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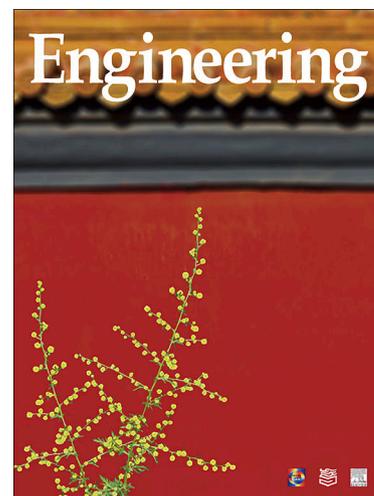
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Changhong Wang, Xueliang Sun

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Views & Comments

The Promise of Solid-State Batteries for Safe and Reliable Energy Storage

Changhong Wang, Xueliang Sun*

Department of Mechanical and Materials Engineering, University of Western Ontario, London, ON, N6A 3K7, Canada

E-mail address: xsun9@uwo.ca

Abstract

Electrochemical power sources such as lithium-ion batteries (LIBs) are indispensable for portable electronics, electric vehicles, and grid-scale energy storage. However, commercial LIBs currently used employ flammable liquid electrolytes, posing serious safety hazards when misused (i.e., overcharged). In addition, the energy density of conventional LIBs is approaching their physiochemical limit. 1 Therefore, developing next-generation energy storage technologies that possess intrinsic safety and high energy density is essential for large-scale energy storage systems. In this context, solid-state batteries (SSBs) have been revived in recent years due to their unparalleled safety and high theoretical energy density. 1-3 However, the development of SSBs has been hindered by several primary challenges, including: (1) lack of appropriate solid-state electrolytes (SSEs) with high ionic conductivity, wide electrochemical window, suitable mechanical properties, and large-scale feasibility; (2) large interfacial resistance with limited interfacial ion/electron transport kinetics; and (3) limited manufacturing processes and technologies for viable SSB production. 4, 5

Keywords: all-solid-state battery, solid-state electrolyte, interface design, practical solid-state pouch cell engineering

1. Introduction

Electrochemical power sources such as lithium-ion batteries (LIBs) are indispensable for portable electronics, electric vehicles, and grid-scale energy storage. However, the currently used commercial LIBs employ flammable liquid electrolytes and thus pose serious safety hazards when misused (i.e., overcharged). In addition, the energy density of conventional LIBs is approaching their physiochemical limit. Therefore, developing next-generation energy-storage technologies with innate safety and high energy density is essential for large-scale energy-storage systems. In this context, solid-state batteries (SSBs) have been revived recently due to their unparalleled safety and high energy density (Fig. 1). However, the development of SSBs has been hindered by several primary challenges [1], including ① a lack of appropriate solid-state electrolytes (SSEs) with high ionic conductivity, a wide electrochemical window, suitable mechanical properties, and large-scale feasibility; ② large interfacial resistance with limited interfacial ion/electron transport kinetics; and ③ limited manufacturing processes and technologies for viable SSB production.

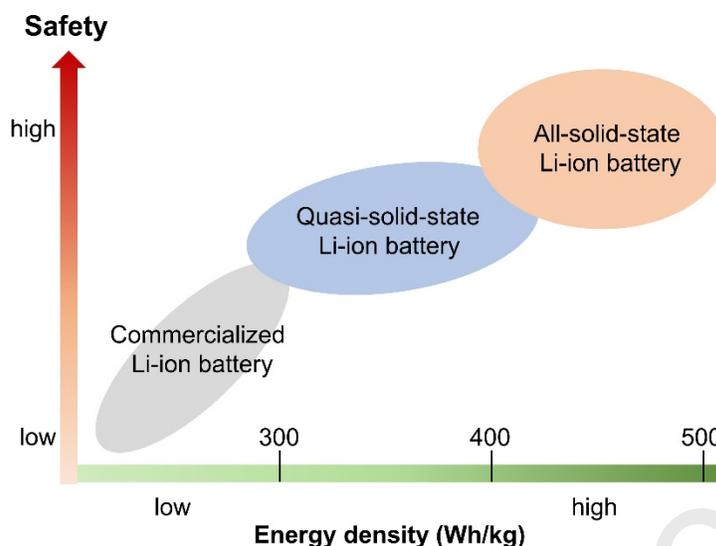


Fig. 1. Overview of the evolution of battery technology.

