International Journal of Education and Science Research Review

E-ISSN 2348-6457

Volume-10, Issue-1 Jan-Feb-2023

P-ISSN 2349-1817

www.ijesrr.org

Email- editor@ijesrr.org

ENHANCING SOLID-STATE LITHIUM BATTERIES WITH METAL OXIDES: CHALLENGES AND INNOVATIONS

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ABSTRACT

Recent advances in all-solid-state battery (ASSB) research have significantly addressed key obstacles hindering their widespread adoption in electric vehicles (EVs). This review highlights major innovations, including ultrathin electrolyte membranes, nanomaterials for enhanced conductivity, and novel manufacturing techniques, all contributing to improved ASSB performance, safety, and scalability. These developments effectively tackle the limitations of traditional lithium-ion batteries, such as safety issues, limited energy density, and a reduced cycle life. Noteworthy achievements include freestanding ceramic electrolyte films like the 25 µm thick Li0.34La0.56TiO3 film, which enhance energy density and power output, and solid polymer electrolytes like the polyvinyl nitrile boroxane electrolyte, which offer improved mechanical robustness and electrochemical performance. Hybrid solid electrolytes combine the best properties of inorganic and polymer materials, providing superior ionic conductivity and mechanical flexibility. The scalable production of ultrathin composite polymer electrolytes shows promise for high-performance, cost-effective ASSBs. However, challenges remain in optimizing manufacturing processes, enhancing electrode-electrolyte interfaces, exploring sustainable materials, and standardizing testing protocols. Continued collaboration among academia, industry, and government is essential for driving innovation, accelerating commercialization, and achieving a sustainable energy future, fully realizing the transformative potential of ASSB technology for EVs and beyond.

Keywords: *batteries; electric vehicles; battery electrolytes; battery manufacturing*

INTRODUCTION

The evolution of energy storage technologies has been pivotal in advancing contemporary technological capabilities, significantly contributing to the development of sustainable energy systems . Historically, energy storage has undergone various phases of innovation, each enhancing the efficiency, safety, and environmental impact . Presently, a notable transition is occurring towards solid-state energy storage, exemplified by the development and implementation of solid-state batteries (SSBs). This shift is driven by two main factors: the recognition of the limitations in traditional energy storage systems, particularly those using liquid electrolytes, like in lithium-ion batteries (LE-LIBs), and substantial progress in materials science, introducing novel materials and fabrication techniques vital for solid-state energy storage systems .

SSBs, using solid electrolytes, offer higher energy densities, crucial for applications ranging from consumer electronics to electric vehicles, and inherently reduce many safety risks associated with liquid electrolytes.

Solid electrolytes also enable the use of more chemically stable and durable electrode materials, extending the lifespan and efficiency of batteries . Liquid electrolyte lithium-ion batteries, despite their high energy density and widespread adoption, face increasing limitations in safety, performance, and environmental impact. Concerns include the flammability of liquid organic electrolytes, thermal runaway risks, dendrite formation during charging, and temperature-dependent ionic conductivity, impacting battery performance and lifespan . Additionally, the extraction of materials like lithium and cobalt poses environmental and social challenges . The end-of-life disposal and recycling of these batteries further exacerbate environmental concerns. Given these constraints, there is a growing interest in exploring alternatives like SSBs, which promise higher safety, improved performance, and environmental compatibility . The transition to solid-state electrolytes in SSBs could foster the development of highvoltage cathodes and anodes, potentially increasing the energy density and broadening the operating voltage window. In this comprehensive review, we concentrate on the significant shift from liquidbased to solid-state systems, highlighting the key technological and scientific advances that have catalyzed this transformation. Our analysis will delve into the pressing demands for more efficient energy storage solutions, the shortcomings of current technologies, and the material science breakthroughs that have facilitated the emergence of solid-state options. Although we cover a diverse array of intricate systems, our objective is to offer an indepth understanding of the fundamental changes reshaping energy storage technologies. Our focus will primarily be on the critical developments in solid electrolytes and anode materials for solid-state batteries (SSBs), with a special emphasis on lithium-metal anodes and their interfaces, elucidating the innovative strides in this particular area of energy storage technology.

