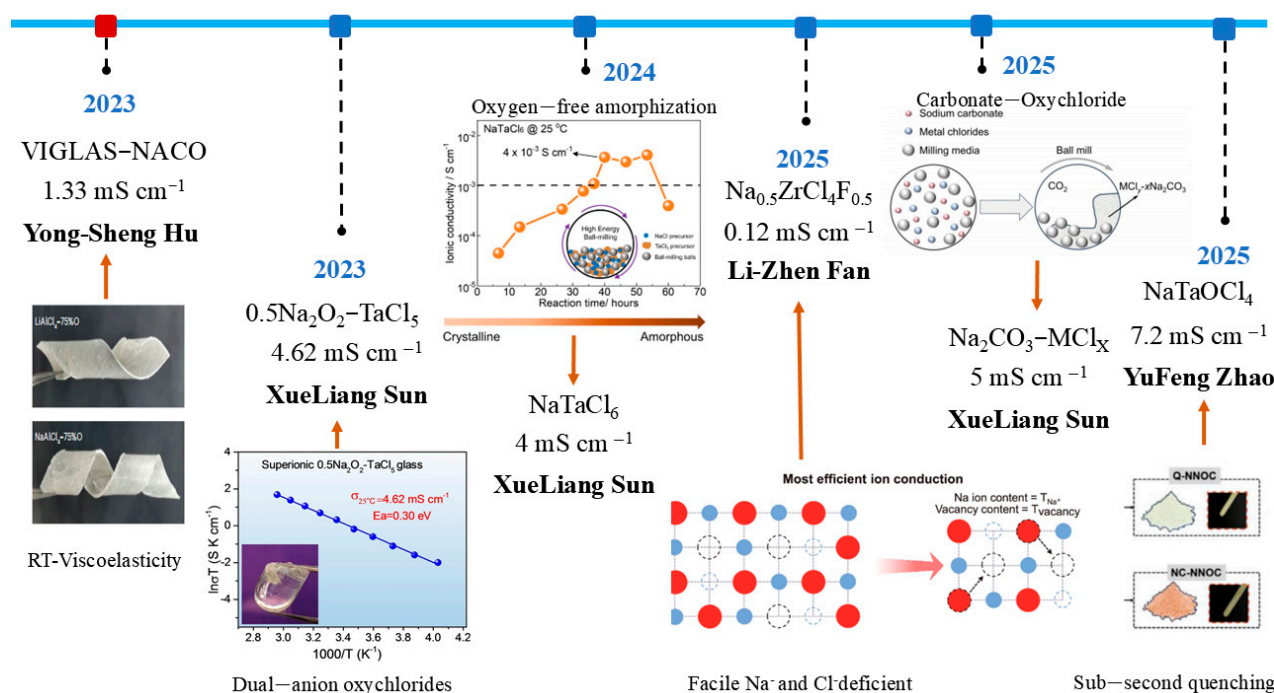


Figure 2. Recent progress in amorphous sodium ion chloride SEs [78–83].

X. Sun's group pioneered a series of TaCl₅-based amorphous sodium ion chlorides, demonstrating that strategic incorporation of oxygen-containing precursors could stabilize glassy networks while boosting conductivity [75,80]. Their 0.5Na₂O₂-TaCl₅ system reached 4.62 mS·cm⁻¹, and NaTaCl₆ achieved ~4 mS·cm⁻¹, with both confirmed fully amorphous by XRD. Here, oxygen from Na₂O₂ acted as a network former, bridging Ta-Cl polyhedra to create a percolating Li⁺/Na⁺ conduction pathway, analogous to how O²⁻ stabilizes silicate or borate glasses. Further innovations included Na₂CO₃-TaCl₅ and related carbonate-chloride hybrids, where CO₃²⁻ induced structural disorder, pushing conductivities up to 5 mS·cm⁻¹ [81]. Meanwhile, L. Fan's team explored mixed-anion design, introducing Na_{0.5}ZrCl₄F_{0.5}, which leveraged the high oxidative stability of F⁻ and high mobility of Cl⁻ to achieve 1.2 × 10⁻⁴ S·cm⁻¹—a modest but conceptually significant step toward anion engineering in amorphous chlorides [82]. The current pinnacle was reached in early 2025 with Y. Zhao's report of NaTaOCl₄, a predominantly amorphous oxychloride delivering an extraordinary 7.2 mS·cm⁻¹ at 25 °C [83]. (Figure 2) Its success stems from oxygen-modulated lattice flexibility, which simultaneously enhances Na⁺ site connectivity, suppresses crystallization, and improves interfacial compatibility with high-voltage cathodes. Collectively, these advances mark a transformative shift: once overlooked, amorphous sodium ion chlorides are now at the forefront of solid electrolyte innovation, proving that with intelligent structural design, even “disfavored” ion-anion combinations can be re-engineered into high-performance materials. This evolution from crystalline limitations to amorphous liberation underscores a new design philosophy for next-generation ASSBs [84].

In this review, we focus on the application and performance of chloride-based materials in ASSBs. The discussion is organized into five key areas: (1) structural classifications of chloride SEs; (2) the impact of synthesis and preparation methods on their physico-chemical properties; (3) a comprehensive analysis of their ionic conductivity and electrochemical stability window; (4) interfacial compatibility with cathode and anode materials; and (5) recent advances in chloride-based ASSBs architectures. Finally, we critically examine the current challenges facing chloride SEs and ASSBs and offer perspectives on future research directions and development opportunities.

2. The Typical Classification of Chloride (Li, Na) Structures: Structure and Ion Transport Mechanism

2.1. Common A_{3-x}MCl₆ (x=0, 1) Type [MCl₆]^{y-}

Currently, the chloride composition that has been most extensively studied is generally the A_{3-x}MCl₆ (x=0, 1) type. The most typical chloride solid electrolyte of this type is Li₃YCl₆; due to its breakthrough progress in 2018, it has sparked the wave of research on chlorides today. Usually, it can be observed that the main structures can be divided into three categories: trigonal [31,39], orthorhombic [85], and monoclinic [32,86]. Li₃YCl₆ belongs to a trigonal system (space group P $\bar{3}$ m1) [30]; it displays a 3D Li⁺ diffusion channel with a preferred 1D path on the c-axis through a shared octahedron (Figure 3), based on a hexagonal close-packed (hcp) anion framework, where Li⁺ ions, metal ions, and vacancies occupy octahedral sites [87]. Furthermore, the conduction mechanism of Li₃YCl₆ is along the tetrahedral interstitial sites on the a-b plane (Figure 3) or directly connect adjacent octahedral positions along the c-axis direction.

For this classical LiMX₆ system, recently, Chen et al. [88] discovered the superior phase transition mechanism triggered by the collective motion of anions in Li₃YCl₆: the “swing motion” of Cl octahedron restricts the one-dimensional diffusion of lithium ions at low temperature and changes to “breathing motion” at high temperature. The octahedron expands along the c-axis to open the ab-plane two-dimensional channel so that the

conductivity increases. Based on this, $\text{Li}_3\text{YCl}_{4.5}\text{Br}_{1.5}$ and $\text{Li}_3\text{GdCl}_3\text{Br}_3$ were designed by Br doping to regulate anion dynamics. Their conductivity reached $6.1 \text{ mS}\cdot\text{cm}^{-1}$ and $11 \text{ mS}\cdot\text{cm}^{-1}$, respectively.

For sodium ion chloride SEs, there are notable structural differences compared to their Li^+ counterparts. For instance, while Li_2ZrCl_6 (LZC) exists in two distinct phases, an α -phase with a trigonal crystal system and a β -phase with a monoclinic crystal system (Figure 4), Na_2ZrCl_6 (NZC) exhibits only a single phase, which crystallizes in the trigonal system [45].

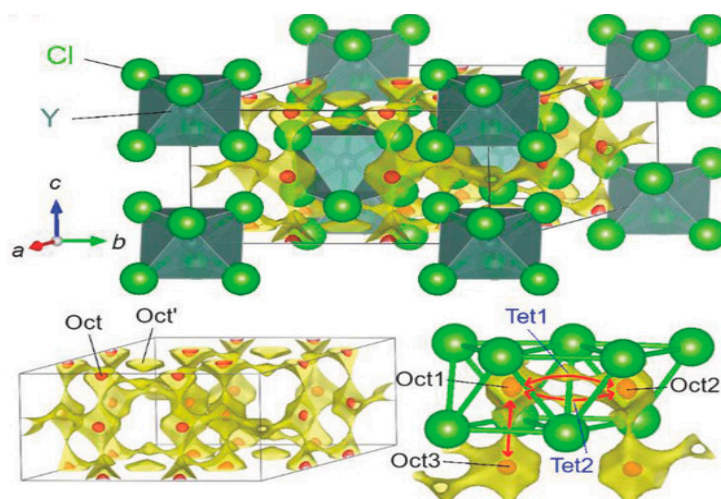


Figure 3. The crystal structures and a calculated BVSE-based lithium-ion potential map of Li_3YCl_6 . Oct means octahedron, Tet means tetrahedron. The arrow refers to the direction of atom movement. Copyright 2018, Wiley-VCH [30].

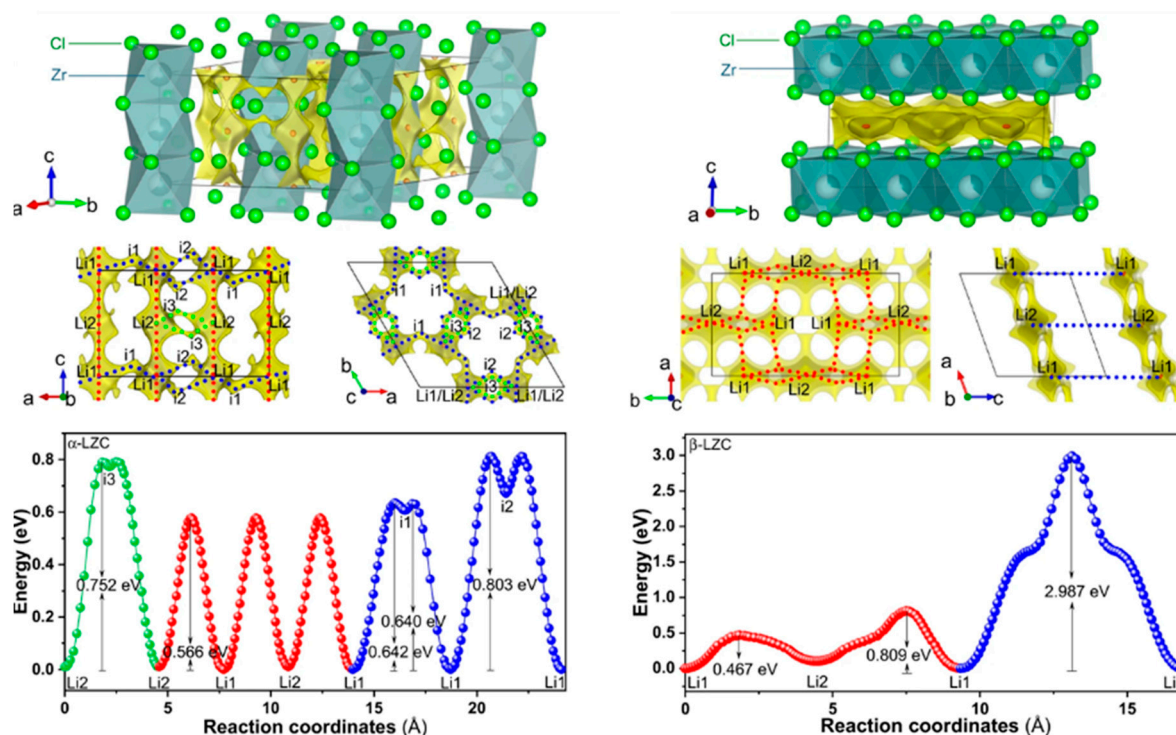


Figure 4. Crystal structures, superimposed with a Li^+ potential map, Li -ion migration pathways, and energy profiles of the migration pathways of α - (Left) and β - (Right) Li_2ZrCl_6 . The energy profiles of different colors in each main figure correspond to the reaction pathways of the same color in the subfigures above them, respectively. Reproduced with permission from ref. [34]. Copyright 2021, Nature Communications.

As for NZC, the migration mechanism of Na^+ ions varies depending on the crystallographic z position ($z = 0$ and 0.5) [89]. In contrast, LZC exists in two polymorphic phases, α -LZC and β -LZC, each exhibiting distinct Li^+ migration characteristics. In α -LZC, the most favorable 1D conduction channel follows the $[\text{Li}_1\text{--Li}_2\text{--Li}_1]$ chain along the $[001]$ direction. Moreover, Li^+ ions can also bridge multiple pathways, including the $[\text{Li}_1\text{--i}_1\text{--Li}_1\text{--i}_2\text{--Li}_1]$, $[\text{Li}_2\text{--i}_3\text{--Li}_2]$ and $[\text{Li}_1\text{--Li}_2\text{--Li}_1]$ chains, to form a three-dimensional (3D) percolating network, enabling efficient ion transport with a low activation barrier of 0.803 eV. By comparison, β -LZC favors Li^+ diffusion primarily within the ab plane, with a migration barrier of 0.809 eV. However, interlayer hopping between adjacent ab planes is significantly hindered by a much higher energy barrier of 2.987 eV (Figure 4) [34], effectively restricting ion transport to two dimensions.

2.2. Anti-Perovskite Type $\text{Cl-B}^2\text{-X}^+$

The study of perovskite materials dates to 1839. In the conventional perovskite structure with the general formula ABX_3 , the X site is occupied by anions (typically oxygen or halides), while the A and B sites are occupied by cations [90]. In contrast, anti-perovskites feature an inverted arrangement: the A and B sites are occupied by anions, and the X site is occupied by cations (Figure 5). Depending on variations in pressure, temperature, and chemical composition, anti-perovskites can adopt various distorted crystal symmetries, most commonly orthorhombic, rhombohedral, tetragonal, or hexagonal phases. However, their ideal, undistorted structure corresponds to the cubic $\text{Pm}\bar{3}\text{m}$ [91]. Li_3OCl and Na_3OCl have the same structure (cubic, $\text{Pm}\bar{3}\text{m}$); however, there are significant differences in ion conduction pathways. Analysis of the simulation results indicates that the nearest Li^+ hop occurred at the edge of the Li_6O octahedron on the (011) plane [92]. Furthermore, Zhao et al. believe that lithium-rich anti-perovskite is a “lithium swamp” that requires “grooves” to channel rapid ion transport. The combination of chemical, electronic, and structural manipulation means the formation of three-dimensional (3D) “channels” that allow for simple Li^+ jumps and transport [93]. As for Na_3OCl , Na^+ with a larger radius (Na^+ : 102 pm versus Li^+ : 76 pm) is beneficial for stabilizing the anti-perovskite structure due to the tolerance factor $t = (r_a + r_x)/[\sqrt{2}(r_b + r_x)]$. Wang et al. found that when a certain vacancy concentration is present, there will be two possible diffusion paths along the $[101]$ and $[001]$ directions [94].

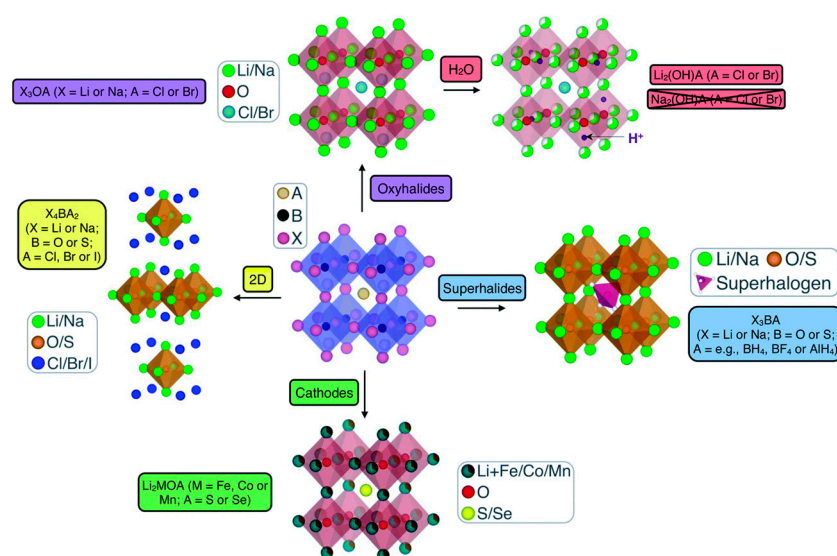


Figure 5. Anti-perovskite structure conversion diagram, reproduced with permission from ref. [90]. Copyright 2021, Royal Society of Chemistry.

2.3. New Zeolite-like Structure $A_xM_yN_zCl_3$: $[SmCl_9]^{6-}$

Lithium (76 pm), indium (80 pm), zirconium (72 pm), and yttrium (90 pm) possess small and similar ionic radii, enabling them to readily form $[MCl_6]^{x-}$ octahedra that pack in either ccp or hcp arrangements. However, as the ionic radius of the metal cation increases—specifically for larger rare-earth elements such as La through Sm—the coordination environment shifts from sixfold to eight- or ninefold coordination (Figure 6a). For instance, $SmCl_3$ adopts a UCl_3 -type structure (space group $P6_3/m$), in which each Sm^{3+} ion is coordinated by nine Cl^- ions, forming a $[SmCl_9]^{6-}$ trigonal prismatic unit. This structure features one-dimensional (1D) vacant channels along the c -axis. These channels, with pore dimensions comparable to those of zeolites, provide a potential framework for rapid ion diffusion [95]. In this architecture, Li^+ migration requires passage through a shared triangular bottleneck before hopping between adjacent distorted octahedral sites. The 1D hexagonal tunnels exhibit an inner diameter of 4.52 Å, with a short distance of only 2.08 Å between neighboring cation vacancies (Figure 6b). Building on this structural motif, Yao et al. [32] recently developed a novel chloride solid electrolyte, $Li_{0.388}Ta_{0.238}La_{0.475}Cl_3$, based on the UCl_3 -type $LaCl_3$ lattice ($P6_3/m$). In this material, Ta^{5+} doping introduces La^{3+} vacancies that interconnect the intrinsic 1D channels, thereby constructing a three-dimensional (3D) Li^+ conduction network. Li^+ ions diffuse rapidly through closely spaced sites within the 1D tunnel. The Li^+ probability density map shows anomalous features, indicating that some Li^+ positions are disordered or dynamically distributed rather than fixed. Computational analysis reveals two distinct migration pathways for lithium ions: the blue path, which represents inter-channel hopping via La vacancies in the ab plane, and the red path, corresponding to intra-channel diffusion along the c -axis. The red path exhibits a significantly lower energy barrier for Li^+ migration (0.09 eV) compared to the blue path (0.31 eV).

