

Advances in Solid-state Batteries: Materials, Interfaces, Characterizations and Devices

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Abstract:

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 material discovery, interface characterizations and device fabrication. This issue of MRS Bulletin focuses on the current state of 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.

Key words:

Solid-State Batteries; Materials, Interfaces, Characterizations, 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). The replacement of SEs for LEs brings several advantages, such as: (a) high modulus to enable high-capacity electrodes (e.g. Li anode); (b) improved thermal stability to mitigate combustion or explosion risks; (c) the potential to simplify battery design and reduce the weight ratio of inactive materials.^{6, 8-10}

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 amongst the automakers (e.g., Toyota, Mercedes, Ford) and battery industries (CATL, Solid Power, QuantumScape) have announced their strong interests and developed roadmaps on the development and commercialization of SSBs.

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 ASSBs 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.¹²⁻¹⁵ 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⁻¹) and a cycle life of over 1000 charges by using an Ag-C anode pairing with Li metal and argyrodite (Li₆PS₅Cl) as the SE material.¹⁶ Such innovations for ASSBs demonstrate their high potential for the future development of batteries with features of high energy density and enhanced safety for vehicle electrification.

Different Chemistries for All Solid-State Batteries (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

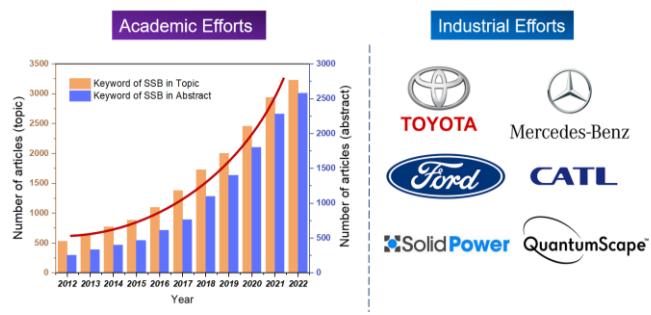


Figure 1. Left: academic efforts. The variation of published research articles related to solid-state batteries (SSBs) (source: data acquired from webofscience.com). Right: industrial efforts. Representative companies (Toyota, Mercedes, Ford, CATL, Solid Power, QuantumScape, etc).

greatly increases the energy density and volumetric energy density compared to conventional LIBs (150 Wh kg⁻¹).¹⁷ 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* (ASSLIBs) using graphite or Li₄Ti₅O₁₂ as the anode,¹⁸ *all solid-state Li metal batteries* (ASSLMBs) with Li metal as the anode,⁶ *all solid-state lithium sulfur batteries* (ASSLSBs) utilizing sulfur as the cathode,¹⁹ and *all solid-state silicon batteries* (ASSSiBs) incorporating Si as the electrode,²⁰ as shown in **Figure 2**.

All-solid-state Li metal batteries (ASSLMBs). The utilization of SEs allows for Li metal as the anode, which shows advantages of high theoretical specific capacity of 3,860 mAh g⁻¹, high energy density in excess of 500 Wh kg⁻¹ and the lowest electrochemical potential of 3.04 V.⁶ With Li metal, ASSLMBs at pack levels can increase the specific energy density of LIBs by 35% and the volumetric energy density by 50%, respectively. 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 lab-level cells.