Advancements and Concepts of Solid-State Batteries (SSBs)

Solid-state batteries (SSBs) represent a significant advancement in energy storage technology, marking a shift from liquid electrolyte systems to solid electrolytes. This change is not just a substitution of materials but a complete re-envisioning of battery chemistry and architecture, offering improvements in efficiency, durability, and applicability . At the core of SSBs are solid electrolytes made of ceramic, polymer, glass, or sulfide materials, facilitating lithium-ion transport between the anode and cathode without the risks associated with liquid electrolytes, such as volatility and combustibility. This solid medium not only enhances safety but also allows for the use of lithium metal as an anode, offering a higher theoretical capacity and a stable interface that prevents dendritic growth . The solid-state design of SSBs leads to a reduction in the total weight and volume of the battery, eliminating the need for certain safety features required in liquid electrolyte lithium-ion batteries (LE-LIBs), such as separators and thermal management systems . This compactness is particularly beneficial for electric vehicles (EVs), where space and weight savings are crucial. Additionally, solid electrolytes in SSBs are more stable and degrade less under cycling conditions, contributing to a longer lifespan and slower decline in battery capacity over time . Research in this field has led to the discovery of materials with exceptional ionic conductivities, rivaling or surpassing those of liquid counterparts. The manufacturing processes for SSBs have also evolved, with new techniques ensuring uniformity and quality in large-scale production . This scalability is vital as the demand for advanced energy storage systems increases with global electrification efforts . In terms of sustainability, SSBs have a more environmentally friendly lifecycle, with solid components being generally more stable, less reactive, and potentially less hazardous than the volatile organic compounds in liquid electrolytes .

OVERVIEW OF ALL-SOLID-STATE BATTERIES

International Journal of Education and Science Research Review
Volume-10, Issue-1 Jan-Feb-2023 E-ISSN 2348-6457 P-ISSN 2349-1817
www.ijesrr.org Email- editor@ijesrr.org

Properties of All-Solid-State Electrolyte Lithium-Ion Batteries

ASSBs represent a significant leap forward in energy storage technology, particularly for EVs, as shown in Table 1. They operate similarly to traditional batteries, with an anode, cathode, and electrolyte facilitating the movement of ions during charging and discharging cycles. However, the main difference lies in the electrolyte material. In all-solid-state batteries, the liquid electrolyte is replaced with a fully solid material that conducts ions between the electrodes. This transition from liquid to solid-state electrolytes (SSEs) fundamentally alters the battery's architecture and performance characteristics. Solid electrolytes are non-volatile, resistant to high temperatures and corrosion, and less reactive with lithium metal, offering the potential for safer, higher-energy-density solutions suitable for the automotive industry . SSEs also exhibit higher thermal stability, enabling safer operation under extreme temperatures—an essential consideration for EV applications wherein batteries are subjected to varying environmental conditions. ASSBs can operate within a broader temperature range, up to about 200 ◦C, compared to traditional batteries .

Table 1. Summary of the advantages (green) and disadvantages (red) of all-solid-state lithium-ion batteries when compared to traditional lithium-ion batteries.

Feature	Traditional Lithium-Ion	All-Solid-State Lithium-Ion
Energy Density	Moderate to high	Potentially higher
Safety	Risk of leakage, flammability	More stable, less risk of leakage
Charging Speed	Moderate	Higher impedance, but potentially faster with advancement
Temperature Range	Limited, can degrade at high temperatures	Wider, more stable at high temperatures
Lifecycle	Moderate (500–1500 cycles)	Longer (Potentially 2–10× Li-Ion)
Manufacturing Complexity	Mature technology, well-established	Emerging, still under development
Cost	Relatively lower	Higher, but expected to decrease
Form Factor	Limited Flexibility	More design flexibility

Commercial Availability	Widely available	Limited, mostly in development

A major limitation of traditional lithium-ion batteries is their charging speed. Although ASSBs have higher impedance, which can impede charging, innovative research is addressing this issue . Developing high ionic conductivity solid electrolytes, such as sulfide-based or oxide-based materials, can reduce impedance. Optimizing electrode- electrolyte interfaces and using thin-film technology for thinner electrolyte layers can enhance ion transport. Advanced manufacturing techniques for defect-free layers and 3D battery architectures to increase reactive surface area help to distribute current more evenly. Combined with advanced electrochemical techniques like pulse charging and sophisticated modeling, these strategies can effectively address impedance challenges, enabling faster charging for ASSBs . In essence, ASSBs offer improved stability, reducing the risk of electrolyte leakage and dendrite formation . This is critical for the automotive industry, in which the size and weight of the battery packs currently limit the range of vehicles. By eliminating the liquid component, ASSBs can theoretically allow for more compact designs and better integration into vehicle architectures, further enhancing their appeal for next-generation EVs. Moreover, SSEs tend to have longer lifespans than their liquid counterparts, which contributes to reduced maintenance costs and greater reliability, making them an attractive option for EV manufacturers and consumers alike. They experience less wear and tear during operation and are more resistant to shocks and vibrations, contributing to increased durability and reliability. The inherent flexibility of ASSB technology opens doors to innovative design possibilities, enabling manufacturers to create lighter, more compact battery packs without compromising performance.

