Solid-State Batteries: Material Challenges and Opportunities

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Abstract. As the demand for safer, more efficient, and longer-lasting energy storage solutions increases, solid-state batteries (SSBs) have emerged as a promising alternative to conventional liquid-based batteries. With their potential to offer higher energy density, enhanced safety, and greater longevity, SSBs are as a key technology for the future of electric vehicles, consumer electronics, and other high-demand applications. This paper explores the material challenges and opportunities associated with SSBs, focusing on the advantages of solid electrolytes, the potential for fast charging, and the flexibility in battery design. Additionally, the paper addresses critical issues such as lithium dendrite formation, interface stability, and the complexities of manufacturing solid-state batteries. Through a comprehensive analysis of current research, this study highlights the energy storage could undergo a revolution with the potential of SSBs while also pinpointing the technical obstacles that need to be overcome in order to achieve commercial viability. The role of young scientists and interdisciplinary research in driving these advancements is also emphasized.

Keywords: Solid-state battery, energy storage, electrochemical stability.

1. Introduction

A battery is a device that provides electricity to power various applications, including radios, toys, and cars. The basic components of a battery are the anode, cathode, and electrolyte, which facilitate a chemical reaction between the anode and cathode during operation. Batteries are generally divided into two types: primary and secondary. Primary batteries, such as lithium and zinc-carbon batteries, are non-rechargeable, while secondary batteries, like lead-acid and solid-state batteries, are rechargeable. In everyday life, batteries are utilized across diverse sectors, including healthcare, transportation, consumer electronics, household and industrial applications, and renewable energy.

This article primarily focuses on solid-state batteries, which use a solid electrolyte for ionic conduction between electrodes, instead of liquid or gel polymer electrolytes found in conventional batteries. Solid-state batteries are considered safer due to their reduced risk of electrolyte leakage and combustion. Additionally, their energy density and lifespan are superior to traditional batteries.

The research presented in this article explores the material obstacles and opportunities associated with solid-state batteries, as well as the potential benefits and limitations of solid-state technology.

2. Basics of Solid-State Batteries

A solid-state battery (SSB)'s structure is illustrated below (Fig. 1), which consists of anode, cathode, solid electrolyte, and separator.

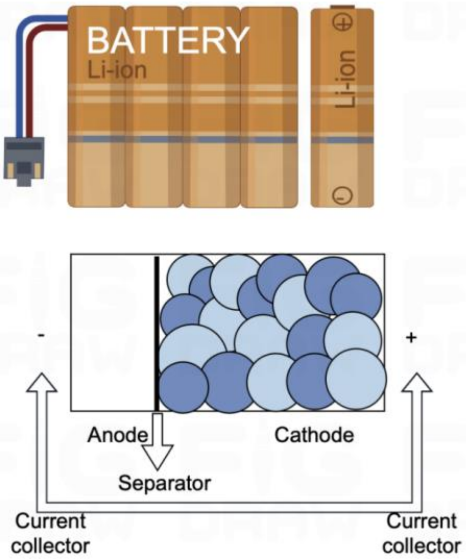

Figure 1. The structure of solid-state battery (Picture/image credit: Original)

The distinctions between conventional liquid-based batteries and solid-state batteries are considerable, as illustrated in Fig. 2. While both types of batteries consist of an anode, cathode, and electrolyte, conventional batteries utilize a free-flowing liquid electrolyte, whereas solid-state batteries employ a solid electrolyte. This fundamental distinction leads to variations in safety, energy density, and manufacturing costs. Overall, solid-state batteries offer superior performance, particularly in terms of safety and energy density.

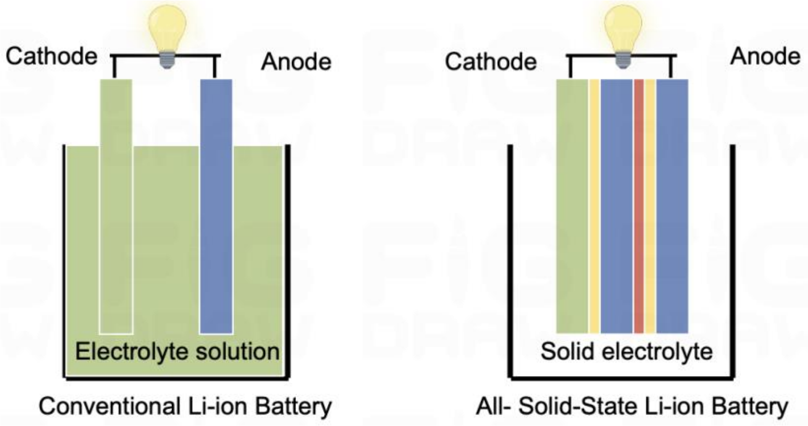

Figure 2. The comparison between solid-state batteries and conventional liquid-based batteries (Picture/image credit: Original)