A series of studies on UCl_3 -type halide solid electrolytes have been published since then. Related studies on the structure of UCl_3 reveal universal design principles for optimizing ion diffusion channels by regulating anion frameworks, which provide important guidance for the development of new SEs in the future. Yao et al. [94] proposed a non-densely packed anion framework represented by the UCl_3 type. Its highly distorted sites increase the energy of stable sites, and the wide channel reduces electrostatic repulsion, which reduces the Li/Na/K migration energy barrier. The experimental verification of Li- UCl_3 -type materials has a high ionic conductivity. Based on the classic LLTC electrolyte, Xu et al. [96] proposed the non-dense pile UCl_3 -type crystalline oxychloride solid electrolyte $Li_{0.388+x}La_{0.475}Ta_{0.238}Cl_{3-x}O_x$. Its 9-coordination framework endows a high oxygen doping degree; when $x = 0.388$, oxygen accounts for 12.9% and remains crystalline. Oxygen atoms preferentially replace Cl around Ta to form Ta-O bonds, compress polyhedra, and expand Li^+ transport channels. The optimized composition $x = 0.15$ has an ionic conductivity of $2.05 \text{ mS}\cdot\text{cm}^{-1}$ at 30 °C, oxidation stability of >5 V, and mechanical density of >93%. The Li_2O layer formed at the interface provides an excellent dendrite suppression ability and a stable Li|SE|Li symmetric battery with a 4000 h cycle. The reversible capacity of ASSBs (NCM811 cathode) based on this electrolyte is increased to $206.4 \text{ mAh}\cdot\text{g}^{-1}$, and soft pack batteries achieve a 71.49 mAh discharge capacity.

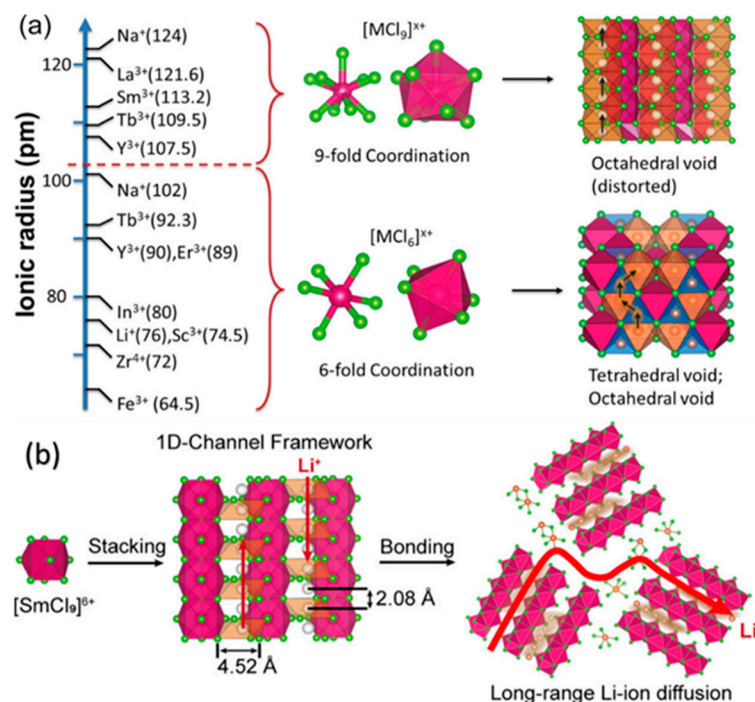


Figure 6. (a) Relationship between the ionic radius of M and the coordination of $[MCl_x]$ polyhedra. (b) Schematic diagram of 1D channel framework composed of $[SmCl_9]^{6+}$ and long-range ion diffusion. Reproduced with permission from ref. The arrow refers to the movement of Li^+ [96]. Copyright 2023, American Chemical Society.

2.4. Superchloride A_aMX_b Type ($a \geq 0$, $b \geq 14$)

“Superchloride” typically refers to lithium–chlorine compounds that no longer meet the general composition rules, and such materials are relatively rare. Representative examples include $LiNb_6Cl_{19}$ (orthorhombic, space group $Pmma$) [97], and Ta_6Cl_{15} (cubic, space group $Ia\bar{3}$) [98]. Among these, $LiNb_6Cl_{19}$ (LNC) adopts a two-dimensional layered structure; along the [100] direction, it consists of stacked LNC sheets in which $LiCl_6$ octahedra share edges with four $NbCl_6$ octahedra belonging exclusively to the first type of Nb^{3+} site. Two crystallographically distinct Nb^{3+} sites exist: the first forms $NbCl_6$ octahedra that share edges with one $LiCl_6$ and three neighboring $NbCl_6$ octahedra, while the second favors a mixed connectivity involving both edge- and face-sharing with adjacent $NbCl_6$ units. The Nb–Cl bond lengths range from 2.40 to 2.61 Å. The parallel arrangement of infinite $[Nb_6Cl_{18}]^n$ ladder-like motifs generates a quasi-one-dimensional framework, within which Li^+ ions occupy linearly aligned voids (Figure 7a). As for Ta_6Cl_{15} , it contains sufficient channels to support ion transportation. (Figure 7b).

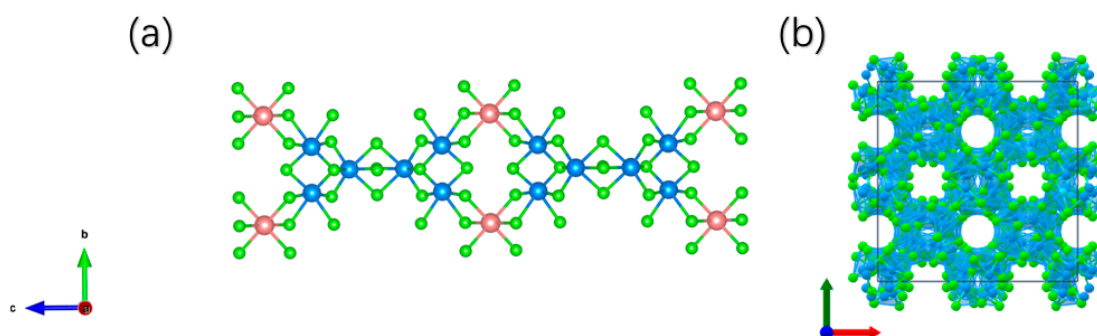


Figure 7. (a) Structure diagram of $LiNb_6Cl_{19}$. The red ball represents Li; The blue ball represents Nb; The green ball represents Cl [97]; (b) structure diagram of Ta_6Cl_{15} . The blue ball represents Ta; The green ball represents Cl [98].

2.5. Amorphous Structure

Amorphous chloride is a recently discovered type of special chloride, named for its lack of a specific structural composition, like glass, for example, MACO ($M = \text{Li/Na}$), reported by the Hu [78] group, which precursor MAlCl_4 ($M = \text{Li/Na}$) exhibits clear crystalline peaks. Oxygen is introduced via a substitution reaction, where Sb_2O_3 displaces the chlorine anions in MAlCl_4 ; it gradually becomes amorphous, leaving only excess NaCl crystalline peaks; and the main phase completely transforms into an amorphous state. The characteristics of amorphous materials are short-range order and long-range disorder (short-range order means that a crystal-like ordered structure is exhibited over a nanoscale region, whereas long-range disorder indicates the absence of structural regularity at the microscale). Similarly, the inorganic amorphous chloride materials prepared by the teams of Sun, Yao, Ma [73–75,77], and others follow the same pattern. Therefore, it is necessary to use *ab initio* molecular dynamics (AIMD) calculations to simulate possible structural distributions for analysis. From the graph, it can be observed that the formation of an amorphous structure is maintained by the introduction of oxygen (Figure 8). The formation of Al-O-Al constitutes the entire inorganic amorphous network, while other forms, such as non-bridging oxygen (the oxygen atom is bonded to only a single atom), also exist in the system. Chlorine alone tends to coordinate with individual aluminum elements and does not contribute to network formation. Therefore, the appropriate oxygen-to-chlorine ratio can adjust the size of the network, while the AlCl_3 groups that do not participate in network construction reduce the glass transition temperature (T_g). Through other characterizations, it is found that bridging oxygen (the oxygen atom is bonded to two atoms like Al-O-Al) shortens the distance between two lithium ions, thereby reducing the ion migration distance. This theory provides excellent guidance for the research on amorphous oxygen halides.

Recently, many studies on halide SEs with amorphous structures have emerged, and strategies for inducing amorphous structure formation by doping fluorine, oxygen, sulfur, nitrogen, etc., have been proposed. By merely adjusting the ratios of sodium ions and various transition metals, the amorphization of the AMX_6 ($A = \text{Li, Na}$)-type halide can be achieved. Meng et al. [99] regulated $\text{Na}_{2.25-x}\text{Y}_{0.25}\text{Zr}_{0.75}\text{Cl}_{6-x}$ ($1.375 \leq x \leq 2.0$), combined with mechanical ball milling; a nanocrystalline-to-amorphous electrolyte was successfully prepared. A decrease in NaCl can induce grain refinement and amorphization, promote Na^+ to occupy prismatic sites preferentially, accelerate inter-site exchange, and significantly reduce the activation energy of ion migration. $\text{Na}_{0.625}\text{Y}_{0.25}\text{Zr}_{0.75}\text{Cl}_{4.375}$ ($x = 1.625$) has room-temperature conductivity of up to $4.0 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which is one order of magnitude higher than that of traditional crystal electrolyte. When the material is matched with a NaCrO_2 cathode, the reversible capacity reaches $97 \text{ mAh}\cdot\text{g}^{-1}$ at a 1C rate, and the capacity retention rate exceeds 78% after 500 cycles. Additionally, Xia et al. [100] proposed an innovative strategy based on Zr doping to induce complete amorphization. By introducing Zr with a larger radius into NaTaCl_6 , an amorphous $\text{Na}_{1.33}\text{Ta}_{0.67}\text{Zr}_{0.33}\text{Cl}_6$ (NTZC) electrolyte was successfully synthesized. This structural transformation not only eliminated high-resistance grain boundaries but also significantly broadened sodium ion transport channels through lattice expansion and distortion of $[\text{TaCl}_6]^-$ octahedra, increasing the room temperature ionic conductivity to $3.4 \text{ mS}\cdot\text{cm}^{-1}$. At the same time, the amorphous material exhibits excellent mechanical flexibility, ensuring a dense and stable interface contact with the cathode. Thanks to this, ASSBs using NTZC electrolytes can be used at high loads ($20.85 \text{ mg}\cdot\text{cm}^{-2}$) and maintain 77.45% capacity after 450 cycles at 0.5C, far exceeding the undoped crystal control group. This work highlights the great potential for the synergistic optimization of ion transport and interface stability through controlled amorphization engineering. Similarly, Fan et al. [101] synthesized $\text{A}_{2-x}\text{M}_{1-x}\text{Ta}_x\text{Cl}_6$ using a mechanochemical method ($A = \text{Li/Na}$, $M = \text{Zr/Hf}$) system; Ta doping induces lattice distortion and forms a

completely amorphous structure at $x = 0.6$. Synchrotron radiation X-ray absorption spectroscopy (XAS) and AIMD simulations reveal that the octahedral distortion of $[\text{TaCl}_6]^-$ shortens the Ta-Cl bond, expanding the Na transport channel; cation disorder eliminates grain boundary resistance and reduces activation energy. Optimized composition $\text{Na}_{1.4}\text{Zr}_{0.4}\text{Ta}_{0.6}\text{Cl}_6$ achieves room-temperature conductivity of $1.95 \text{ mS}\cdot\text{cm}^{-1}$, two orders of magnitude higher than crystalline standard, and has oxidation stability $> 4 \text{ V}$. In an ASSBs, the electrolyte matches with a $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode, and the capacity retention rate of 1000 cycles at 0.5C is 86%, which verifies that the amorphous structure improved the interface stability.

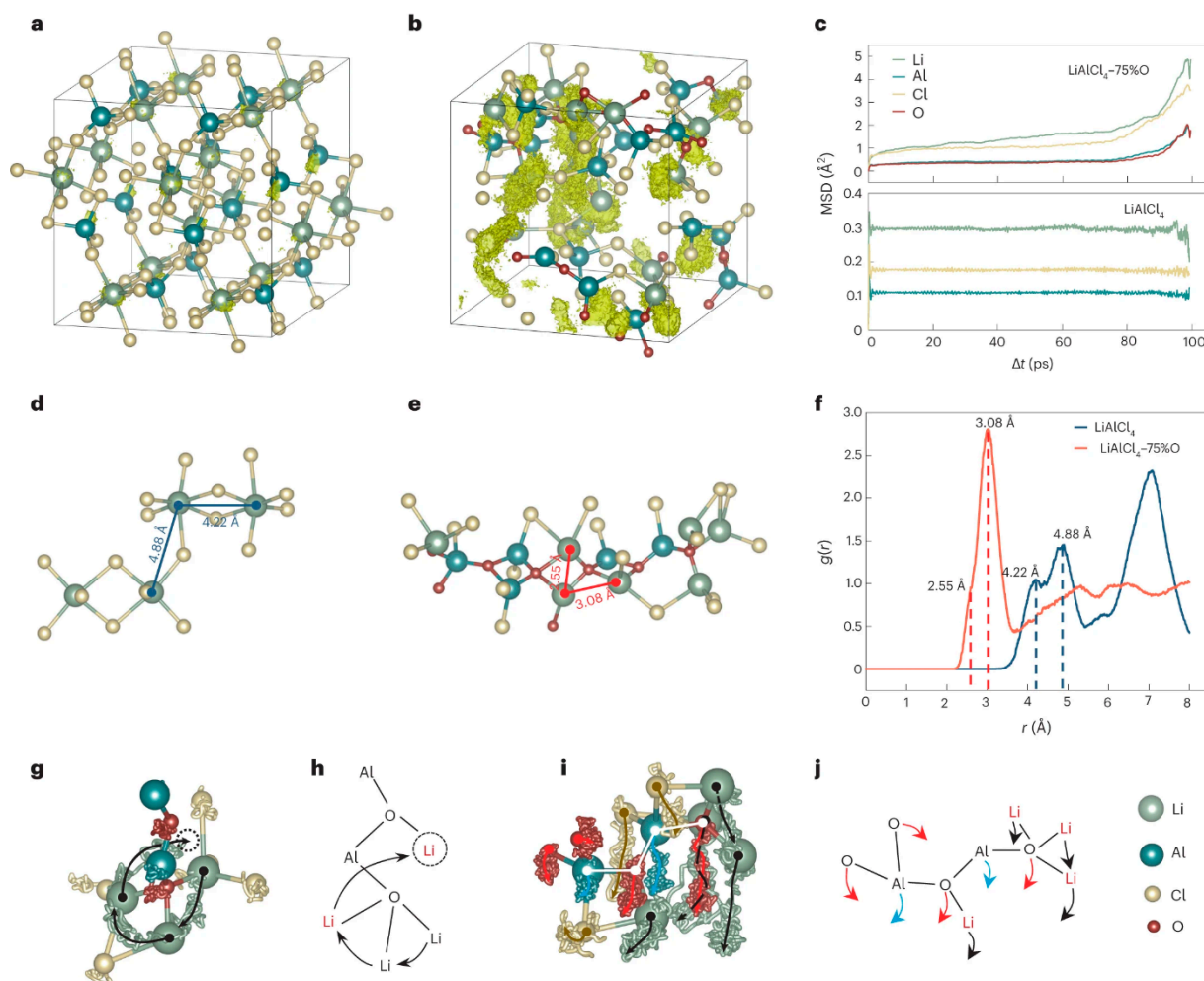


Figure 8. (a,b) The atom position distribution of Li in LiAlCl_4 (a) and LACO75 (b). Green, blue, yellow, and red spheres represent Li, Al, Cl, and O, respectively. (c) The MSD of Li, Al, Cl, and O in LiAlCl_4 and LACO75 at 100 ps. (d,e) Microstructural fragments with the shortest Li^+ transition distances of LiAlCl_4 (d) and LACO75 (e). (f) RDF of Li-Li in LiAlCl_4 and LACO75 . The r represents the distance between different Li ions. (g,h) Movement trajectories of Li, Al, Cl, and O elements in a hopping event (g) and corresponding schematic diagram of Li^+ migration (h). (i,j) Movement trajectories of Li, Al, Cl, and O elements on a swinging Al-O-Al segment (i) and the corresponding schematic diagram denoting the movement directions of all the elements (j). The arrows in (h,j) signify the moving directions of elements [78]. Copyright 2023, Nature Energy.

The doping of fluorine elements not only helps to form fluorine-rich interfaces, improving the performance of batteries, but also plays a role in inducing amorphous states in certain systems. Fan et al. [82] proposed a design strategy of “sodium deficiency/chlorine deficiency”. By precisely controlling the vacancy and carrier concentration in the

lattice, the conductivity enhancement of several orders was realized. The conductivity of $\text{Na}_{0.5}\text{ZrCl}_{4.5}$ electrolyte synthesized based on this strategy reached $8.1 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at room temperature. The calculation revealed that the optimized structure formed a three-dimensional ion permeation network with a lower migration barrier, which provided a theoretical basis for the improvement of performance. To further improve electrochemical stability, the F element is introduced to induce amorphization, and the interface compatibility is enhanced while maintaining high conductivity ($1.12 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$). The all-solid-state sodium battery assembled by using the fluorinated electrolyte $\text{Na}_{0.5}\text{ZrCl}_4\text{F}_{0.5}$ can still maintain 94.4% of the initial capacity after 300 cycles at room temperature, highlighting the great potential of this design strategy in developing SEs with high ionic conductivity and long-term cycle stability. By introducing a different fluorine source from the aforementioned one, Li et al. [102] proposed a fluoride modification strategy to successfully synthesize a $2\text{NaF}\cdot\text{ZrCl}_4$ electrolyte with an amorphous nanocrystalline composite structure by introducing NaF into Na_2ZrCl_6 . The fluorination strategy significantly enhanced the amorphous degree of the material and optimized the local coordination environment of Na^+ . The structural remodeling increased the ionic conductivity at room temperature to $2.35 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$. The improved performance can be attributed to F weakening the Coulomb binding of Na migration and forming a rapid, three-dimensional ion transport network in the amorphous matrix. It can form a stable fluoride interface layer, effectively inhibiting side reactions. An ASSB based on this electrolyte can still maintain 81.1% of the initial capacity after 600 cycles at room temperature and exhibits excellent rate performance.