Types of Solid-State Electrolytes

SSEs can be categorized into three main types: inorganic solid electrolytes, solid polymer electrolytes, and composite solid electrolytes. A summary of these different electrolytes is provided in Table 2.

Table 2. Summary of features for the different types of the three different types of solid-state electrolytes—inorganic solid electrolytes, solid polymer electrolytes, and composite solid electrolytes. The different electrolyte materials result in changes in electro-chemical properties for the associated batteries.

Feature	Inorganic Solid Electrolytes	Solid Polymer Electrolytes	Composite Solid Electrolytes
Electrolyte Material	Ceramic	Polymers	Combination of Ceramics and Polymers
Ionic Conductivity	High	Moderate	Values are potentially between those of inorganic solid electrolytes and solid polymer electrolytes based on composition
Electronic Conductivity	Low	Moderate	
Thermal Stability	Excellent	Moderate	
Chemical Stability	Excellent	Moderate	

Electrochemical Window	Wide	Narrow	
Durability	Brittle	Flexible	
Cost	Expensive	Moderate	

Inorganic solid electrolytes include ceramic materials such as oxides, sulfides, and phosphates. These materials are renowned for their high ionic conductivity and excellent thermal and chemical stability. In particular, inorganic oxide electrolytes have gained extensive attention due to their high ionic conductivity, low electronic conductivity, excellent chemical stability, broad electrochemical window, and high safety features . However, their brittleness and high manufacturing costs pose significant challenges. Efforts to improve their mechanical properties and reduce costs are ongoing, with research focusing on novel material compositions and manufacturing techniques.

Solid polymer electrolytes (SPEs), often based on polymers, offer greater flexibility and easier processing compared to inorganic counterparts. They are generally less expensive to produce but typically exhibit lower ionic conductivity and thermal stability . Despite these limitations, their flexibility and cost-effectiveness make them attractive for various applications. Research is focused on enhancing the ionic conductivity of SPEs through the incorporation of plasticizers, nanofillers, and copolymer blends. Composite solid electrolytes aim to combine the advantages of both inorganic and polymer electrolytes. These materials seek to balance high ionic conductivity with mechanical flexibility and stability. This hybrid approach is an emerging area of research, holding significant promise for the future development of ASSBs. By integrating the strengths of both types of electrolytes, composite solid electrolytes could potentially overcome the individual limitations of inorganic and polymer materials, paving the way for more efficient and durable ASSBs . Current research is exploring various hybrid configurations, such as ceramic-polymer composites, to achieve optimal performance characteristics.

Challenges in Integrating All-Solid-State Batteries

Manufacturing Processes

While ASSBs hold significant promise, several challenges need to be addressed to make them commercially viable. Unlike traditional lithium-ion batteries with liquid electrolytes, ASSBs require the precise fabrication of solid electrolyte layers, which involves intricate synthesis methods and high-temperature processing. This complexity not only increases production costs but also poses technical challenges in scaling up manufacturing for mass production. Designing solid electrolyte materials with tailored properties poses another challenge. Researchers aim to balance ionic conductivity, mechanical strength, thermal stability, and compatibility with electrode materials. Achieving this balance often requires iterative experimentation and optimization. Moreover, scaling up production while maintaining material quality and consistency presents additional obstacles . Traditional manufacturing methods, such as powder pressing or sintering, may not be suitable for producing thin, defect-free electrolyte layers with high ionic conductivity. Developing novel manufacturing techniques, such as solutioninfusion methods, self-assembly processes, or tape-casting methods, requires overcoming technical hurdles and ensuring reproducibility at scale. This transition from laboratory-scale synthesis to large-scale production necessitates the careful consideration of factors such as cost, efficiency, and quality control to enable the widespread adoption of ASSB technology.