2. Solid-state electrolyte

As a core material of SSBs, many SSEs based on various anion chemistries (S^{2-} , O^{2-} , X^- ($X = F, Cl, Br, \text{ and } I$), etc.) have been reported over the last few decades, some of which include sulfide-, oxide-, solid polymer-, halide-, anti-perovskite-, and borohydride-based SSEs. Each class of SSE has its own pros and cons. For example, sulfide electrolytes (i.e., $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$, $25 \text{ mS}\cdot\text{cm}^{-1}$) exhibit the highest ionic conductivity at room temperature, but they suffer from poor air stability and toxic gas (i.e., H_2S) release when exposed to the ambient environment. Furthermore, the cost of sulfide electrolytes is still far from satisfying industrial requirements. Therefore, improving the air stability and reducing the cost of sulfide electrolytes are crucial prerequisites for developing their SSB technology.

In contrast, oxide electrolytes possess favorable air stability, high ionic conductivity ($1 \text{ mS}\cdot\text{cm}^{-1}$), and wide electrochemical windows. Nonetheless, the high elastic modulus of oxide electrolytes restricts their device integration [2]. Thus far, oxide electrolytes have been successfully used to develop quasi-SSBs (with some liquid electrolytes or gel polymer electrolytes). It should be mentioned that the typical oxide electrolyte, $Li_7La_3Zr_2O_{12}$, is chemically sensitive to carbon dioxide (CO_2) and water (H_2O), leading to the formation of Li_2CO_2 and $LiOH$ on its surface and resulting in poor interfacial lithiophilicity [3]. Borohydride electrolytes show good ionic conductivity, but their low thermal stability and susceptibility to releasing hydrogen (H_2) are worrisome for practical applications. Anti-perovskite electrolytes demonstrate excellent stability against lithium (Li) metal, but their ionic conductivity at room temperature still needs improvement [4]. Considering the mechanical properties of SSEs, solid-state polymer electrolytes are considered to be the most feasible for large-scale battery manufacturing, despite their insufficient room-temperature ionic conductivity ($\sim 10^{-6} \text{ S}\cdot\text{cm}^{-1}$). So far, a 30 kW·h lithium metal polymer (LMP) battery has been commercialized by Bolloré and successfully integrated into their Bluecar, providing a driving range of 250 km in urban use and a maximum speed of $120 \text{ km}\cdot\text{h}^{-1}$.

Recently, solid-state halide electrolytes have been widely reported; these electrolytes exhibit relatively high ionic conductivity ($> 1 \text{ mS}\cdot\text{cm}^{-1}$), high oxidation stability ($> 4 \text{ V}$ against Li^+/Li), and favorable mechanical softness (similar to that of sulfide electrolytes) [5–7]. For example, our group developed new wet-chemistry methods to synthesize halide electrolytes and systematically investigated their structure-to-property relationship [6–8]. Nazar's group [9] demonstrated the high-voltage stability ($> 4.8 \text{ V}$ versus Li^+/Li) and ultra-long cycling stability of SSBs using a halide electrolyte ($Li_2In_{1/3}Sc_{1/3}Cl_4$). Although halide-based SSBs demonstrate outstanding electrochemical performance, their moisture vulnerability and interfacial instability toward next-generation anodes (e.g., Li metal) remain extremely challenging. Moreover, it is essential to develop low-cost halide electrolytes with good atomic economy.

Despite the various SSEs that have been developed based on different anion chemistries, a perfect SSE that can satisfy all the criteria of SSBs is still lacking. Therefore, continuous efforts should be put to bolster existing SSEs and develop innovative alternatives. In addition, designing composite SSEs that combine the advantages of inorganic and organic materials is an important research direction [2]. Meanwhile, scholars in this field are encouraged to understand the structure-to-property relationship of SSEs by using first-principles calculations and advanced characterization techniques, which will offer mechanistic insights into the ion-transport mechanism and crystal structure of SSEs.

3. Interface design

Since an ideal SSE has yet to be developed for SSB applications, SSBs based on existing SSEs suffer from grand interfacial challenges, including insufficient ionic contact caused by point-to-point solid-solid ionic contact, detrimental interfacial reactions, physical contact loss caused by the volume change of active materials upon the charge/discharge process, and lithium dendrite-penetrating SSEs. In this section, we highlight the interfacial challenges of SSBs, while providing some promising strategies and future perspectives regarding the cathode and anode, respectively (Fig. 2(a)).

