Nanomaterials in Solid-State Batteries: Enhancing Safety and Performance

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Abstract. Solid-state batteries (SSBs), utilizing solid electrolytes instead of liquid ones, represent a promising advancement in energy storage technology due to their higher energy density and enhanced safety. Despite their potential, SSBs face significant challenges such as high interfacial resistance, low ionic conductivity, and high production costs. Recent advancements in nanomaterial technology have offered innovative solutions to these issues. Nanomaterials with high specific surface areas and controllable morphologies optimize interfacial contact, reduce resistance, and enhance ionic conductivity through efficient ion transport channels. Additionally, surface modifications and doping improve the chemical and thermal stability of SSB components, extending battery life and preventing adverse reactions. Although initial preparation costs are high, advancements in production technology and large-scale manufacturing are expected to lower these costs, facilitating commercialization. Future research should focus on new nanostructure designs, nanocomposites, and interfacial engineering to further enhance battery performance and safety. Understanding the influence of nanomaterials on safety performance and improving thermal and mechanical shock resistance are crucial for the reliable implementation of solid-state batteries in practical applications.

Keywords: Solid-state battery, nanomaterials, ionic conductivity, interface stability, mechanical properties, safety.

1. Introduction

SSBs embody a cutting-edge battery technology that utilizes a solid electrolyte, marking a departure from the conventional liquid electrolyte employed in traditional lithium-ion batteries. In SSBs, all components, including the positive electrode, negative electrode, and electrolyte, are solid. The working principle involves energy storage and release through chemical reactions between the electrodes, similar to conventional batteries, but with a different ion transmission mechanism.

Traditional lithium-ion batteries face limitations in energy density improvement due to inactive components like binders, conductive agents, and packaging materials. Additionally, the use of combustible organic liquid electrolytes poses thermal runaway safety risks. In contrast, SSBs, utilizing solid electrolytes, providing greater energy density and enhanced safety characteristics, represent a promising future for battery development. SSBs encompass two primary types: all-solid-state electrolyte batteries (ASSBs) and hybrid solid/liquid electrolyte batteries (HSLBs) [1], and the initial investigation into PEO-based polymer ASSBs dates back to 1978 [2].

The incorporation of nanomaterials in SSBs can significantly enhance ionic conductivity. Nanoscale inorganic fillers in polymer electrolytes create continuous ion transport channels, reducing ion transport resistance. Furthermore, nanostructures increase the contact area between the electrolyte and electrodes, improving ion transport efficiency at the interface. Nanomaterials also bolster the mechanical stability of SSBs by forming composite electrolytes with a combination of rigid inorganic fillers and flexible polymer matrices, resisting external stresses and deformation.

The unique size effects of nanomaterials, such as increased specific surface area, provide more ion transport channels and active sites, enhancing ionic conductivity—a crucial factor in the performance of SSBs. Nanomaterials' high mechanical strength and toughness also mitigate crack propagation in electrolytes or electrode materials, improving battery cycle life, safety, and resistance to failure under extreme conditions.

This paper will examine the challenges faced by SSBs and the role of nanomaterials in enhancing solid-state battery performance such as ionic conductivity, interfacial stability, mechanical properties and safety. And future directions and innovations in solid-state batteries using nanomaterials are discussed.

2. Challenges in Solid-State Battery Technology

While SSBs offer numerous advantages over conventional batteries, they also face significant challenges. One of the primary challenges is the ion transport efficiency in solid-state electrolytes. Compared to liquid electrolytes, solid-state electrolytes generally exhibit lower ionic conductivity, which limits the charge/discharge rate and power density of ASSBs. The primary factors contributing to this issue encompass inadequate ionic conductivity within the solid electrolyte, as well as elevated interfacial resistance occurring at the junction between the electrolyte and electrode materials. Additionally, the stability of the electrode-electrolyte interface critically affects the lifespan and safety of SSBs. The transition from a solid-liquid interface in conventional batteries to a solid-solid interface in SSBs introduces higher contact resistance and more complex interfacial reactions.

Ceramic-based solid electrolytes have been widely studied for their high ionic conductivity and chemical stability. However, their high hardness and strength are offset by poor toughness, making them prone to fracture under external stresses. During the charging and discharging cycles, the electrolyte must accommodate volume changes and stresses, which can lead to the brittleness-induced rupture of ceramic electrolytes, compromising the safety and reliability of the battery. Furthermore, the brittleness of ceramic materials presents challenges in processing, requiring specialized equipment and techniques, thereby increasing production costs and process complexity.

