



# Advances in solid-state batteries: Materials, interfaces, characterizations, and devices

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Solid-state batteries with features of high potential for high energy density and improved safety have gained considerable attention and witnessed fast growing interests in the past decade. Significant progress and numerous efforts have been made on materials discovery, interface characterizations, and device fabrication. This issue of *MRS Bulletin* focuses on the current state of the art of solid-state batteries with the most important topics related to the interface issues, advanced characterizations, and electrode chemistries, aiming to provide a comprehensive perspective for the interface and characterization challenges for high-performance solid-state battery devices.

## Becoming “solid” in battery technology

Rechargeable batteries continue to be a key technology to meet the rapidly growing demands of clean energy resources in the global market, including electric vehicles (EVs) and mobile computing applications. High energy density and improved safety metrics are among the essential requirements for next-generation energy-storage systems. Among the alternatives, all-solid-state batteries (ASSBs) utilizing inorganic solid electrolytes (SEs) have become one of the most promising candidates due to their enhanced safety compared to conventional Li-ion batteries (LIBs) with liquid electrolytes (LEs). There are several advantages of using SEs: (1) high modulus to enable high-capacity electrodes (e.g., Li anode); (2) improved thermal stability to mitigate combustion or explosion risks; and (3) the potential to simplify battery design and reduce the weight ratio of inactive materials.<sup>1–3</sup>

In the last decade, there has been a remarkable rise in research activities in academia as well as significant interest from industrial players. **Figure 1** shows the ever-increasing number of published research articles with the topic on solid-state batteries (SSBs), in which almost an exponential growth is illustrated in yearly columns. In comparison to 255 articles in

2012, the number of articles has expanded by 10 times to 2581 in 2022. Stimulated by this rapid growth of innovations, many companies among the automakers (e.g., Toyota, Mercedes, Ford) and battery industries (e.g., Samsung, CATL, Solid Power, QuantumScape, Factorial Energy) have announced their strong interests and roadmaps on the development and commercialization of SSBs.<sup>4</sup>

From the academic perspective, significant research advancements have been made within the past decade, mainly focusing on (1) the discovery of novel materials, specifically solid superionic conductors; (2) the interface characterization and stabilization; and (3) the demonstration of electrochemical cycling in ASSB devices. There are several important review articles that summarize these achievements, challenges, and strategies related to the materials, interfaces, and devices for the development of ASSBs.<sup>5–8</sup> In the industry, one example is Samsung, which in 2020 announced a high-performance ASSB prototype (Ah-class pouch cells) designed to achieve a high energy density (900 Wh L<sup>-1</sup>) and a cycle life of greater than 1000 charges using an Ag–C anode pairing with Li metal and argyrodite (Li<sub>6</sub>PS<sub>5</sub>Cl) as the SE material.<sup>9</sup> Such innovations for ASSBs demonstrate their high potential for the future

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development of batteries with features of high energy density and enhanced safety for vehicle electrification.

### Different chemistries for ASSBs

ASSBs are bulk-type solid-state batteries that possess much higher energy/power density compared to thin-film batteries. In solid-state electrochemistry, the adoption of SEs in ASSBs greatly increases the energy density and volumetric energy density compared to conventional LIBs ( $250 \text{ Wh kg}^{-1}$ ).<sup>10</sup> Pairing the SEs with appropriate anode or cathode materials is crucial to achieve good cycling performance. Depending on the selection of materials at the anode and cathode, ASSBs can generally include all-solid-state Li-ion batteries using graphite or  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as the anode,<sup>11</sup> all-solid-state Li-metal batteries with Li metal as the anode,<sup>2</sup> all-solid-state lithium sulfur batteries utilizing sulfur as the cathode,<sup>12</sup> and all-solid-state silicon batteries incorporating Si as the electrode,<sup>13</sup> as shown in Figure 2.<sup>2</sup>

### All-solid-state Li-metal batteries

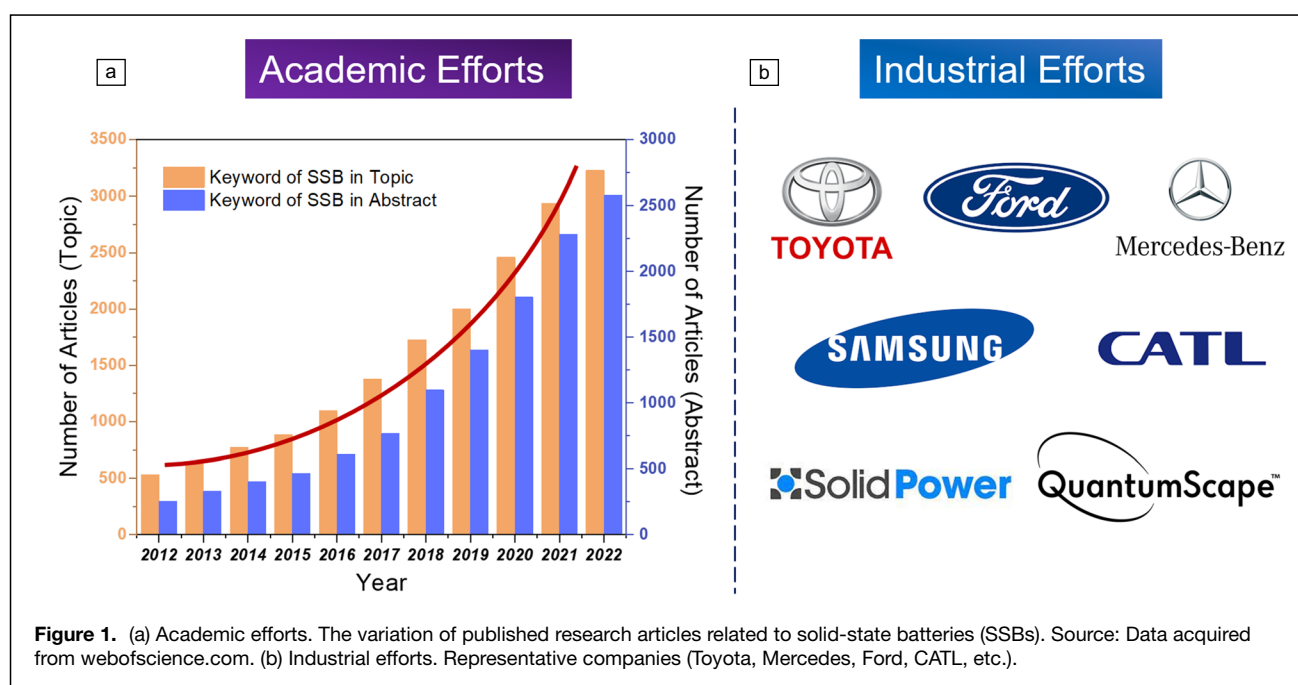
The utilization of SEs allows for using Li metal as the anode, which shows high theoretical specific capacity of  $3860 \text{ mAh g}^{-1}$ , high energy density ( $>500 \text{ Wh kg}^{-1}$ ), and the lowest electrochemical potential of 3.04 V versus the standard hydrogen electrode (SHE). With Li metal, all-solid-state Li-metal batteries (ASSLMBs) at pack levels can increase the specific energy density of LIBs by 35% and the volumetric energy density by 50%, respectively.<sup>2</sup> Although Li dendrites could still penetrate SEs via grain boundaries and voids, interface engineering has been employed as an efficient strategy to ensure stable cycling in laboratory-level cells.

### All-solid-state Si batteries

Silicon (Si) is one of the other promising anode materials due to its theoretical specific capacity of  $3590 \text{ mAh g}^{-1}$ , worldwide abundant resource and electrochemical potential (0.06 V versus  $\text{Li/Li}^+$ ) being close to Li metal. Rapid capacity decay occurs when using LEs due to the huge volume expansion ( $>300\%$ ) during the lithiation. Nevertheless, SEs provide a unique opportunity to form stable and passivating SEI at the interface and enable the use of Si anodes in ASSBs.<sup>14–16</sup> In 2021, Meng et al. reported the micro-silicon ( $\mu\text{-Si}$ ) anode (carbon-free), NMC 811 ( $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ ) cathode, pairing with argyrodite SE, and the full cell was found to deliver 80% capacity retention after 500 cycles under a high current density of  $5 \text{ mA cm}^{-2}$  (area capacity of  $11 \text{ mAh cm}^{-2}$ ).<sup>15</sup> Zhu et al. studied nano-Si coupled with single-crystal NMC (stabilized with  $\text{Li}_2\text{SiO}_x$ ) and argyrodite SE ( $\text{Li}_6\text{PS}_5\text{Cl}$ ) and found that the full cell with a mass loading ( $10 \text{ mg cm}^{-2}$ ) delivered a high capacity of  $145 \text{ mAh g}^{-1}$  at C/3 and stable cycling for 1000 cycles.<sup>14,17</sup> Besides, Wu et al. demonstrated that hard carbon-stabilized Si anode-ASSBs with NMC811 cathode at a loading of  $5.86 \text{ mAh cm}^{-2}$  could deliver stable cycles at a 1 C rate.<sup>16</sup>

### Discovery and development of solid ionic conductors

Solid-state ionic conductors, as an indispensable component in ASSB structure, play a significant role in determining the cyclability and performance of cells. Generally, SE materials can be divided into inorganics, polymers, and composites. Among them, inorganic SEs have gained intensive research interests and a variety of materials have been developed,<sup>18–21</sup> including oxides, sulfides, halides, and borohydrides.



The ideal SE materials are expected to hold several important features (**Figure 3**),<sup>22–24</sup> such as high ionic conductivity ( $>10^{-3}$  S  $\text{cm}^{-1}$ ) at room temperature (RT); low electrical conductivity to avoid self-discharge; a wide electrochemical stability window; good chemical/electrochemical stability toward the electrodes; low interfacial resistance; low toxicity and environmentally benign character; improved mechanical properties and reliability; and economic processing of materials and cost-effective manufacturing. Intensive efforts have been devoted to the conductivity and (electro) chemical stability of SEs by doping chemistry and adopting different synthetic approaches (e.g., solid-state reaction and liquid-based method).

There are several inorganic SE materials to achieve ionic conductivity competitive with that of LEs. A major milestone was the report in 2011 of  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS)<sup>25</sup> sulfide with RT ionic conductivity of 12 mS  $\text{cm}^{-1}$  and a later report in 2016 on a LGPS-type solid solution ( $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ ) shows an ionic conductivity of 25 mS  $\text{cm}^{-1}$ .<sup>26</sup> Other representative inorganic SE materials include garnet-type oxide ( $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ , LLZO),<sup>21,27</sup> NASICON-type (e.g.,  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ , LATP),<sup>28</sup> sulfides such as argyrodites ( $\text{Li}_6\text{PS}_5\text{X}$ ),  $\text{Li}_3\text{PS}_4$ ,<sup>29</sup> and halides, such as  $\text{Li}_3\text{InCl}_6$ .<sup>30</sup>

For different types of SE materials, they were found to exhibit unique advantages, yet they also encounter specific challenges for their application within ASSBs. For example, sulfide SEs possess a notably high ionic conductivity ( $>1$  mS  $\text{cm}^{-1}$ ), favorable mechanical deformability (ductility), low-cost nature, and the potential to accommodate electrode volume changes at the interface.<sup>29,31</sup> However, they also grapple with drawbacks such as moisture sensitivity, a relatively narrow electrochemical potential window, and require protective environment for the processing, as well the

passivate layer toward to oxide cathode.<sup>5,32</sup> Similarly, oxide SEs show great chemical stability with cathodes, nevertheless, they are brittle and exhibit poor contact at the interface. Halide SEs display high chemical stability with high-voltage oxide cathodes, but they have instability issues at the interface toward the Li metal.

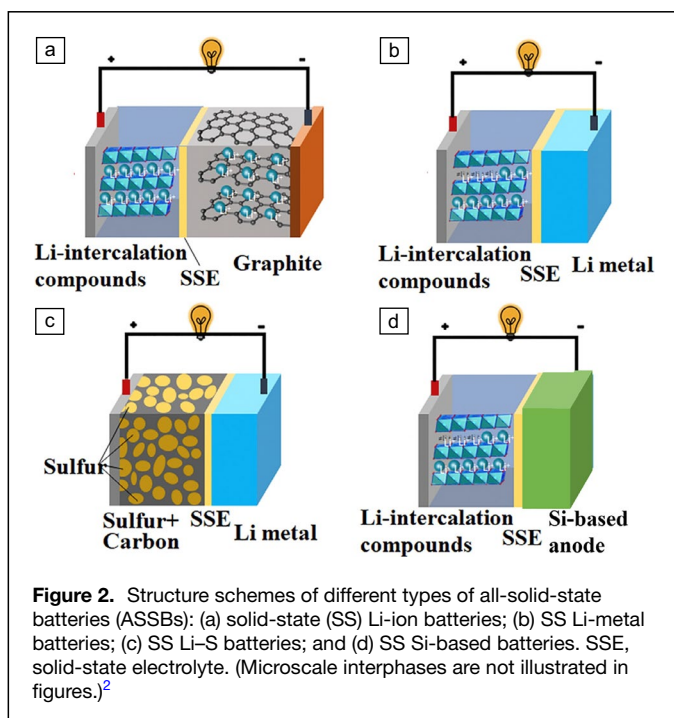
To overcome these challenges of SEs, doping chemistry and interface engineering have been widely explored. Specifically, aliovalent elemental doping can significantly improve both ionic conductivity and stability. In 2022, Nazar et al. reported  $\text{Li}_2\text{In}_x\text{Sc}_{0.666-x}\text{Cl}_4$  halide SE exhibited both impressive conductivity (2.0 mS  $\text{cm}^{-1}$  at RT) and great compatibility with oxide cathode ( $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$ ), leading to stable 3000 cycles with 80% capacity retention (at loading of 1.325 mAh  $\text{cm}^{-2}$ ).<sup>34</sup> Later,  $\text{Li}_{6.8}\text{Si}_{0.8}\text{As}_{0.2}\text{S}_5\text{I}$  sulfide was reported to show enhanced air and electrochemical stability (long cycle life of 62,500 cycles at 2.44 mA  $\text{cm}^{-2}$ ).<sup>33</sup>

So far, there is no single SE material that can meet all the requirements (high conductivity, chemical/electrochemical stability, interface stability to electrodes) to ensure ASSBs with practical applicable performance; therefore, research efforts on the exploration of novel SEs materials should be continued. Computational screening could assist for the discovery of new Li-ion conductors based on lattice dynamics or high-entropy mechanism.<sup>35,36</sup> Additionally, there are also other factors to consider from a practical perspective, including (1) use more economical materials to reduce the dependency on rare-earth elements; (2) environmentally benign materials and process for battery manufacturing and recycling; and (3) the applicability of SEs for industrial electrode fabrication conditions.<sup>24</sup>

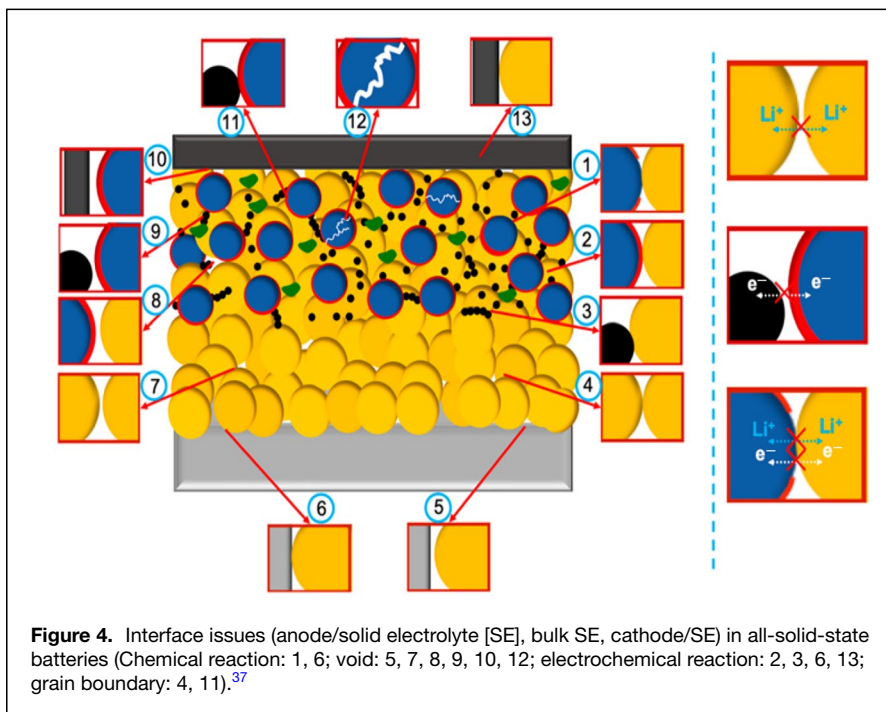
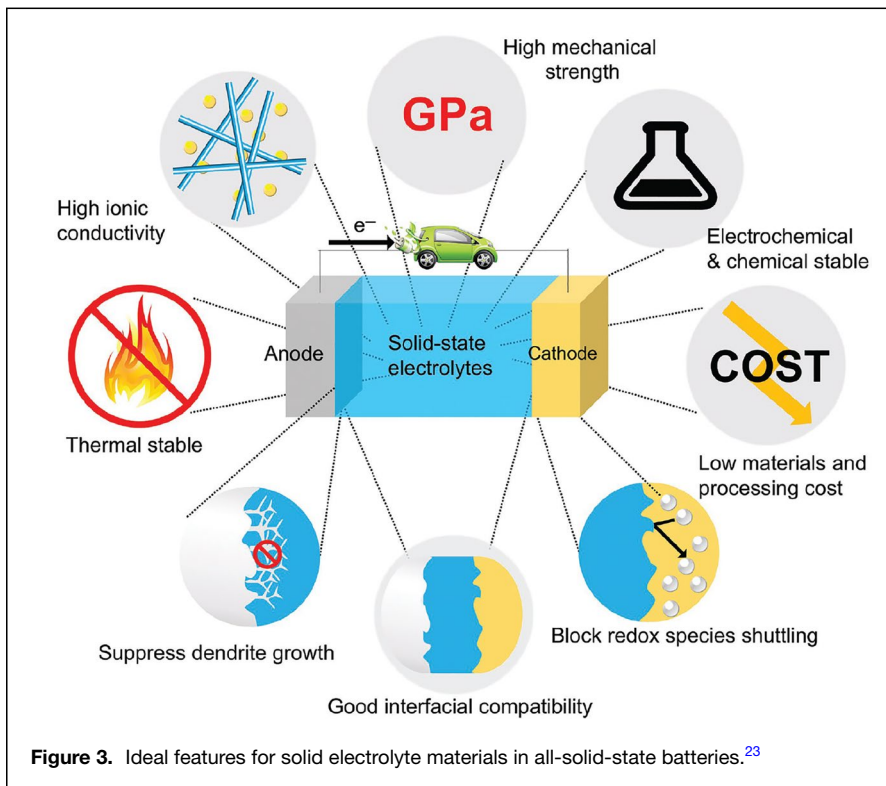
## Interfacial issues and strategies

In addition to the conductive property, interface behavior stands out as another crucial factor that determines the successful cycling or failure of ASSBs. There are various types of interfaces in ASSBs (**Figure 4**):<sup>37</sup> anode/SE pellet, cathode/SE pellet, nano-interfaces inside bulk SE, and interface in composite cathode (active material/SE particles). At the anode/SE interface, the high reactivity (e.g., Li metal) or the volume expansion (e.g., Si) of anode forms unstable interfaces and result in huge interface resistance. Within the bulk SEs, inorganic SE crystals face challenges coming from grain boundaries, voids, and impurity phase, which not only hinder the ion transport but also provide the pathways for Li dendrite growth. At the cathode/SE interface, the presence of multiple components introduces further complexity; moreover, the mismatch of the SEs' electrochemical window with high-voltage cathode materials also causes interface instability.

Interface issues in ASSBs are complicated, as they involve a blend of factors, including interfacial reactions and mechanical degradation. Numerous important review articles have been reported in ASSBs,<sup>38–40</sup> shedding light on the intricate nature of the interface challenges. The main interface issues include (1) limited physical contact diminishes the effective interaction area and obstructs the efficient ion transport across the interface.







The origin of poor physical contact can be traced to the high modulus of inorganic SEs or the stress/strain changes arising from the distinct volume expansion of electrode material; (2) sluggish charge transfer due to poor (electro)chemical stability at SE/electrode interfaces, causing the decomposition of SEs or unstable SEI layer; and (3) Li dendrites formation that resulted from nonuniform current deposition at the interface, which penetrate

along the grain boundaries of inorganic SEs (e.g., garnet oxide, argyrodite sulfide). The first two issues lead to high interfacial resistance, resulting in rapid capacity decay of ASSBs, while the presence of Li dendrite at the interface can trigger internal short circuits within the batteries.

Extensive studies have been focused on the interface issues in ASSBs and a broad range of strategies have been explored to address or mitigate them.<sup>41,42</sup> The primary principles are to prevent undesirable reactions, creating an interlayer that facilitates ion transport while electronically insulating and preserving mechanical integrity. The popular strategies include specially designed artificial interlayer (or buffer layer) and engineered structure designs that aim to stabilize the interface and mitigate the side reactions. On the anode side, protective interlayers such as alloy phase (e.g.,  $\text{Li}_x\text{In}_y$ ,  $\text{Li}_x\text{Ag}_y$ ) have proven effective in stabilizing Li metal and preventing dendrite growth.<sup>43,44</sup> For cathodes, thin coatings (e.g.,  $\text{LiNbO}_2$ ,  $\text{Li}_2\text{SiO}_x$ ) applied on the surface of cathode active materials (CAMs) have been successful in suppressing unfavorable side reactions, particularly those between sulfide SEs and oxide cathode.<sup>14,45</sup> Additionally, engineered structural designs, such as gradient or core cell structures, can also modify the interface to address interfacial side reactions.<sup>21</sup>

### Advanced characterization techniques

To pursue high-performance ASSBs, advanced characterization techniques play a significant role in gaining fundamental understanding of the bulk, surface, and interface chemistry at both the materials and device levels. Specifically, *operando* and *in situ* characterization techniques provide a precious and unique opportunity to scrutinize the dynamic interphase structure and phase changes during electrochemical processes. Moreover, by elucidating the interfacial phenomena and electrochemical mechanisms, *operando* characterizations also facilitate the rational design and optimization of ASSB components.<sup>46–48</sup>

A range of representative characterization techniques are available that offer morphological and structural information

for materials and device-level analysis. These techniques include scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), transmission x-ray microscopy (TXM), x-ray tomography (XT), and solid-state nuclear magnetic resonance (ss-NMR). Zhu et al. utilized *operando* x-ray absorption near-edge structure (XANES) spectroscopy and *ex situ* x-ray nanotomography (XnT) to investigate the structure evolution of the nano-Si composite anodes.<sup>17</sup>

There are also some characterization techniques that are sensitive to detect (electro)chemical environment at the surface and interface in ASSBs. These techniques include x-ray photoelectron spectroscopy (XPS), synchrotron XPS, x-ray absorption spectroscopy (XAS), interface x-ray scattering, Auger electron spectroscopy (AES), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), Raman spectroscopy, and extreme-ultraviolet second harmonic generation (XUV-SHG). For examples, XPS spectra during Li deposition on LGPS reveal the chemical compositions ( $\text{Li}_3\text{P}$ , Ge,  $\text{Li}_2\text{S}$ ) at the unstable interface.<sup>49</sup> Using XUV-SHG and XPS characterizations, it is found that the reduction in Li interfacial mobility at the surface is due to the intrinsic changes in LLTO cage vibrational modes.<sup>50</sup> In addition, neutron scattering techniques, including neutron diffraction (ND) and neutron imaging, have better sensitivity to light elements such as lithium because they are based on interaction with atomic nuclei rather than electrons (Figure 5).<sup>51</sup>

Advanced characterization techniques have made significant contributions toward investigating ion distribution, migration behaviors, and chemo-mechanical evolution at solid–solid interfaces in ASSBs. Gaining a fundamental understanding of interfacial phenomena and processes can further guide the design principles of SEs and efficient interfacial engineering strategies. Elucidating the complex interfacial changes occurring in ASSBs through advanced *operando* techniques is key to enabling their practical application. By providing critical insights into the dynamic electrochemical mechanisms, advanced interface characterization will facilitate the rational design and optimization of SEs and interfaces to enhance ASSB performance.

### ASSBs device configuration design

The replacement of LEs by SEs provides new opportunities on the device configuration: (1) ASSBs have the potential to be assembled directly in parallel layer stacking or sheet-type cell for the package (Figure 6).<sup>42,52</sup> Specifically, bipolar mode fabrication of ASSBs enables the internal connection for a series of unit cells, reducing the mass ratio of current collectors.<sup>52</sup> (2) ASSBs can work under high temperatures,<sup>26</sup> thus the cooling system can be removed at the cell package. To achieve full potential of ASSBs, the new design of battery configuration still needs more development effort.

The design and fabrication of ASSB devices should consider the following factors. (1) Processing diversity. The processing techniques are strongly dependent on SE materials. For example, sulfide sheets can be densified to device stacks

through cold calendaring, whereas oxide sheets require high-temperature annealing for densification. (2) Stress/strain accumulation. The volumetric changes for electrode materials during cycling cause the occurrence of stress and strain at the SE/electrode interface. (3) Stack pressure. Stack pressure plays an important role to form intimate contact at the SE/electrode interface, thus optimal stack pressure (e.g., 5 MPa) sometimes is required to achieve high-performance ASSBs.<sup>53</sup> Nevertheless, the stacking pressure should not be too high to increase the manufacturing cost of the cell package.

To date, the integration of SEs into full ASSB devices is still at the early stage. To achieve high energy density of ASSBs, the SE materials should be efficiently processed to thin sheets<sup>54</sup> rather than thick pellets, and the portion of SEs in composite cathode should be minimized, but still maintain effective ion transport.

### Challenges to practical application of ASSBs

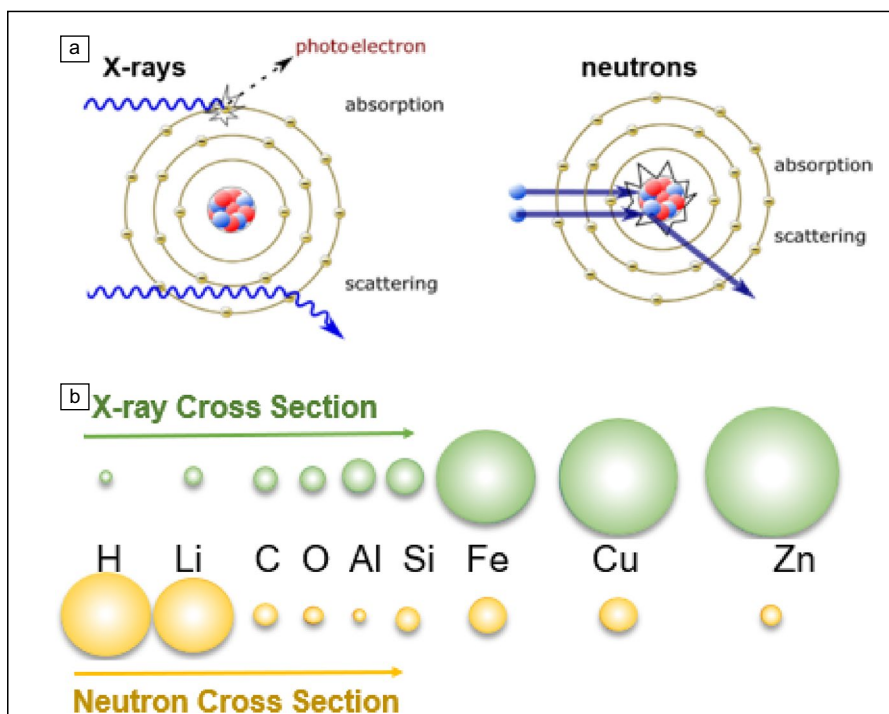
In the past decade, advanced materials and interface design had been successfully validated in laboratory-level ASSBs to exhibit excellent electrochemical cycling performance, although some operations are under conditions such as temperature and pressure. There are still several challenges on the road toward the practical applications of ASSBs (Figure 7).<sup>55</sup>

#### High loading of cathode active materials

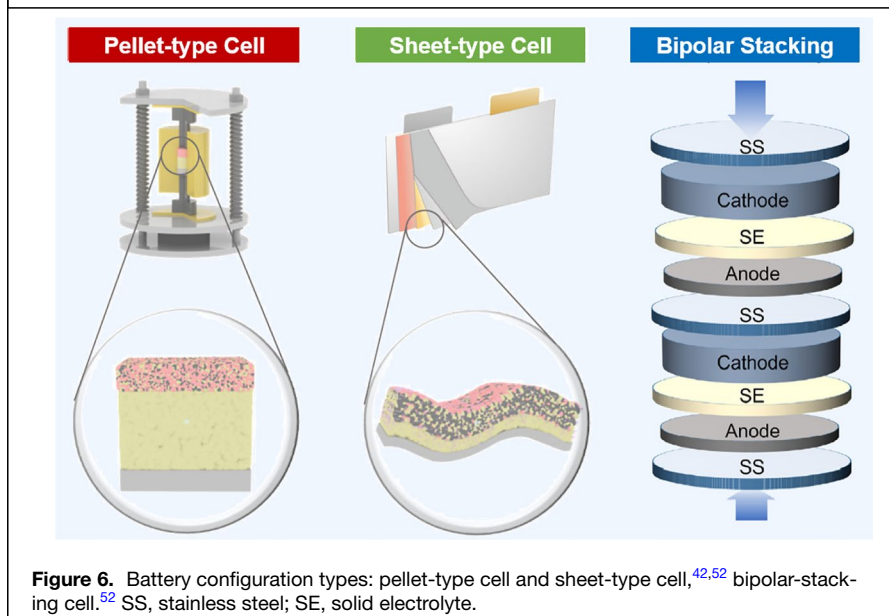
To realize the full potential of ASSBs, high mass loading of active materials (e.g., areal capacity  $>3 \text{ mAh cm}^{-2}$ ) in electrodes is required to be competitive with conventional LIBs. However, chemo-mechanical degradation problem and low utilization of active materials occur in the high-loading composite cathode. Currently, a high composition of SE ( $>25 \text{ wt\%}$ ) often happens in the cathode for ASSBs compared to LE composition in the commercial LIBs.<sup>56</sup> The optimization principles of cathode composition are to reduce the content of SEs while maintaining high conductivity (both ionic and electronic) in the electrode. In addition, advanced coating techniques involving the selection of appropriate technology and the materials (e.g., binder or solvent) as well as the conductive additives are important to ensure the efficient ionic and electronic conduction in thick electrodes. Dry electrode technologies could hold great potential for industrial application of ASSBs.

#### Fast charging of high-loading ASSBs with high-capacity retention

For the promising applications of ASSBs, fast charging within tens of minutes (i.e., 4C) is preferred. Nevertheless, although the SEs can present high ionic conductivity at RT, poor battery cycling performance or battery failure for ASSBs have been often observed when cycling under high current density (e.g.,  $>1 \text{ mA cm}^{-2}$ ). Such failure is mostly caused by internal short circuiting from the growth and propagation of Li filaments inside SEs. The related issues include irreversible side reactions between Li anode and SE; structural degradation of cathode



**Figure 5.** (a) Mechanisms for x-rays and neutrons interacting with the outer electron shells of the atoms. (b) Sketch of the x-ray and neutron total cross sections of several atoms.<sup>51</sup>



**Figure 6.** Battery configuration types: pellet-type cell and sheet-type cell,<sup>42,52</sup> bipolar-stacking cell.<sup>52</sup> SS, stainless steel; SE, solid electrolyte.

active materials (CAMs); crack generation after repeated cycling at the cathode; and the formation of cracks within the bulk SEs. To address these problems, enhanced kinetics for ion transport at the interface and achieving homogeneous Li stripping/deposition are important to achieve a viable fast charge performance.<sup>57</sup>

### Scaling up from laboratory scale to industrial applications

There are still large gaps between practical applications of ASSBs to scale up from laboratory-level cells, which have

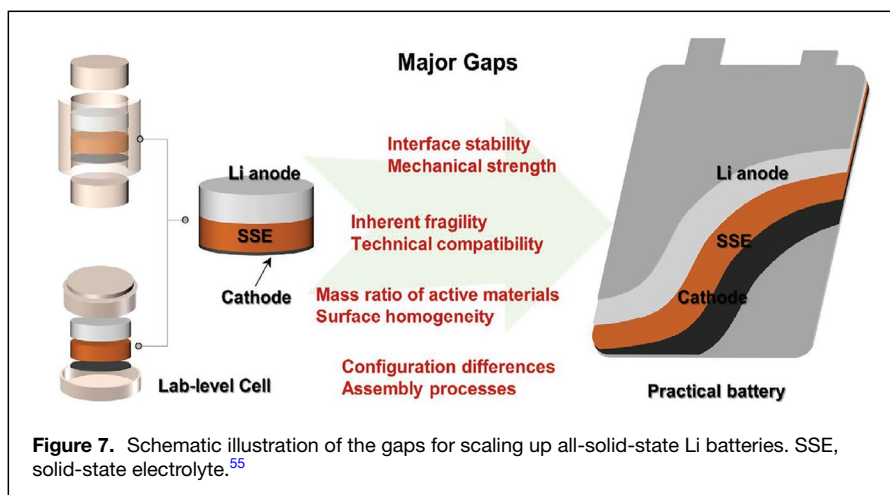
been discussed in several review articles.<sup>55,58</sup> Significant challenges include the following: (1) The mass production of SE materials and large area SE sheets with thin thickness (<50 μm). The cost of raw materials and the manufacturing, as well as the quality of thin SE sheets should be considered. (2) The efficient integration of SE processing into thick electrode preparation for the fabrication of practical ASSBs. (3) For ASSBs with Li-metal anode, more economic and efficient approaches are needed to prepare thin Li film and adopt interface engineering strategy to ASSBs. (4) New battery configurations and assembly strategies are needed to achieve low cost of manufacturing while maintaining high performance.

In summary, there have been several review articles to discuss the scale-up from materials' perspectives and provide valuable insights toward the commercialization of ASSBs.<sup>21,31,56,59,60</sup> In the near future, we believe rapid technological innovation and advancement are expected to realize the successful manufacturing of ASSBs for practical applications.

### In this issue

This issue covers recent advances across various aspects of ASSBs, focusing on the most important topics related to interface issues, advanced characterizations, and electrode chemistry. In the past decade, much progress has been made in materials discovery, interface engineering, characterization techniques, and device fabrication. A variety of SE materials have been discovered, including sulfides, oxides, and halides, each with unique advantages and limitations. Interface engineering strategies appear promising for stabilizing interfaces. Advanced characterization provides valuable insights into interfacial phenomena and mechanisms during battery cycling. Additional *in situ* and *operando* techniques can help guide design optimizations. Impressive ASSB cycling performance achieved in laboratories validates new materials and interface designs. In 2018, a *MRS Bulletin* special issue titled “Frontiers of Solid-State Batteries” greatly summarized the solid-state electrolyte materials and interface.<sup>3</sup> Although ASSBs show potential for enabling safe,





**Figure 7.** Schematic illustration of the gaps for scaling up all-solid-state Li batteries. SSE, solid-state electrolyte.<sup>55</sup>

high energy density batteries, more research efforts across materials, interfaces, characterization, and engineering are needed to bridge the gaps from fundamental laboratory studies to large-scale industrial fabrication and deployment. This issue provides the most recent understanding on interface challenges, electrode, and advanced characterizations in ASSBs. Following are highlights for each article:

The article by Li<sup>61</sup> discusses the fundamental limitations of interface reactions for ASSBs with sulfide SEs. The primary focus of this article centers on exploring the fundamental principles regarding how electrochemical interface reactions are locally coupled with mechanical and transport properties impacting battery performance, giving opportunities to design electrolyte and interface coating materials for advanced solid-state batteries. Qi et al.<sup>62</sup> highlight the Kelvin probe force microscopy (KPFM) as a tool to image the local potential at interfaces inside ASSBs. The authors draw analogies with electron transport in metal/semiconductor interfaces and show a model system characterization and band diagram modeling that could pave the road to connect the interface potential drop and charge-transfer kinetics in ASSBs. The article by Yao et al.<sup>63</sup> discusses the chemical and mechanical origins of interface instability between electrodes and halide SEs in ASSBs. The authors provide a systematical review of interface instability that causes the capacity decay in halide-based ASSBs and propose the perspectives and future directions to resolve such instability at the interface.

Zhu et al.<sup>64</sup> highlight the use of neutron imaging as a non-destructive and powerful approach for the *operando* visualization of ASSBs, specifically on the interface. The authors conclude that neutron imaging provides valuable insights into the dynamics of Li in ASSBs. In addition, Jang and Meng et al.<sup>65</sup> discuss the important characterization tools and methodologies that can shed light on the main degradation mechanisms in ASSBs at various length scales; ranging from interfacial issues at the material level to system-level challenges at the more practical cell level. The authors recommend a full suite of tools ranging from electrochemical and chemical analysis to microscopy and discuss their

capabilities toward accelerating design as well as limitations.

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## Author contributions

All authors contributed to content design and writing of the manuscript, revisions, and editing. All authors read and approved the final manuscript.

## Conflict of interest

The authors declare no conflict of interest.

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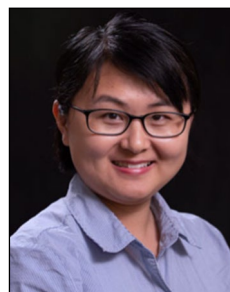
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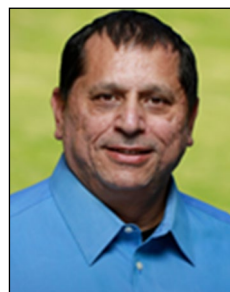
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