Review Article

Interfacial challenges in all-solid-state lithium batteries
Yonglin Huang, Bowen Shao and Fudong Han

Abstract

This mini-review provides a current opinion on interfacial challenges in solid-state batteries (SSBs). We focus our discussion on the effects of mechanical instability, chemical instability, electrochemical instability, and space charge layer formation on the interfacial resistance of SSBs. We highlight that the resulting interfacial resistance of SSBs arises from the coupling of all these effects. Quantifying the exact contribution of each effect to the overall interfacial resistance can be very difficult, if not impossible, because all these effects occur simultaneously during battery operation, but the dominant source, which varies with different electrode/electrolyte combinations, will need to be determined for future development of SSBs.

Addresses
Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, 110 Eighth Street, Troy, NY, 12180, USA

Corresponding author: Han, Fudong (hanf2@rpi.edu)

Introduction
The development of novel batteries has mainly transitioned to the concept of solid-state batteries (SSBs) which are believed to be able to provide higher energy density and safety than the conventional liquid-electrolyte-based batteries (LEBBs). Nevertheless, the commercialization of SSBs has proven difficult owing to challenges in both manufacturing and fundamental understandings of the technology [1]. The critical role of interfaces between electrodes and electrolytes has been appreciated in the battery community, and significant progresses have been made to optimize the interfaces between electrodes and liquid electrolytes [2].

Although many approaches used in LEBBs have been demonstrated to be also effective to lower the interfacial resistance between electrodes and solid electrolytes (SEs), the interfacial resistances in many SSBs remain too high for practical applications [3], highlighting the importance of understanding the fundamental differences of the interfaces in LEBBs and SSBs. Although many comprehensive reviews on various interfaces of SSBs have been published [3—7], here we aim to provide a brief overview on the effects of mechanical instability, chemical and electrochemical instabilities, and space charge layer formation on the interfacial resistance of SSBs. SSBs based on two well-studied SE systems, namely, Li-garnet-oxide $Li_7La_3Zr_2O_{12}$ (LLZO) [8] and lithium thiophosphate, $Li_2S—P_2S_5$ [9] as well as their derivatives [10,11], will be focused on to frame the discussion of this review.

Mechanical instability
One key difference between the interfaces in LEBBs and SSBs is that SEs are not flowable and infiltrative like liquid electrolytes, so inherently, it is much more difficult to achieve intimate contact between electrodes and SEs. The interfacial contacts in the electrodes are quite different depending on the electrode geometry. For cathodes, a composite of electrode active material, SE, and sometimes carbon additive is usually fabricated, and therefore an intimate three-dimensional contact is desired, whereas a two-dimensional contact should be maintained between the SE and planar Li metal anode. For SSBs with garnet-oxide SEs, a sintering step is usually needed for the fabrication of cathode composites to achieve a good contact between electrodes and SEs. Low melting-point sintering additives such as Li_3BO_3 [12] and $Li_{2.3}B_{0.7}C_{0.3}O_3$ [13] have been developed to lower the sintering temperature to mitigate the chemical instability between electrodes and SEs during sintering process. In terms of the cell fabrication, lithium thiophosphate-based SEs are superior in their mechanical properties owing to their low elastic modulus [14], so cathode composites using them as the SEs can be fabricated simply by pressing at room temperature [14,15]. Approaches to integrating the Li anode into the battery are different depending on the chemical stability between SEs and Li metal: for garnet-oxide SEs that have an excellent stability with Li metal, a high pressure seems to be necessary to achieve the intimate contact between Li metal and garnet-oxide

SEs [16], whereas minimum pressure is required to attach Li with thiophosphate-based SEs which can strongly react with Li [17,18].