All solid-state Si batteries (ASSSiBs). Silicon (Si) is one of the other promising anode materials due to its impressive theoretical specific capacity of 3,590 mAh g⁻¹, worldwide abundant resources and electrochemical potential (0.06 V vs. Li/Li⁺) being close to Li metal. With LEs, the huge volume expansion (>300 %) during the lithiation causes a rapid capacity decay of batteries. Nevertheless, SEs provide a unique opportunity to potentially form stable and passivating SEI at the interface and enable the use of Si anodes in ASSBs.²¹⁻²³ In 2021, Meng et al. reported the use micro-silicon (μ -Si) anode (carbon free), NMC 811 (LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂) cathode, pairing with argyrodite SE, and the full cell (μ -Si|SE|NMC811) was found to deliver 80% capacity retention after 500 cycles under a current density of up to 5 mA cm⁻² (area capacity of 11 mAh cm⁻²).²² Zhu et al. studied nano-Si coupled with single-crystal NMC (stabilized with Li₂SiO_x) and argyrodite SE (Li₆PS₅Cl), and found that the full cell with a mass loading (10 mg cm⁻²) delivered a high capacity of 145 mAh g⁻¹ at C/3 and stable cycling for 1,000 cycles.^{21,24} Besides, Wu et al. demonstrated that hard carbon stabilized Si anode-ASSBs with NMC811 cathode at a loading of 5.86 mAh cm⁻² could deliver stable cycles at a 1 C rate.²³

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.^{25,26} Among them, inorganic SEs have gained intensive research interests and a variety of materials have been development, which can be classified into oxides, sulfides, halides, borohydrides, etc.²⁷⁻³⁰

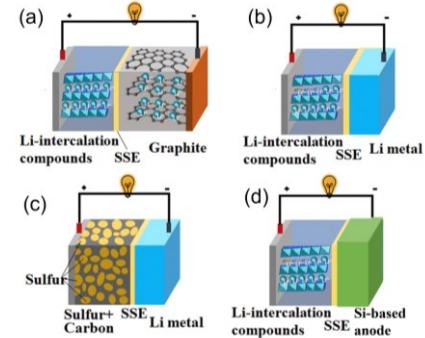


Figure 2. Structure scheme of different types of ASSBs: (a) Li-ion batteries; (b) Li metal batteries; (c) Li-S batteries, and (d) Si-based batteries.⁶ (Microscale interphase are not illustrated in the schematic figures)

The ideal SE materials are expected to hold several important features (**Figure 3**),³¹⁻³³ including high ionic conductivity ($>10^{-3}$ S 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 (anode and cathode); low interfacial resistance; low toxicity and environmentally benign character; improved mechanical properties (modulus) and reliability; economic processing of materials and cost effective manufacturing, etc. There have been intensive efforts focusing on the conductivity and (electro)chemical stability of SEs by tuning their compositions, doping chemistry, and adopting different synthetic approaches (e.g., solid-state reaction and liquid-based method).

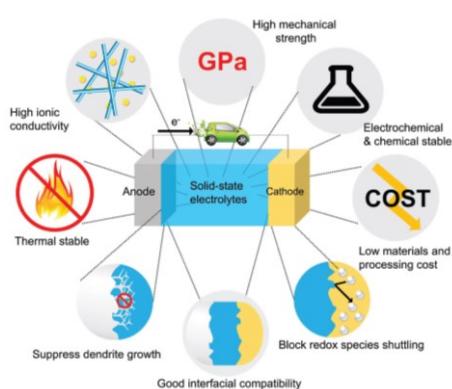


Figure 3. Requirements for ideal SE materials in ASSBs.¹

sulfide such as argyrodites ($\text{Li}_6\text{PS}_5\text{X}$),³² $\text{Li}_3\text{Y}(\text{Br}_3\text{Cl}_3)$,⁴⁰ etc.

For different type 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 (>10 mS cm $^{-1}$), favorable mechanical deformability (ductility), low cost nature, and the potential to accommodate electrode volume changes at the interface.^{41, 42} 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 towards to oxide cathode.^{12, 43} 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 towards the Li metal.