Stability

Another crucial aspect is establishing strong adhesion and chemical and electrochemical stability at the interfaces between the solid electrolyte and the electrode materials [18,21]. This is essential for maintaining an efficient charge transfer between the electrodes and the electrolyte, which impacts the battery's overall performance. Achieving this often involves employing specialized manufacturing techniques and engineering strategies specifically tailored to control the deposition of materials and enhance interface compatibility. Moreover, mechanical compatibility is a significant concern in ASSBs, particularly in applications like EVs where the batteries may be subjected to various mechanical stresses and vibrations . If the mechanical properties of the solid electrolyte and electrode materials are not adequately matched, it can lead to problems such as delamination or cracking, which can compromise the structural integrity of the battery and ultimately affect its performance and safety. Thermal management is another important component for ASSBs, especially in high-power applications like EVs. Heat generation during charging and discharging can significantly affect battery performance, safety, and lifespan. To address this, solid electrolytes and electrode materials must demonstrate robust thermal stability, capable of withstanding elevated temperatures without degradation or triggering thermal runaway.

All these challenges are illustrated in Figure 1. Overall, achieving compatibility between solid electrolytes, electrode materials, and cell design is essential for ensuring reliable performance and safety in real-world applications, particularly in the demanding automotive sector.

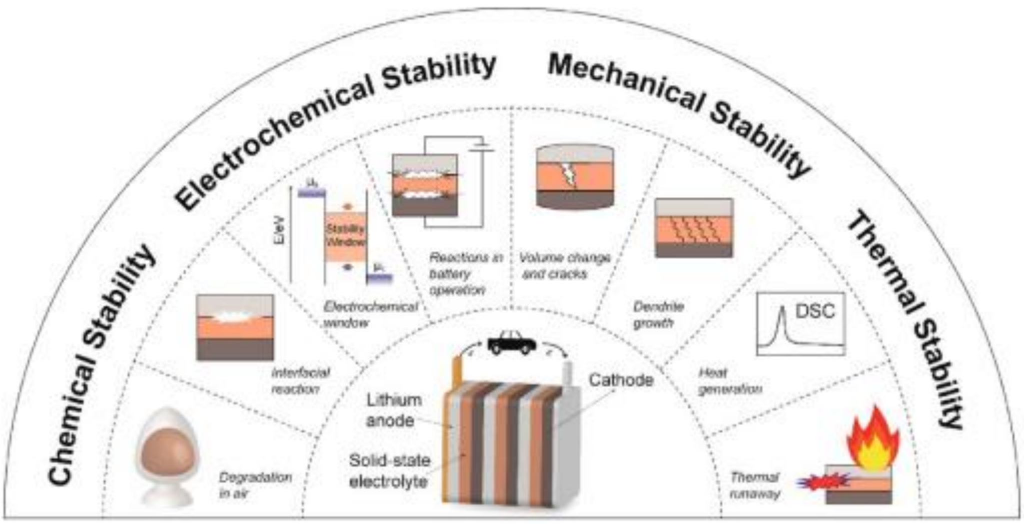

Figure 1. The different stability issues associated with solid state batteries, including chemical, electrochemical, mechanical, and thermal stability. Each stability issue is associated with the underlying properties of the battery chemistry. Reprinted (adapted) with permission from [12]. Copyright © 2024 American Chemical Society.

Safety Considerations

Safety remains a top priority in integrating ASSBs into consumer electronics, electric vehicles, and grid storage systems. The widespread adoption of EVs depends on addressing safety risks like battery fires, prevalent in traditional liquid-electrolyte lithium-ion batteries due to their flammable organic electrolyte. Safety concerns for ASSBs remain a significant hurdle, particularly related to exothermic side reactions between the anode, cathode, and SSE. These reactions can generate substantial heat, potentially leading to thermal runaway, a condition where the temperature of the battery increases uncontrollably. The SSE, which is meant to provide stability and safety, can sometimes exacerbate the issue if not properly managed, as it can react vigorously with lithium metal at high temperatures, further amplifying the risk of fire or explosion.