Based on the extensive research already conducted on oxygen halides, significant progress has also been made in the study of their amorphous forms in recent years. Sun et al. [103] introduced oxygen into zirconium-based halides such as Li_2ZrCl_6 , which can effectively control the amorphous degree from 46.0% to 89.5%, forming a unique Zr-O/Cl polyhedral angle-sharing network structure. A synthesized, highly disordered, but locally ordered structure, such as $\text{Li}_3\text{ZrCl}_4\text{O}_{1.5}$, significantly reduces the lithium-ion migration energy barrier and achieves a room temperature ionic conductivity of $1.35 \pm 0.07 \text{ mS}\cdot\text{cm}^{-1}$, which is one order of magnitude higher than that of quasi-crystalline Li_2ZrCl_6 . Quasi-crystalline Li_2ZrCl_6 was prepared via a one-step ball milling method, and some highly disordered regions exist in its crystalline structure. In addition, amorphization gives the material excellent mechanical deformability, which allows it to be cold-compacted without cracks and have enhanced electrochemical stability, with an oxidation window of up to 4.1 V. ASSBs constructed based on these amorphous SEs in combination with high-voltage cathodes exhibit high-rate performance (3C , $78 \text{ mAh}\cdot\text{g}^{-1}$) and long cycle stability (>300 cycles, capacity retention $>90\%$). Similarly, Zhang et al. [104] proposed an innovative “anion engineering” strategy. By co-introducing F^- and O^{2-} into Zr-based halides, high-performance $\text{Li}_{2.5}\text{ZrCl}_5\text{F}_{0.5}\text{O}_{0.5}$ (LZCFO) superconductors were successfully constructed. The thermodynamic and kinetic oxidation stability of the material was significantly improved by this strategy. At the same time, the introduction of O^{2-} induced the formation of highly disordered amorphous localized structures, which opened a low energy barrier path for Li^+ transport, thus achieving a room temperature ionic conductivity of $1.17 \text{ mS}\cdot\text{cm}^{-1}$ while maintaining high oxidation stability. LZCFO-based ASSBs exhibit excellent cycle stability at high voltages. The key lies in the fact that the in situ fluorine-rich cathode electrolyte interface (CEI) effectively inhibits interfacial side reactions and protects the structural integrity of the cathode materials. Also within the framework of LZC, Li et al. [105] proposed a novel cation–anion co-engineering strategy. By introducing a Cu^{2+} cation and an O^{2-} anion simultaneously to modify Li_2ZrCl_6 , amorphous oxychloride $\text{Li}_{2.1}\text{Zr}_{0.95}\text{Cu}_{0.05}\text{Cl}_{4.4}\text{O}_{0.8}$ was successfully synthesized. This strategy significantly increased the amorphous content of the material to 88.2% and optimized the local coordination environment. The ionic conductivity at room temperature was greatly increased from $4 \times$

$10^{-4} \text{ S}\cdot\text{cm}^{-1}$ to $2.05 \text{ mS}\cdot\text{cm}^{-1}$. Advanced characterization techniques and AIMD simulation reveal that the performance improvement is due to the “weak trap” effect of Cu^{2+} , which reduces the Li migration barrier, and the $[\text{Zr}_{0.95}\text{Cu}_{0.05}\text{Cl}_a\text{O}_b]^{(a+b-3.9)-}$ polyhedral structure induced by O^{2-} , which broadens the ion transport channel. The ASSBs based on this electrolyte can still maintain 90.3% of the initial capacity after 1000 cycles at room temperature and exhibit excellent rate performance. After Sun et al. proposed $x\text{Na}_2\text{O}_2\text{-TaCl}_5$ electrolytes [106], Saneyuki et al. [107] revealed oxygen-mediated structural modulation and ion transport mechanism by systematically regulating the oxygen content in $x\text{Na}_2\text{O-TaCl}_5$ glass electrolytes. It was found that the introduction of oxygen could significantly increase ionic conductivity, reaching $4.1 \text{ mS}\cdot\text{cm}^{-1}$ at room temperature, revealing a three-stage change rule: the conductivity soared due to the decrease in activation energy at low oxygen content; the conductivity increased steadily due to the increase in carrier concentration at medium oxygen content; and the conductivity plummeted due to the increase in non-bridge oxygen at high oxygen content. The structure analysis shows that oxygen atoms exist in two forms: bridging oxygen (Ta-O-Ta) and non-bridging oxygen. The proper amount of oxygen connects isolated octahedra in the form of bridging oxygen (Ta-O-Ta) to construct a disordered network and increase the free volume of Na^+ transfer, while excess oxygen forms a large amount of non-bridging oxygen, and its strong Coulomb interaction becomes the bottleneck of ion transfer. This work not only clarifies the dual role of oxygen in the glass network but also provides a guiding principle for the rational design of multi-anion SEs, which focuses on the regulation of anion coordination environment.

As an element in the same group as oxygen, sulfur can also play a similar role in inducing amorphousness. Zhao et al. [65] designed and prepared a new class of Na-Zr-S-Cl sulfur–chlorine dianion solid electrolytes. By precisely adjusting the anion ratio of sulfur to chlorine, two amorphous electrolytes with different local structures were successfully constructed: Cl-deficient $\text{Na}_2\text{S-1.3ZrCl}_4$ and Cl-rich $\text{Na}_2\text{S-3.3ZrCl}_4$. A high ionic conductivity of $4.89 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ is realized with a Cl-rich structure, which was attributed to the unique $[\text{Zr-S}_2\text{-Zr-S}_2]$ sulfur bridge structure and low Na^+ transport barrier. However, structural differences lead to significantly different physicochemical properties: $\text{Na}_2\text{S-1.3ZrCl}_4$ has superior thermal stability, mechanical strength, and interface stability with a high-voltage layered cathode. The initial interface reaction products can be reversed in the electrochemical process, effectively inhibiting side reactions. Hence, ASSBs using $\text{Na}_2\text{S-1.3ZrCl}_4$ achieved breakthrough cycling performance, with capacity retention exceeding 76.6% after 600 cycles at 0.1C; the capacity is still $52 \text{ mAh}\cdot\text{g}^{-1}$ after 1400 cycles at 0.3C, and its performance is at the forefront of the report. Conversely, the poor interface stability of Cl-rich $\text{Na}_2\text{S-3.3ZrCl}_4$ leads to battery failure. This work not only opens a new system of sulfur–chlorine mixed anion electrolytes but also reveals the regulation mechanism of the anion ratio on structure and performance, which provides important guidance for the design of next-generation high-performance solid electrolytes.

Due to the excellent performance of Li_3N , many scholars have also shown great interest in nitrogen halides. Han et al. [108] designed and synthesized a new class of amorphous nitrogen halide dianionic electrolytes, $\text{Li}_{3x}\text{MC}_y\text{N}_x$ ($\text{M} = \text{Ta}$ or La), using the mechanistic method. Among them, tantalum-based LTCN ($3x = 1.25$) exhibited excellent room-temperature ionic conductivity of up to $7.34 \text{ mS}\cdot\text{cm}^{-1}$. Synchrotron radiation pair distribution function and low-temperature electron microscope analysis confirmed that the introduction of nitrogen successfully induced amorphous formation and critically stretched the Ta-Cl bond length while forming Ta-N bonds. This remodeling of the localized structure significantly broadens the Li^+ transport channel and proposes a “dynamic horizontal bar” transport mechanism. ASSBs based on this electrolyte achieve stable cycling at high rates of 1C, high cutoff voltages of 4.5 V, and low temperatures of -20°C , highlighting the great potential of amorphous dianion design in the development of electrolytes with high

ionic conductivity and wide electrochemical windows. In a zirconium-based system, Cao et al. [109] proposed an innovative nitrogen–chlorine dianion framework design, which successfully induced the structural transition from crystalline to amorphous phase by introducing N^{3-} into Li_2ZrCl_6 , and synthesized $Li_{1.3}ZrN_{0.4}Cl_{4.1}$ electrolyte. This amorphization strategy eliminated grain boundary resistance and significantly improved the intrinsic stability of the material by forming Zr–N bonds. Thanks to this, the room-temperature ionic conductivity of the electrolyte achieved an order of magnitude leap, reaching 3.01 mS cm^{-1} , while the upper limit of oxidation stability was greatly increased to 4.8 V. When matched with a high-nickel layered oxide cathode, the constructed ASSB maintained 95.1% capacity after 150 cycles at 0.2C and exhibited an ultra-long cycle life of more than 3000 cycles at 3C.

The above amorphization strategies can be extended to the poly-anionic system, and universal rules can be derived. Pan et al. [110] proposed a new electrolyte design paradigm based on a one-dimensional $ZrCl_4$ chain. The Lewis acidity of $ZrCl_4$ is used to promote the dissociation of lithium salts such as Li_3PO_4 and release free Li. Meanwhile, its unique octahedral chain structure provides an isotropic fast transmission channel for Li. Synchrotron radiation X-ray total scattering and solid-state nuclear magnetic resonance spectroscopy (NMR) analysis confirm that the insertion of Li_3PO_4 will destroy some Zr–Cl bonds and form [Zr–O] bonds, thus dynamically adjusting the chain spacing and local environment of chain $ZrCl_4$. Molecular dynamics simulations further revealed the transport mechanism of Li^+ hopping along Cl atomic sites between chains. The electrolyte achieved ionic conductivity as high as 1.2 mS cm^{-1} , a Li^+ transfer number of 0.9, and a wide electrochemical window, and it exhibited stable cycling performance in the full cell. Especially, this design significantly reduced the lithium content in the electrolyte, which has the advantage of low cost. The concept of “inorganic polymer” is not only suitable for Li/Na ion conductors but also opens an innovative path for synergistic optimization of ion transport and migration numbers through host matrix engineering, providing universal guidance for the development of high-performance SEs. In order to overcome the bottleneck of lattice compatibility in traditional solid electrolyte doping modification, Sun et al. [111] proposed a new design paradigm of “solid dissociation”, which uses van der Waals crystals (van der Waals crystals are crystals formed solely by the bonding of van der Waals forces, which include intermolecular forces, including dispersion forces, orientation forces, and induction forces, with hydrogen bonds present in some cases) with a low-dimensional structure, such as $ZrCl_4$, as a “solid solvent” to dissolve various lithium salts through strong Lewis acid–base interaction to form amorphous ionic conductors with long-range disorder and short-range order. They propose solid dissociation in which halide van der Waals materials act as solid solvents to dissolve salts, forming amorphous ion-conductive solids. Using this approach, they not only discovered 73 materials, with 40 exhibiting ionic conductivities exceeding 1 mS cm^{-1} , but also analyzed atomic-scale interactions between solvents and salts, uncovering dynamic structural rearrangements that enable solid dissociation. Across diverse solvent–salt pairs, consistent ionic environments emerge, revealing universal mechanisms governing ion transport in this system. Analogous to the compositional tuning of liquid electrolytes, solid dissociation allows for the targeted engineering of SEs for specific application conditions. Distribution function and extended X-ray absorption fine structure characterization reveal that anions such as PO_4^{3-} form mixed coordination environments with metal cations such as Zr^{4+} in solvents, inducing unique “lithium bond-rich” regions. Solid-state NMR and AMID simulations confirm that lithium ions achieve ultrafast migration through breaking and forming lithium bonds, and their energy barrier is significantly lower than that of traditional octahedral site hopping paths. Through a flexible combination of solvents and solutes, customized electrolytes can be successfully applied to ultrafast charging, low temperature (-50°C),

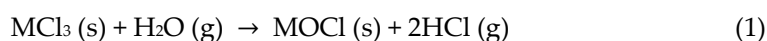
and 4.8 V high-voltage ASSBs and demonstrate improved air stability and cost competitiveness. Solid dissociation provides unprecedented flexibility and universality for the engineering of SEs.

3. Classification of Main Synthesis Methods for Chlorides

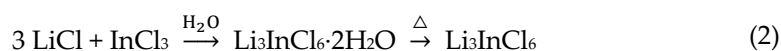
The preparation of chloride SEs considers the characteristics of the material itself and is generally carried out in a protective atmosphere of inert gas while controlling humidity. Based on the current research and modification of chlorides, the preparation types can be divided into three categories: liquid-assisted preparation, solid-state multifunctional preparation, and two-phase co-preparation (co-melting) [29]. According to the development concept of the new era, requirements such as low energy consumption, low cost, and environmental friendliness are particularly important for the preparation process [112,113]. At present, our focus is on how to achieve large-scale industrial production or simple and easy-to-repeat techniques. The new liquid-phase synthesis techniques demonstrate the potential for industrial preparation, and although traditional solid-state reactions are limited to the requirements of protecting the atmosphere, they still have advantages. Although commercialization is still far away, the need to address the possibility of low-temperature and small-scale solid-state processing for electrolyte synthesis may be at a turning point [114]. In addition, we should also pay attention to the impact of preparation methods on the structure and properties of materials, hoping to uncover the connections and secrets within them.

3.1. Liquid Assisted Preparation

The liquid phase method can be used for the synthesis of sulfide solid and organic polymers [115–118]. A few chlorides can be synthesized in this way based on their own characteristics. Previous studies have found that when attempting to dehydrate some chlorides (La–Yb), hydrolysis reactions occur on their own. The hydrolysis equation is [119,120]



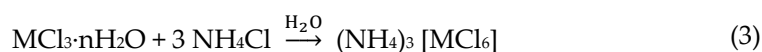
Nevertheless, wet synthesis still has the following advantages: (1) reduced reaction time and temperature, making it easily used for large-scale production; (2) effectively controlled size/morphology; (3) a wet slurry that can be used as a surface-ion-conductive coating for electrode material particles [5]. Next, we will introduce two examples of the typical wet synthesis of chlorides. Li et al. [32] reported for the first time that chloride Li_3InCl_6 can be synthesized in water. In addition, the ion conductivity was measured to be as high as $2.04 \text{ mS}\cdot\text{cm}^{-1}$ at room temperature, and there was no significant change in the ion conductivity after it was dissolved again in water. Although it cannot be adapted to lithium metal, it can come into direct contact with the high-voltage oxide cathode. To briefly summarize the preparation process, the commercial products LiCl and InCl_3 were dissolved in a molar ratio of 3:1 in deionized water at room temperature. Then, the obtained solution was naturally dried in air to obtain the precursor, and the precursor was dried in a vacuum at 200°C for four hours to obtain the finished product. The reaction process is as follows [32]:



Surprisingly, Na_3InCl_6 can also be synthesized through this water-medium method. During the drying process, the author found that if not carried out under vacuum conditions, even with inert gas argon protection, impurities will be generated, which should be avoided. In addition, the synthesis method using water as a medium can easily produce up to 110 g of this high-purity chloride in massive quantities while also possessing high

ionic conductivity. In an air humidity tolerance test of Li_3InCl_6 , it was found that even after 24 h of exposure to low-humidity content (3–5%), the main body could still maintain its initial phase, and the conductivity did not significantly decrease. Then, under high-humidity content (30%), the conductivity sharply decreases, and after 24 h, it mostly transforms into $\text{Li}_3\text{InCl}_6 \cdot 2\text{H}_2\text{O}$. Meanwhile, all samples can be restored to Li_3InCl_6 after reheating. The special performance of material Li_3InCl_6 can be attributed to the reversible dehydration/hydration behavior between Li_3InCl_6 and $\text{Li}_3\text{InCl}_6 \cdot 2\text{H}_2\text{O}$ under certain conditions. However, the decrease in overall ionic conductivity can be attributed to a small amount of Li_3InCl_6 decomposing into In_2O_3 and LiCl without ionic conductivity [121].

Sun et al. were inspired by the route of the industrial synthesis of anhydrous ammonium chloride (MCl_3 , M = trivalent metals) and used ammonium-assisted wet chemistry to prepare various chloride SEs in 2021 [33]. The synthesis process is simply summarized as waiting for the raw material to be completely dissolved in deionized water and drying at 80 °C using a glass oven under vacuum conditions. The obtained powder is pressed into sheets in a glove box and annealed for five hours. The reaction is as follows ($\text{M} = \text{Y}^{3+}$, Sc^{3+} , Er^{3+} , etc.) [33,122]:



Ammonium chloride is used as a coordination agent to combine YCl_3 to form an intermediate. After heat treatment, the intermediate will react with LiCl to form the desired product. The successful synthesis of materials such as Li_3ScCl_6 , Li_3YCl_6 , and Li_3ErCl_6 indicates that, compared to water synthesis, ammonium-assisted wet preparation has generality and can obtain materials with submicron sizes and decent ionic conductivity. When assembling Li_3YCl_6 and Li_3ScCl_6 into full batteries for testing, it was found that neither can directly adapt to lithium metal, but both can be used together with uncoated high-voltage cathode materials. However, the author did not mention humidity tolerance or mass production in the article. From this, it can be inferred that although this method can be applied to the production of various chlorides, the moisture resistance and large-scale preparation of its products are still limited. As shown in the above two representative articles, liquid-phase-assisted preparation has the potential for large-scale production. Using a large amount of inexpensive deionized water as a solvent can greatly reduce the cost of raw materials, and some solvents in ammonium-assisted preparation can be recycled. In addition, the author believes that, compared to solid-state synthesis, wet preparation can introduce several times the amount of microstrain, which is beneficial for the transport of lithium ions [33].

3.2. Solid-State Preparation

Solid-state synthesis is the most used method in material preparation, whether it is oxides, sulfides, or chlorides [15,17,123]. The solid-state synthesis of chlorides can be divided into three categories based on different operating conditions: direct sintering, ball milling (BM), and ball milling with annealing (BMA) [124]. The direct sintering method usually involves simply grinding the raw materials and pressing them into pieces or placing them in a crucible and sintering them in a muffle furnace. The ball milling method usually controls the operating speed and milling time of the ball mill to obtain the desired product characteristics. The reaction is achieved through strong collisions between raw materials, the inner wall of the spherical tank, and grinding beads, resulting in a narrow particle distribution (amorphous/quasi-crystalline) of the material. In addition, products that cannot be obtained through other preparation methods can also be generated. The ball milling method can cause structural changes and introduce more defects, which may

not all be good for ion conductivity [125]. For materials with good crystalline (ZrCl_4 and YCl_3), repeated mechanical milling facilitates the formation of a stable metastable state, namely the quasi-crystalline state, introducing partially highly disordered regions while preserving the main crystalline structure. In contrast, for materials with poor crystallinity (TaCl_5), repeated mechanical milling tends to induce the formation of an amorphous state. However, the ball milling method requires a significant amount of time and energy consumption, and the small pieces of the grinding ball that break may contaminate the product. Ball milling with annealing adds an annealing process after ball milling, typically carried out in a quartz container. While this additional process inevitably increases both time and cost, the resulting enhancement in ionic conductivity often justifies the extra effort. However, in some cases, it can have adverse effects [124].

Through comparison, we can have a better understanding of different preparation methods. Li_3InCl_6 can not only be synthesized through novel water-media methods but can also be obtained using conventional ball milling and annealing methods. Compared to the convenience and low cost of wet synthesis, the ball milling method requires the raw materials to be ball-milled at a speed of 500 rpm for 24 h. At the same time, annealing treatment requires pressing the milled products into sheets at a pressure of 200 MPa, maintaining them for a certain temperature range under vacuum conditions for a period, and then cooling them to room temperature. The above processes are all carried out in an argon atmosphere [126]. The ion conductivities of Li_3InCl_6 obtained using the above three methods are $2.04 \text{ mS}\cdot\text{cm}^{-1}$, $8.37 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, and $1.49 \text{ mS}\cdot\text{cm}^{-1}$, respectively (Table 1). The difference in ion conductivity between aqueous synthesis and ball milling plus annealing is not significant, and the three products have the same structure, but there are differences in crystallinity and moisture tolerance. However, there is currently no evidence to suggest that changes in humidity tolerance are related to preparation methods.

