

Solid-State vs. Liquid Electrolytes: A Comparative Review

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Abstract:

Considering the increasingly stringent safety and energy density requirements of lithium-ion batteries, scientists have focused more on solid-state lithium-ion battery research in recent years. Solid-state electrolytes (SSEs) have emerged as a transformative solution to the intrinsic limitations of conventional liquid electrolytes, particularly in mitigating safety hazards and enhancing energy density for next-generation batteries. This review systematically contrasts the fundamental mechanisms of SSEs and liquid electrolytes, demonstrating how SSEs address critical challenges. Firstly, the superior thermal stability eliminates flammable components, fundamentally preventing thermal runaway chains. Secondly the robust mechanical properties physically suppress lithium dendrite penetration. Finally, the extended electrochemical windows enable stable operation with high-voltage/high-capacity electrodes. Despite these advantages, interfacial resistance and high manufacturing costs remain key barriers to large-scale adoption. Future advancements hinge on innovative interface engineering, scalable synthesis of stable SSE materials (e.g., oxygen-doped sulfides), and system-level designs such as bipolar stacking. Emerging applications in multivalent-ion batteries and solid-state lithium-sulfur systems are also discussed as pivotal frontiers for sustainable energy storage.

Keywords: Solid-state electrolytes; liquid electrolytes; thermal stability; dendrite suppression; thermal runaway mitigation

1. Introduction

The innovation in energy storage technology is a core driver for the widespread adoption of electric vehicles (EVs), the integration of renewable energy into the grid, and the sustained advancement of portable electronics [1]. Among various storage technologies,

lithium-ion batteries (LIBs), owing to their high energy density and relatively long cycle life, have become the dominant market choice [2].

However, as the demand intensifies for batteries offering longer range, faster charging, and, crucially, enhanced safety, the inherent limitations of conventional liquid-based LIBs are increasingly exposed,

posing critical bottlenecks to their further evolution. Safety, the most fundamental and vital requirement for batteries, faces severe challenges due to the presence of flammable organic solvents in liquid electrolytes — incidents of fires or even explosions triggered by thermal runaway are frequently reported, causing not only property damage but also posing significant risks to human life [3].

Concurrently, to achieve higher energy density for extending the runtime of devices per charge or increasing the driving range of EVs, the industry is actively pursuing high-voltage cathode materials (e.g., lithium-rich manganese-based, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) and high-capacity anode materials (e.g., silicon-based anodes, lithium metal). Regrettably, conventional liquid electrolytes, constrained by their limited electrochemical stability window and severe parasitic reactions with highly reactive electrodes (especially lithium metal), struggle to accommodate these high-performance materials, acting as a stumbling block to the leap in energy density [4].

It is against this backdrop that Solid-State Electrolytes (SSEs) have emerged as the highly anticipated core material for next-generation batteries. By eliminating flammable liquid components, SSEs promise to fundamentally enhance the intrinsic safety of batteries [5]. Their wider electrochemical stability window paves the way for pairing with high-voltage/high-capacity electrodes, unlocking the potential for significantly higher energy density. Moreover, their solid nature offers the possibility to physically suppress lithium dendrite growth. Consequently, gaining a deep understanding of and systematically comparing the core working mechanisms of liquid electrolytes and SSEs, dissecting their respective strengths, limitations, and performance in practical applications, is of paramount importance for accelerating the development and deployment of the next generation of safe, high-performance batteries [6]. This review aims to synthesize the progress in this dynamic field, providing a clear perspective for future technological breakthroughs.

2. Liquid Electrolytes: Composition, Mechanisms, and Inherent Challenges

Liquid electrolytes (LEs) are fundamental components of commercial lithium-ion batteries (LIBs), typically comprising lithium salts dissolved in organic carbonate solvents. Their core function is to facilitate reversible lithium-ion (Li^+) transport between the electrodes while electronically insulating them. Ion conduction relies on the solvation of Li^+ ions by solvent molecules, forming solvation sheaths, and occurs through solvent rearrangement and ion diffusion/migration within the liquid phase

[4].

The evolution of LEs has been driven by the need to overcome critical performance barriers:

Establishing Foundational Stability: Early developments focused on achieving reversible Li^+ transport and stable solid-electrolyte interphase (SEI) formation on graphite anodes. EC-based electrolytes with LiPF_6 emerged as the dominant paradigm, where EC forms a protective SEI layer preventing solvent co-intercalation and graphite exfoliation, while LiPF_6 provides adequate conductivity and passivates aluminum current collectors [4, 7, 8].

Compatibility with Advanced Electrodes: To enable higher energy density silicon anodes and high-voltage cathodes ($>4.2\text{V}$), research shifted towards interfacial stabilization using functional additives. Examples include fluoroethylene carbonate (FEC) to form robust LiF -rich interphases on silicon and suppressants like 1,3-propane sultone (PS) to mitigate salt decomposition at high voltages [7, 8].

Enabling Lithium Metal Anodes: Targeting ultra-high energy density, recent efforts concentrate on suppressing lithium dendrite growth. Strategies like “solvent-in-salt” and localized high-concentration electrolytes minimize free solvents and form stable aggregate structures, improving Li plating efficiency and enabling lithium-metal full cells [9, 10].

Despite continuous optimization, LEs suffer from inherent limitations that critically impact safety and energy density:

Thermal Instability: The flammable organic solvents (e.g., EC/DMC) have low flash points ($<40^\circ\text{C}$) and decompose violently at elevated temperatures (e.g., $\sim 150^\circ\text{C}$), generating gases (CO_2 , HF) and acting as the primary trigger for thermal runaway cascades, as evidenced by decomposition rates significantly exceeding those of cathodes [10].

Uncontrolled Li Dendrite Growth: The dynamic nature of the SEI and inhomogeneous Li^+ flux can lead to inhomogeneous lithium deposition. Dendrites, under stress ($>5\text{ MPa}$), readily penetrate separators, causing internal short circuits [11].

Narrow Electrochemical Window: Conventional LE systems oxidize at voltages typically below $4.3\text{ V vs. Li}^+/\text{Li}$. Operating with high-voltage cathodes ($>4.5\text{V}$) accelerates electrolyte decomposition and transition metal dissolution from the cathode, leading to severe capacity fade [12]. This intrinsic voltage limitation restricts the use of high-capacity, high-voltage electrode materials. These fundamental challenges of LEs regarding safety hazards and energy density bottlenecks underscore the impetus for exploring solid-state electrolytes as a transformative solution.

3. Solid-State: Fundamental Distinc-

tions from Liquids

3.1 Definition and characteristics of SSEs

Solid-State Electrolytes (SSEs) represent the cornerstone material for next-generation batteries promising enhanced safety and energy density. Fundamentally, they are solid ionic conductors that selectively facilitate the transport of charge-carrying ions (e.g., Li^+ , Na^+ , Mg^{2+}) between the cathode and anode within a battery cell while blocking electronic conduction, thereby enabling electrochemical cycling. In stark contrast to conventional Liquid Electrolytes (LEs), SSEs exhibit fundamental differences in physical state, microstructure, ion transport mechanisms, and consequently, their functional properties. SSEs are inorganic, organic, or composite ionic conductor materials existing in the solid state (crystalline, glassy, or glass-ceramic). Their defining characteristics, which underpin their advantages over LEs, include: (1) Solid State: Absence of flow, fundamentally eliminating flammable organic solvent components and enhancing intrinsic safety [5]. (2) Ionic Conduction: Possessing appreciable ionic conductivity. While achieving room-temperature conductivity comparable to liquids (typically 10^{-3} to 10^{-2} S/cm) remains a key target and is realized primarily in sulfide-based SSEs [6], many other SSE types exhibit lower conductivities that still meet application requirements, especially at elevated temperatures or in thin-film configurations. (3) Electronic Insulation: Exhibiting extremely low electronic conductivity, preventing internal short circuits and enabling stable electrochemical operation [5, 6]. (4) Wide Electrochemical Window: Typically offering a broader electrochemical stability window ($>5\text{V}$ for many oxides) than LEs ($<4.5\text{V}$), enabling compatibility with higher voltage/capacity cathode materials [5, 6].

3.2 Physical State, Microstructure, and Classification of SSEs

Liquid Electrolytes (LEs): Consist of lithium salts (e.g., LiPF_6) dissolved in organic solvents (e.g., EC, DMC), forming a homogeneous liquid phase. Ion transport relies on the solvation of Li^+ ions by solvent molecules, forming solvation sheaths, and occurs through solvent molecule rearrangement and ion diffusion/migration within the solution. Their structure is inherently dynamic and fluid [13]. Solid-State Electrolytes (SSEs): Possess distinct physical states and microstructures that fundamentally govern their ion transport mechanisms and functional properties. These states include rigid lattice structures (crystalline), disordered network structures (amorphous/glassy), or composites thereof (e.g., glass-ceramic). Ion transport occurs within the solid matrix, primarily dependent on the

specific microstructure:

3.2.1 Crystalline SSEs

Ion migration occurs via “hopping” between predefined sites within specific channels of the crystal structure (e.g., 3D networks in garnets, interlayer gaps in layered oxides, 1D channels) or through vacancy defects. Representative materials include:

- (1) Oxide SSEs (e.g., garnet LLZO/ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, perovskite LLTO, NASICON LATP): Offer exceptional chemical/electrochemical stability (especially against air and lithium metal) and outstanding thermal stability ($>1000^\circ\text{C}$), with a wide electrochemical window ($>5\text{ V}$). However, they typically exhibit moderate room temperature ionic conductivity (10^{-6} - 10^{-3} S/cm), are rigid and brittle leading to poor solid-solid contact, and require high-temperature sintering ($>1000^\circ\text{C}$), increasing cost and hindering thin-film fabrication.
- (2) Crystalline Sulfide SSEs (e.g., LGPS/ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, argyrodite LPSCl/ $\text{Li}_6\text{PS}_5\text{Cl}$): Boast very high room temperature ionic conductivity (10^{-3} - 10^{-2} S/cm, rivaling liquids). Their inherent deformability facilitates good electrode contact via cold pressing or low-temperature annealing ($<300^\circ\text{C}$). Drawbacks include poor air/chemical stability (reacting with moisture/air to generate toxic H_2S), often requiring interface modification for stability against lithium metal, a relatively narrower electrochemical window necessitating protective layers for high-voltage cathodes, and potential high raw material costs.

3.2.2 Amorphous (Glassy) SSEs

Ion diffusion occurs along energetically favorable pathways facilitated by the relatively open structure and large “free volume” in the disordered network. The ratio of network formers (e.g., P_2S_5) to network modifiers (e.g., Li_2S) critically influences ionic mobility. Representative materials include:

- (1) Sulfide Glass SSEs (e.g., Li_2S - P_2S_5): Share the high conductivity potential of crystalline sulfides and good deformability. Similar drawbacks regarding chemical stability (H_2S generation), interfacial compatibility, and electrochemical window apply. Processing often involves melt-quenching or mechanical milling.
- (2) Polymer SSEs (primarily PEO-based complexes with Li salts like LiTFSI): Provide excellent flexibility, processability, and film-forming ability at relatively low cost, ensuring good electrode interface compatibility, especially with lithium metal. Their significant limitations stem from the amorphous polymer matrix: low room temperature ionic conductivity (typically $<10^{-4}$ S/cm, requiring operation at 60 - 80°C), a relatively narrow electrochemical window ($<4\text{V}$), lower mechanical strength/modulus lim-

iting dendrite suppression capability, and inferior thermal stability compared to oxides/sulfides.

3.2.3 Composite SSEs

Composite SSEs combine materials from different categories to leverage synergistic effects. Typically comprise inorganic fillers (e.g., LLZO, LLTO, LGPS nanoparticles) dispersed in a polymer matrix (e.g., PEO), or inorganic fillers within ionic liquid gels. Ion transport may involve conduction through the polymer matrix (enhanced by segmental motion and interfacial effects), conduction through the inorganic particles themselves, or along particle-particle/polymer interfaces. Examples include PEO blended with LLZO or LGPS particles. They aim to combine advantages like polymer processability with inorganic conductivity/modulus/stability. Challenges include ensuring uniform filler dispersion and stable interfacial properties, mitigating long-term phase separation risk, and addressing safety concerns if residual liquid components are present. Glass-ceramics (e.g., some $\text{Li}_2\text{S-P}_2\text{S}_5$ based materials heat-treated to form nanocrystals within a glass matrix) can also be considered a type of composite material.

3.2.4 Thin-Film SSEs

Thin-Film SSEs are a special category characterized by fabrication into ultra-thin, dense layers (e.g., via sputtering, PLD). Amorphous LiPON (Lithium Phosphorus Oxynitride) is the prime example, offering exceptional interfacial homogeneity and electrochemical stability, making it suitable for micro-batteries. However, applicability is limited by very low room temperature ionic conductivity ($\sim 10^{-6}$ S/cm) and complex, expensive fabrication processes. While often amorphous, thin-film techniques can also produce crystalline SSE layers.

4. Advantages and Challenges of SSEs

4.1 How SSEs solve the problems of LEs

4.1.1 Intrinsic Thermal Stability: Breaking the Thermal Runaway Chain

The fundamental thermal safety weakness of liquid electrolytes lies in the flammability of their organic solvents. Solid-state electrolytes, particularly oxides like garnet-type LLZO ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$), address this issue at its root due to their inorganic nature. Critical high-temperature synchrotron X-ray diffraction studies (Janek group) directly demonstrated that LLZO maintains its crystal structural stability up to 1000°C. This stands in stark contrast to liquid electrolytes (e.g., 1M $\text{LiPF}_6/\text{EC:DMC}$), which undergo violent decomposition and gas evolution (e.g., CO_2 peak intensity reaching 1200 a.u.) at relatively

mild temperatures around 150°C. Similarly, polymer SSEs such as cross-linked PEO-PEGDA also exhibit non-flammability and retain structural integrity at 150°C, as validated by combustion tests [14]. This exceptional thermal stability stems from the complete absence of flammable organic solvent components in SSEs, thereby fundamentally breaking the characteristic “thermal decomposition - gas evolution/expansion - thermal runaway” chain reaction pathway prevalent in liquid systems. Practical safety test results validate this advantage: full cells employing LLZO SSEs successfully pass the stringent UL 1642 nail penetration test, with their surface temperature rise effectively limited to only 22°C, significantly lower than that of liquid electrolyte-based batteries (typically exceeding 300°C) [15].

4.1.2 Mechanical Dendrite Suppression: Fulfilling the Dendrite Blocking Criterion

Lithium dendrite penetration leading to short circuits is a major failure mode in liquid batteries, particularly lithium metal batteries. SSEs, especially sulfides with excellent deformability (e.g., $\text{Li}_6\text{PS}_5\text{Cl}$, LPSCl), address this challenge by providing a robust mechanical barrier. Pioneering observations by the Kato group using high-resolution operando transmission electron microscopy (TEM) revealed that when subjected to enormous stress (up to 18 GPa) from lithium dendrite tips, LPSCl could accommodate dendrite growth through significant elastic deformation without catastrophic fracture. This behavior contrasts sharply with the brittle solid electrolyte interphase (SEI) formed in liquid electrolytes, which fractures under stresses as low as 5 MPa. The core mechanism behind this lies in the high shear modulus of LPSCl (~ 18 GPa), which significantly exceeds twice the shear modulus of lithium metal, thereby satisfying the dendrite mechanical blocking criterion proposed by Monroe and Newman [16]. Oxide SSEs like LLZO ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) achieve dendrite suppression via high shear modulus (~ 60 GPa), enabling stable cycling at 0.5 mA/cm^2 for 300 hours in symmetric cells [17]. Thin-film amorphous LiPON ($\text{Li}_{2.9}\text{PO}_{3.3}\text{N}_{0.4}$) demonstrates exceptional interfacial homogeneity, preventing dendrite initiation over 5,000 cycles at 1 mA/cm^2 in solid-state micro-batteries [18]. This effective mechanical blocking is reflected in practical electrochemical performance: Li/LPSCl/Li symmetric cells can cycle stably for over 1000 hours at current densities as high as 2 mA/cm^2 without short-circuit failure, whereas analogous systems using liquid electrolytes typically fail within 200 hours even at 0.5 mA/cm^2 [19].

4.1.3 High-Voltage Compatibility: Constructing Stable Cathode Interfaces

Achieving compatibility with high-voltage cathode materials (e.g., Ni-rich layered oxides like NMC) is crucial for increasing energy density. SSEs can effectively suppress interfacial side reactions and transition metal dissolution at high voltages by in-situ forming or pre-constructing passivating layers at the cathode interface that are ionically conducting but electronically insulating. A classic and mechanistically well-understood example comes from the work of the Goodenough group. They significantly enhanced interfacial stability by constructing an artificial cathode electrolyte interphase (CEI) layer of the fast ion conductor Li_3OCl on LiCoO_2 (LCO) or NMC cathode materials. Detailed characterization (including electrochemical testing and materials analysis) demonstrated that this Li_3OCl interfacial layer effectively prevents the dissolution and migration of transition metal ions (e.g., Co^{3+} , Mn^{2+}) from the cathode material into the electrolyte during high-voltage cycling. The mechanism involves: Li_3OCl itself being an excellent lithium-ion conductor (Li^+ conductivity can reach $\sim 10^{-3}$ S/cm), ensuring efficient Li^+ transport; simultaneously, it acts as a physical and chemical barrier, isolating direct contact between the high-voltage cathode active material and the electrolyte, thereby inhibiting oxidative decomposition reactions. Moreover, LLZO-coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) cathodes reduce interfacial resistance to $23 \Omega\cdot\text{cm}^2$ and show 92% capacity retention after 100 cycles at 4.4V, outperforming liquid electrolytes by 40% [20]. Benefiting from this stable interface design, full cells using Li_3OCl -coated LCO or NMC cathodes paired with sulfide SSEs (e.g., $\text{Li}_2\text{S-P}_2\text{S}_5$) exhibit significantly improved cycling stability at a high cut-off voltage of 4.3 V (vs. Li^+/Li), with much superior capacity retention compared to uncoated counterparts or cells using liquid electrolytes [21].

4.2 Challenges and Mitigation Advances of SSEs

4.2.1 Interfacial challenges

The high interfacial resistance ($>100 \Omega\cdot\text{cm}^2$) between solid-state electrolytes (SSEs) and electrodes remains a primary obstacle. This stems from poor physical contact and chemical incompatibility. For instance, garnet-type LLZO reacts with ambient moisture to form insulating Li_2CO_3 passivation layers, which increase interfacial resistance by over 200 $\times$ (from $<10 \Omega\cdot\text{cm}^2$ to $>2,000 \Omega\cdot\text{cm}^2$) and severely limit critical current density to $<0.2 \text{ mA}/\text{cm}^2$ [22]. Sulfide SSEs like $\text{Li}_6\text{PS}_5\text{Cl}$ undergo electrochemical decomposition at Ni-rich cathodes (e.g., NMC811), generating highly resistive $\text{Li}_2\text{S}/\text{P}_2\text{S}_5$ interphase that accelerates transition metal dissolution. As quantified by X-ray photoelectron spectroscopy (XPS), this degradation causes 40%

capacity fade within 50 cycles at 4.3V [23].

4.2.2 Recent Mitigation Advances

The latest solutions include interface engineering and process innovation. Interface engineering: Atomic layer deposition (ALD) of ultrathin Al_2O_3 ($<5 \text{ nm}$) on LLZO surfaces decomposes Li_2CO_3 via the reaction: $\text{Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3 \rightarrow 2\text{LiAlO}_2 + \text{CO}_2$. These transforms insulating layers into ion-conductive LiAlO_2 , reducing interfacial resistance from $>1,000 \Omega\cdot\text{cm}^2$ to $<20 \Omega\cdot\text{cm}^2$. Consequently, critical current density increases by 300% to $0.6 \text{ mA}/\text{cm}^2$, enabling stable cycling of the cells. Process innovation: Solvent-assisted sintering using $\text{LiOH-B}_2\text{O}_3$ flux lowers LLZO densification temperature by 300°C (from $1,200^\circ\text{C}$ to 900°C). This reduces energy consumption by 40% and mitigates Li evaporation, facilitating the fabrication of crack-free $80\text{-}\mu\text{m}$ thick membranes. Roll-to-roll compatibility of this process has been demonstrated for 10-m-long SSE tapes, advancing scalable manufacturing [24].

5. Conclusion

Solid-state electrolytes (SSEs) address the intrinsic limitations of liquid electrolytes through three core mechanisms: intrinsic thermal stability, mechanical dendrite suppression, and high-voltage compatibility. Validations include nail-test temperature rise of only 22°C (vs. $>300^\circ\text{C}$ for liquids), critical dendrite-penetration current density of $2 \text{ mA}/\text{cm}^2$ (vs. $<0.5 \text{ mA}/\text{cm}^2$ for liquids), and $>40\%$ improvement in capacity retention at high voltage. Nevertheless, interfacial issues dominate SSE performance limitations, with resistance often exceeding $100 \Omega\cdot\text{cm}^2$ due to poor physical contact (e.g., LLZO/Li metal) and electrochemical degradation. Material costs (e.g., sulfide SSE synthesis cost $\sim \$50/\text{kWh}$) also remain barriers to scalability. Recent advances in interfacial engineering and process innovation offer promising pathways: atomic layer deposition (ALD) of ion-conductive coatings reduces LLZO interfacial resistance by 98% ($<20 \Omega\cdot\text{cm}^2$), and solvent-assisted sintering lowers LLZO processing temperatures by 300°C , enabling crack-free thin films ($80\mu\text{m}$) and scalable roll-to-roll production.

Future priorities demand in situ interface construction (e.g., ALD- Al_2O_3) to reduce resistance below $10 \Omega\cdot\text{cm}^2$ and graded interfaces to mitigate stress. Material development requires optimized oxide sintering (e.g., microwave) for $<20\mu\text{m}$ LLZO and atmosphere-stable sulfides (e.g., O-doped $\text{Li}_6\text{PS}_5\text{ClO}_x$) to suppress H_2S . Manufacturing must scale solution-processed sulfide SSEs to $<\$20/\text{kWh}$, while system integration needs bipolar stacking exceeding $400 \text{ Wh}/\text{kg}$ and $>95\%$ La/Zr recovery. Additionally, exploring multivalent systems (e.g., Mg^{2+} diffusion in

MgSc₂Se₄) and solid-state Li-S batteries (sulfide SSEs suppress polysulfide shuttling >99%) is critical.

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