To overcome these challenges, *doping chemistry* and *interface engineering* have been widely explored. Specifically, aliovalent elemental doping can significantly improve their ionic conductivity as well as their stability. For instance, $\text{Li}_{6.8}\text{Si}_{0.8}\text{As}_{0.2}\text{S}_5\text{I}$ sulfide shows enhanced air and electrochemical stability (long cycle life of 62,500 cycles at 2.44 mA cm $^{-2}$).⁴⁴ In another case, $\text{Li}_2\text{In}_x\text{Sc}_{0.666-x}\text{Cl}_4$ ($0 < x < 0.666$) from halide family SEs exhibits both impressive conductivity (2.0 mS cm $^{-1}$ at RT) and great compatibility with oxide cathodes, leading to successful 3,000 cycles with 80% capacity retention with $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$ cathode at a cell loading of 1.325 mAh cm $^{-2}$.⁴⁵

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 may assist for the discovery of new Li-ion conductors based on lattice dynamics or high-entropy mechanism.^{46, 47} In addition, there are also other factors to consider from a practical application perspective, including (i) use more economical materials to reduce the dependency on rare-earth or expensive materials/elements; (ii) manufacturing scalability; and (iii) environmentally benign materials and process for battery recycling; (iv) the applicability of SEs for industrial electrode fabrication conditions.^{33, 48}

Interfacial Issues and Strategies.

In addition to the conductive property, interface behavior stands out as another crucial factor that determines the performance of ASSBs, ultimately leading to either successful cycling or failure. There are various types of interfaces in ASSBs (**Figure 4**)³: 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 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 the growth of Li dendrite. At the *cathode/SE interface*, the presence of multiple components introduces further complexity to the interfaces. 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,⁴⁹⁻⁵³ shedding light on the intricate nature of the interface challenges. The main interface issues include: (1) *limited physical contact*. This issue 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 and strain changes arising from the distinct volume expansion of electrode material); (2) *sluggish charge transfer*. Interfaces between SE and electrodes impede charge transfer due to poor (electro)chemical stability, causing the decomposition of SEs or unfavorable electronically conductive SEI layer; and (3) *Li dendrites formation*. Non-uniform current deposition at the interface contributes to the nucleation and growth of Li dendrites, 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 interface can trigger internal short circuits within the batteries.

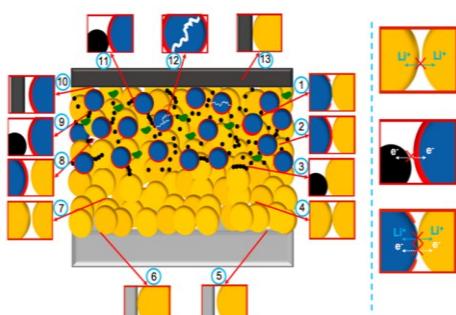


Figure 4. Interface issues (anode/SE, bulk SE, cathode/SE) in ASSBs.³

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.^{2, 54} 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 involve specially designed artificial interlayer (or buffer layer), and engineered structure designs that aim to stabilize interface and mitigate the side reactions. *On the anode side*, protective interlayers such as alloy phase (e.g. Li_xIn_y , Li_xAg_y) have proven effective in stabilizing Li metal and preventing dendrite growth.^{55, 56} *For cathodes*, thin coatings (e.g. LiNbO_2 , Li_2SiO_x) applied on the surface of CAM have been successful in suppressing unfavorable side reactions, particularly those between sulfide SEs and oxide cathode.^{21, 51} Additionally, engineered structural designs such as gradient or core cell structures, can also modify the interface to address interfacial side reactions.³⁰

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.. By elucidating the interfacial phenomena and electrochemical mechanisms, advanced *Operando* characterizations facilitate the rational design and optimization of ASSB components, leading to enhanced performance.⁵⁷⁻⁵⁹

A range of representative characterization techniques are available that offer morphological and structural information for battery 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), solid-state nuclear magnetic resonance (ss-NMR), etc.. Zhu et al. utilized operando X-ray absorption near-edge structure (XANES) spectroscopy, ex-situ scanning electron microscopy (SEM), and ex situ X-ray nanotomography (XnT) to investigate the structure evolution of the nano-Si composite anodes.²⁴