For the practical implementation of ASSBs, solid electrolytes are imperative to exhibit high ionic conductivity, minimal electronic conductivity, an extensive electrochemical stability window, robust stability at the electrode/electrolyte interface, resilience against environmental factors such as air and moisture, and robust mechanical stability capable of withstanding dendrite growth [3]. There are various types of solid electrolytes, including oxide, sulfide, polymer, and emerging halide solid electrolytes.

Oxide-based solid electrolytes (OSEs) exhibit superior ionic conductivity, robust mechanical properties, and outstanding thermal stability, making them highly desirable in battery technology. OSE can be categorized into crystalline and amorphous, common crystalline oxide electrolytes include chalcocite, NASICON and garnet; amorphous forms include LiPON and some of its derivatives. However, the solid-solid interface between the electrolyte and electrodes in ASSBs frequently gives rise to contact issues, thereby necessitating the implementation of interfacial engineering strategies to enhance their cycling performance.

Sulfide solid electrolytes exhibit excellent ionic conductivity but are unstable in contact with lithium metal, requiring an interfacial protection layer to prevent continuous electrolyte degradation. Additionally, their poor air stability and thermodynamic instability with certain electrodes limit their practical application. Among the various electrolysis systems that have garnered significant attention, those utilizing lithium sulfide as a foundation, including Li_2S-SiS_2-P_2S_5 and Li_2S-P_2S_5-LiI, stand out prominently [4, 5]. Currently, Li_2S-P_2S_5-type solid electrolytes (LPS), crafted utilizing varying molar ratios of the corresponding reagents, are among the most intensely researched materials. These electrolytes can be synthesized in diverse phases, including glass, glass-ceramic, and ceramic forms [6].

Polymer solid electrolytes are flexible and easy to fabricate. Among the realm of polymer-based solid-state electrolytes, PEO holds a pioneering position as one of the first polymers identified to conduct lithium ions. Its glass transition temperature of -67°C, significantly lower than room temperature, enables the facile formation of an amorphous structure at ambient conditions. This amorphous structure is highly conducive to the efficient conduction of cations, making PEO an attractive material for solid-state battery applications [7]. Since then, more polymer electrolyte systems such as PC, PVDF, PDMS, PAN, etc. have been applied to solid-state electrolytes. Yet their low ionic conductivity and narrow voltage window hinder large-scale use. As a result, composite polymer electrolytes are often developed by combining polymers with other materials to enhance electrochemical performance.

Halide solid electrolytes (SEs) exhibit outstanding electrochemical oxidative stability, but research on these materials remains limited. Numerous lithium-ion halide solid-state electrolytes (SSEs) featuring high ionic conductivity, attaining values as high as 10^{-2} S cm^{-1}, have been successfully developed. Among these, notable examples include Li_3YCl_6, Li_3InCl_6, Li_3ScCl_6, Li_2ZrCl_6, and $LiTaOCl_4$, along with several others. Recently, the realm of sodium halide SSEs has expanded to include novel compounds like Na_2ZrCl_6, Na_3YCl_6, Na_3ErCl_6, $NaAlCl_4$, along with their derivatives, showcasing a growing interest in this class of materials. Despite exhibiting oxidation stability on par with lithium halides, these sodium halide-based SSEs exhibit notably lower sodium ionic conductivity, approximately 10^{-5} S cm^{-1} at room temperature, highlighting a key area for potential improvement [8].

3. Role of Nanomaterials in Enhancing Ionic Conductivity

Nanomaterials significantly enhance ionic conductivity in solid-state batteries by optimizing electrode structures and improving reactivity and ion transfer, thus enhancing electrochemical properties such as capacity, energy density, and cycle life. Nanocoatings can increase electrode conductivity, reduce resistance, and improve charge transfer efficiency.

Nano-engineering enables the design of materials with layered or porous structures. Layered structures provide space for reversible ion intercalation, mitigating volume expansion, while porous structures increase specific surface area, facilitating more ion transport channels and accelerating ion transport rates. The surface effect promotes ion adsorption and diffusion, enhancing ion pathways. Doping and surface modification can alter the chemical composition and physical properties at grain boundaries, reducing the potential barrier and improving electron transport efficiency.

For example, nanowires, nanofibers, and nanotubes in lithium battery anodes can create ion transport channels, potentially enhancing cycling performance by 3–8 times and capacity retention by 2–4 times compared to conventional materials [9].