3. Advantages and Challenges of the Solid-State Batteries (SSBs)

3.1. Fast Charge

Due to their unique transport, thermal, and mechanical properties, solid electrolytes may be able to overcome the barriers to fast charging that are associated with safety, performance, and degradation in liquid-based counterparts [1]. Additionally, by replacing the graphite anode with a lithium metal anode, solid-state batteries (SSBs, Figure 1) can achieve gravimetric and volumetric energy densities that are 40% and 70% higher, respectively, than those of lithium-ion batteries (LiBs). These systems' separate development is strongly encouraged by the potential for high energy content and fast charging [1].

One of the primary limitations to the fast charging of lithium batteries is the concentration polarization in liquid electrolytes [1]. Salt concentration window in liquid electrolytes is relatively narrow for optimal ionic conductivity, leading to significant concentration gradients during high charge [1]. Asymmetric concentration distributions are the consequence of these gradients between the cathode and anode, while ionic conductivity is limited due to local depletion of carriers [2]. The overlapping of ion solvation shells occurs within the negative electrode due to high salt concentrations, further restricting ion mobility within the positive electrode [1]. In contrast, by bypassing concentration gradients, inorganic solid electrolytes (ISEs) can provide both high energy densities and fast charging rates [1].

However, in SSBs, the interfaces between the electrode materials and the solid electrolyte are where the dynamic processes play a crucial role, as instabilities at these solid-solid interfaces can cause kinetics to be impaired, resulting in capacity or power fading [1].

3.2. Electrochemical Stability

A key aspect of solid electrolytes is the evidence suggesting that favorable decomposition pathways for argyrodite-, garnet-, and NASICON-type solid electrolytes are indirect rather than direct. This occurs through the delithiation state of the solid electrolyte, producing thermodynamically stable decomposition products [3]. These findings indicate that the electrochemical stability window of solid electrolytes is significantly broader than that observed in direct decomposition [3]. Additionally, it has been observed that the silver crystal metastable (de)lithiation phase contributes to the (ir)reversible cycling capability of all-solid-state batteries, fully explaining the redox activity of solid electrolytes. This insight is crucial for guiding the interface and material design of all-solid-state batteries [3].

A different study utilized calculations based on first principles to determine the thermodynamic electrochemical stability window of solid electrolytes and developed an experimental method using lithium-carbon batteries to evaluate the intrinsic electrochemical stability period of these materials [4]. $Li_{10}GeP_2S_{12}$ and $Li_7La_3Zr_2O_{12}$ were selected as model materials for sulfide and oxide solid electrolytes, respectively [4]. The findings address the most grueling problems of interface stability and resistance in high-performance solid-state batteries, providing valuable directions for future development [4].

However, the formation of lithium dendrites (Fig. 3) presents a significant challenge. Solid electrolytes don't completely prevent the growth of lithium dendrites while charging, resulting in a short circuit if the dendrites reach the cathode [5].

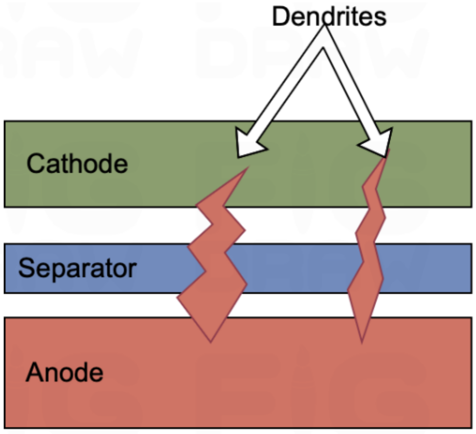

Figure 3. Lithium dendrite formation [4]

3.3. Shape Customization

SSBs are capable of offering a wide range of shapes and sizes, allowing them to be manufactured in diverse forms, unlike liquid electrolytes, which are limited by the possibility of leakage [2]. However, the manufacturing process of SSBs is challenging, this is causing a rise in costs that is preventing mass production and integration of these batteries for everyday use [6]. Unlike lithium-ion batteries (LiBs), which use liquid electrolytes, SSBs utilize solid electrolytes, and their manufacturing process differs accordingly. Depending on the specific type, SSBs can utilize various materials, including oxides and sulfides. For instance, sulfide-based solid electrolytes, a common type, moisture causes them to degrade quickly and make them highly sensitive to air, producing requires strict humidity control and specialized facilities, like dry rooms [7].