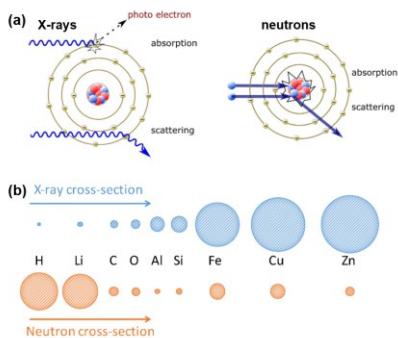


Figure 5. (a) Mechanisms for X-rays and neutrons interacting with the outer electron shells of the atoms.⁵ (b) Sketch of the relative x-ray and neutron total cross sections of several atoms.⁷

scattering, Auger electron spectroscopy (ToF-SIMS), Raman spectroscopy, extreme-ultraviolet-second-harmonic generation (XUV-SHG), etc. For examples, XPS spectra recorded during Li deposition on LGPS reveal that the chemical compositions (Li_3P , Ge, Li_2S) at the unstable interface.⁶⁰ By using XUV-SHG and XPS, it is found that the reduction in Li interfacial mobility at the surface due to the intrinsic changes in LLTO cage vibrational modes.⁶¹ In addition, Neutron scattering techniques, including neutron diffraction (ND) and neutron imaging, have better sensitivity to light elements such as lithium since they are based on interaction with atomic nuclei rather than electrons (**Figure 5**).

Advanced characterization techniques have made significant contributions towards 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 and sheet-type cell for the package (**Figure 6**). Also, bipolar mode fabrication of ASSBs enables the internal connection for a series of unit cells, reducing the mass ratio of current collectors and enhance the energy density.¹¹ (2) ASSBs can work under high temperatures,⁸ thus the cooling system can be removed at the design of cell package

On the other side, the fabrication of ASSB devices should consider the following factors. (1) *Processing diversity*. The processing techniques are possibly very different dependent on SE materials. For example, sulfide sheets can be densified to device stacks through high-pressure calendaring, while oxide sheets required high temperature annealing for densification. (2) *Stress/strain accumulation*. The different levels of volumetric changes for electrode materials during cycling causes the occurrence of stress and strain at the SE/electrode interface. For instance, *Operando* stress measurement of ASSBs with various anode materials (Li metal, graphite, and Li₄Ti₅O₁₂) revealed that the cell with Li metal exhibited much higher level of stress than the other two due to the largest volumetric changes.⁶² (3) *Stack pressure*. Stack pressure plays an important role to form intimate contact at SE/electrode interface or between material within the electrode, thus sometimes external stack pressure is required to achieve high performance ASSBs, but high stacking pressure may increase the manufacturing cost of cell package. The effect of different stack pressure (5-25 MPa) has been studied on the cycling of ASSLMBs, and it is suggested that 5MPa is optimal pressure since it not only enables proper contact between Li metal/SE but also useful to prevent pressure-induced Li dendrites.⁶³

So far, 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 rather than thick pellets, and the portion of SE in composite cathode should be minimized but still maintain effective ion transport.² Additionally, the new design of battery configuration also needs more development effort, specifically the commercialization level ASSBs device configuration.

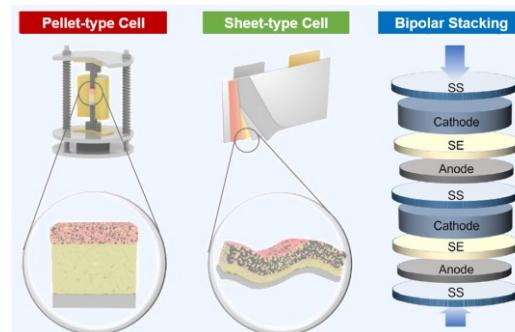


Figure 6. Battery configuration types: pellet-type cell and sheet-type cell;² bipolar-stacking cell.¹¹

Challenges to Practical Application of ASSBs.

In the past decade, advanced materials and interface design had been successfully validated in lab-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.

(1) High loading of cathode active materials (CAM). 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 cathode (consisting of CAM, SE, binder and conductive additive). The *optimization principles of cathode composition* are to reduce the content of SEs while maintaining high conductivity (ionic and electron) in the electrode. In the current cathode design, a high composition of SE ($> 25 \text{ wt\%}$) often happens in ASSBs compared to LE composition in the commercial LIBs.⁶⁴ On the other hand, *advanced coating techniques* that 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 cathode electrodes. In the near future, dry electrode technologies may hold great potential for industrial application of ASSBs.⁶⁵

(2) 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 ($> 10 \text{ mS cm}^{-1}$) at RT, poor battery cycling performance or battery failure for ASSBs have been often observed when cycling under high energy 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.⁷² Compared to the requirement on ionic conductivity, *the stability and resistance* at the interface are more critical parameters to realize fast charging capability.⁶⁶ Various issues include: irreversible side reaction at the interface between Li metal and SE materials at the anode; structural degradation of CAMs; crack generation after repeated cycling at the cathode; and the formation of cracks within SEs which provide the pathways or the internal location for reduction of Li in 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.

(3) Scaling up from lab-scale to industrial applications. There are still large gaps between practical application of ASSBs to scale up from lab-level cells, which have been discussed in couple review articles.^{4, 67} Significant challenges include: (1) the mass production of SE materials and the preparation of large area SE sheets with thin thickness ($< 50 \mu\text{m}$). The price of raw materials and the cost for processing need to be considered. High quality SE sheets with surface

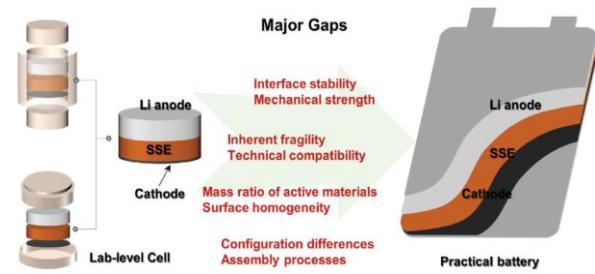


Figure 7. Schematic illustration of the gaps for the scale-up of solid-state lithium batteries.⁴

homogeneity and internal defect control are required. (2) the efficient integration of SE processing steps with thick electrodes to fabricate practical ASSBs with high energy density and power density. (3) For ASSBs with Li metal anode, more economic and efficient approaches are needed to prepare thin Li film and mitigate the high reactivity of Li metal by interface engineering to ASSBs. (4) New battery configurations and assembly strategies are needed to ensure low cost of manufacturing while maintaining high performance. External pressures can be added but should be minimized to reduce the additional costs.

In summary, there have been several review articles to discuss the scale up from materials' perspectives and provide valuable insights regarding the utilization of sulfide SEs, oxide SEs, as well as electrode fabrications processes towards to the commercialization of ASSBs.^{30, 41, 64, 68} 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 Special Issue

This special 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. For instance, a MRS Bulletin special issue in 2018 titled “Frontiers of solid-state batteries” had summarized the solid-state electrolyte materials and device architectures. 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 labs validates new materials and interface designs. While ASSBs show potential for enabling safe, high energy density batteries, more research efforts across materials, interfaces, characterization, and engineering are needed to bridge the gaps from fundamental lab studies to large-scale industrial fabrication and deployment. Following are highlights for each article:

At the interface, the article by Li [] discusses the fundamental limitations of interface reactions for ASSBs with sulfide Ses. The primary focus of this article focuses 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. [] highlight the Kelvin probe force microscopy (KPFM) as a tool to image the local potential at interface 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. [] 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.

For the anode, Westover et al. [] focus on tailoring the Li metal to achieve high performance of ASSBs, specifically the synthesis approach, microstructure, surfaces, impurities, mechanics, and alloying strategies to optimize Li anode. The authors also look at the impact the long-term cycling on the evolution of Li metal in ASSBs.

For the advanced characterization, Zhu et al. [] highlight to use 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 concentration, reaction mechanisms, and transport constraints in ASSBs, contributing to the evolution of high battery performance. In addition, *Jang and Meng et al. []* 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 towards accelerating design as well as limitations.

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Author Contribution Statement

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

Conflicts of Interest

The authors declare no conflict of interest.

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