In sulfide solid electrolytes, Li_2S-P_2S_5-type solid electrolytes (LPS) are widely studied. Doping these electrolytes with carbon-group sulfides or lithium halides can significantly enhance their properties. Solid electrolytes conduct ions, typically cations, anions, or ion defects, with negligible electronic conductivity. Contrary to the swift ionic transport observed in liquid electrolytes, solid electrolytes rely on the diffusion of vacancies for ionic conduction, leading to a comparatively lower level of ionic conductivity. This limitation in conductivity hampers their widespread practical adoption [10].

The ionic conductivity in solid electrolytes commonly adheres to a temperature-dependent behavior governed by the Arrhenius law, formulated as $\sigma T = \sigma o \exp (Ea/KBT)$. Here, T represents the absolute temperature, σo is an exponential prefactor, Ea signifies the ion migration activation energy, and KB denotes the Boltzmann constant. This equation underscores a linear relationship between the logarithm of conductivity (lg σT) and the reciprocal of temperature (1/T), illustrating the sensitivity of conductivity to temperature changes [11]. The distribution of particle sizes plays a pivotal role in influencing not only the ionic conductivity but also the stability of the interface between the electrolyte and electrode. Consequently, meticulously optimizing this distribution is imperative for ensuring effective interaction between the electrode and electrolyte, as well as the development of a uniform and stable interface. For example, using Li_2S and P_2S_5 in an 80:20 molar ratio, ball-milled in an inert atmosphere at 370 rpm for 20 hours, resulted in an electrolyte with 2×10^{-4} S cm^{-1} conductivity. Heating this electrolyte above its crystallization temperature to 250°C increased its conductivity to 9×10^{-4} S cm^{-1} at room temperature, attributed to a microcrystalline glass structure that reduces grain boundary impedance and enhances Li ion mobility [10].

4. Improving Interface Stability with Nanomaterials

The development of composite electrolytes (CEs) is a key strategy for enhancing the interfacial performance of SSBs. Incorporating nanomaterials into electrolytes can significantly improve ionic conductivity, interfacial stability, and inhibit side reactions. Nanocoatings can also prevent lithium dendrite formation, reducing the risk of short-circuiting and improving battery safety and stability. Micronization of solid electrolyte particles enhances the electrode-electrolyte mixing state, increasing the capacity of all-solid-state batteries (ASSBs). Nanocoatings increase the specific surface area of the electrode, providing more active sites for electrochemical reactions, improving reaction rates, and enhancing electrode-electrolyte interactions.

Polymer electrolytes (PEs), particularly those based on polyvinylidene fluoride (PVDF), are highly preferred due to their excellent electrode compatibility, simplicity in mass production processes, and economical cost. PVDF-based electrolytes are notable for their good lithium dissociation ability, high dielectric constant, mechanical properties, and thermal stability. In a study by Liang et al., a PVDF-based PE was prepared using a mixed solvent system of propylene carbonate (PC) and N,N-dimethylformamide (DMF). The research revealed that PC possesses the capability to modulate the solvation arrangement and expedite the dissociation process of lithium oxalyldifluoroborate (LiODFB). The organic-inorganic interfacial layer that arises from the decomposition of PC and LiODFB on the surface of the Li anode improves interfacial adhesion and mitigates adverse reactions between residual DMF and the Li anode [12].

Zhang and his team have introduced an innovative composite solid electrolyte (CSE) with PEO as the main matrix and the incorporation of succinonitrile (SN) and zinc oxide nanoparticles (NP) to enhance its overall performance. This enhancement is based on two main aspects: first, it promotes the development of a LiF-rich elastic solid electrolyte interphase (SEI) by anchoring bis(trifluoromethanesulfonyl)imide (TFSI) anions to ZnO, which strengthens the interface. Secondly, it restricts escaping SN molecules and promotes the self-polymerization of SN, which improves the charge transfer efficiency. The resulting ionic conductivity reached 1.1×10^{-4} S cm^{-1} at room temperature, and the $LiFePO_4$ (LFP) full cell exhibited excellent stability, withstanding more than 800 cycles at a rate of 0.5 C, demonstrating its ultra-durability. This study provides insights that can guide the development of cutting-edge solid-state lithium metal batteries (SSLMB) based on PEOs [13].

5. Enhancing Mechanical Properties via Nanoscale Engineering

Nanocomposite solid electrolytes, which combine polymer electrolytes with nanoinorganic fillers, are an advanced class of materials synthesized through a composite process involving multiple nanomaterials and polymer matrices. Nanostructures play a crucial role in enhancing mechanical properties by redistributing mechanical stresses and preventing crack propagation. Their high specific surface area and interfacial strength act as barriers to crack growth, forcing cracks to change direction or consume more energy to continue expanding. According to the Hall-Petch relationship, materials with smaller grain sizes exhibit higher mechanical strength, including tensile strength, hardness, and plasticity. In such materials, the increased grain boundaries enhance resistance to dislocation buildup, thereby increasing yield strength and reducing grain deformation stress.