Advancements in 3D printing technology have introduced significant design and manufacturing freedoms for batteries. This technology allows for the creation of batteries with tailored properties, including the ability to modify internal structures, maintain consistent shapes, and enhance power capabilities and energy density [8]. A review on the development of 3D printing technology in the field of customizable batteries highlights the basic concepts and unique advantages of 3D printing. The study examines five representative 3D printing technologies, exploring their working mechanisms, material requirements, manufacturing precision, and technical characteristics. An in-depth analysis covers three fundamental levels of customizable batteries: pore structure, component architecture, and interface, as well as battery appearance and mechanical deformation capabilities [8]. The results indicate that 3D-printed customizable batteries hold significant potential for practical applications.

4. Material Challenges and Solutions in Solid-State Batteries

4.1. Solid Electrolytes

Solid electrolyte is an essential component of all-solid-state lithium batteries (ASSLBs) as it enhances safety by replacing the highly flammable liquid electrolyte [9]. Various types of solid electrolytes are available, including NASICON-type, garnet-type, perovskite-type, LISICON-type, LiPON-type, Li3N-type, sulfide-type, argyrodite-type, anti-perovskite-type, and others [10].

Whereas balancing conductivity and stability in these materials is challenging. Inorganic electrolytes primarily fall into two categories: oxide-based and sulfide-based solid electrolytes, both characterized by high-temperature ionic conductivity [11]. A few sulfide-based electrolytes have an ionic conductivity that is equivalent to or greater than that of liquid electrolytes, but they are highly susceptible to environmental conditions [11]. Each type has its limitations, hindering widespread application. For instance, in the presence of lithium metal anodes, NASICON and perovskite Li+ ion conductors exhibit poor chemical stability [11]. Garnet-based electrolytes are stable against lithium metal but are sensitive to moisture and CO2, leading to byproduct formation on their surfaces [11]. Additionally, the rigidity and brittleness of inorganic solid electrolytes are common problems, this leads to poor contact at the electrode/electrolyte interface, which is a significant obstacle to practical application [11].

To improve the energy density of solid-state batteries, researchers have explored the use of high-voltage cathodes. However, these cathodes are confronted with issues like low electrochemical stability, poor chemical stability at the cathode-electrolyte interface, poor mechanical contact, and gas evolution, all of which can compromise battery performance and lead to failure, thus hindering commercialization [12]. To address these issues, the development of cathode materials is crucial, with strategies such as coating protection, synthetic modification, and structural improvement being employed to enhance electrochemical performance [12].

4.2. Interface Issues

The dendritic growth of lithium metal is a significant concern, as dendrites can penetrate the separator between the cathode and anode, causing sudden battery failure and the unwanted release of heat, thereby increasing the fire hazard due to short-circuiting [13]. Additionally, when preparing solid cathodes, the interface quality between the cathode active material (CAM) and binder (SE) must be carefully considered to ensure good electrochemical performance [13]. Unlike traditional lithium-ion batteries (LIBs), lithium ions in all-solid-state batteries (ASSBs) can only be transferred through the limited areas where CAM and SE particles are in direct contact [14]. Consequently, the extent of these contact areas greatly affects the electrochemical performance of ASSBs.

To enhance the energy density of solid-state batteries, high-voltage cathodes are often used [14]. However, these cathodes present challenges such as low electrochemical stability, poor chemical stability at the cathode-electrolyte interface, poor mechanical contact, and gas evolution [14]. These issues can degrade battery performance and even lead to battery failure, impeding the commercialization of solid-state batteries [13]. The development of cathode materials is crucial for addressing high-voltage cathode failure, with strategies such as coating protection, synthetic modification, and structural improvement being employed to enhance electrochemical performance [14].

The stability of solid electrolytes in a variety of situations has been accurately predicted using computational models based on ab initio calculations [15]. Moreover, for various SSB interfaces, a sizable amount of experimental data has been gathered, which can be integrated with computational predictions to provide a deeper understanding and analysis of interface reactions. These insights can guide future development, since it has been discovered that a limited number of chemical and physical concepts can adequately explain both interfacial reaction products and electrochemical stability, which can help ensure a stable interface to a certain extent [15].