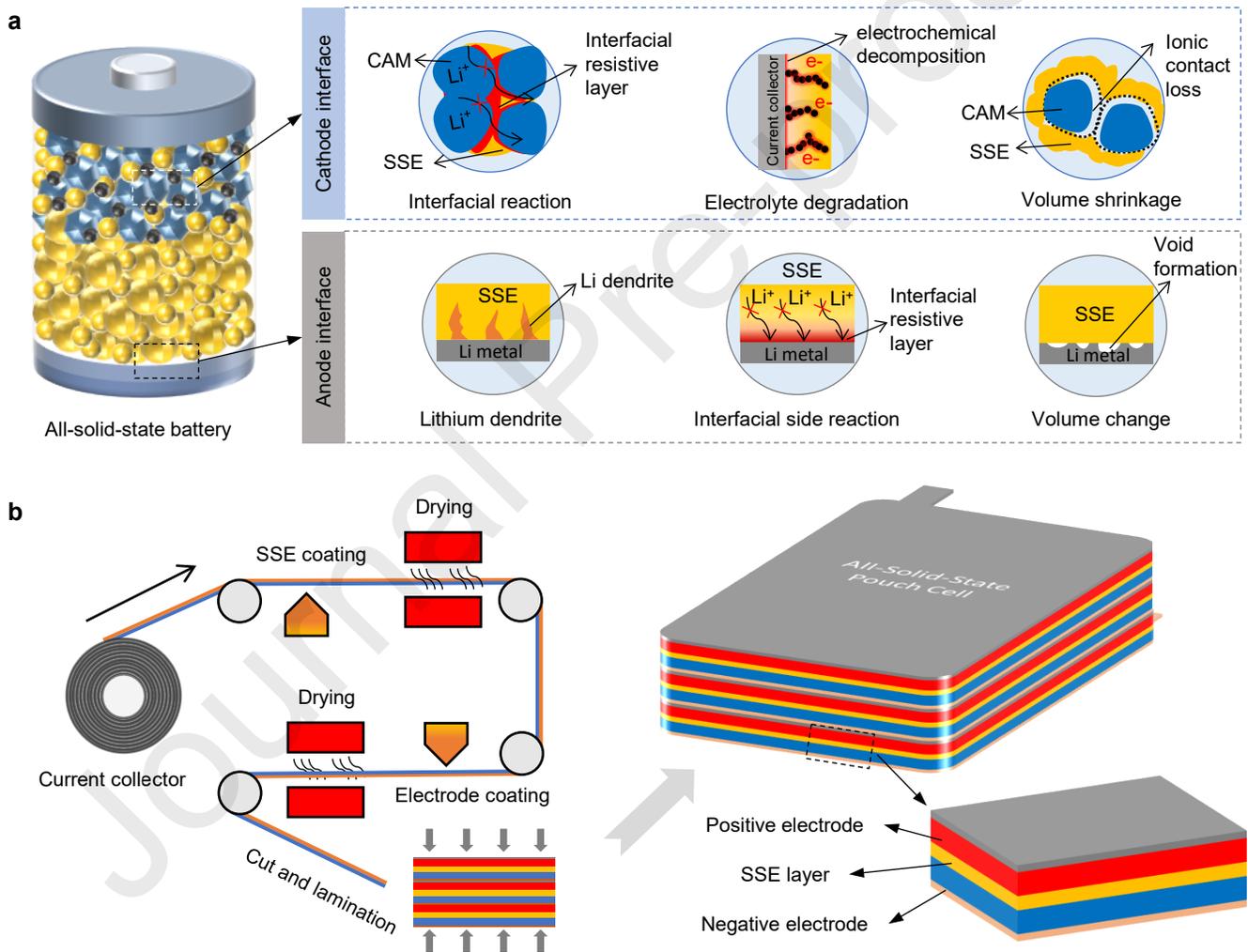


Fig. 2. (a) The configuration of an all-solid-state battery highlights the interfacial challenges; (b) a slurry coating process to fabricate practical multilayer all-solid-state pouch cells.

(1) **Cathode-related strategies and future perspectives.** At the cathode interface, the space charge effect caused by the difference in intrinsic electrochemical potential between the cathode and SSE is a well-recognized factor that impedes interfacial charge transport. Depositing a dielectric buffer layer at the interface can effectively mitigate the space charge

effect [1]. In addition, interfacial side reactions between cathode active materials (CAMs) and SSEs result in a resistive interfacial layer (Fig. 2(a)), which significantly hinders interfacial ion/electron transport. An interfacial coating layer with high ionic conductivity is highly desirable to prevent cathode side reactions. However, a full understanding of how to rationally design ideal interfacial coating materials is lacking, especially regarding ionic conductivity, mechanical properties, and electronic conductivity. The volume change of electrode materials is also a significant challenge that leads to physical contact loss. Although external pressure can help mitigate these issues, considerable pressure is not very feasible for practical applications. Adding wet agents is a good solution; however, the chemical compatibility between the wet agent and other components in the composite must be carefully examined. Moreover, conductive carbon is typically required to construct continuous electron pathways in electrode composites. However, such electron-conductive agents can also cause SSE decomposition, particularly for sulfide electrolytes. Therefore, balancing the interfacial ion and electron transport inside the electrode composite is paramount for realizing SSBs with a high power density and a long cycle life.

Most cathode materials that have been widely investigated for SSBs are LiCoO_2 and high-nickel (Ni) cathodes. Cobalt-free cathodes should be developed in the near future in order to avoid issues related to cobalt resources. In addition, high-capacity cathodes (e.g., sulfur, oxygen) need to be developed. Advanced characterization techniques, such as high-resolution transmission electron microscopy (TEM), synchrotron analysis, cryo-TEM, and distribution of relaxation time (DRT) [10], are crucial for understanding the interfacial degradation mechanism and interfacial charge transport kinetics.