One-dimensional nanomaterials are particularly effective in mitigating issues related to volume changes in electrodes. Their unique structure facilitates stress dispersion and provides void space to buffer volume changes during charging and discharging. This helps prevent capacity loss due to crushing and aggregation, thereby enhancing electrode stability and active material utilization. The successful application of one-dimensional nanomaterials in lithium batteries has demonstrated their ability to extend battery cycle life by accommodating electrode volume changes.

Kim et al. investigated the morphology, crystallinity, and lithium super ionic conductivity of wet-milled (WM) and hand-milled (HM) $Li_{10}GeP_2S_{12}$ (LGPS) [14]. HM-LGPS, with a d50 of 1.32 μm, comprises particles with a size of several tens of micrometers (Figure 1).

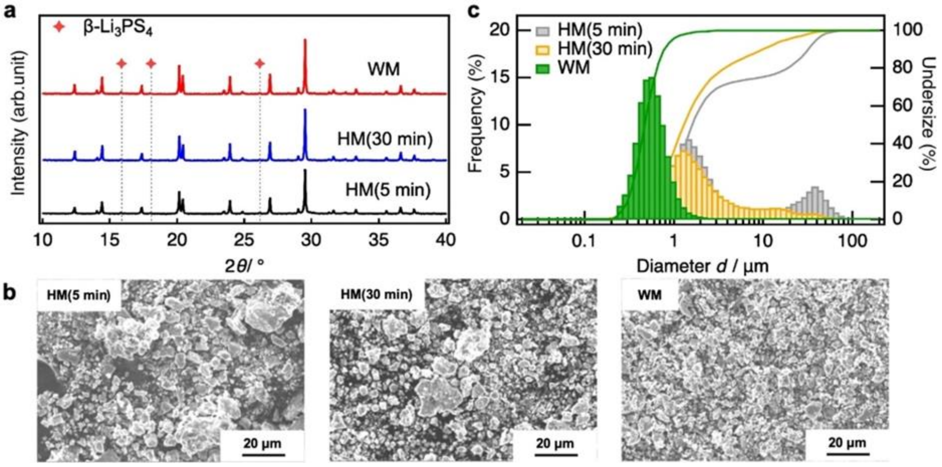

Figure 1. a) XRD patterns, b) SEM images (magnification factor: ×1000), and c) dispersed particle-size distributions of Li10.35Ge1.35P1.65S12 pulverized under different milling conditions [14]

The mechanical strength of this LGPS layer is relatively low around the coarse particles, resulting in crack formation (owing to the mechanical stress induced by the large volume changes in In-Li). In contrast, WM-LGPS, with a d50 of 0.51 μm, exhibited a narrow size distribution with no coarse particles. The small grains with relatively high mechanical strength suppress crack formation; consequently, excellent electrochemical stability was observed during the charge-discharge cycling of In-Li with WM-LGPS.

Li et al. utilized porous adhesive poly (ethylene vinyl acetate) (PEVA) scaffolds in conjunction with polytetrafluoroethylene (PTFE) binders to intricately interlace sulfide solid electrolytes, crafting freestanding films with exceptional attributes: an ultra-thin thickness of 40 μm, an impressive ionic conductivity of 1.1 mS cm^{-1}, and a robust tensile strength reaching 74 MPa. These ultrathin solid electrolyte (SE) films facilitated the construction of all-solid-state lithium batteries (ASSLBs) that boasted an extraordinary energy density of 354.4 Wh kg^{-1}, calculated based on the entire battery assembly's weight. This study underscores the importance of cathode composite design and highlights the need to consider the mechanical properties and interfacial stability of ultrathin sulfide SE films for achieving safe, fast-charging, and high-energy-density batteries [15].

6. Safety Improvements of Solid-State Batteries by Nanomaterials

The application of nanomaterials in the field of SSBs has brought significant improvements in reducing fire risks and thermal management.

For reduction in fire risks, in conventional liquid batteries, the electrolyte consists mainly of salt and organic solvents, which are prone to evaporation and can cause fires. The electrolyte in SSBs, on the other hand, is solid, which inherently reduces the risk of fire. Further, the application of nanomaterials can further reduce or replace these flammable components. Dendrite growth is an undesirable phenomenon within batteries, and when metallic dendrites connect the anode and cathode of a battery, they can cause short circuits, which in turn can lead to battery failures and even fires. And nanomaterials can form extremely thin protective layers at the interface of solid-state batteries, and these layers can act as barriers to inhibit dendrite growth, thus preventing short circuits and fires.