5. Applications and Future Prospects

5.1. Applications of Solid-State Batteries

SSB offer numerous advantages over liquid-based batteries (Table 1), including high ionic conductivity, thermal stability, suppression of dendrite growth, high mechanical strength, good interfacial compatibility, prevention of redox species shuttling, and low material and processing costs. They also exhibit electrochemical and chemical stability (Fig. 4), making them promising candidates for use in electric vehicles, smartphones, and other advanced technologies. Additionally, the use of high-voltage cathodes in solid-state batteries can significantly enhance energy density, resulting in higher energy storage capacity and longer lifespans compared to liquid batteries.

Table 1. Comparison of various types of lithium batteries

Battery type	Liquid state	Semi-solid state	Solid state
Upper energy density	Low (<300 Wh/kg)	Medium (>400 Wh/kg)	High (>500 Wh/kg)
Diaphragm	Requires	Requires	It is not necessary
Current cost of production	Lower	Intermediate	Higher
Upper limit of electrolyte chemistry window	Narrow (<4.3V)	Intermediate	High (> 5V)
Liquid content	>10%	<10%	0
Lithium metal negative electrode compatibility	Poor	The inhibition of lithium crystallization is weak	Strong inhibition of lithium crystallization
Safety (heat stability, needle resistance)	Heat limit 140-180 ℃, acupuncture immediately burning	Thermal limit >180 ℃	Heat stability>300 ℃, immune to acupuncture and even shear

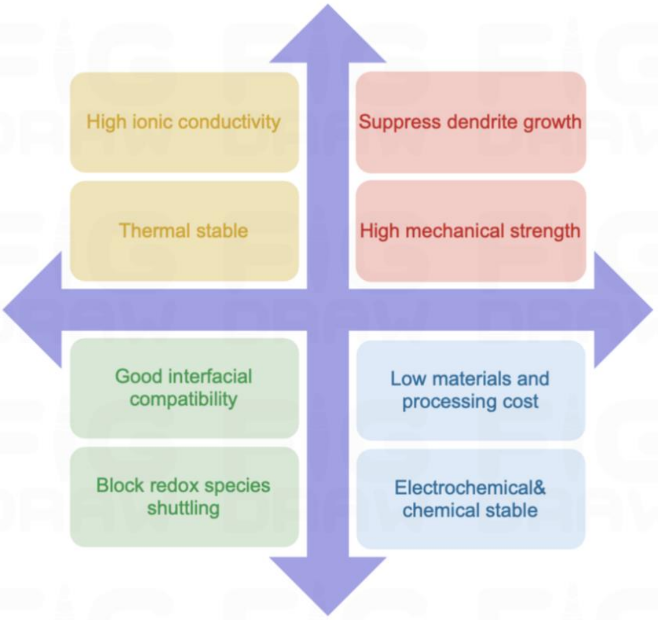

Figure 4. The advantages of solid-state batteries (Picture/Image credit: Original)

5.2. Future Research Directions

Future research on SSBs should prioritize improving solid electrolytes to enhance ionic conductivity, mechanical flexibility, and interfacial compatibility, while also addressing the stability challenges of high-voltage cathodes to boost energy density and battery lifespan. Additionally, developing scalable, cost-effective manufacturing processes will be crucial for making SSBs commercially viable. The active involvement of young scientists and students is essential in this endeavor, as they bring fresh ideas and innovative approaches to tackle these challenges. By exploring novel materials, advancing computational modeling, and participating in interdisciplinary research, they can significantly contribute to the development of SSBs, ultimately helping to make this technology a practical and widespread solution for future energy storage needs.

6. Conclusion

Superior to conventional liquid-based batteries, solid state batteries (SSBs) have several advantages over them, such as increased energy density, enhanced safety, and extended lifespans. SSBs are a potential development in energy storage technology. Their unique properties, such as high ionic conductivity, thermal stability, and resistance to dendrite growth, position them as a key technology for future applications in electric vehicles, consumer electronics, and other high-demand areas. However, SSBs also face significant challenges, particularly in terms of material stability, interface compatibility, and manufacturing processes.

Addressing these challenges requires focused research on improving solid electrolytes, enhancing the performance of high-voltage cathodes, and developing cost-effective manufacturing techniques. The role of young scientists and interdisciplinary research is critical in overcoming these obstacles and driving the innovation needed to make SSBs a commercially viable and widespread technology.

Overall, while SSBs offer a promising future, continued research and development are essential to fully realize their potential and address the technical limitations that currently hinder their widespread adoption. By advancing both the fundamental materials science and the practical engineering aspects of SSBs, the technology can become a cornerstone of future energy storage solutions.

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