(2) Anode-related strategies and future perspectives. At the anode interface, most SSEs are susceptible to reduction when paired with a lithium metal anode, as the lithium anode has the lowest electrochemical potential (-3.04 V versus standard hydrogen electrode (SHE)). To address this issue, interfacial coatings have been developed to prevent side reactions. Similar to a liquid system, Li dendrites have been widely observed in SSBs, probably related to poor interfacial solid-solid contact, the electronic conductivity of SSEs (10^{-8} – 10^{-10} $\text{S}\cdot\text{cm}^{-1}$), voids, and random surface and bulk defects formed during SSE preparation [2]. Several promising strategies that can suppress Li dendrite formation include constructing a Li host with a high diffusivity (i.e., alloy anodes) and adding an interfacial wetting agent that regulates Li deposition behaviors [11].

Nevertheless, very limited areal capacity (0.1 – 0.5 $\text{mA}\cdot\text{h}\cdot\text{cm}^{-2}$) is typically tested in Li/SSE/Li symmetrical cells, which is unrealistic for practical applications [12]. Some Li/SSE/Li cells have even demonstrated a very high critical current density (CCD), above which Li dendrites will penetrate through the SSE layer and cause internal short-circuits. The current test protocol for CCD is always under the minimal capacity, which should be reconsidered. Moreover, most previous work is based on thick lithium metal, which is derived from practical applications. Future work should utilize a thin Li layer (e.g., 30 μm). As thin Li metal suffers from significant volume change upon cycling, advanced strategies to accommodate the volume change of a thin Li metal anode are highly desirable.

Although using a Li metal anode significantly boosts the energy density of SSBs, the safety of solid-state lithium metal batteries needs to be carefully evaluated [13]. Apart from Li metal, other anode materials such as graphite, Si/C, silicon, and alloys (e.g., tin (Sn)) should be developed in parallel for SSB applications [14]. Anode-free SSBs are another promising direction, as demonstrated by Samsung, even though they present grand challenges [15].

4. All-solid-state batteries

Many research groups have reported encouraging electrochemical results for SSBs, some of which include high-power all-solid-state batteries using superionic sulfide conductors, high-energy long-cycling all-solid-state lithium metal batteries enabled by silver-carbon composite anodes [15], carbon-free high-loading silicon anodes enabled by sulfide SSEs [14], and high-areal-capacity, long-cycle-life 4 V ceramic all-solid-state Li-ion batteries enabled by chloride SSEs [9]. Although these contributions hold great promise for SSB technology and development, they are not necessarily indicative of future success, as lab-scale SSBs are typically tested using high-pressure model cells with a low capacity of 1 – 2 $\text{mA}\cdot\text{h}\cdot\text{cm}^{-2}$, which cannot be used for practical applications. Thus far, demonstrations of SSBs in pouch cell configuration have not been widely reported, other than by a few research groups and several up-and-coming companies such as QuantumScape, Solid

Power, Samsung, and Toyota. For commercial manufacturing, advanced fabrication processes must be developed, such as wet slurry coating (Fig. 2(b)) and dry electrode processes, which require systematic engineering to improve the chemical compatibility between polymeric binders, organic solvents, and various SSEs. In addition, a low self-discharge rate of SSBs (< 2% in one month) should be realized for large-scale energy-storage systems. Most SSBs are currently fabricated with and tested under high pressure, leading to many engineering issues in practical applications. Therefore, eliminating pressure reliance during SSB fabrication and operation should also be considered.

5. Conclusion

In summary, SSBs have taken the world by storm due to their intrinsic safety and high theoretical energy density. However, SSBs suffer significant challenges at the material, interface, and full-cell levels. At the material level, SSEs with high ionic conductivity, wide electrochemical stability, good chemical stability, and large-scale feasibility should be continually sought after. Meanwhile, interdisciplinary characterizations and theoretical calculations (e.g., machine-learning-assisted material selection) should be employed to search for an ideal SSE and comprehend its ion transport mechanism. At the interface level, interfacial charge transport should be tailored to achieve fast kinetics and long-term stability. The failure mechanism should also be explored in order to further improve interface strategies. At the full-cell level, many efforts are focused on improving the electrochemical performance of SSBs. While this is important, equivalent efforts should be made in parallel to develop economic and high-throughput fabrication processes that can enable large-scale SSB manufacturing. Furthermore, a comprehensive analysis of SSBs, such as their self-discharge behavior, thermal stability, pressure reliance, and cost, is crucial for their successful commercialization. We hope this perspective will encourage joint efforts from academia and industry to make a difference in SSB technology.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: