Nanostructured Solid Electrolytes for Enhanced Safety and Performance of Battery Materials

Yangsongyue Cui

Department of QMES, Northwestern Polytechnical University, Xi’an, Shaanxi, 710072, China

2021304054@mail.nwpu.edu.cn

Abstract. Solid-state batteries (SSB) have garnered significant attention by reason of their potential advantages over traditional liquid electrolyte batteries, including higher energy density, enhanced safety, and reduced volume. However, the development and implementation of solid electrolytes confront several challenges, such as lower ionic conductivity, dendrite formation, and interface stability issues. This review explores the current advancements in solid electrolytes (SLs), with a focus on nanostructured materials, including solid polymer electrolytes (SPEs), solid inorganic electrolytes (SIEs), and composite solid electrolytes (CSEs). The review highlights the benefits of nanostructuring in improving mechanical intensity, ionic conductivity and thermostability. Key methods for synthesizing nanostructured solid electrolytes (NSLs), such as the sol-gel method and 3D printing, are discussed. Additionally, the review addresses critical challenges, including the high cost of materials and manufacturing processes, and proposes future research directions to overcome these barriers. The purpose is to comprehensively understand the current status and future potential of NSL in promoting SSB technology.

Keywords: Solid electrolyte, limitation of battery materials, nanostructured materials.

1. Introduction

All batteries consist of two electrode layers and one electrolyte layer. Recent research has increasingly focused on the complexity of electrolyte components, which can be categorized into liquid electrolytes, mixed electrolytes, and SLs [1-3]. As shown in Figure 1. SLs have garnered significant attention due to their advantages over liquid electrolytes, including higher energy density, enhanced safety, and reduced volume, owing to the absence of solvent interference [1]. However, SLs also face several challenges. Current research suggests that nanostructures can significantly improve the ionic conductivity of SLs, enhance the stability of electrolyte/electrode interfaces, suppress dendrite nucleation and growth, and improve mechanical properties [2]. This article primarily explores the current development, advantages, classification, and limitations of SLs, with a particular focus on the role of nanostructures in enhancing the performance of solid-state electrolytes.

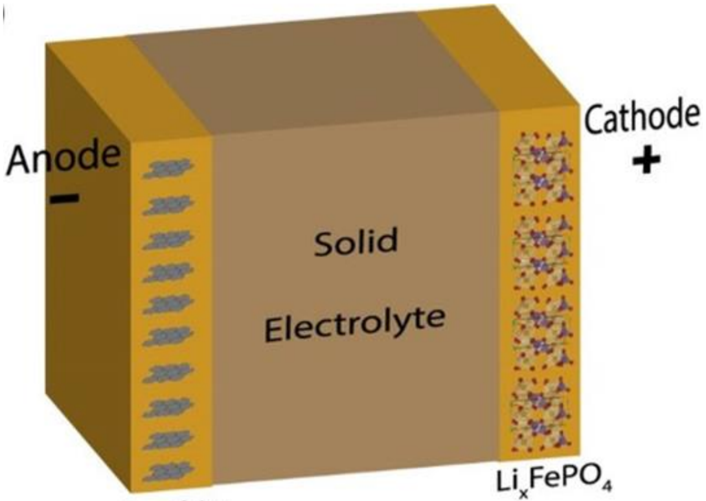

Figure 1. Schematic diagram of solid-state battery [4]

2. Fundamental Challenges in Solid Electrolytes

Solid-state electrolytes face several key challenges that impact their performance and reliability. As shown in Figure 2. One major issue is the stability of the electrode-electrolyte interface. The interface's structure and composition differ from those of bulk materials, which can suppress the performance of the interface and, consequently, the battery's overall efficiency. Ensuring stable and effective contact at this interface is crucial for optimal battery operation [1, 4]. Another significant challenge is the dendritic growth of metal electrodes [1, 3, 5]. Uneven deposition of metals can result in the formation of dendrites, which may penetrate the solid electrolyte and reach the cathode. This can lead to short circuits, posing a serious safety risk and limiting the practical application of SSB. Controlling dendritic growth is essential to enhance the safety and longevity of these batteries [4]. Additionally, the contact points between the electrode and solid electrolyte can lead to the generation and diffusion of cracks. The sensitivity of electrode materials to stress can cause crack propagation and even delamination at the interface, which can significantly degrade the battery's mechanical integrity. This issue adversely affects critical battery performance parameters, including energy density and cycling stability, making it a major focus area for improving solid-state battery technology [4].

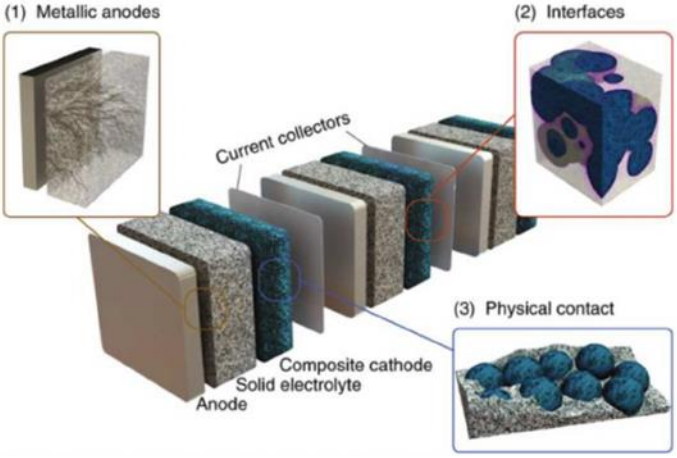

Figure 2. Microscopic schematic diagram of three challenges faced by SSB [5]

3. Types of Solid Electrolytes

3.1. Solid inorganic electrolytes

SIEs typically use ceramics and other inorganic substances. Figure 3 shows the microstructure of a solid inorganic electrolyte. SIEs have high modulus, conductivity, and thermal stability. The solid inorganic electrolyte is a single-ion cationic conductor. Compared with traditional liquid electrolytes, it has higher charge transfer efficiency due to its high transfer number [6, 7].

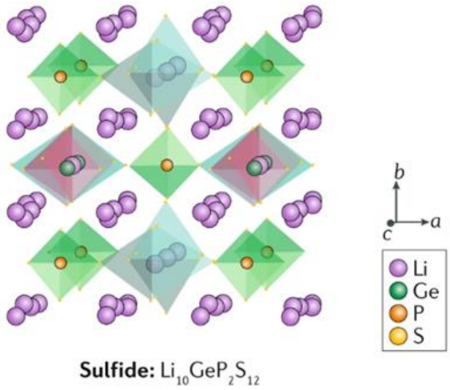

Figure 3. The microstructure of common SIEs [6]

SIEs offer numerous advantages, but there are still challenges that limit their widespread application. As shown in Figure 4, one significant issue is their high brittleness, which leads to dendrite growth in metal electrodes. This growth can cause fractures in the SIEs, complicating mechanical manufacturing processes [6]. Additionally, the poor contact between solid electrodes and the electrolyte often results in inefficient charge transfer at the interface, further reducing the overall performance of the battery [6-8].

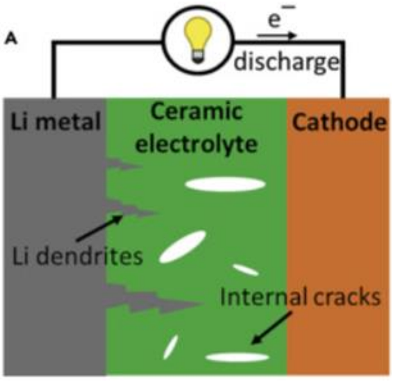

Figure 4. The environment faced by SIEs in lithium batteries [7]

Another challenge is the relatively high cost of SIEs, which can hinder their commercial viability. A key focus of current research is finding ways to enhance the mechanical strength of these electrolytes to prevent dendrite-induced fractures. However, increasing strength often compromises ionic conductivity, creating a need to balance these two critical properties. Researchers are actively exploring methods to optimize both conductivity and strength to improve the practicality of SIEs in advanced battery technologies [8].

3.2. Solid Polymer Electrolytes

Solid polymer electrolytes are composed of high molecular weight polymers. Divided into artificial synthetic and natural polymer materials. Figure 5 shows the microstructure of a common solid organic electrolyte. SPE has multiple advantages compared to SIE. Including ease of synthesis, low mass density, high chemical stability, low cost, and environmentally friendly [6, 8].