To address these challenges, researchers are developing advanced materials and engineering solutions. One approach involves creating more stable solid electrolytes that are less reactive with lithium metal, such as sulfide-based electrolytes, which show promise due to their thermal stability and ionic conductivity, as discussed by Rui et al. Further, certain composite electrolytes can combine the benefits of inorganic and organic components, enhancing both mechanical and thermal stability . Xiao et al. detailed another approach of using different coatings and interlayers to create protective barriers at the interfaces between the electrolyte and the electrodes, reducing the likelihood of adverse reactions . Moreover, advanced thermal management systems are being integrated into ASSB designs to dissipate heat more effectively, ensuring that any exothermic reactions that do occur do not lead to catastrophic failure . These innovations collectively aim to mitigate the safety risks while harnessing the full potential of ASSB technology. Another safety concern is thermal runaway from electrolyte decomposition at high temperatures, especially when used in EV batteries. Incorporating additives like borosilicate glass (BG) into the solid electrolyte matrix enhances the structural integrity and thermal shock resistance of ASSBs . This minimizes the risk of electrolyte cracking or delamination, which can trigger thermal runaway, especially under mechanical stress or rapid temperature changes during EV operations. Internal short circuits and battery fires can also occur due to dendrite formation, common in lithium-metal batteries. Thin, defect-free solid electrolytes with short Li-ion diffusion distances effectively inhibit dendrite growth, addressing this issue and enhancing battery safety . While solid electrolytes offer inherent advantages in terms of reduced flammability and enhanced thermal stability compared to liquid electrolytes, ensuring comprehensive safety standards and regulatory compliance is essential. Addressing safety concerns related to dendrite formation, internal short circuits, and thermal management under various operating conditions is critical for gaining consumer confidence and regulatory approval. By addressing safety challenges through innovative research and development, ASSBs pave the way for safer and more sustainable transportation solutions, driving the widespread adoption of electric vehicles.

Cost and Scalability

Balancing performance requirements with cost considerations is crucial for commercial viability. The current fabrication methods for solid electrolytes and electrodes are often resource-intensive and costly, limiting the economic viability of large-scale production. These high costs primarily stem from the need for specialized equipment, high-purity materials, and precise synthesis conditions, which increase the overall manufacturing expenditure . Therefore, it is imperative to develop cost-effective synthesis routes, optimize material utilization, and streamline manufacturing processes to reduce production costs and expedite the commercialization of ASSBs.

Energy Density

For ASSBs to provide the greatest benefit to EVs, they need to have a significantly higher energy density, as the low energy density of modern Li-ion batteries with liquid electrolytes limits the range and increases the weight of EVs. ASSBs replace these liquid electrolytes with solid materials, enabling the use of lithium metal anodes instead of conventional graphite anodes. Lithium metal has a much higher theoretical capacity, significantly boosting the overall energy density of the battery. Researchers have achieved energy densities exceeding 350 Wh/kg with solid-state configurations, compared to the 150–250 Wh/kg typical of current commercial lithium-ion batteries . Innovations in materials science have played a crucial role in these advancements. The development of solid electrolytes with high ionic conductivity, such as sulfide-based and oxide-based materials, has been pivotal. These solid electrolytes not only enhance ionic transport within the battery but also offer better stability and compatibility with high-capacity electrodes. Additionally, the integration of novel composite materials and nanostructures can mitigate issues like dendrite formation, which can cause short circuits and degrade battery life, further allowing for improved energy density . The introduction of high-capacity cathode materials, such as nickel-rich layered oxides and lithium-rich compounds, further complements the high-energy-density potential of solidstate batteries . The practical implementation of solid-state lithium-ion batteries is also seeing progress through advances in manufacturing techniques. Methods like cold sintering and the use of thin-film deposition technologies are enabling the scalable production of solid-state batteries with uniform and defect-free interfaces . These techniques ensure better contact between the solid electrolyte and electrodes, reducing interfacial resistance and enhancing overall battery performance.

Recent Advances

In the pursuit of ASSB technology, researchers have explored various approaches to enhance the performance and safety of SSEs. These efforts have led to significant breakthroughs in material design, processing techniques, and performance optimization.