For Li_3InCl_6 , annealing after ball milling can indeed improve to a certain extent ion conductivity. Nevertheless, annealing is not good for Li_2ZrCl_6 and Na_2ZrCl_6 . It is evident from Table 1 that once annealing treatment is applied, the ion conductivity drops sharply by three orders of magnitude. Interestingly, annealing not only changes the crystallinity of the former but also its crystal structure, while the latter undergoes none of the aforementioned additional changes. Hiram et al. believe that the difference in ionic conductivity in Na_2ZrCl_6 is due to heat treatment, which causes the strong bonding between sodium and chloride ions and a lack of interconnection between sodium atoms at the 6 h site. Regarding the reason for the difference in Li_2ZrCl_6 , Ma and Jung et al. [34,127] share similar views, both believing that heat treatment leads to structural changes that increase migration barrier energy and narrow ion migration channels. The most important thing is that the metastable and nonperiodic features generated by ball milling are suppressed by annealing treatment, resulting in drastic changes in ion conductivity. However, it is difficult to determine which part of the aperiodic region is the main contributor to ion conductivity. Compared to the above preparation methods, there is another method that is commonly used in chloride synthesis, which is the co-melting method. Both the Sun and Nazar teams [38,128] have used this simple and user-friendly method to prepare $\text{Li}_2\text{Sc}_2\text{Cl}_7$; the ion conductivity of the obtained products is above $1 \text{ mS}\cdot\text{cm}^{-1}$.

Recently, some have proposed a new synthesis process, where the material is sintered and then quenched, which helps to form an amorphous structure and has advantages such as enhancing ionic conductivity and improving interface stability [129]. This study has proposed a toughening strategy based on defect engineering by adjusting halide electrolyte $\text{Li}_{2.5}\text{Y}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$; the mechanical robustness was improved significantly. The results showed that rapid quenching treatment could introduce a high density of dispersed defects without changing the intrinsic ionic conductivity of the material compared with slow cooling. Synchrotron radiation-computed tomography, atomic-force microscopy, and

Williamson–Hall analysis confirm that the quenched samples have a higher Young’s modulus and microstrain, which are due to a smaller grain size, greater lattice distortion, and higher amorphous-phase content. In the electrochemical performance evaluation, ASSBs with quenched electrolytes exhibit significantly improved cycle stability and rate performance because the electrolyte effectively suppresses the interface powdering and porosity caused by the electrode volume effect, maintaining the integrity of ion transport channels for a long period. Additionally, Zhao et al. [83] studied the regulation of oxygen halides using sub-second quenching strategies such as NaNbOCl_4 . This process breaks the Nb–O–Nb bridging oxygen bonds through rapid cooling, induces NbO_2Cl_4 octahedral distortion and non-bridging oxygen formation, and builds a highly disordered ion transport network, which increases the room temperature conductivity to $1.51 \text{ mS}\cdot\text{cm}^{-1}$ (Nb) and $7.2 \text{ mS}\cdot\text{cm}^{-1}$ (Ta), while maintaining a high oxidation stability of 4.43 V. Structure characterization and machine learning simulations confirm that short-range disordered structures reduce Na migration activation energy and inhibit the precipitation of the NaCl impurity phase. The capacity retention of the full cell based on this electrolyte reaches 82.61% after 250 cycles at 0.5C, which can be attributed to the excellent interface compatibility due to its low Young’s modulus (8.2 GPa). This work provides a new paradigm for the design of low-cost and high-performance solid electrolytes, but further optimization of the scale-up process and thermal stability is needed.

In summary, we currently adopt a cautious stance toward annealing treatment and must evaluate its suitability on a case-by-case basis, depending on the specific material (Table S1, in Supplementary Materials). While products synthesized via ball milling exhibit certain unique characteristics, their yield is inherently limited by the capacity of the milling vessel and the size of the milling media. Moreover, ball milling entails high energy consumption and prolonged processing times, issues that are difficult to avoid. Conventional solid-state sintering, though capable of large-scale production, presents its own challenges, including the difficulty of maintaining large-volume vacuum environments, poor homogeneity in bulk products, and stringent humidity control requirements. Furthermore, the choice of precursor should be aligned with the selected synthesis method, as different routes can lead to distinct crystal structures and, consequently, divergent electrochemical properties. Therefore, for any target halide-based solid electrolyte, a systematic investigation is essential: the optimal synthesis strategy must be identified and the process parameters carefully tuned to achieve optimum performance. We have summarized the basic information of typical electrolytes in Table 1.

Table 1. Basic information on preparation products.

Chlorides	Structure	Synthesis	Ionic Conductivity $10^{-3} \text{ S cm}^{-1}$	Air/Moisture Tolerance	Ref.
Li_3InCl_6	Monoclinic rock-salt (C2/m)	Water-mediated synthesis (heat at 200°C for 4 h)	2.04 (25°C)	Dry air/3–5% humidity	[32]
Li_3InCl_6	Monoclinic rock-salt (C2/m)	Ball-milling (500 rpm for 24 h)	0.84 (25°C)	Dry air/1% humidity	[126]
Li_3InCl_6	Monoclinic rock-salt (C2/m)	Ball-milling (500 rpm for 24 h), annealing (260°C for 5 h)	1.49 (25°C)	Dry air/1% humidity	[126]
Li_3ScCl_6	Monoclinic (C2/m)	Co-melting at 650°C for 12 h	3.02 (25°C)	Avoid air exposure	[38]

Li_3ScCl_6	Monoclinic (C2/m)	Ammonium-assisted wet chemistry + annealing (500 °C for 5 h)	1.25 (25 °C)	Avoid air exposure	[33]
Li_2ZrCl_6	Trigonal (P3m1)	Ball-milling (at 600 rpm for 10 h)	0.40 (30 °C)	Dry air	[127]
Li_2ZrCl_6	Monoclinic (C2/m)	Ball-milling (at 600 rpm for 10 h), annealing (260 °C for 12 h)	5.7×10^{-3} (30 °C)	Dry air	[127]
Na_2ZrCl_6	Trigonal (P3m1)	Ball-milling (at 600 rpm for 10 h)	1.8×10^{-2} (30 °C)	Avoid air exposure	[89]
Na_2ZrCl_6	Trigonal (P3m1)	Ball-milling (at 600 rpm for 10 h), annealing (400 °C for 12 h)	6.9×10^{-5} (30 °C)	Avoid air exposure	[89]
$\alpha\text{-Li}_3\text{ZrCl}_6$	Trigonal (P3m1)	Ball-milling (at 500 rpm for 45 h)	0.81 (25 °C)	N ₂ with 5% relative humidity	[34]
$\text{Li}_x\text{Ta}_y\text{La}_z\text{Cl}_3$	UCl ₃ (P63/m)	Ball-milling (at 400 rpm for 16 h)	3.02 (30 °C)	Not mentioned	[35]
$\text{Li}_{2+x-y}\text{ZrCl}_{6-x-y}\text{O}_x$	Amorphous	Ball-milling (at 600 rpm for 45 h)	2.42 (25 °C)	Not mentioned	[77]
$x\text{Li}_2\text{O-MCl}_y$ (M = Ta or Hf)	Amorphous	Ball-milling (at 500 rpm for 10 h)	6.6 (25 °C)	Not mentioned	[74]
LTC·Li-X (X = F, Cl, O, OH, O ₂).	Amorphous	Ball-milling	4–7 (25 °C)	Not mentioned	[76]
NaTaCl_6	Amorphous	Ball-milling (at 600 rpm for 40 h)	4 (30 °C)	Not mentioned	[79]
$0.5\text{Na}_2\text{O}_2\text{-TaCl}_5$	Amorphous	Sintered at 450 °C for 12 h	4.62 (25 °C)	Not mentioned	[75]
$\text{NaAlCl}_{2.5}\text{O}_{0.75}$	Amorphous	Sintered at 250 °C for 1 h	1.33 (25 °C)	Not mentioned	[78]
$\text{LiAlCl}_{2.5}\text{O}_{0.75}$	Amorphous	Sintered at 250 °C for 1 h	1.52 (25 °C)	Not mentioned	[78]

4. Further Investigation of Ion Conductivity and Electrochemical Stability Window

Ionic conductivity remains a critical and unavoidable focus in the development of SEs. High ionic conductivity reflects low activation energy for ion migration and the presence of well-connected pathways that enable rapid ion transport, key factors that directly influence battery performance [43]. In the field of chloride-based SEs, progress has been hard-won: early materials exhibited conductivities on the order of 10^{-5} S·cm⁻¹, and achieving the first milestone of >10 mS·cm⁻¹ required substantial breakthroughs in composition and structure design. Today, most crystalline lithium electrolytes achieve conductivities of around 1 mS·cm⁻¹ (Figure 9). However, sodium-based crystalline chlorides still lag, largely due to structural constraints and the larger ionic radius of Na⁺. Notably, introducing structural disorders, such as through amorphization, can dramatically enhance Na⁺ mobility. As a result, amorphous sodium ion chloride SEs are now approaching the ionic conductivity levels previously seen only in crystalline lithium systems, offering promising pathways toward high-performance all-solid-state sodium batteries.

To further improve ion conductivity, various methods have been attempted from different perspectives. With a simple and highly operational approach, changing the synthesis conditions or synthesis path can effectively change it. But in fact, this is the result

obtained by changing the microscopic conditions; for example, low-crystallinity samples can generally be obtained through ball milling, while high-crystallinity products can be obtained through annealing treatment, and more importantly, the structure and even the phase can undergo changes [34,89,127]. The above is not universal, and different materials may have specific needs. In Section 3, it was mentioned that adding annealing treatment to some materials after ball milling can effectively improve their conductivity. Nevertheless, some have the opposite effect, reducing them by one or two orders of magnitude instead. Wu et al. [130] summarized basic key points on doping, and improved ion conductivity by controlling the doping elements and content to change the ion occupancy rate or adjusting the concentration of vacancies. It is useful to partially replace high-valence elements with low-valence elements for charge compensation, thereby increasing the lithium-ion content. In addition, high-valence elements can also be used to replace low-valence elements to introduce extra vacancies. Furthermore, the local disorder caused by doping promotes the disorder of sublattices, thereby enhancing ion conductivity.

Jung et al. [127] used trivalent Fe^{3+} to replace Zr^{4+} , and after achieving good results, attempted to replace Zr^{4+} with trivalent Cd^{3+} and V^{3+} . From the material composition, compared to the undoped raw material, the increase in lithium content in $\text{Li}_{2.25}\text{Zr}_{0.75}\text{Fe}_{0.25}\text{Cl}_6$ will also drive an increase in the amount of charge carriers. The Coulomb repulsion between Li and other metal cations in undoped materials increases the activation barrier for Li^+ transport. Replacing Zr^{4+} with Fe^{3+} can alleviate the Coulomb repulsion and lower the activation barrier for Li^+ transport. It can also reduce the overall size of the central atomic polyhedron, which is conducive to conversion into larger Li^+ channels and improves ion migration ability. Nazar et al. [58] replace the trivalent central metal ion with Zr^{4+} , and as the doping content gradually increases, the crystal structure changes accordingly from trigonal ($P\bar{3}m1$) to orthorhombic ($Pnma$). An additional tetrahedral Li site is generated in the third phase, and the site occupancy is only 20%, showing a significant vacancy population. At first, the ionic conductivity of Li_3ErCl_6 ($x=0$) is $8.7 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 25°C , and the third pure phase is obtained while also obtaining the maximum ion conductivity, $1.1 \text{ mS}\cdot\text{cm}^{-1}$ when $x = 0.367$. Recently, Hu explored the influence of cation disorder and related migration on ion conductivity based on Li_3ScCl_6 . By partially replacing Zr elements, the migration channels along the C-axis were broadened, and the migration barrier was reduced. Moreover, the substitution adjusted the concentration of lithium ions/vacancies, resulting in higher room-temperature ion conductivity [131]. To study the relationship between the structure and ionic conductivity of the solid electrolyte, $\text{Li}_3\text{MgCl}_{2+x}$, they used neutron diffraction by manipulating the value of x to influence the crystal structure [132]. Starting from crystallographic parameters, they analyzed the reasons for the variation in ionic conductivity with changing x values. Their paper reveals that crystallographic parameters influence Li^+ transport differently at different stages. In the initial stage ($2 \geq x \geq 1.6$), the increase in the Debye–Waller factor (DWF) of Li and the length of the Li–Cl bond led to increased ionic conductivity. During the middle stage ($1.6 \geq x \geq 1.4$), the increase in Li and DWF, along with a higher concentration of vacancies, had a more pronounced effect on facilitating Li^+ transport, overcoming the negative impact of reduced unit cell parameters and shorter Li–Cl bond lengths. In the final stage ($1.4 \geq x \geq 1$), changes in all crystallographic parameters restricted Li^+ transport, resulting in decreased ionic conductivity. This may provide some guidance for understanding how chloride crystal structures direct ionic conductivity. By introducing Ta and other high-valence elements into Li_3InCl_6 , a series of high-performance electrolytes such as $\text{Li}_{2.6}\text{In}_{0.8}\text{Ta}_{0.2}\text{Cl}_6$ were successfully prepared [133]. This strategy created many Li^+ vacancies through charge compensation effect, significantly reducing the Li^+ migration activation energy, thus obtaining a room temperature ionic conductivity of up to $4.47 \text{ mS}\cdot\text{cm}^{-1}$. Meanwhile, the formation of strong Ta–Cl bonds effectively improves the oxidation stability of the lattice and broadens the oxidation

initiation potential to 5.13 V. (vs. Li/Li⁺). ASSBs assembled based on this electrolyte exhibited excellent cycle stability even at a high voltage of 4.6 V, with 70% capacity retention and rate performance after 1400 cycles. Others have designed Li₂Zr_{0.75}Ta_{0.2}Cl₆ by replacing less high-valence Ta with lower-valence Zr, which introduces abundant Zr vacancies while maintaining charge balance and high lithium content [134]. The bond valence points energy (BVSE) calculations confirm that these structural vacancies construct additional low-energy barrier ion transport channels within the non-lithium-centered octahedral framework, forming an efficient three-dimensional permeation network, increasing the ionic conductivity to 1.74 mS·cm⁻¹. The electrolyte shows excellent compatibility with a high-nickel, single-crystal cathode and achieves unprecedented cycle stability, including more than 12,000 cycles at 5C high rate and capacity retention higher than 80% after thousands of cycles under high-load conditions, more than 20 mg·cm⁻².

Furthermore, Arumugam et al. [135] proposed a new class of oxygen halide solid electrolyte: NaNbCl_{6-2x}O_x. The ionic conductivity of NaNbCl₄O synthesized by the mechanochemical method is as high as 1.03×10^{-4} S·cm⁻¹ at room temperature, which is nearly two orders of magnitude higher than that of pure halide NaNbCl₆. The introduction of oxygen promotes the transformation of isolated [NbCl₆]⁻ octahedra into polymer chain [NbCl₄O]⁻ anions, reshaping the local transport environment of sodium ions, which is the structural source of the remarkable increase in conductivity. More groundbreaking is that the electrolyte exhibits redox activity; XPS confirms reversible Nb⁵⁺/Nb⁴⁺ pairs, making it both an ionic conductor and an extra capacity carrier. Coupling this “redox active electrolyte” with a Co-free Ni layered oxide cathode, the full cell achieves a high discharge capacity of 155 mAh·g⁻¹ at room temperature, confirming its great potential for increasing battery-level energy density. Apart from adjusting synthesis conditions and doping, researchers have adopted techniques for controlling material composition. Liang et al. [38] studied the conductivity differences caused by the variation in X in Li_xScCl_{3+x} (X = 2.5, 3, 3.5, 4). The research results demonstrate that the basic octahedral configuration will not change with X, but the dense packing mode will shift from ccp to hcp. The increase in X can obtain more lithium ions and reduce the blocking effect of Sc ions, but it can also reduce the vacancy concentration. Li₃ScCl₆ exhibits the best ionic conductivity (3.2 mS·cm⁻¹).

Sun et al. [66] designed crystalline oxyhalide Li₃Ta₃O₄Cl₁₀ (LTOC). The uniqueness of this material lies in its anionic sublattice: oxygen atoms shared by angles form a helical skeleton, and terminal chlorine atoms create a low-coordination Li⁺ environment. This structure induces the formation of continuous “tetrahedral–tetrahedral” Li⁺ transport channels, whose energy barriers are significantly lower than those involving octahedral sites in traditional halides. Thanks to this, LTOC exhibits a record room-temperature ionic conductivity of 13.7 mS·cm⁻¹, which surpasses most liquid electrolytes and has oxidation stability > 4.9 V. LTOC-based ASSBs not only achieve a long-life cycle at high voltages but also exhibit excellent rate performance and cycle stability at extreme low temperatures of −50 °C. This work confirms that anionic sublattice engineering can effectively integrate the advantages of different anions and opens a new paradigm for designing next-generation solid electrolytes with high ionic conductivity, wide electrochemical windows, and environmental adaptability.

Considering ion conductivity alone, this does not have much advantage compared to other oxides, sulfides, etc. The sulfide series, which is far ahead of others, is unparalleled, and the sodium superionic conductor (NASICON) series of oxides is not to be outdone. There is still much room for improvement in chloride, but more investment and research support are needed to continue promoting it.

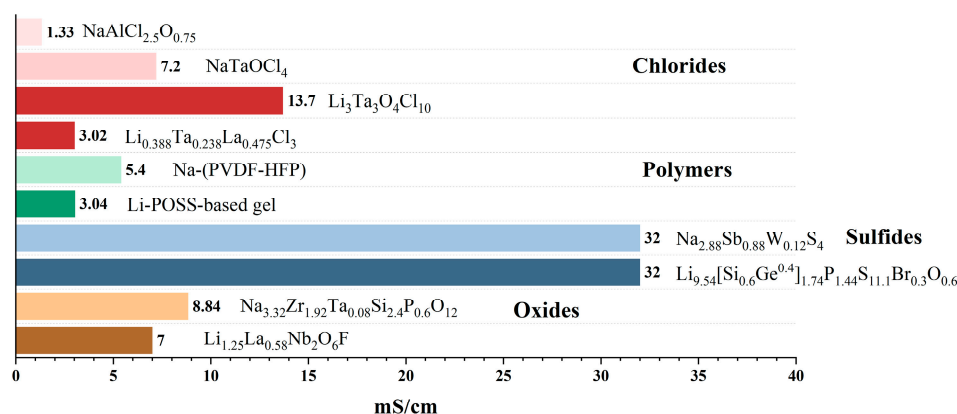


Figure 9. Schematic diagram of ion conductivity of different typical SEs [35,60,78,79,136–148].

Ion conductivity is not the only criterion for evaluation, but it is also important for the suitability of electrodes (i.e., electrochemical stability window—ESW). There are various opinions on the measurement of electrochemical stability windows, and some have provided clear explanations from a computational perspective. In the three common calculation methods currently used—the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) method, the phase stability method, and the stoichiometry stability method—the HOMO-LUMO method combines the connection between phase stability method and stoichiometry stability method. The different directions considered by the phase stability method and stoichiometric stability method lead to differences; the former considers the equilibrium voltage of the solid electrolyte decomposition reaction, while the latter considers the insertion and extraction from the SSE structure. The phase stability window is more accurate than the quantitative stability window, but there are exceptions to everything [149]. The width of the electrochemical stability window determines whether the solid electrolyte can adapt to high-oxidation voltage cathode materials or metal anodes with strong reducibility. In experiments, sulfides were initially considered to have a short ESW, through theoretical calculations it was found that they did not have good stability themselves; rather, the decomposition products of the electrolyte formed a passivation layer on the surface, which affected the reaction process [150]. More scholars have conducted in-depth computational research and found that the electrochemical stability window of general solid electrolyte materials is not wide, especially for sulfides [151–153]. It has been proposed that the excellent electrochemical stability observed in experiments is not the intrinsic thermodynamic characteristics of materials but the kinetic factors resulting from the slow decomposition process of materials [154]. There is no doubt that parts of oxides and polymers have a wide electrochemical stability window, and the anionic groups in them can withstand high oxidation voltages to maintain the stability of the solid electrolyte [155,156]; high-voltage oxidation stability is usually limited by the anions with the lowest ionization potential, following the order $\text{N}^{3-} < \text{P}^{3-} < \text{H}^- < \text{S}^{2-} < \text{I}^- < \text{O}^{2-} < \text{Br}^- < \text{Cl}^- < \text{F}^-$ [3]. Furthermore, for polymers, electrochemical stability can be further improved by adding inorganic fillers or using stable groups in the main chain [157–159]. Figure 10 presents the electrochemical windows of several common types of SEs.

The high-entropy strategy provides a new way to solve the bottleneck of the high-pressure stability of halide solid electrolytes. Luo et al. [160] introduced multiple elements into Li_3InCl_6 (Y/Er/Yb) doping and successfully synthesized high-entropy $\text{Li}_{2.75}\text{Y}_{0.16}\text{Er}_{0.16}\text{Yb}_{0.16}\text{In}_{0.25}\text{Zr}_{0.25}\text{Cl}_6$ (HE-LIC). Neutron diffraction and PDF analysis confirmed that lattice distortion induced local structural reconstruction: on the one hand, the Li-Cl

bond was prolonged, the Li^+ migration barrier was reduced, and the ionic conductivity was increased to $1.17 \text{ mS}\cdot\text{cm}^{-1}$; on the other hand, the Cl^- distribution was restricted, the oxidation kinetics was suppressed, and the electrochemical window was widened to 4.4 V. The HE-LIC-based ASSB achieves an initial capacity of $185 \text{ mAh}\cdot\text{g}^{-1}$ and a 50-cycle retention rate of 91.6% at a high voltage of 4.6 V, significantly better than traditional Li_3InCl_6 .

Although halides have always been criticized because their high-conductivity phases cannot be maintained at room temperature, the excellent electrochemical stability of chlorides can easily be matched with high-voltage cathodes to obtain greater energy density. According to the lowest ionization potential of anions just mentioned, some calculations have found that chlorides have large band gaps and exhibit good stability on the cathode side, which can fully meet the requirements of 4 V cathode materials compared to oxides and sulfides [31]. From the changes in valence states, when the central metal ion of the chloride is at its highest valence, except for the chloride ion itself, which can continue to be oxidized, none of the other metal ions will lose electrons anymore [161]. Therefore, according to the calculation results, it was found that most chlorides have almost the same oxidation potential [31,85]. After experimental verification, the difference between the calculated values and the experimental results is very small. Whether the measured electrochemical window is consistent with the practical one requires specific verification tests. [162,163].

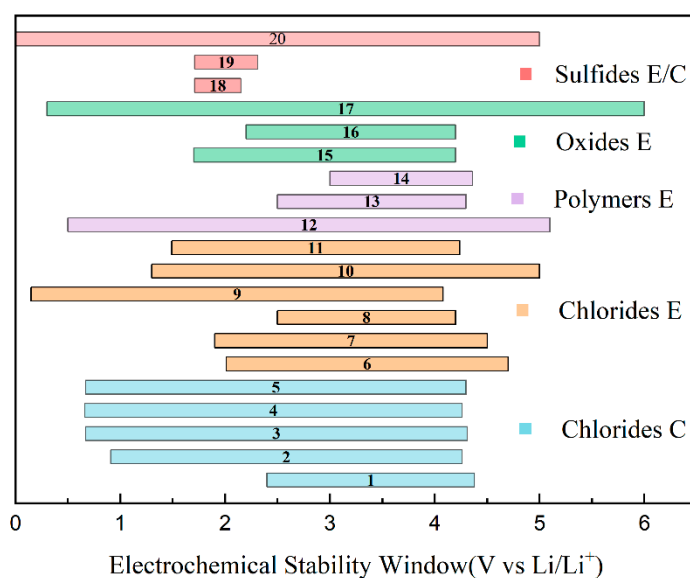


Figure 10. Comparison diagram of electrochemical stability window. The suffix “C” denotes values obtained from theoretical calculations, and the suffix “E” denotes those derived from experimental tests. The corresponding materials from 1 to 20 are Li_3InCl_6 , Li_3ScCl_6 , Li_3ErCl_6 , Li_3YCl_6 , Li_3HoCl_6 , LiAlTaCl_4 , Li_3YCl_6 , Li_3InCl_6 , Li_3ScCl_6 , Na_2ZrCl_6 , NaAlCl_4 , PEO + 2%vol LPS, PEG-distearate-4, C-PEGR, LiAlTiPO_4 , LiAlGePO_4 , NaSiZrPO_4 , LiGePS_4 , Li_3PS_4 , and NPAS [30,32,33,35,68,89,123,124,137,149,152,157,164,165].

Although the oxidation potential of most chlorides is similar, the reduction potential determined by metal ions is quite different, which leads to a difference in the electrochemical stability window width. Now, the outer orbital of anions in chlorides can no longer accommodate extra electrons, so it has an insignificant effect on the reduction potential. In recent years, research direction has mainly focused on how to match lithium sodium metal anodes and further reduce the reduction potential of solid electrolytes to stabilize cycle performance.

5. Compatibility with Electrode Materials

After a chloride solid electrolyte is assembled into a battery, the actual electrochemical stability window may change due to the solid–electrolyte interphase (SEI) generated by the reaction between the electrode and the solid electrolyte [5,166]. In addition, the rapid migration of Li^+/Na^+ at the interface between the electrode and the solid electrolyte is also a key factor affecting the performance of the entire battery. The interface pressure, interface contact, and interface reaction directly lead to the fluctuation of interface impedance [5]. Therefore, compatibility with electrode materials cannot be merely considered a reaction.

5.1. Pursuing High-Voltage Cathode Materials

Given the excellent oxidation stability of chloride itself, its overall level is second only to fluoride. Most chloride oxidation potentials are around 4.2 V, while common cathode materials have operating potentials between 2.8 V and 4.3 V [85]. In the 1990s, some scholars used LiAlCl_4 in combination with LiCoO_2 cathode material, and no other coating materials were used on the surfaces of the cathode materials. The assembled battery only experienced slight capacity degradation, but at that time, this material was not taken seriously due to low ion conductivity [54]. In 2018, Li_3YCl_6 was first used in combination with uncoated LiCoO_2 , achieving a high initial Coulombic efficiency (CE) of 94.8% while maintaining good ion conductivity ($5.1 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$). The high initial CE means that the electrolyte is stable in contact with the cathode and has good interface compatibility. The interface resistance between the cathode and the electrolyte is only $16.8 \Omega\cdot\text{cm}^2$ [30]. This excellent performance proves that chloride is not as low in oxidation stability as expected [167], and scholars began to match chlorides with different cathode materials. In addition to the common LiCoO_2 , $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ series cathode materials are often used in conjunction with chlorides to gain higher capacity. Nazar et al. formed a composite cathode material with $\text{Li}_{2.7}\text{Yb}_{0.7}\text{Zr}_{0.3}\text{Cl}_6$ (LYZC) and $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622) in a ratio of 2:8. The initial discharge capacity can reach $170 \text{ mAh}\cdot\text{g}^{-1}$, and the upper limit of stable cyclic potential can reach 4.3 V. However, due to cracking in NCM622 particles and a decrease in contact with LYZC, the internal resistance increases, resulting in a slight decrease in capacity [168]. Furthermore, Sun et al. [32] combined Li_3InCl_6 synthesized from a simple water medium with $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811). The full cell achieved stable cycling over 70 cycles, with a reversible capacity exceeding $154 \text{ mAh}\cdot\text{g}^{-1}$, and an initial CE of 84.2%. Moreover, Sun et al. used $\text{LiNi}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}\text{O}_2$ (NCM83) with a higher nickel content ratio than NCM811 to match $\text{Li}_{2.556}\text{Yb}_{0.492}\text{Zr}_{0.492}\text{Cl}_6$. The results show that the initial CE is 91.5%, and the maximum discharge capacity is as high as $209.8 \text{ mAh}\cdot\text{g}^{-1}$ (0.1C). After 50 cycles, the capacity retention was 78%, and the discharge capacity was still $141.8 \text{ mAh}\cdot\text{g}^{-1}$ under the condition of 3C in the rate test [161]. In addition to the common cathode materials mentioned above, LiNiCoAlO series cathodes are also used by many scholars [87,127,169]. Others have also attempted to use Se-based cathode materials [57], and some have even mixed a small amount of carbon with chloride (Li_3TiCl_6) [170] as the cathode composite. However, despite offering an innovative approach, the materials mentioned above cannot deliver high energy density due to their low operating voltage. Although chloride SEs can support a cycling cutoff voltage of around 4.5 V, chloride ions above 4.3 V will begin to oxidize and generate lithium-deficient metal chlorides (InCl_3 , etc.) that lack sufficient Li^+ transport pathways, as well as the continuous consumption of SEs, which will deteriorate the overall battery performance [31].

To sum up, in order to achieve a higher matching of high-voltage cathode materials, it is necessary to modify them. Sun et al. [171] proposed a dual halogen element strategy that improves its oxidation stability by replacing some of the chlorine elements in the

original composition with fluorine elements. Although the material itself is still limited by the upper limit of the chloride ion oxidation potential of 4.42 V, its actual electrochemical stability window depends on the passivation interface generated spontaneously in situ. Considering that $\text{Li}_3\text{InCl}_{4.8}\text{F}_{1.2}$ can achieve an ultra-high anodic limit over 6 V, an attempt was made to apply a cutoff voltage of 4.8 V (vs. Li/Li^+) to battery testing. The test results showed that the maximum reversible capacity reached $203.7 \text{ mAh}\cdot\text{g}^{-1}$, and the initial CE was 89.2%, although after 70 cycles, capacity decay was caused by the unstable structure of LiCoO_2 when the voltage exceeded 4.47 V. The characterization results of F K-edge XAS, synchrotron-based scanning transmission X-ray microscopy (STXM), and thermodynamic analyses showed that the passivated LiF layer generated during the first cycle maintained the stability of the following cycles. According to the flat F k-pre-edge feature, excluding LiInF_4 and InF_3 , there were weak metal ligand bonds. Several positions were selected on the surface of the cathode particles, and the corresponding F K-edge spectra showed that the E_0 values of these spectra were the same as those of standard lithium fluoride, indicating that LiF was the main compound of the cathode electrolyte interphase (CEI) layer; this prevents the cathode from continuing to react with the solid electrolyte. During the charging and discharging process, the decomposition energy of LiF against LCO is always 0 meV, which creates interface stability under ultra-high voltage conditions. Although chloride itself has high oxidation resistance due to the presence of chloride ions, the corresponding materials of sodium ions or lithium ions are still very different.

For sodium ion chloride solid electrolyte materials, $\text{Na}_{0.85}\text{Mn}_{0.5}\text{Ni}_{0.4}\text{Fe}_{0.1}\text{O}_2$ (NMNFO), $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ (NVOPF), $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP), and NaCrO_2 (NCO) are currently known to be used as the cathode for full battery performance testing. Compared to Na_3PS_4 ($\sim 933 \Omega$), Na_2ZrCl_6 has a smaller interface impedance with the cathode ($\sim 320 \Omega$), and the formation of an interphase on the cathode and solid electrolyte side contributes to an increase in ionic conductivity (about an order of magnitude). To explore the evolution of the underlying interface, ex situ photoelectron spectroscopy was used to detect the spectra of Zr 3d and Cl 2p, and there was no significant change after 10 cycles, which confirmed the stability of the Na_2ZrCl_6 and cathode interface when in contact with NaCrO_2 up to $\sim 3.6 \text{ V}$ (vs. Na/Na^+). In contrast, S 2p and P 2p XPS spectra all show SO_4^{2-} , PO_4^{3-} , bridging sulfur (P-[S]_n-P), and P_2S_5 originating from Na_3PS_4 . Again, compared to Na_3PS_4 , the interface impedance of Na_2ZrCl_6 is much lower than expected. The results of X-ray photoelectron spectroscopy are like those above, and Na_3PS_4 produces a series of derivatives, indicating poor interfacial stability [89].

Besides, some ultra-high voltage cathodes which are used in liquid battery, such as LiCoPO_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, have shown significant potential (Figure 11). The redox potential of LiCoPO_4 is as high as 4.8 V (vs. Li/Li^+), with a theoretical capacity of $167 \text{ mAh}\cdot\text{g}^{-1}$ [172]. Moreover, the operating voltage of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is also about 4.7 V (vs. Li/Li^+), with an energy density of $650 \text{ Wh}\cdot\text{kg}^{-1}$ [173]. Figure 11 partly lists some representative cathode materials that may not yet have been combined with chlorides. We hope to find more research in this area in the future to further increase the number of cathode materials available.

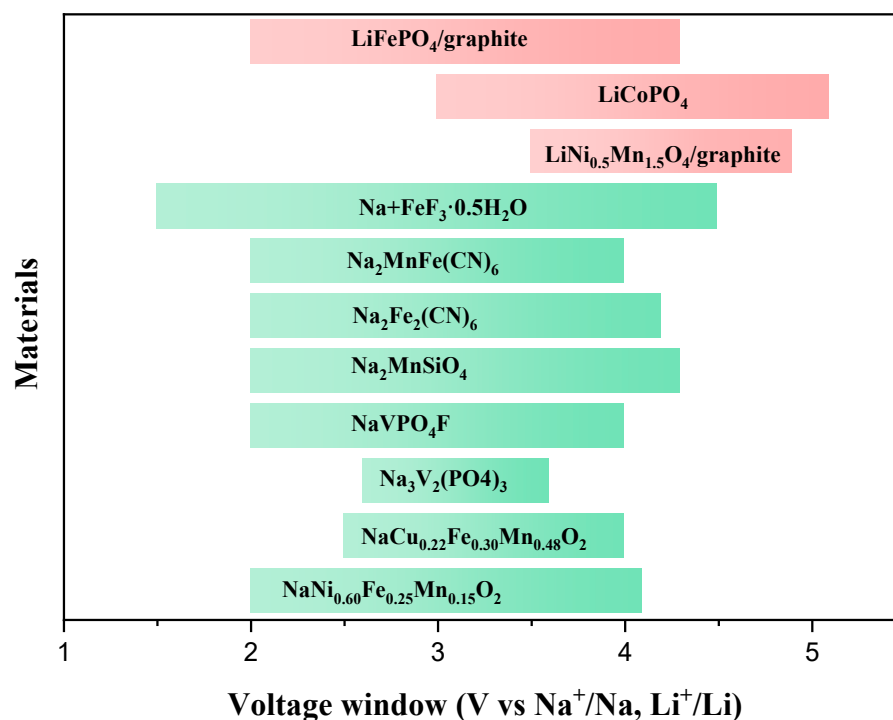


Figure 11. Operating voltage diagram of cathode materials [14,68,116,117,124,137,140,142,146,174,175].

5.2. Anode Misery: Improving the Stability of Lithium/Sodium Metal

Lithium metal, as an ideal anode material, has attracted much attention. It has the lowest redox potential (−3.04 V, compared with the standard hydrogen electrode), which means that high energy density can be achieved with a high-voltage cathode. At the same time, it also has high volumetric and gravimetric (theoretical) energy densities of 2061 mAh·cm^{−3} and 3860 mAh·g^{−1}, respectively [10]. Although its redox potential is low enough, it is not good for chloride SEs. We have discussed, above, how the reduction potential of chlorides depends on the non-lithium metal ions in them, and that anions have little effect currently [161]. Therefore, when chloride SEs are paired with lithium metal, reactions inevitably occur. Some scholars have conducted research specifically on instability, investigating the interface reaction products between Li₃YCl₆ and lithium metal. Research has found that the reduced metal Y provides electronic conductivity, while LiCl provides ionic conductivity. These two products form a mixed conductive phase, allowing the reaction to continue until the chloride electrolyte or lithium metal is consumed first [176,177]. Based on this, we believe that non-self-limiting interface is incompatible with lithium metal anodes compared to the passivation interface. Non-self-limiting refers to a chemical/electrochemical process (e.g., side reaction, dendrite growth, phase transition) that cannot stop spontaneously and will continue to proceed even without external intervention, usually leading to progressive degradation of material performance or structural failure. And passivation is a chemical or electrochemical process in which a thin, non-reactive, and protective solid layer forms spontaneously on the surface of a material when exposed to a specific environment.



For Li_3InCl_6 , the generated In will form an alloy with lithium and disperse in LiCl. The continuous rapid decomposition of Li_3InCl_6 leads to the rapid growth of the interphase, which is harmful to the overall battery resistance [176]. Ma et al. conducted symmetrical battery tests (Li/ Li_2ZrCl_6 /Li) on Li_2ZrCl_6 and lithium metal and found a similar situation to Li_2ZrCl_6 and Li_3InCl_6 , confirming the non-self-limiting nature of the mixed conductive phase (LiCl and Zr) [34]. It is worth noting that although chloride SSEs contain high-valence metal elements with different degrees of reactivity with lithium metal anodes, their compatibility still depends on the actual reduction potential of the central metal in the halide electrolyte [124]. Despite the embarrassing situation, many scholars are still planning to overcome this difficulty, one after another. In 2014, it was discovered that Li_3OCl with an anti-perovskite structure exhibited stability toward lithium metals [90], and Li_2OHCl also exhibited stability in 2016 [178]. Furthermore, Sun et al. reported, for the first time, that Li-M-Cl series chlorides (Li_3ScCl_6) can be directly in contact with lithium metals for symmetrical battery testing. Despite the high polarization voltage during the testing process, the entire testing duration exceeded 2800 h [38]. For some inherently stable metal-free chlorinated nitrides ($\text{Li}_9\text{N}_2\text{Cl}_3$ [179]), a stable symmetrical battery cycle can also be achieved without additional processing (Figure 12).

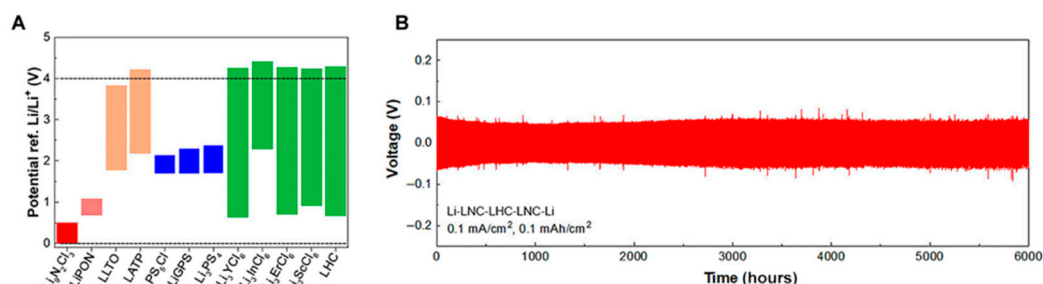


Figure 12. Investigation of all-solid-state lithium symmetric cells: $\text{Li}_9\text{N}_2\text{Cl}_3$. (A) Calculated thermodynamics intrinsic electrochemical windows of different electrolytes (B) a current density of 0.1 mA/cm^2 [179]. Copyright 2023, Science Advances.

Moreover, Yao et al. [35] developed a new type of $\text{Li}_{0.388}\text{Ta}_{0.238}\text{La}_{0.475}\text{Cl}_3$ chloride and successfully combined it with a lithium metal anode. It ran stably for over 5000 h in symmetrical battery testing, and the interface impedance was finally stable at around $610 \Omega\cdot\text{cm}^2$ through time-resolved impedance spectroscopy. In the full battery test, it has successfully operated for 100 cycles at a 4.35 V cutoff voltage. By studying the valence changes in elements at the interface between the solid electrolyte and lithium metal through X-ray photoelectron spectroscopy, it was found that, compared to the large reduction in the In element in Li_3InCl_6 [176], only a small amount of Ta (13.4%) was reduced on the interphase surface. Similarly, only up to 8.4% of La was reduced on the surface, demonstrating good resistance to reduction. At this point, the small amount of La and Ta metal generated is not sufficient to form a continuous conductive network, thus meeting the requirements for anode stability. Meanwhile, through SEM observation, it was found that the tight interface contact between the dense nanocrystalline solid electrolyte and lithium metal is also the key to ensuring anode stability. It can also be seen from the data for the symmetric battery that the corresponding polarization potential under different current densities is low, indicating that the interface between the solid electrolyte and the lithium metal is stable, and the reaction is contained. Compared with metal-free chlorinated nitrides, we selected $\text{Li}_{0.388}\text{Ta}_{0.238}\text{La}_{0.475}\text{Cl}_3$, as it is compatible with both the anode and cathode.

In addition to the reduction resistance of the material itself mentioned above, other means can also be used to achieve the same goal. Faced with the strong reducibility of

lithium metal, researchers prefer to use Li-In alloy [30,127], or a mixture of $\text{Li}_{11}\text{Sn}_6$ and Li_3PS_4 [58], to stabilize the interface, but some scholars have found out that the alloy layer has a lower diffusion rate, and the lithium concentration will decrease in the interlayer area near the interface, leading to an increase in overpotential [10,180]. Some scholars have also used an intermediate protective layer to insert a layer of $\text{Li}_6\text{PS}_5\text{Cl}$ between the chloride electrolyte and the lithium metal, and the reaction between $\text{Li}_6\text{PS}_5\text{Cl}$ and the lithium metal has self-limiting properties to stabilize the interface [33,176]. This method may introduce additional interface impedance. Of course, besides lithium metal, there are other potential anode materials that may be suitable for chloride electrolytes, such as silicon [181,182], silicon composite anode [183,184], high entropy oxides [185], three-dimensional hierarchically porous MoS_2 foam [186], and so on.

Apart from lithium metals, sodium metals still have potential. Their redox potential is -2.71 V, slightly higher than that of lithium metal. However, the volumetric and gravimetric (theoretical) energy density of sodium metal is only one-third of that of lithium metal [187]. Nevertheless, it still has significant advantages compared to other anode materials. At present, there are few reports on sodium ion chloride electrolytes, and according to existing reports, Na-Sn alloy has been used as the negative electrode [89,123]. In the middle of a layer of sulfide (Na_3PS_4), NASICON [78,79] material has been used to help stabilize the sodium metal anode while providing good ionic conductivity. Other representative anode materials, such as hard carbon [188,189], graphite [190], $\text{NaAlTi}_3\text{O}_8$ [191], MoS_2 [186], and $\text{Na}_{0.6}(\text{Cr}_{0.6}\text{Ti}_{0.4})\text{O}_2$ [192], have the potential to be paired with sodium ion chloride electrolytes. Regarding the construction of stable solid electrolytes for metal anodes, Sun's team provided their viewpoint: when combining metal ions with iodine ions with significant polarizability, it is difficult to chemically reduce these materials [193]. However, this is also faced with a problem of two choices: whether to withstand the high-voltage cathode or become compatible with the metal anode. To date, two main strategies are available for pursuing anode stability. First, the development of novel intrinsic anode-stable materials (e.g., $\text{Li}_9\text{N}_2\text{Cl}_3$). Second, the implementation of modification strategies for alloy anodes and electrolytes (Figure 13).

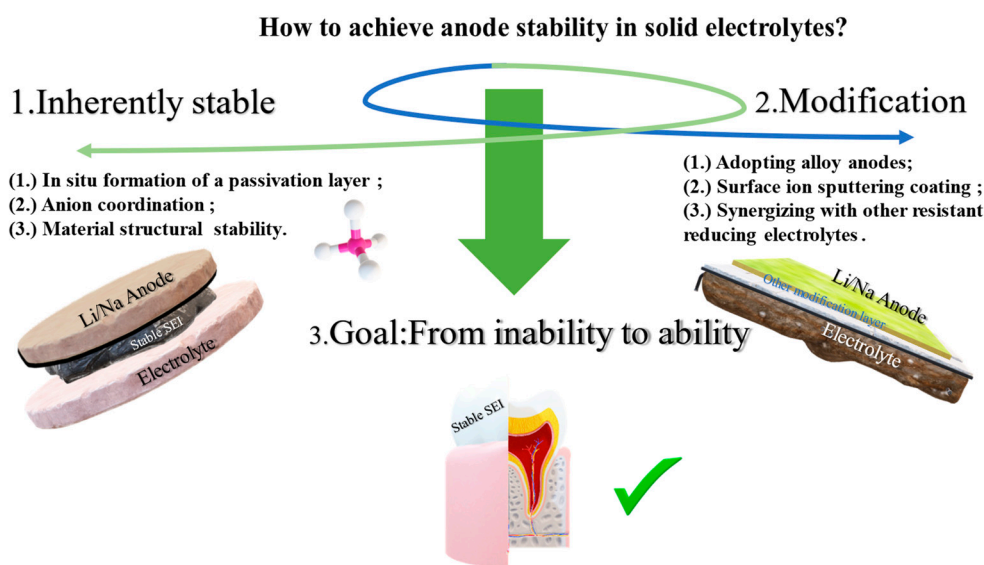


Figure 13. Investigation of all-solid-state lithium symmetric cells.

6. General Characterization Techniques

Next, a brief introduction to some common characterization tools will help us better understand and comprehend the characteristics of these materials. This involves issues related to the material surface that we are more concerned about, such as morphology, interphase thickness, chemical composition, elemental valence states, and distribution [194]. X-ray diffraction (XRD), solid-state nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) are the commonly used characterization tools that we will discuss later.

XRD is applicable to most materials and is commonly used to qualitatively determine the phase composition and to determine the content and structure of components, for example, in general synthesis, detecting the generation of target chlorides or determining whether the material structure undergoes changes under external conditions and observing the types of reaction products in electrode studies [195,196]. For the crystalline structure of halide solid electrolytes, XRD and its refined spectra can accurately analyze the basic structural information by using the peak position and peak intensity. By using in situ and synchrotron X-ray techniques to track the evolution of Li_3InCl_6 under humid air conditions, and by monitoring the shift of XRD peak positions and the appearance of new phases (such as the hydrated form of $\text{Li}_3\text{InCl}_6 \cdot 2\text{H}_2\text{O}$ or In_2O_3 impurities), its unique reversible dehydration/hydration behavior can be revealed, providing an intuitive structural basis for understanding its humidity tolerance mechanism [121]. For synthesized amorphous materials, the broadened part can be easily identified using XRD, which is direct evidence of the formation of an amorphous structure [82,102]. Similarly, XRD is also intuitive for studying the structure of cathode and anode. Lee et al. [197,198] conducted a basic structural study of silicon negative electrode materials using XRD. They found that after processing, the material still maintained a cubic structure and did not transform into amorphous or other phases.

Usually, researchers use nuclear magnetic resonance (NMR) technology to determine the local structure and kinetics of electrodes. The distribution of Na^+/Li^+ ions in the material and the electrochemical reaction mechanism can be clearly explored using $^{23}\text{Na}/^{7}\text{Li}$ nuclear magnetic resonance [199]. Yao et al. revealed the interexchange strength of lithium ions at two different sites using 2D exchange NMR spectroscopy. At $x = 0.388$, the two peaks with the highest intensity are off-diagonal, imply an ultrafast Li^+ exchange between channel sites and La vacancy [35]. This discovery strongly supports the low ion migration energy barrier and high ion conductivity of this material. The concept of “solid-state dissociation” has also benefited from verification by NMR. By analyzing the local chemical environment of Li^+ , it was confirmed that Li^+ forms a unified, rich lithium bond environment dominated by Cl^- (a ~ 0.5 ppm resonance peak) under different salt–solvent combinations, revealing that low coordination numbers and weak lithium bonds are the essence of superionic conduction ($\text{Li}_2\text{SO}_4\text{--ZrCl}_4$, $2/3\text{Li}_3\text{PO}_4\text{--ZrCl}_4$, $\text{Li}_2\text{CO}_3\text{--ZrCl}_4$, $\text{Li}_2\text{O--ZrCl}_4$ and ZrCl_4). By tracking the evolution of peaks during the formation of the structure and changes in conductivity during the solid-state dissociation process, and by reversing the targeted design of the electrolyte based on the subtle displacement differences of different solvents, this provides key structural evidence for the excellent electrochemical behaviors of the electrolyte, such as high ion conductivity, a wide operating temperature range, high rate performance, and high voltage compatibility [111].

X-ray photoelectron spectroscopy (XPS) is applied to detect the surface and interface chemical environment of electrodes [200]. In general research, it is used to detect changes in the combined states of elements to determine the reduction resistance of metal elements in electrolytes [176] or to compare before and after exposure in humidity/air stability tests [126]. Janek et al. [176] conducted an in-depth study of the interfaces between Li_3InCl_6 and Li_3YCl_6 and lithium metal using XPS. By analyzing the changes in the chemical states of

the In and Y elements in the XPS spectra, it was found that In^{3+} and Y^{3+} were reduced to metallic elements, while Cl was converted into LiCl. These products formed a mixed ionic/electron conductor interface layer, which made the reduction reaction non-self-limiting, resulting in a continuous increase in interface impedance and battery failure. This experimental finding directly explains the mechanism of the instability of chlorides toward lithium metal at the atomic level. For the anode side, Jung et al. [89] conducted XPS studies on the interface stability of chlorides (Na_2ZrCl_6), sulfides (Na_3PS_4), and NaCrO_2 as cathode. After multiple cycles, the Cl 2p and Zr 3d spectra showed almost no changes, indicating the integrity of the chloride interface, while the control group Na_3PS_4 detected a large amount of sulfur- and phosphorus-containing oxidation products, proving that the chlorides have higher intrinsic stability.

Scanning electron microscopy (SEM) plays a crucial role in studying surface morphology. Its observation ranges from a few millimeters to a few nanometers, and the resolution is generally 6 nanometers, requiring the observed sample to have conductivity. The interface contact integrity, interface thickness, and even some crack defects between the electrode and electrolyte can be clearly observed [194]. SEM characterization can serve as a crucial link connecting the microstructure, mechanical properties, and electrochemical behavior of connection materials. For instance, by studying the morphology of the quenched (LiYzr-Q) and slowly cooled (LiYzr-N) electrolytes, it was observed that the grain refinement and high-density defects in the quenched samples could enhance the mechanical deformation ability of the material. Moreover, the SEM images of the microstructural evolution of the cathode composite materials before and after cycling show that the particles and interface of LiYzr-Q after cycling are in good contact without obvious cracks, while LiYzr-N presents many cracks, particle fragmentation, and interface peeling. These cracks directly lead to a reduction in the contact area between the cathode and the LiYzr-Q electrolyte, hindering the ion transmission path, and explaining the reasons for the continuous increase in internal impedance and continuous decrease in the capacity of the battery assembled with a LiYzr-N electrolyte compared to a LiYzr-Q electrolyte, as well as poor battery cycle stability. Here, SEM reveals the microscopic mechanism behind the decline in electrochemical performance and corroborates the mechanism of defect-enhanced toughening [129].

7. Overall Research Progress on Chloride All-Solid-State Batteries

7.1. Air/Humidity Stability

The air/humidity stability of materials plays a crucial role in practical electrolyte production and battery assembly processes. Long-term use of inert atmosphere protection is not conducive to large-scale operations and cost control [201,202]. Most SEs have issues with air or humidity stability, especially for sulfides, which have been criticized for air stability [203]. Structural damage, toxic H_2S production, and capacity degradation cannot be underestimated [24,204]. For oxide electrolytes, there is a trend of slow reaction with moist air, generating LiOH and Li_2CO_3 with ion resistance [130,205]. Even PEO polymer SEs that are chemically stable to both water and air are easily oxidized under pure oxygen conditions [25]. It is worth noting that chloride electrolytes can generally remain stable in dry air atmospheres. Because the oxidation potential of Cl^- is much higher than that of O^{2-} , O_2 in the air cannot oxidize chloride ions [202]. In addition to focusing on the condition of dry air, moisture resistance is also a concern.

As far as we know, Li_3InCl_6 [32,121,126] and Li_2ZrCl_6 [34] have been reported to have good moisture resistance and can withstand certain humidity conditions. The moisture resistance mechanism of Li_3InCl_6 has already been discussed in Section 3, so it will not be further elaborated here. The experimental results showed that after 24 h of exposure to a nitrogen atmosphere with a humidity content of 5%, there were no changes in XRD or

XPS results, no notable changes in ion conductivity, and no need to recover after humidity exposure. The authors believe that Li_2ZrCl_6 has better stability than Li_3InCl_6 in an atmosphere with 5% humidity content [34]. Mo et al. provided us with very novel material design guidance on humidity stability. They first studied simple binary-phase LiCl and NaCl , found that LiCl exhibited poor humidity stability. They measured humidity stability through hydrolysis reaction energy and found that ternary chlorides generally have humidity stability because they exhibit positive hydrolysis reaction energy. Nevertheless, given most of the reported results, the actual situation is not as optimistic as the authors think, and there are also significant deviations. It is practical for element In to have the highest hydrolysis reaction energy while corresponding to the best humidity stability, but element Zr exhibits excellent moisture resistance corresponding to lower hydrolysis reaction energy. The abnormalities of other elements will not be elaborated here [206].

Since the first reported case of chloride used in all batteries in the last century, it was not until 2023 that, except for a few chlorides that can be directly prepared in air (need to be dried in vacuum), the preparation, characterization, and battery assembly of almost all chlorides need to be carried out in an inert gas atmosphere (this also includes Li_2ZrCl_6 and Li_3InCl_6 mentioned above). The above results suggest that it is necessary to store the chloride electrolyte in an inert atmosphere to ensure the optimal performance of the battery. Therefore, even if the stability and partial humidity resistance of chlorides in dry air are leveraged for industrial-scale production, the assembly of full cells remains impractical. Determining how to improve long-term air stability and humidity resistance is crucial for the storage and production of finished products, as well as the assembly of full batteries. Wang et al. attempted to reveal the conditions that affect air/humidity stability from different perspectives. Firstly, considering that the absorbed moisture comes from the solid–gas interface, it was found that compacting powder into pellets can greatly improve the moisture resistance of a sample. Secondly, the authors explored the effects of particle size [207] and concluded that the smaller the particle, the faster the water absorption rate, leading to a worse stability situation. Finally, to further improve the air/humidity stability of Li_3InCl_6 , the authors decided to artificially add a protective layer to its surface and deposit it through powder atomic-layer deposition. The water absorption rate of Li_3InCl_6 coated with Al_2O_3 in the air decreased by 25% compared to the initial value, and the deliquescence time increased by seven times [208]. In addition, some scholars have proposed improving the air/humidity stability of materials by doping moisture-resistant elements (In) [209], but this is essentially a conversion to Li_3InCl_6 . According to previous references, Li_3InCl_6 and Li_2ZrCl_6 are currently two known chloride electrolytes with good moisture resistance; it is worth considering whether doping both In and Zr elements at the same time, or whether doping one alone can truly improve stability. At present, the air stability of sodium ion chloride has not been reported.

The moisture resistance of chlorides has a significant impact on their manufacturing and large-scale machining. Materials with good moisture resistance, such as Li_3InCl_6 and Li_2ZrCl_6 , can be synthesized using low-cost liquid-phase processes mediated by water, without the need for expensive inert gas protection. The requirements for large-scale production and processing are relatively relaxed. This can be completed in a conventional drying room without the need for extremely anhydrous equipment. During storage and transportation, there is no need for strict sealing conditions, significantly reducing the cost of large-scale production. It has been reported that a universal and scalable water-assisted synthesis strategy, applied to Al-based chlorides with cheap and readily available raw materials, only requires “manual mixing + low-temperature heating”. Compared to the high-temperature annealing or high-energy ball milling strategies required for materials with poor moisture resistance, this process is simpler, energy consumption is significantly reduced, the equipment cost is low, and its kilogram-scale production feasibility has been

verified, meeting the efficiency and cost requirements of industrial large-scale production [210].

Materials with moderate moisture resistance, such as Li_3YCl_6 , Li_3ScCl_6 , and Li_3ErCl_6 , have been discussed previously and can be synthesized using ammonium-salt-assisted liquid-phase synthesis. However, the atmosphere requirements for large-scale processing are still somewhat high compared to materials with good moisture resistance. The intermediate process should strictly shorten the amount of time that the electrolyte powder is in contact with the air, and the precursors and the synthesized materials should all undergo drying treatment, increasing the complexity of the process and the cost. Materials with poor moisture resistance, such as Na_2ZrCl_6 , must be synthesized in a water-free and oxygen-free glove box (water and oxygen content < 0.1 ppm). The precursors also need to be strictly anhydrous. The environmental control costs for large-scale production, transportation, and storage are extremely high, making it difficult to achieve a continuous production line. Currently, it is only applicable to basic laboratory research and does not have industrial value.

7.2. High-, Low-, and Room-Temperature Battery Performance

The high- and low-temperature performance of batteries is also an important practical indicator, and it is inevitable to encounter sudden temperature drops in winter or hot weather in summer in daily life. In addition, having a wide operating temperature is more advantageous for special purposes, such as military weapons and equipment requiring normal operation in extremely cold or hot conditions. However, the development of the high- and low-temperature performance of batteries currently faces problems. In low-temperature environments, reversible capacity degradation caused by huge interface impedance is inevitable, and ion conductivity will further decrease [211]. Slow diffusion of lithium ions in electrolytes is often considered the main reason for unsatisfactory LIB performance under low-temperature conditions [212]. High-temperature operation is a double-edged sword that can reduce energy barriers and increase ion diffusion rates. Furthermore, it can also worsen side reactions at the electrode–electrolyte interface and be dangerous [213]. Usually, we maximize battery life by balancing competing degradation mechanisms, such as lithium plating at low temperatures and SEI layer growth at high temperatures, when operating at optimal temperatures ($\sim 30^\circ\text{C}$) [214]. Although lead–acid batteries (-30 – 0°C) and some special high-temperature molten salt batteries ($\sim 90^\circ\text{C}$) can meet the conditions of operating at high and low temperatures, they cannot match the portability and large-scale applicability of lithium-ion batteries [211]. Typically, a significant feature of SEs at low temperatures is a significant decrease in ion conductivity [215]. To improve the ionic conductivity of polymers, a method of reducing crystalline is generally used to enhance the movement of organic molecular chains. However, due to the low ionic conductivity of the polymer itself, it is not suitable for too-low environmental temperatures. The above methods have been proven to be effective between 0 and 25°C [216]. Recently, some scholars have reported that polymer ion conductivity reached $2.2 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at -20°C , and a dual-layer SEI strategy was adopted on the lithium metal anode, achieving a capacity retaining of over 75% at -20°C , compared to the first discharge capacity ($151 \text{ mAh}\cdot\text{mg}^{-1}$) [217].

At present, the main low-temperature research focuses on polymer solids and organic solvents, and there are few reports on inorganic solids, as the inherently low ionic conductivity of solids still needs to be maintained by increasing temperature. Operation at low temperatures is not a strength of SEs. Deng et al. gave us a new idea to improve the performance of chloride ASSBs at low temperatures, that is, to adjust the electronic conductivity of the composite cathode instead of improving the ion conductivity in a conventional way. The authors believe that although the further decrease in electrolyte electron

conductivity caused by low temperature helps to avoid self-discharge and stabilize lithium metal anodes, it is not conducive to electron transfer on the cathode side. It has been proven that adding an appropriate number of carbon nanotubes (CNTs) on the cathode side is beneficial for charge transfer without damaging the interfacial stability of the electrolyte (Li_3InCl_6). The initial discharge capacity under the condition of 0.6C at $-10\text{ }^\circ\text{C}$ is $77.6\text{ mAh}\cdot\text{g}^{-1}$, and the capacity retention rate at 0.4C after long-term 300 cycles is 89.2%. In addition, electrochemical analysis shows that the addition of CNTs can significantly increase charge transfer kinetics, resulting in a higher rate capability [218]. Liang et al. obtained an optimal ion conductivity component by adjusting the ratio of lithium to metal elements: $\text{Li}_{3-3x}\text{Ho}_{1+x}\text{Cl}_6$ ($0.04 \leq x \leq 0.2$). At room temperature, the ion conductivity is $1.3\text{ mS}\cdot\text{cm}^{-1}$. They formed a composite cathode with $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ and $\text{Li}_{2.73}\text{Ho}_{1.09}\text{Cl}_6$ in a ratio of 7:3. At 0.025C and $-10\text{ }^\circ\text{C}$, the ASSB of NMC811/ $\text{Li}_{2.73}\text{Ho}_{1.09}\text{Cl}_6$ /In exhibited a reversible capacity of $142\text{ mAh}\cdot\text{g}^{-1}$ and an initial CE of 79.4%. The entire battery also exhibited good cycling performance, with a specific capacity of $90\text{ mAh}\cdot\text{g}^{-1}$ for 100 cycles [219].

In the last century, the first all-solid-state chloride battery was tested at $100\text{ }^\circ\text{C}$, but its poor performance did not attract much attention [54]. Recently, a study revealed that a $\text{VCl}_3\text{-Li}_3\text{InCl}_6\text{-C}$ composite cathode exhibited a reversible charging capacity of $162.5\text{ mAh}\cdot\text{g}^{-1}$. Considering that Li_3InCl_6 also has high ion conductivity at low temperatures ($>10^{-4}\text{ S}\cdot\text{cm}^{-1}$, $-25\text{ }^\circ\text{C}$), the temperature range for full battery testing is between -30 and $60\text{ }^\circ\text{C}$. When the battery is cycled at $-30\text{ }^\circ\text{C}$, it exhibits significant polarization, with a reversible capacity of only $79\text{ mAh}\cdot\text{g}^{-1}$. However, operating at $60\text{ }^\circ\text{C}$ can reduce energy barriers, with a reversible capacity of $169\text{ mAh}\cdot\text{g}^{-1}$, which is twice the low-temperature reversible capacity [220]. In addition to battery performance, Jia et al. investigated the thermal stability of rock-salt-type Li_3InCl_6 and anti-perovskite-type Li_2OHCl with cathode materials at high temperatures. The results indicate that Li_3InCl_6 and Li_2OHCl are stable for some common cathodes and anodes (LiCoO_2 , LiMn_2O_4 , graphite, silicon-carbon, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) at $170\text{ }^\circ\text{C}$, which almost covers most of the operating temperature range [221]. Compared to lithium-ion chloride SEs, sodium-ion chloride has lower ion conductivity ($\sim 10^{-5}\text{ S}\cdot\text{cm}^{-1}$) combined with a high cycling temperature ($60\text{ }^\circ\text{C}$), which can effectively improve the initial CE, capacity, rate performance, and long-term cycling capacity retention [89,123]. At present, there is limited research on the high- and low-temperature performance of chloride SEs, mainly due to the incomplete development of this system in full batteries. Thus, most of them operate near room temperature [222–224].

In view of the good conductivity ($\sim 1\text{ mS}\cdot\text{cm}^{-1}$) and strong oxidation resistance ($\sim 4\text{ V}$) of chlorides at room temperature, the performance of chloride batteries at room temperature is also remarkable. In 1992, LiAlCl_4 was first assembled into a full battery with an average discharge capacity of only $68\text{ mAh}\cdot\text{g}^{-1}$ and no more than 200 cycles. The charge and discharge voltage range is 1.7–2.7 V. During the discharge process, LiCoO_2 experiences a serious polarization phenomenon [54]. Compared with the achievements of the last century, 2018 can be regarded as a new breakthrough, with the mixture of LiCoO_2 (LCO) and LYC as the cathode layer, LYC as the SE layer, and In-Li alloy as the anode. In terms of capacity, it can almost reach $130\text{ mAh}\cdot\text{g}^{-1}$, and the charge and discharge voltage range is about 2–3.5 V. In terms of magnification performance, there is also a capacity retention rate of about 80% at 1C. Moreover, there is no significant polarization phenomenon under good ionic conductivity. However, compared with other systems of SEs, there is still a lot of room for improvement [30]. Hiram and Juhyoun used $\text{NaCrO}_2(\text{NCO})$ as the cathode for Na_2ZrCl_6 and NaAlCl_4 [89,123]. The maximum discharge capacity of Na_2ZrCl_6 combined with NCO is $111\text{ mAh}\cdot\text{g}^{-1}$, the initial CE is 93.1%, and its stable operating potential is up to 3.6 V. A NaAlCl_4 solid-state battery using NCO electrode exhibited a high initial discharge capacity of $114\text{ mAh}\cdot\text{g}^{-1}$, and the initial CE was 95.2%, with an excellent capacity retention rate of up to 82.0% after 300 cycles [54]. Recent reports on SEs for

sodium-ion chloride have shown good performance at room temperature, thanks to the excellent ionic conductivity provided by their amorphous structure. The two sodium-ion chloride materials reported by the team led by Sun [75,79] could achieve stable cycling for 500 and 1500 cycles at room temperature. Particularly, the NaTaCl₆ material demonstrated stable cycling at a high rate of 3C for 4000 cycles at a controlled temperature of 60 °C, with a capacity retention rate of 81%. The inorganic flexible chloride solid electrolyte, which was first proposed by Hu [78], can achieve stable cycling for up to 600 cycles at a rate of 1C at 60 °C, with a capacity retention rate of 85%. Furthermore, the as-assembled batteries enable operation without external pressure by virtue of the intrinsic viscoelasticity of the material. This proves the potential of amorphous sodium-ion chloride for stable long-term cycling. Further detailed battery performance data are presented in Table 2.

Table 2. Performance of solid-state batteries.

Cathode	Electrolyte	Anode	Con (10 ⁻³ S/cm)	Long-Cycle Data			Ref.
				Volt (V)	(Cycle, Retention, Capacity, Tem/°C and Rate)		
LiNi _{0.88} Co _{0.11} Al _{0.01} O ₂	Li ₂ ZrCl ₆	Li–In	0.40 (30 °C)	3–4.3	100-91.3%-170mAh/g-0.5C	30	[127]
LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂	Li ₂ ZrCl ₆	Li–In	0.81 (NM)	2.2–3.8	200-99.9%-149 mAh/g-1C	25	[34]
LiCoO ₂	Li _{2.633} Er _{0.633} Zr _{0.367} Cl ₆	Li ₁₁ SN ₆	1.4 (25 °C)	2.5–4.3	200-99%-80 mAh/g-0.5C	RT	[58]
LiCoO ₂	Li _{5/3} Cr _{1/3} Zr _{1/3} Cl ₄	Li–In	0.313 (RT)	2.5–4.3	650-72.6%-72 mAh/g-0.5C	25	[222]
LiNi _{0.85} Co _{0.1} Mn _{0.05} O ₂	Li _{2.6} Zr _{0.4} Lu _{0.6} Cl ₆	Li–In	1.8 (NM)	2.5–4.8	180-75%-151 mAh/g-0.5C	30	[223]
LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂	Li _{0.388} Ta _{0.238} La _{0.475} Cl ₃	Li	3.02 (30 °C)	2.2–4.3	100-81.6%-130 mAh/g-0.44C	30	[35]
LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂	Li ₃ InCl ₆	In	2.04 (25 °C)	1.9–3.8	70-99%-150 mAh/g-0.1C	25	[32]
SE–LHoC–C	Li ₃ HoCl ₆	Li	1.05 (RT)	1–3	750-99%-402 mAh/g-0.1C	25	[57]
LiCoO ₂ + LNOC	LNOC/Li ₃ YCl ₆	Li–In	10.7 (RT)	2.5–3.6	100-97%-120 mAh/g-0.3C	25	[60]
LiNi _{0.90} Co _{0.05} Mn _{0.05} O ₂	Li _{2.375} Sc _{0.375} Hf _{0.625} Cl ₆	Li–In	2.2 (RT)	2.8–4.3	200-82.7%-160.6 mAh/g-0.5C	30	[131]
LiNi _{0.88} Co _{0.11} Al _{0.01} O ₂	Li ₃ YbCl ₆	Li–In	1.5 (RT)	3.0–4.3	1000-83.6%-160 mAh/g-0.5C	30	[87]
LiCoO ₂	Li ₃ ScCl ₆	In	3 (RT)	1.9–3.6	160-99.2%-104.5 mAh/g-0.1C	25	[38]
LiCoO ₂	Li ₂ Sc _{2/3} Cl ₄	Li–In	1.5 (RT)	3.0–4.3	110-99.8%-170 mAh/g-0.1C	NM	[128]
LiNi _{0.83} Co _{0.11} Mn _{0.06} O ₂	1.6Li ₂ O–TaCl ₅	Li–In	6.6 (25 °C)	1.9–3.8V	2400-90.7%-100 mAh/g-2C	25	[74]
LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂	Li _{1.75} ZrCl _{4.75} O _{0.5}	Li–In	2.42 (25 °C)	2.18–3.68	2082-70.34%-70.2 mAh/g-5C	25	[77]
LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂	Li ₃ Zr _{0.75} OCl ₄	Li–In	1.35 (25 °C)	2.8–4.3	700-80.9%-100 mAh/g-5C	25	[225]
LiNi _{0.88} Co _{0.09} Mn _{0.03} O ₂	Li _{2.5} Zr _{0.5} In _{0.5} Cl ₆	Li–In	1.8 (30 °C)	3.0–4.3	100-86.4%-175 mAh/g-0.1C	30	[226]
LiCoO ₂	Li _{2.22} Zr _{1.11} Cl _{5.33} O _{0.67}	Li–In	1.03 (RT)	2.4–3.6	200-99.8%-110 mAh/g-0.5C	25	[227]
LiCoO ₂	LiAlCl ₄	TiS ₂	NM	0–2.3	160-90%-60 mAh/g-NM	100	[54]
Li ₃ TiCl ₆	Li ₂ ZrCl ₆	Li–In	1 (25 °C)	2.2–2.8	2500-62.3%-70 mAh/g-10C	25	[170]
Li ₃ TiCl ₆	Li ₃ TiCl ₆	LTC	1 (25 °C)	0.2–2.0	2500-50.8%-50 mAh/g-10C	25	[170]
LiNi _{0.91} Co _{0.06} Mn _{0.03} O ₂	LiTaCl ₆	Li–In	10.95 (RT)	2.7–4.3	2500-93.8%-214 mAh/g-2C	NM	[73]
(NCM91)	LiTaCl ₅ F	Li–In	4.37 (RT)	2.7–4.3	2500-96.1%-223 mAh/g 2C	NM	[73]
(NCM91)	LiTaCl ₅ O _{0.5}	Li–In	7.75 (RT)	2.7–4.3	2500-95.3%-220 mAh/g-2C	NM	[73]
(NCM91)	LiTaCl ₆	Li–In	10.95 (RT)	2.7–4.8	200-90.15%-229 mAh/g-0.3C	NM	[73]
(NCM91)	LiTaCl ₅ F	Li–In	4.37 (RT)	2.7–4.8	200-92.81%-240 mAh/g-0.3C	NM	[73]
(NCM91)	LiTaCl ₅ O _{0.5}	Li–In	7.75 (RT)	2.7–4.8	200-92.5%-238 mAh/g-0.3C	NM	[73]
LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	LAC075	Li	1.05 (30 °C)	2.8–4.3	600-72%-125 mAh/g-1C	30	[78]
Na ₃ (VO) ₂ (PO ₄) ₂ F	NAC075	Na	1.05 (30 °C)	3.0–4.3	600-83.5%-106mAh/g-1C	30	[78]
Na ₃ V ₂ (PO ₄) ₃	NaTaCl ₆	Na ₁₅ Sn ₄	4 (RT)	2.7–3.8	250-88%-90 mAh/g-0.2C	RT	[79]
Na _{0.85} Mn _{0.5} Ni _{0.4} Fe _{0.1} O ₂	0.5Na ₂ O ₂ –TaCl ₅	Na ₁₅ Sn ₄	4.62 (RT)	2.5–3.8	500-66%-70 mAh/g-0.1C	RT	[75]
NaCrO ₂	NaAlCl ₄	Na ₃ Sn	0.0039 (30 °C)	2.0–3.5	500-82%-112 mAh/g-1C	30	[123]

NM—not mentioned.

7.3. Manufacturing and Cost

Generally, an ASSB is assembled into a sandwich structure, in which the anode layer and the composite cathode layer are sandwiched between the solid electrolyte layer, like two pieces of bread in a sandwich [5]. The slurry-coating process is often used in the manufacturing process of pouch batteries to achieve the large-scale production of ASSBs. However, polar solvents and binders can have a certain impact on chloride inorganic SEs [228]. Traditional slurry-casting manufacturing in SSB has issues of brittleness, solvent sensitivity, and ion transport obstruction. The solvent-free method can reduce energy consumption and eliminate the drying step. In addition, organic solvents are generally toxic and can cause damage to the environment. Considering the cost, expenses need to be reduced to a certain extent throughout the entire process, from raw materials to cell assembly. Compatibility is suitable for inorganic/polymer SEs, as well as meeting the needs of thick electrodes and reducing binder content [229]. Wang et al. used the solvent-free method for the first time to fabricate freestanding ultra-thin chloride bilayer solid electrolyte membranes. Using polytetrafluoroethylene (PTFE) fibrilization technology, based on only 0.5 wt% PTFE, 99.5 wt% SE powder can be easily interwoven into plastic elastic sheets. Then, $\text{Li}_6\text{PS}_5\text{Cl}$ and Li_3InCl_6 can be prepared as large films with a thickness of 15–20 μm using roll-to-roll pressing. Given the use of solvent-free processes, the high ionic conductivity of inorganic SEs (i.e., $\text{Li}_6\text{PS}_5\text{Cl}$ and Li_3InCl_6) can be well maintained above 1 $\text{mS}\cdot\text{cm}^{-1}$. In the assembly of an entire battery, considering that Li_3InCl_6 has high oxidation stability, it is combined with LiCoO_2 to form a sheet electrode through a solvent-free method. The configuration of all-solid-state pouch batteries is $(\text{Li}_3\text{InCl}_6@\text{LiCoO}_2/\text{Li}_3\text{InCl}_6 + \text{Li}_6\text{PS}_5\text{Cl}/\text{Graphite}@\text{Li}_6\text{PS}_5\text{Cl})$. The initial capacity is $121.2 \text{ mAh}\cdot\text{g}^{-1}$, with a CE of 71.8%. After 50 cycles of testing, this kind of battery still has 75% capacity retention. The assembled pouch battery can also successfully light an LED, indicating that this dry electrode/electrolyte technology has great potential in engineering all-solid-state pouch batteries using chloride electrolytes [230].

In addition to the solvent-free method mentioned for constructing pouch batteries, Xiao et al. attempted a fabrication method similar to the in situ polymerization of polymer-based solid electrolytes [231], carefully stacking and sintering chloride SEs and electrodes together. Compared to in situ polymer solidification, this does not require external conditions to initiate solidification, but the expected goal is consistent, which will hopefully form good contact with the electrode interface before solidification. In traditional assembly methods, the poor contact between inorganic SEs and electrode materials requires the application of high temperature and pressure to avoid the presence of voids and reduce interface impedance [232]. This method involves melting the low-melting-point solid electrolyte into a liquid state (300 $^{\circ}\text{C}$) and then injecting it into the packaged battery to allow it to penetrate the electrode, forming a good contact similar to an organic electrolyte. In terms of equipment, existing equipment can continue to be used, reducing the threshold for industrialization [59].

Besides optimizing the battery manufacturing process, determining how to maximize the control and compression of battery costs is a crucial step in achieving commercialization. For chloride SEs, LiCl is an important raw material composition, and other metal chlorides affect the overall cost of electrolytes. Wang et al. investigated the price and crustal content of some elements suitable for chloride SEs and found from the results that the In element, which is known to have good moisture resistance, as a rare element, has low content and a high price, which increases the cost of electrolytes [29]. Therefore, minimizing the use of elements such as In and Sc and developing a more affordable metal chloride combination is a worthwhile goal, for example, Li_2ZrCl_6 , NaAlCl_4 , Li_2TiCl_6 , and so on. Hu et al. [77] recently reported that $\text{Li}_{1.75}\text{ZrCl}_{4.75}\text{O}_{0.5}$ does not contain any expensive raw materials or precious metal elements commonly used in other chlorides. The synthesis of $\text{Li}_{1.75}\text{ZrCl}_{4.75}\text{O}_{0.5}$ can be directly satisfied by cheaper materials such as LiCl , ZrCl_4 , and Li_2O ,

among which Li_2O may also be obtained through the reaction or decomposition of cheaper compounds (Li_2CO_3 and LiOH). The estimated prices of representative chloride materials, Li_3InCl_6 , Li_3ScCl_6 , and $\text{Li}_2\text{In}_{1/3}\text{Sc}_{1/3}\text{Cl}_4$, are 380.26 USD/kg, 9468.84 USD/kg, and 4418.10 USD/kg, respectively. Compared to these three more expensive typical chlorides, if $\text{Li}_{1.75}\text{ZrCl}_{4.75}\text{O}_{0.5}$ uses the three raw materials $\text{LiOH}\cdot\text{H}_2\text{O}$, LiCl , and ZrCl_4 , the cost of chloride SEs can be as low as 11.60 USD/kg.

Shao's group [222] used density functional theory (DFT) for simulation calculations and experimental optimization to study the lattice chemical properties of Li_2CrCl_4 . By introducing high-valency cations, $\text{Li}_{5/3}\text{Cr}_{1/3}\text{Zr}_{1/3}\text{Cl}_4$ was synthesized, which greatly improved ionic conductivity and provided a good electrochemical window compared to the original material. The raw materials used consist of elements that are abundant and inexpensive. Based on sodium-based Na_2ZrCl_6 , Atsushi [233] obtained an amorphous solid electrolyte by combining different sodium salts (Na_2SO_4 , Na_3PO_4 , Na_2WO_4 , Na_4SiO_4 , or Na_3VO_4) with ZrCl_4 through ball milling and for the first time reported the use of polyanions to weaken the bond between sodium ions and chloride ions, thereby achieving higher ionic conductivity ($1.6 \text{ mS}\cdot\text{cm}^{-1}$). Moreover, the use of industrial raw materials can significantly reduce production costs.

In addition, the team led by Hu [78] has developed a new inorganic viscoelastic solid electrolyte that enables the operation of an ASSB without the need for additional pressure. During the material preparation process, by simply mixing and heating the raw materials (sodium salt/lithium salt and AlCl_3) to remove impurities, a transparent and pure precursor can be obtained. This step can be scaled up to ensure the uniformity of the materials. The prepared MACO, after rolling, can yield inorganic thin film sheets at polymer film thickness, significantly reducing the thickness of the electrolyte. The low melting point of the MACO material ensures a good interface contact between the electrode and the solid electrolyte (Figure 14). Moreover, the team opted for resource-rich raw materials such as NaCl , AlCl_3 to reduce the cost (Figure 15). This concept fully embodies the idea of low cost. Furthermore, vigorously developing sodium-ion chloride materials to avoid the use of lithium elements can also significantly reduce costs, but the performance needs to be improved.

For high-energy ball milling, reducing the synthesis time can significantly lower the cost. Xiao et al. [234] recently developed the Zr-based oxyhalide electrolyte LZC by introducing inexpensive Ta_2O_5 as a "catalyst" and oxygen source, achieving minute-scale synthesis and high ionic conductivity. Ta_2O_5 drives the amorphization of ZrCl_4 during ball milling and forms a core-shell structure: the surface of the Ta_2O_5 crystal nucleus is covered with an amorphous shell rich in [Ta-O-Zr]-bridged oxygen and [Ta-O]-non-bridged oxygen, which cooperatively optimizes the Li^+ migration path.

The interface conduction mechanism enables LZC to meet the practical conductivity of $1.1 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ within 18 min, and the assembled battery is compatible with the uncoated LiCoO_2 cathode. The 450 cycle capacity retention rate exceeds 80%, ball milling is further prolonged to 5 h, the conductivity is improved to $2.02 \text{ mS}\cdot\text{cm}^{-1}$, and 2000 stable cycles at 3C high rate are supported. The strategy reduces the cost by replacing Li_2O with cheap Ta_2O_5 and verifies the universality of the Nb_2O_5 system. Li et al. [81] developed sodium carbonate-oxychloride SSEs ($\text{MCl}_y\cdot x\text{Na}_2\text{CO}_3$) through the decomposition of Na_2CO_3 in high-energy ball milling to produce CO_2 gas acceleration reaction kinetics; a $\text{TaCl}_5\cdot 1.2\text{Na}_2\text{CO}_3$ conductivity of $1.11 \text{ mS}\cdot\text{cm}^{-1}$ was synthesized in 10 min, and a $\text{TaCl}_5\cdot 0.5\text{Na}_2\text{CO}_3$ conductivity of $5.01 \text{ mS}\cdot\text{cm}^{-1}$ was optimized in 10 h, which is the highest conductivity in sodium electricity so far. The structure characterization reveals that [TaOCl] polyhedra are dispersed in the amorphous matrix, and polynuclear anion clusters such as $[\text{Ta}_2\text{O}_4\text{Cl}_3]^-$ are formed by bridging oxygen to construct an efficient Na transport network. The SSEs have a wide electrochemical window, an oxidation window of 4.24 V, and

excellent cathode compatibility. When matched with O3-type cathodes, they achieve 92% capacity retention for 300 cycles. This gas-accelerated synthesis strategy can be extended to the Nb/Hf/Zr/Al system, providing a new paradigm for the large-scale preparation of sodium ion SSEs with low cost and high performance. However, compared with conventional oxide SEs, chlorides have consistently maintained high costs; therefore, it is hoped that their superior performance can compensate for this drawback. Large-scale fabrication remains a critical challenge to be addressed [235].

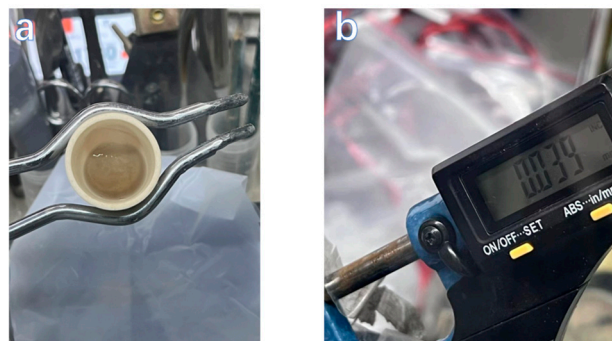


Figure 14. Experimental process photos of MAC and MACO. (a) the melting state of MAC; (b) thickness of the MACO film.

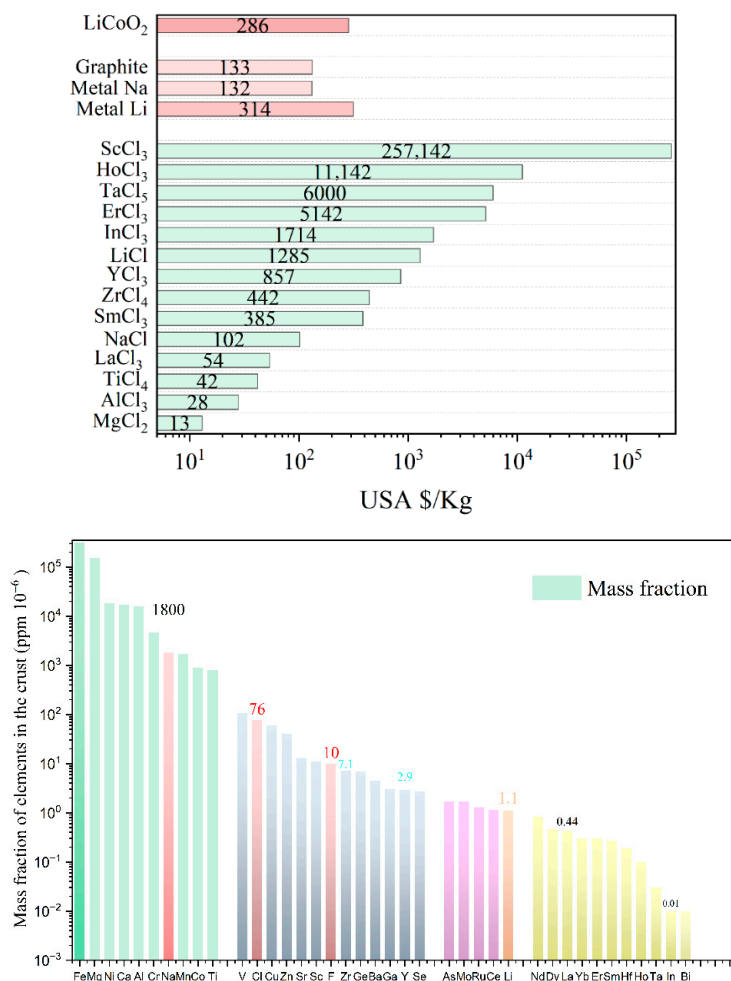


Figure 15. Mass fraction diagram of crustal elements and laboratory-level raw material prices. (Data collection from Wiki).

8. Prospects and Challenges

This review systematically elaborates on the research origins and development course of chloride solid electrolytes, which have evolved from the simplest alkali metal chlorides (LiCl and NaCl) to divalent, trivalent, and even pentavalent transition metal chlorides (MgCl_2 , AlCl_3 , and TaCl_5), making the research selection more diversified. Chlorides are not perfect solid electrolytes, yet their overall performance is more balanced in comparison with other counterparts: oxides suffer from extremely high interfacial impedance, sulfides have potential toxicity, polymers exhibit low ionic conductivity, and borohydrides are restricted by high raw material costs. Thus, chlorides have no particularly severe drawbacks and still retain ample room for further improvement. We have presented an outlook on the future development of ASSBs in Figure 16.

- (1) From a structural perspective, lithium ions with a small ionic radius display excellent ionic migration performance in the traditional crystalline framework of chlorides, but amorphized structures also exert a certain enhancing effect on lithium ion transport; to accommodate sodium ions with a larger ionic radius and pursue higher conductivity, the research and development of chlorides has gradually expanded toward amorphization and structural disordering. The formation of amorphous phases is promoted through the incorporation of nonmetallic elements (F, O, S, N) or the decrease in crystallinity by means of high-energy ball milling. For materials with good crystallinity (ZrCl_4 , YCl_3), repeated mechanical milling facilitates the formation of a stable metastable state, namely the quasi-crystalline state, introducing partially highly disordered regions while preserving the main crystalline structure. In contrast, for materials with poor crystallinity (TaCl_5), repeated mechanical milling tends to induce the formation of an amorphous state.
- (2) The differences between preparation methods and their impact on material properties were explored. The amorphous state provides a broader and more flexible ionic conduction network for Na^+ . The short-range order and long-range disorder structure enable it to maintain a favorable coordination environment for ion transport at short ranges, while the long-range disorder avoids the obstruction of periodic crystal boundaries and specific defects on ion conduction. Through high-entropy cation doping or mixed anion substitution, introduce a large amount of configurational entropy or chemical disorder within the crystal to simulate the diverse local environment of the amorphous state. Design crystalline structures with wide migration channels such as the UCl_3 type, whose framework itself possesses wide one-dimensional channels, and then through doping create three-dimensional connectivity, approaching the openness of the amorphous structure in structure. To date, the highest reported ionic conductivity of lithium-ion chloride electrolytes has reached $13.7 \text{ mS}\cdot\text{cm}^{-1}$, ref. [66] while that of sodium ion chloride electrolytes has also attained $7.2 \text{ mS}\cdot\text{cm}^{-1}$ [83]. According to simulation, result showed that the ion conductivity of $\text{Li}_3\text{Y}(\text{Br}_3\text{Cl}_3)$ was as high as $22.3 \text{ mS}\cdot\text{cm}^{-1}$ [235]. Can sodium ion chloride electrolytes break the $10 \text{ mS}\cdot\text{cm}^{-1}$ barrier? And can lithium ion chloride electrolytes surmount the $20 \text{ mS}\cdot\text{cm}^{-1}$ threshold? The goals may be achieved through further optimization of crystalline structures or directional regulation of disordered structures.
- (3) We focused on the compatibility between chloride and electrode materials, especially high-voltage cathode materials and metal anodes. To meet the demand for high energy density, the electrolyte must remain stable at a high voltage of 4.3 V to minimize the occurrence of side reactions. We can adopt the following strategies to enhance oxidation stability: (1). Partially replace Cl^- with anions with higher electronegativity and greater reactivity (such as F^- , O^{2-}) from the fundamental elements. (2). Select chloride precursors with high voltage tolerance, such as ZrCl_4 . Even if the electrolyte

itself slightly decomposes at high voltages, a thin and dense, highly ion-conductive CEI layer is formed in situ on the cathode surface. (3). Conduct coating modification on cathode materials to reduce their oxidizability. At present, only a small number of chloride solid electrolytes can withstand the reducibility of metal anodes, and the strategies adopted for this purpose are generally as follows: (1). The use of non-metallic precursors (e.g., Li_3N) for synthesizing solid electrolytes can avoid the reduction of metal anodes. (2). Using intrinsic strongly electronegative metal elements (such as Y, Sc, La series, etc.) or elements that can in situ form a passivation interface layer (such as Si, F, O, etc.) (3). Coating certain chlorides or other active substances (such as PI_3) to anode. Mitigate the corrosion of solid electrolytes by metal anodes, analogous to cathode coating. Owing to the high reactivity of metallic sodium, no sodium ion chloride electrolytes capable of withstanding metallic anodes have yet been developed. However, in consideration of safety issues, and more importantly, the future research direction remains the development of electrolytes compatible with safe carbon anodes, tin anodes and other alternative anode materials.

- (4) The overall performance of chloride ASSBs is also a focus of attention, such as that related to air/humidity stability, high- and low-temperature performance, assembly, and cost. Regarding the currently perplexing issue of air/humidity stability, we consider the following strategies to be relatively effective: (1). Using surface atomic layer deposition to form a protective layer on the surface of the halide. (2). Using water-insensitive organic polymers (such as PTFE, PVDF) or water-stable lithium salts (such as LiF) to in-situ coat the chloride powder can form a physical barrier, significantly reduce its water absorption rate and improve its air stability. Elevated-temperature conditions are generally beneficial for the operation of all-solid-state batteries, enabling favorable capacity utilization. In contrast, the decline in ionic conductivity of electrolytes at low temperatures leads to range loss, and it is therefore imperative to maximize the intrinsic ionic conductivity to achieve a conductivity margin at low temperatures.
- (5) How to reduce the external pressure applied to ASSBs during operation? Aluminum-based viscoelastic electrolytes provide a solution. The reliance on external pressure can be significantly reduced by virtue of the intrinsic properties of the material itself. Can more room-temperature viscoelastic electrolytes be developed to meet our demands for diverse performance characteristics, such as the high ionic conductivity of tantalum-based materials and the oxidation resistance of zirconium-based materials? The utilization of low-cost chlorides (e.g., Zr-based, Al-based) can yield substantial cost savings, yet the accompanying performance disparities also merit careful consideration. The remaining performance gaps are included: (1). The ionic conductivity of Zr/Al-based materials typically ranges from 10^{-4} to $10^{-3} \text{ S}\cdot\text{cm}^{-1}$, slightly lower than the top materials of In/Sc-based ones. (2). Some Zr/Al-based chlorides are more sensitive to humidity, and their moisture resistance and air stability are slightly inferior to In-based chlorides. To bridge these gaps, ion doping can be adopted, introducing other transition metal ions such as Ta^{5+} , La^{3+} , Hf^{4+} , etc. or introducing N^{3-} , O^{2-} , F^{-} to optimize the local coordination environment. Partially or completely amorphizing Zr/Al-based chlorides through mechanochemical or composition design to eliminate grain boundary impedance is also an effective means to improve performance. The recently emerging amorphous chloride SEs demonstrate that even sodium ions exhibit high ionic conductivity when freed from the constraints of the intrinsic crystal lattice. However, the highly disordered structure hinders the conventional methods of guiding the further development of new materials. Emerging machine learning is expected to help address the design challenges of amorphous materials, where artificial intelligence (AI) can be leveraged for high-throughput screening and

performance prediction of new materials based on experimentally derived rules and design requirements. In any case, chloride SEs have certain advantages in ionic conductivity, stability, ductility, etc. They are potential candidates to meet the requirements of the future development of ASSBs.

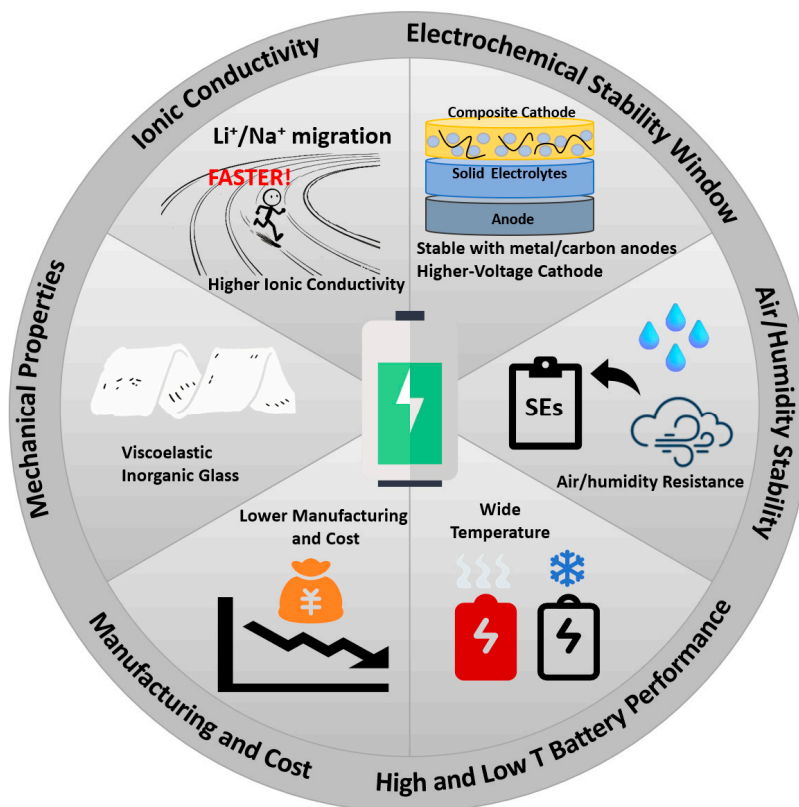


Figure 16. Prospect of future development of ASSBs.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/batteries12020051/s1>. Table S1: Basic information about common chlorides.

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