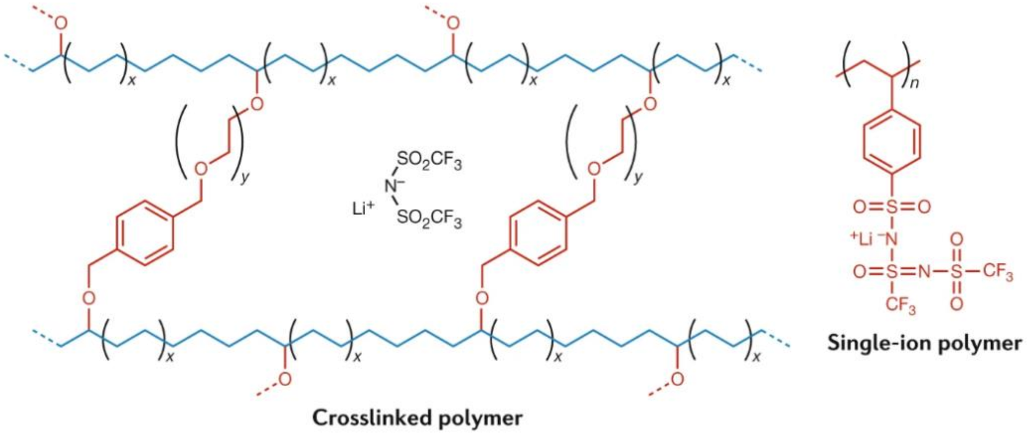

Figure 5. The microstructure of common SPEs [6]

The low conductivity of SPEs has been a major research topic recently. To address this deficiency, it is necessary to balance the strength and conductivity of SIE. Researchers have developed CSEs.

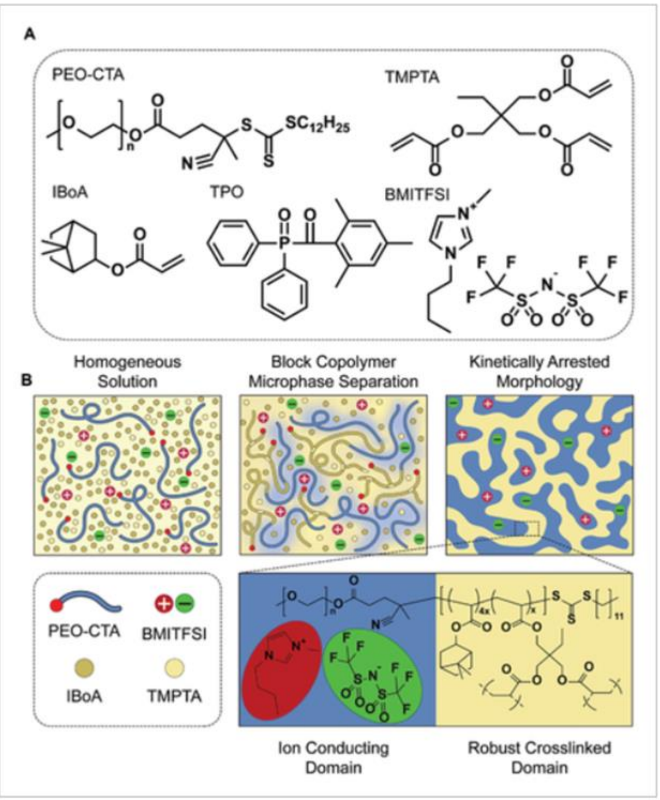

Figure 6. Overview of PIMS Process Flow [9]

The incorporation of nanostructures in SPEs can significantly enhance both ionic conductivity and mechanical properties. Utilizing aggregation-induced microphase separation (PIMS) technology (As shown in Figure 6), continuous nanoscale ion conductive channels can be embedded within a rigid cross-linked polymer network. This structure provides an efficient pathway for ion transport. The combination of a rigid cross-linked styrene/divinylbenzene (S/DVB) network with a polyethylene oxide (PEO) domain allows the material to maintain a high elastic shear modulus while also exhibiting excellent ionic conductivity. SPEs with nanostructures can achieve ionic conductivities as high as $\sigma = 3 \times 10^{-4}$ S cm^{-1} at room temperature. The high strength of these electrolytes is crucial for improving the cycling stability of electrochemical devices, as it helps inhibit the growth of lithium dendrites in lithium batteries, thereby enhancing overall device performance and safety [9].

3.3. Solid Polymer Electrolytes

CSEs are composed of one or more polymer matrices combined with inorganic reinforcements, such as ceramics or lithium salts. These reinforcements can significantly enhance specific properties of SPEs [8]. For example, active fillers like lithium salts can increase ionic conductivity, while passive fillers like ceramics reform thermal and mechanical properties, maintaining essential flexibility and thermostability during battery operation [9]. CSEs consist of one or more polymer matrices and reinforcements. Reinforcements can usually be inorganic materials such as ceramics or lithium salts [9, 10]. Adding reinforcement can improve specific SPE performance, such as increasing ion conductivity (active fillers), and improving thermal and mechanical properties (passive fillers) to maintain essential flexibility and thermostability during cell operation. In the latest study, the maximum ionic conductivity of UV-curable PUA with a LiTFSI content of 30% by weight at room temperature reached 0.0032 mS/cm.

The improvement of ion conductivity is not the only focus of current research. In addition, other functions related to CSEs are also being developed. Such as self-healing performance, flame retardancy environmental friendly, etc., as shown in Figure 7. Crosslinking sodium alginate in a PEO matrix filled with LiTFSI can produce a solid electrolyte with flame retardant ability and improved mechanical stability and also has a stable electrochemical platform of up to 4.6 V [11]. Yellow yarrow gum is a complex mixture of natural polysaccharides mainly collected from the legume shrub plant Astragalus membranaceus. Has good thermal stability and antioxidant properties. It can dissolve in water and form a viscous gel-like solution. Yellow yarrow gum can be used to manufacture water-based SLs with minimal environmental impact. SLs with high stability, ionic conductivity, and a stable electrochemical platform up to 3.4V can be obtained by filling lithium nitrate [12].

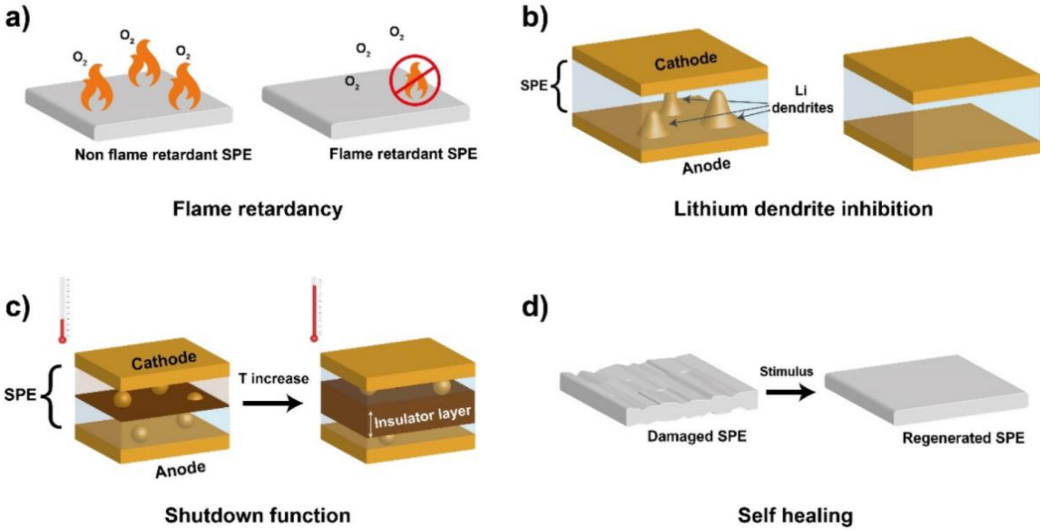

Figure 7. Other properties of CSEs under development [13]

3.4. Synthesis Method of Nanostructured Solid Electrolyte

The methods of synthesizing nanostructures can be divided into the polymer composite method, nano template method, advanced manufacturing technology, in-situ polymerization and self-assembly method, and sol-gel method [14, 15].

The polymer composite method is the process of combining inorganic ceramic nanoparticles with a polymer matrix to form a nanocomposite solid electrolyte. The nano solid electrolyte synthesized by this method combines the high ionic conductivity of inorganic ceramics with the good processability and mechanical properties of polymers [14]. Nanotemplates such as porous membranes, nanofibers, etc. can be used to guide the formation of nanostructures in SPEs. This method can accurately control the porosity and morphology of the electrolyte [14]. Thus, suitable ion conductivity and mechanical properties for SSB can be obtained. Advanced manufacturing methods mainly include 3D printing and electrospinning technology. They are typically used for synthesizing more complex nanostructures. The nanostructures manufactured using these two methods are more precise [13, 14].

The use of 3D printing technology to manufacture SLs with nanostructures involves several critical steps. Initially, resin formulations are designed to achieve suitable electrochemical and mechanical properties, ensuring they are amenable to the manufacturing process. These formulations must balance the need for high ionic conductivity with sufficient mechanical strength and stability. In a recent study, ion-conducting channels with nanostructures were created using the aggregation-induced microphase separation (PIMS) process, a self-assembly technique. This process was implemented using a digital light processing (DLP) 3D printer. The printer utilizes visible light-mediated polymerization reactions to directly print the liquid resin formulations into solid structures. During printing, the resin rapidly solidifies, forming a solid polymer electrolyte with nanostructures. This approach allows for precise control over the architecture of the electrolyte, potentially enhancing its ionic conductivity and mechanical properties [13].

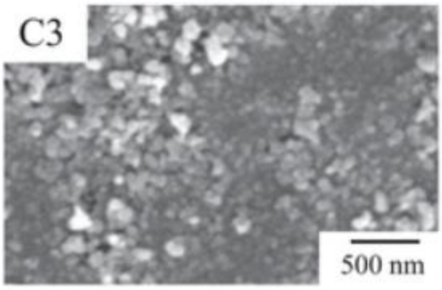

Figure 8. $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ SLs SEM picture prepared by gel method [15]

A team synthesized $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ SLs (The microstructure is shown in Figure 8) using the sol-gel method with titanium sources. [15] The synthesis of nanomaterials via the sol-gel method involves several crucial steps. First, a precursor solution is prepared using suitable metal salts/metal alkoxides, which are dissolved in a solvent, such as water or alcohol. Chelating agents, stabilizers, and other auxiliary agents are added to this solution to control the reaction process and the performance of the final product. The precursor solution then undergoes hydrolysis, alcoholysis, or chelation reactions, gradually transforming into a sol, which is a uniform solution or colloidal suspension of precursor molecules in the solvent. Next, the sol is converted into a gel by adjusting parameters such as pH, temperature, or time, forming a three-dimensional network structure. This gel formation involves continuous solid network synthesis through condensation and cross-linking reactions between the precursor molecules. The gel is aged under controlled conditions to further consolidate its network structure. The solvent in the gel is subsequently removed using techniques such as supercritical drying, freeze drying, or conventional drying, resulting in either a xerogel or aerogel. The final step involves heat-treating the xerogel or aerogel at high temperatures to remove any residual organic matter, enhance crystallinity, and induce the desired phase transitions. This heat treatment is crucial for developing SLs with excellent ionic conductivity [16]. As shown in Figure 9.

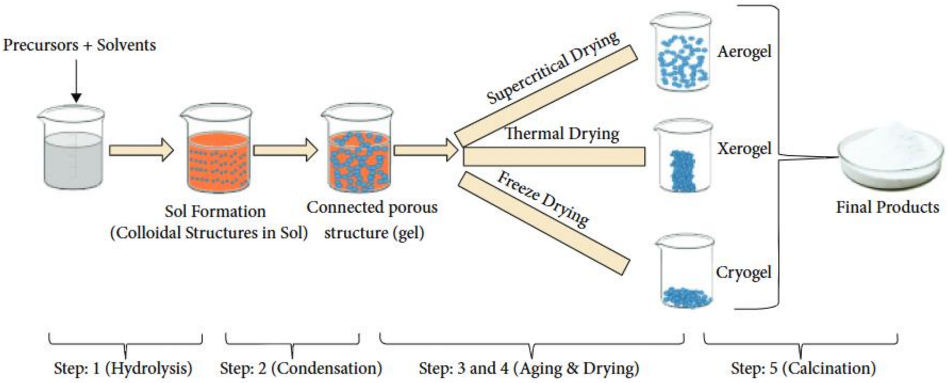

Figure 9. Synthesis of Nanomaterials by gel method [16]

4. Enhancements in Safety and Performance Through Nanostructuring in Solid Electrolytes

4.1. Enhancing Ionic Conductivity Through Nanostructuring

Nanostructuring modifies the microstructure of SLs to increase the density of ionic pathways and reduce path length. This alteration is achieved through the integration of nanoscale features such as particles, fibers, or layers, which can reshape the conduction landscape and enhance the overall ionic flux. The reduced dimensionality and increased surface area of nanostructured materials facilitate shorter and more numerous ionic pathways, effectively lowering the energy barriers associated with ion migration across interfaces. PEO-based block copolymers are the most widely studied type of nanostructured polymer electrolytes. Polystyrene b-polyethylene oxide (PS-b-PEO) block copolymers form nano-layered structures through self-assembly. The PEO layer serves as the ion conductive phase, while the PS layer serves as the mechanical support phase. This structure significantly improves ion conductivity while maintaining a certain mechanical strength. PEO is prone to crystallization at low temperatures, leading to a decrease in ionic conductivity. But when using nanostructures. The movement of PEO chains is limited at the nanoscale. It makes it difficult to form a complete crystal structure, thus maintaining high ionic conductivity [17]. In addition, when using PEO as the matrix and ceramics as fillers to prepare CSEs. It can be observed that the ion conductivity of the composite solid electrolyte is significantly improved when the size of the ceramic filler is reduced [14]. As shown in Figure 10 below:

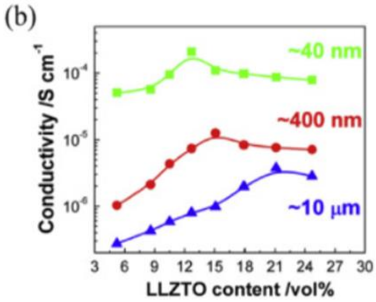

Figure 10. The functional relationship between the ionic conductivity of PEO: LLZTO ICEs and the volume fraction of LLZTO particles at different particle sizes [14]

4.2. Addressing Interfacial Challenges

The interface between the electrode and electrolyte in SSB is critical for efficient charge transfer and overall battery stability. Nanostructuring at this interface has proven to be an effective approach to address these challenges by promoting better mechanical contact and enhancing electrochemical stability. Techniques such as the deposition of nanoscale interlayers or the creation of interfacial nanostructures have been employed to augment physical contact and reduce interfacial resistance. Additionally, nanostructured interfaces can significantly enhance the stability and durability of the electrolyte-electrode interface, which in turn improves the battery's charge-discharge efficiency and lifespan. These advancements are essential for the exploitation of more reliable and high-performance SSB.

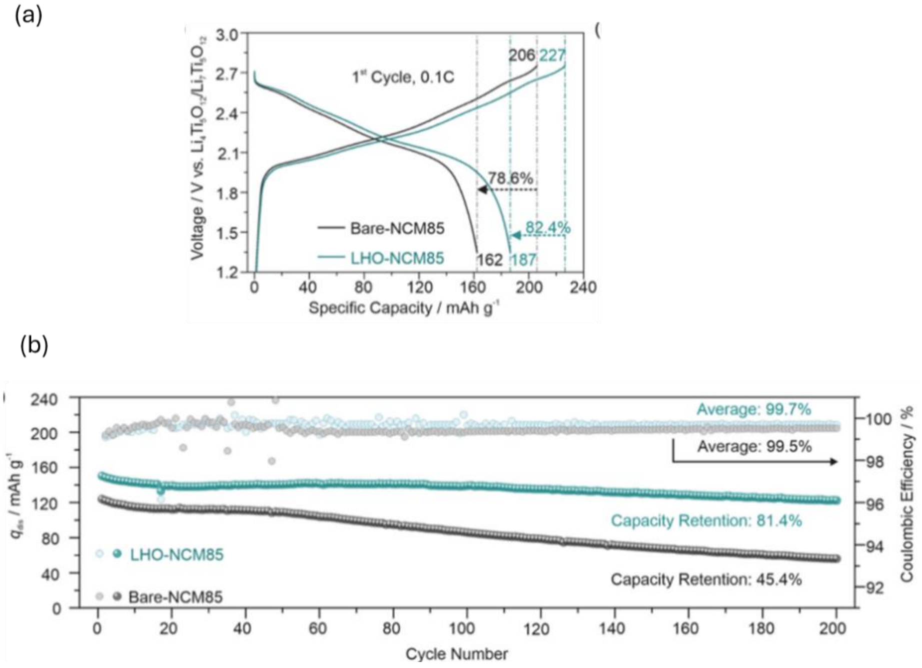

Figure 11. (a) Comparison of voltage platforms between LHO-NCM85 and bare NCM85 electrode materials. (b) Comparison of cycling performance between LHO-NCM85 and bare NCM85 electrode materials [18]

For elevating the interface performance between SLs and electrodes using nanoparticle coatings. Ruizhuo Zhang and his team uniformly coated the NCM85 electrode surface with LHO nano coatings (Li_2HfO_3 and HfO_2 nanoparticles). By exhibiting higher specific discharge capacity and Coulomb efficiency during the cycling process, as well as smaller voltage drop and higher average voltage.As shown in Figure 11. This indicates that the nanoparticle coating can effectively suppress side reactions at the interface and reduce resistance accumulation. Improved the cycling performance and specific capacity of the battery [18].