Inorganic Solid Electrolytes

A study by Ren et al. reviewed sulfide-based ASSBs, which show promise in improving safety and high energy density, as discussed in Section 3 . However, their practical application faces numerous challenges, with key issues including material instabilities, interfacial failures, and transport and mechanical problems within composite electrodes. In particular, sulfide solid electrolytes suffer from air instability and limited electrochemical stability, complicating mass production. Strategies such as H_2S absorbents, element substitution, surface engineering, and sulfide-polymer composites improve air stability but often reduce ionic conductivity. Meanwhile, buffer layers can mitigate electrochemical instability. Cathode materials face electrochemo-mechanical degradation, and anode materials have issues with volume expansion and interface stability. Interfacial problems, such as the space-charge layer effect and mechanical instability, impede ion/electron transport. Their analysis recommends constructing buffer layers and innovative interfacial designs to mitigate these issues. Composite electrodes need optimized microstructural design to improve transport and mechanical stability. Despite progress, existing sulfide-based ASSBs still fall short of what is required by EVs for rate performance and cycle life. Collaborative efforts among universities, research institutes, battery manufacturers, and material suppliers are crucial for advancing sulfide-based ASSBs. A study by Jiang et al. introduced a different approach, using freestanding ceramic electrolyte film based on Perovskite-type $Li_{0.34}La_{0.56}TiO_3$ (LLTO) with a thickness of 25 µm . This thin electrolyte film significantly reduces internal resistance by shortening the ion travel distance between electrodes.

Consequently, it enhances energy density, power output, and charging/discharging rates, making it particularly suitable for high-performance applications like EVs. Moreover, the thin LLTO film allows for higher packing densities of active materials within the battery, further optimizing energy density and extending the range of EVs. Another breakthrough involves creating ultrathin solid electrolyte membranes using ZrO2 nanowires and Li3InCl6 through a solution-infusion method . These membranes, also with a thickness of 25 µm, represent a significant departure from conventional SSE layers, which typically range from 500 to 1000 µm thick . This reduction in thickness translates to a substantial decrease in internal resistance, potentially enabling a remarkable increase in energy density by up to 300%. These membranes are free of organic components, ensuring outstanding thermal stability and safety. Recent studies have also explored the integration of borosilicate glass (BG) as a secondary phase into an electrolyte consisting of sodium superionic conductor (NASICON) to enhance the mechanical properties and density. NASICON is an inorganic material renowned for its exceptional ionic conductivity, making it a key component in solid electrolytes for various electrochemical devices . The integration of BG into NASICON solid electrolytes addresses the critical limitations of conventional NASICON electrolytes, such as low fracture toughness and density . The resulting ceramic electrolytes exhibit a fracture strength of 74 MPa, 2.38 times that of pure NASICON, and a relative density of 97.17%, achieved under pressureless sintering conditions. Furthermore, when integrated into ASSBs with LiFePO4 cathodes and metallic Li anodes, these electrolytes demonstrate excellent cycling stability, with a discharge specific capacity of 154.5 mA·h·g –1 and Coulombic efficiency approaching 100% after 100 cycles. Yang et al. found garnet-based ASSBs to be promising, owing to their high energy density and safety features. However, the widespread adoption of these batteries faces challenges, primarily from the accumulation of Li2CO3 contaminants on the surface of the SSE . These contaminants can impair battery performance by hindering interface contact and promoting dendrite formation . Li et al. focused on investigating the growth process of Li2CO3 on the surface of the solid-state electrolyte Li6.4La3Zr1.4Ta0.6O12 (LLZTO) and proposed an innovative approach for effectively removing these contaminants as shown in Figure 2. This approach involves immersing LLZTO electrolytes in pure CH3COOH (acetic acid) for a brief duration of 1 min . This treatment effectively removes Li2CO3 contaminants from the surface of the electrolyte, significantly reducing the interface resistance between lithium and LLZTO from 5542 to 5 Ω cm2 .