And for thermal management, the electrolyte of solid-state batteries has relatively poor thermal conductivity, which limits its performance in high-power applications and can lead to overheating of the battery. And nanomaterials can improve the thermal stability of electrolytes in a number of ways. For instance, in the work of Zhang et al., to mitigate the adverse side reactions triggered by flame-retardant aluminum diethylphosphonite (ADP) during cycling, it is encapsulated within a protective urea-formaldehyde (UF) shell. This core@shell structured ADP@UF is then integrated with poly (ethylene oxide) (PEO), resulting in a composite that exhibits exceptional thermal stability [16]. And utilizing nanopore structures can increase the specific surface area of the electrolyte, thereby improving its thermal conductivity. In addition, some nanomaterials have inherently good thermal conductivity properties and can be used directly as thermal management materials.

Nanomaterials can also be used to develop localized cooling techniques for thermally sensitive spots in solid-state batteries. By introducing nano-refrigerants or nano-heat pipes in these hot spots, more precise temperature control can be realized to prevent the battery from overheating. And the application of nanomaterials can also facilitate the design of novel heat dissipation structures. For example, miniature fans or heat pipes made with nanotechnology can more effectively dissipate the heat generated inside the battery, thus keeping the battery operating within a safe temperature range.

7. Future Directions and Innovations

Recent years have witnessed remarkable progress in the research on nanostructured solid electrolytes, making them a focal point in battery technology. Multi-level nanostructured solid electrolytes have demonstrated superior performance, enhancing both the cycle life and power density of batteries. The incorporation of nanomaterials into electrolytes has proven particularly effective, with nanoporous metals being extensively studied for their unique pore structure, large specific surface area, and excellent electrical conductivity. These materials significantly improve energy density and cycle life by enhancing electrode-electrolyte contact and reducing lithium-ion and electron diffusion paths.

In terms of safety and stability, solid-state electrolytes offer better thermal and chemical stability compared to their liquid counterparts. They are less prone to combustion and explosion under extreme conditions such as high temperatures, overcharging, and short circuits, thereby reducing safety risks. Additionally, solid electrolytes can effectively inhibit lithium dendrite growth, mitigating the risk of internal short circuits.

The preparation process of nanostructured electrolytes is continuously being optimized, which is expected to reduce production costs. ASSBs are emerging as promising contenders to conventional lithium-ion batteries, providing benefits including increased energy density, improved safety features, and a prolonged operational lifespan. Nevertheless, several challenges persist, hindering their widespread commercial adoption. While nanostructured electrolytes perform well in laboratory settings, their material properties, including ionic conductivity, mechanical strength, and stability, need further enhancement for commercial applications. Moreover, the complex manufacturing process requires specialized technical knowledge and equipment, making process optimization and efficiency improvements crucial for commercial viability. High production costs also pose a significant barrier, necessitating strategies to reduce expenses while maintaining performance standards.

The burgeoning demand for high-performance batteries, fueled by the widespread adoption of new energy vehicles, renewable energy storage systems, and portable electronic devices, underscores the vast market potential for nanostructured electrolytes. Significant progress has been made in the commercialization of ASSBs, marking an important milestone in energy storage technology. Collaboration among upstream and downstream enterprises in the solid-state battery industry is intensifying, fostering a complete industrial chain system. This cooperation is expected to reduce production costs, improve product quality, and enhance competitiveness, paving the way for the widespread adoption of nanostructured solid electrolytes in the battery industry.

8. Conclusion

Recent advancements in nanomaterial technology have addressed key challenges in solid-state batteries, including high interfacial resistance, low ionic conductivity, poor material stability, and high costs. Nanomaterials, with their high specific surface area and controllable morphology, optimize interfacial contact between solid-state electrolytes and electrodes, reducing interfacial voids and resistance. Nanostructural designs, such as nanoparticles and nanowires, enhance ionic conductivity by creating efficient ion transport channels. Furthermore, surface modification, doping, or capping of nanomaterials improves chemical and thermal stability, preventing decomposition and extending battery life. Although the initial preparation costs are high, advancements in production technology and large-scale manufacturing are expected to lower costs, promoting commercialization. Future research should explore new nanostructure designs, nanocomposites, and interfacial engineering to further optimize battery performance and safety. In-depth studies on the influence of nanomaterials on safety performance and measures to improve thermal and mechanical shock resistance are also crucial for ensuring the reliability of solid-state batteries.

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