Junbao Kang and his team prepared porous ferroelectric ceramic BIT NFs using electrospinning technology and high-temperature calcination process. It was mixed as a nanofiller in the PEO/LiTFSI system to prepare a composite solid electrolyte‘ Due to its high piezoelectric constant, BIT is a ferroelectric ceramic. Its ferroelectricity and piezoelectricity help promote the dissociation of lithium salts and achieve uniform deposition of lithium ions at the electrolyte/lithium negative electrode interface. Thereby inhibiting the growth of lithium dendrites. The porous structure (As shown in Figure 12) of CSEs ensures good contact with the polymer matrix, constructs a long-range and continuous organic-inorganic interface and provides sufficient contact sites. This promotes rapid ion transport. At 50°C, the ionic conductivity of the electrolyte is 6.25×10^{-4} S cm^{-1} [19].

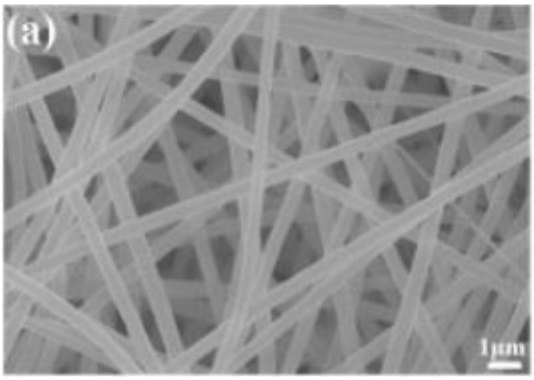

Figure 12. SEM images of BIT NFs [19]

4.3. Improvements in Mechanical and Thermal Properties and Safety

The enhanced surface area and modified thermal pathways in nanostructured electrolytes contribute to better heat dissipation, which is crucial for maintaining operational stability and preventing thermal degradation.

The porous nanostructure composite electrolyte was developed by Junbao Kang's team as mentioned earlier. This increases the specific surface area of the electrolyte, thereby improving heat transfer efficiency. Moreover, the porous structure implies excellent heat dissipation performance. This can maintain the battery at a relatively low-temperature level during operation, greatly improving the safety and cycling performance of the battery.

Incorporating nanostructured ceramics or polymers within the electrolyte matrix has been shown to distribute mechanical stresses more evenly and introduce ductility to otherwise brittle materials. Reducing Fire and Leakage Risks: NSLs eliminate the risks of leakage and flammability associated with liquid electrolytes due to their stable solid state.

In Jiulin Hu's team's research, g-C_3N_4 porous microspheres were used as fillers to prepare composite electrolytes. G-C_3N_4 is composed of many two-dimensional nanosheets stacked together, which gives it a high-strength skeleton with high strength (shear modulus of approximately 21.6 GPa). High mechanical strength nanofillers can effectively inhibit the growth of lithium dendrites, as they can provide stronger support structures and prevent local breakthroughs of lithium dendrites [20].

In addition to suppressing dendrite growth to avoid battery short circuits and improve safety. In Mi Xu's research, a reinforced concrete architecture was constructed by embedding highly conductive PDIL into a robust CCNF network. Achieve ultra-high mechanical strength and enhance mechanical robustness. This directly enhances the safety of SLs, preventing electrolyte failure or battery failure caused by physical damage [21].

5. Conclusion

Currently, nano-solid electrolytes still lag behind liquid electrolytes in terms of ionic conductivity. Additionally, the issue of bonding between the electrode and the solid electrolyte interface remains unresolved. Future research will focus on developing new nano-solid electrolyte materials and optimizing their structure, as well as reducing the impedance at the electrode-solid electrolyte interface. Another critical challenge preventing the widespread adoption of SSB is their cost. Research efforts are needed to develop low-cost, high-performance nano solid electrolyte materials and to reduce production costs through optimized manufacturing processes and improved material utilization rates. The establishment of a comprehensive industrial chain will be crucial in addressing these challenges and promoting the broader adoption of SSB.

With the rapid development of new energy technology, SSB, as the next generation of high-performance and high-safety energy storage devices, is gradually becoming a research hotspot. This article delves into the significant improvement in battery performance and safety through the use of nano-solid electrolyte materials. Although SLs face many challenges, recent research has optimized them in various aspects through nanomaterials, including ion conductivity, mechanical properties, safety, and thermal stability. In future research, reducing material costs and simplifying synthesis methods to form an industrial chain in the production of SSB will be extremely important directions for future development.