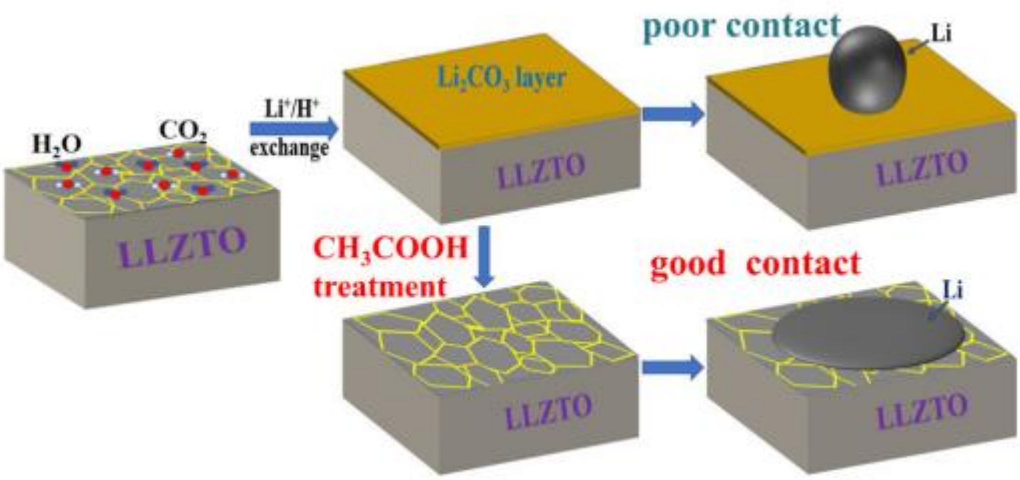

Figure 2. Schematic of approach recommended by Li et al. for removing Li_2CO_3 contaminants on the LLZTO surface by exposing it to acetic acid (CH_3COOH) for short durations. Reprinted (adapted) with permission from [14]. Copyright © 2024 American Chemical Society.

In another study, Guo et al. synthesized lithium garnet oxide (LLZO) nanosheets and self-assembled them into thin, defect-free, and freestanding LLZO laminar inorganic solid electrolytes (LLISE) . These LLISEs exhibited an ultrahigh ionic conductance of 0.17 S and an impressive energy density of 340 Wh kg^{-1}, while maintaining a compressive strength of 3.2 GPa. Particularly noteworthy is the performance of Li symmetrical cells assembled with LLISE, which exhibited excellent cycling stability, retaining a discharge specific capacity of 143.2 mAh g^{-1} even after 200 cycles.

Solid Polymer Electrolytes

The development of SPEs represents a significant advancement in ASSB technology. These electrolytes combine the mechanical flexibility and processability of polymers with the enhanced safety and stability of solid-state systems. Recent innovations have focused on improving the ionic conductivity, mechanical strength, and overall performance of SPEs, making them increasingly viable for practical applications. One notable development by Xue et al. is the introduction of an SSE consisting of glass fiber-reinforced polyethylene oxide (PEO) with lithium fluoride (LiF) and succinonitrile (SN) additives (GP-LiF-SN). This SSE combines amorphous poly(ethylene oxide)-based electrolyte with a glass fiber reinforcement and nano-LiF and succinonitrile (SN) additives . The incorporation of SN, which maintains a plastic crystalline phase over a wide temperature range, contributes significantly to the mechanical robustness and safety of the composite electrolyte. The high polarity of SN molecules facilitates the dissolution of lithium salts, enhancing the ionic conductivity of the electrolyte. Additionally, the inclusion of a solid plasticizer improves the plasticity and viscosity of the composite electrolyte, promoting better interfacial contact between the electrolytes and electrodes. This innovation addresses not only the mechanical stability but also enhances the electrochemical performance, making it a promising candidate for practical ASSB applications. Another breakthrough in ASSB technology has been achieved with the development of a new solid polymer electrolyte, polyvinyl nitrile boroxane (PVNB), through in situ polymerization via a thermally initiated free-radical reaction as shown in Figure 3. This process involves the electron-deficient boron in cyclic boroxane groups and cyano in acrylonitrile, which immobilize the anion to enhance the Li-ion transference number. The lone-pair electrons of cyano in acrylonitrile coordinate with transition-metal ions, preventing them from taking electrons from the ethylene oxide (EO) chain segment and inhibiting the decomposition of the solid polymer electrolyte. By incorporating boron and cyano groups, PVNB forms stable interfaces, improving cycling stability and flameretardant properties. For instance, a configuration of PVNB electrolyte-based solid-state batteries yields notable results, with cells maintaining 80% capacity after 1000 cycles at a high rate of 5C. A significant challenge in the development of SPEs is balancing membrane thickness and mechanical strength. Thicker membranes often provide better mechanical stability but at the expense of increased internal resistance and reduced ionic conductivity. To overcome this trade-off, Li et al. pioneered a protic solvent-penetration induced self-assembly tech- nique . This approach enables the fabrication of membranes with thicknesses below 5 μm while maintaining a tensile strength of 556.6 MPa, which is significantly higher compared to most reported layered materials with a single component. These ultrathin membranes have been utilized to produce the thinnest SSE at 3.4 μm thickness, allowing Li-S batteries to cycle over a thousand times at a high rate of 1C.

Composite Solid Electrolytes

Recent advancements in hybrid solid electrolytes have significantly improved the performance and scalability of ASSBs. These electrolytes combine the high ionic conductivity of inorganic materials with the flexibility and processability of polymers, making them suitable for mass production and practical applications. A notable advancement involves the large-scale preparation of ultrathin, flexible SSEs. By combining typical scraping and hot-pressing processes, Liang et. al. successfully impregnated a polyethylene oxide (PEO)/Li-salt (LiTFSI) electrolyte into a porous poly(tetrafluoroethylene) (PTFE) matrix, creating an ultrathin, highly dense composite polymer electrolyte commonly referred to as PLP-HP [40]. The hot-pressing process ensures a densely impregnated PEO/LiTFSI conductive network, while the PTFE matrix provides excellent mechanical properties and high thermal stability. This results in a composite electrolyte with thicknesses as low as 6 µm, significantly reducing internal resistance and enhancing battery performance. The Li/Li symmetrical cell with a 14.5 µm thick electrolyte shows stable cycling for over 900 h at 60 ◦C without lithium dendrite growth. Additionally, the $LiFePO_4$/Li full cell can cycle more than 500 times with a Coulombic efficiency exceeding 99.9% at 0.5C and 60 ◦C. The 6 µm thick electrolyte further demonstrates a superior rate performance, enabling the battery to operate at 30 ◦C with a reversible capacity of around 135 mAh g^{-1} at 0.2C. This study provides a scalable and cost-effective approach for producing highperformance ultrathin composite polymer electrolytes, essential for the commercialization of solid-state lithium-metal batteries. The development of flexible and solvent-free polymer electrolytes has also advanced hybrid ASSBs . These electrolytes enhance lithium-ion transport and maintain electrochemical stability, crucial for high-performance batteries. By incorporating lithium salts into a polymer matrix with garnet-type ceramic electrolytes, researchers have achieved higher Li^+ conductivity while ensuring electrolyte stability. Manthiram et al. have established critical correlations among composite structures, polymer dynamics, and lithium-ion transport, enhancing the understanding of ion transport mechanisms . The integration of garnet-type ceramic electrolytes, like $Li_7La_3Zr_2O_{12}$ (LLZO), into polymer matrices addresses brittleness and processing difficulties, creating a composite material with high ionic conductivity and mechanical flexibility. These hybrid electrolytes improve interfacial properties, facilitating smooth ion transfer and reducing resistance. provides a summary of the different research efforts for designing composite electrolytes for ASSBs. Similar to solid polymer electrolytes, the amount of research is not as extensive as inorganic solid electrolytes; regardless, the scientific advancements in this area will contribute to the field and advance ASSBs.

CONCLUSIONS

Recent advancements in ASSB research signify a substantial leap forward in addressing the critical challenges hindering the widespread adoption of this technology, particularly in electric vehicles (EVs). Key innovations, such as the development of ultrathin electrolyte membranes, the incorporation of nanomaterials for enhanced conductivity, and novel manufacturing techniques, have significantly improved the performance, safety, and scalability of ASSBs. These advancements offer promising solutions to the limitations of traditional lithium-ion batteries, including safety concerns, limited energy density, and reduced cycle life. Notable developments include the introduction of freestanding ceramic electrolyte films, such as the 25 µm thick LLTO film, which significantly enhances energy density and power output. Innovations in solid polymer electrolytes, like the GP-LiF-SN composite and the PVNB electrolyte, have improved mechanical robustness and electrochemical performance. Hybrid solid electrolytes have combined the best properties of inorganic and polymer materials, leading to improved ionic conductivity and mechanical flexibility. The scalable preparation of ultrathin composite polymer electrolytes, exemplified by the PLP-HP, demonstrates the potential for high-performance, cost-effective ASSBs. However, despite these remarkable achievements, several challenges remain. Optimizing manufacturing processes to reduce costs and enhance scalability is crucial. Enhancing electrode-electrolyte interfaces to minimize resistance and maximize efficiency is another key area needing further research. The exploration of sustainable materials and production methods to mitigate environmental impacts is also essential. Additionally, standardizing testing protocols and establishing regulatory frameworks will be vital to ensuring the safety and reliability of ASSB technology. Continuing the collaboration between academia, industry, and government stakeholders is essential for driving innovation, accelerating technology commercialization, and facilitating the transition towards a sustainable energy future. By addressing the remaining challenges and capitalizing on the opportunities presented by solid-state battery research, the full potential of this transformative technology can be realized, ushering in a new era of clean, efficient, and reliable energy storage for electric vehicles and beyond.

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