References

[1] Sen S, Richter F H. Typology of battery cells–from liquid to solid electrolytes. Advanced Science, 2023, 10 (33): 2303985.

[2] Tu Z, Nath P, Lu Y, et al. Nanostructured electrolytes for stable lithium electrodeposition in secondary batteries. Accounts of chemical research, 2015, 48 (11): 2947-2956.

[3] Zhang Z, Han W Q. From Liquid to Solid-State Lithium Metal Batteries: Fundamental Issues and Recent Developments. Nano-Micro Letters, 2024, 16 (1): 24.

[4] Famprikis T, Canepa P, Dawson J A, et al. Fundamentals of inorganic solid-state electrolytes for batteries. Nature materials, 2019, 18 (12): 1278-1291.

[5] Wang L, Li J, Lu G, et al. Fundamentals of electrolytes for SSB: challenges and perspectives. Frontiers in Materials, 2020, 7: 111.

[6] Zhao Q, Stalin S, Zhao C Z, et al. Designing solid-state electrolytes for safe, energy-dense batteries. Nature Reviews Materials, 2020, 5 (3): 229-252.

[7] Lutkenhaus J L, Flouda P. Ceramic Electrolytes Get “Tough” on Lithium Metal Batteries. Matter, 2020, 3 (1): 14-15.

[8] Barbosa J C, Goncalves R, Costa C M, et al. Toward sustainable solid polymer electrolytes for lithium-ion batteries. ACS omega, 2022, 7 (17): 14457-14464.

[9] Barbosa J C, Gonçalves R, Costa C M, et al. Metal–organic frameworks and zeolite materials as active fillers for lithium-ion battery solid polymer electrolytes. Materials Advances, 2021, 2 (12): 3790-3805.

[10] Yu X, Manthiram A. A review of composite polymer-ceramic electrolytes for lithium batteries. Energy Storage Materials, 2021, 34: 282-300.

[11] Kale S B, Nirmale T C, Khupse N D, et al. Cellulose-derived flame-retardant solid polymer electrolyte for lithium-ion batteries. ACS Sustainable Chemistry & Engineering, 2021, 9 (4): 1559-1567.

[12] Yu X, Manthiram A. Sustainable battery materials for next-generation electrical energy storage. Advanced Energy and Sustainability Research, 2021, 2 (5): 2000102.

[13] Lee K, Shang Y, Bobrin V A, et al. 3D printing nanostructured solid polymer electrolytes with high modulus and conductivity. Advanced Materials, 2022, 34 (42): 2204816.

[14] Hu C, Shen Y, Chen L. Recent advances in nanostructured composite solid electrolyte. Current Opinion in Electrochemistry, 2020, 22: 51-57.

[15] Kotobuki M, Koishi M. Preparation of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ solid electrolyte via a sol-gel method using various Ti sources. Journal of Asian Ceramic Societies, 2020, 8 (3): 891-897.

[16] Bokov D, Turki Jalil A, Chupradit S, et al. Nanomaterial by sol-gel method: synthesis and application. Advances in materials science and engineering, 2021, 2021 (1): 5102014.

[17] Glynos E, Pantazidis C, Sakellariou G. Designing all-polymer nanostructured solid electrolytes: Advances and prospects. ACS omega, 2020, 5 (6): 2531-2540.

[18] Zhang R, Ma Y, Tang Y, et al. Conformal Li_2HfO_3/HfO_2 Nanoparticle Coatings on Layered Ni-Rich Oxide Cathodes for Stabilizing Interfaces in All-SSB. Chemistry of Materials, 2023, 35 (17): 6835-6844.

[19] Kang J, Yan Z, Gao L, et al. Improved ionic conductivity and enhancedinterfacial stability of solid polymer electrolytes with porous ferroelectric ceramic nanofibers. Energy Storage Materials, 2022, 53: 192-203.

[20] Hu J, Tian J, Li C. Nanostructured carbon nitride polymer-reinforced electrolyte to enable dendrite-suppressed lithium metal batteries. ACS Applied Materials & Interfaces, 2017, 9 (13): 11615-11625.

[21] Dou H, Xu M, Zhang Z, et al. Biomass Solid-State Electrolyte with Abundant Ion and Water Channels for Flexible Zinc–Air Batteries. Advanced Materials, 2024: 2401858.