Even if intimate interfacial contact has been achieved for the as-fabricated SSB, maintaining the contact during battery operation is also challenging, as shown in Figure 1. Most cathode and anode active materials experience volume change during charge and discharge. The exact magnitude of volume change depends on the structure and the storage mechanism of the electrodes, and unfortunately, a higher capacity usually comes with a higher volume change [19,20]. Moreover, the volume change of the electrodes is usually neither isotropic nor uniform within the electrode composites [19,21]. Although the volume change of the electrodes has been reported to facilitate ionic transport owing to the consolidation of SEs [16,22], in most of the cases, the volume change of the electrodes deteriorates the performance of SSBs. Contact loss (Figure 1(a)) and crack formation (Figure 1(b)) have been observed even in the electrode composites consisting of low-volume-change (a few percent) layered transition metal oxide cathodes and soft lithium thiophosphate SEs [23,24]. Crack formation was also observed at the interface between

the cathode layer and SE layer for LLZO-based solid-state batteries (Figure 1(c)) [25]. Even though Li metal is considered relatively soft, the morphologies of the Li electrode both at the interface with the SE and within the bulk Li are highly dynamic, with the formation of pores/voids even under high-pressure and high-temperature operating conditions (Figure 1(d)) [16,26−29]. In addition, coatings on cathode particles can be broken by high local stress [22,30]. Pulverization of electrodes has also been reported [19]. Although degradation of battery performance caused by the volume change of electrodes has also been observed in LEBBs, the mechanical degradation in SSBs is expected to be much more severe because liquid electrolytes can flow into the gaps or cracks, and the flow of liquid electrolytes can help accommodate the stress generated in the electrodes.

One promising strategy to address the mechanical instability is to develop electrodes with no apparent volume change. Two nearly zero-strain layered transition metal oxides, NCM361 (30 wt.% Ni, 60 wt.% Co, and 10 wt.% Mn) and NCM271 (20 wt.% Ni, 70 wt.% Co, and 10 wt.% Mn), have been developed by Janek et al. [31], and the cathodes demonstrated excellent cycling

Figure 1
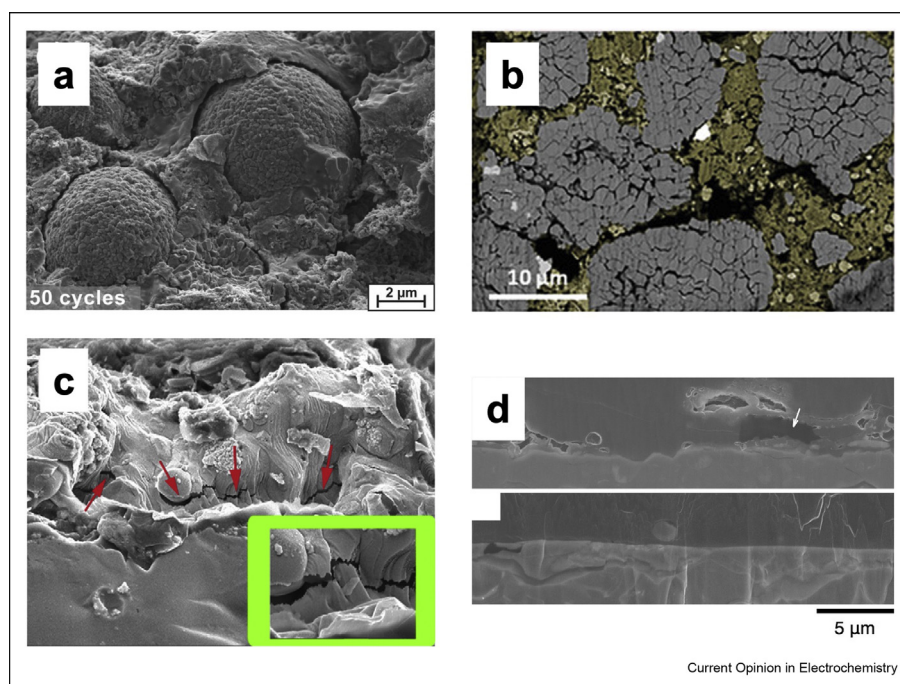
Illustrations of mechanical instability. (**a**) The contact loss between NCM particles and Li_3PS_4 SE after 50 cycles in a composite cathode [23]. Reproduced from Koerver et al. with permission. Copyright 2017 American Chemical Society. (**b**) The cross-sectional image of poly-crystalline $NCA/Li_6PS_5Cl_{0.5}Br_{0.5}$ electrode composite after 100 cycles. The charge and discharge voltage range is 3.0−4.3 V versus Li^+/Li [24]. Reproduced from Han et al. with permission. Copyright 2021 John Wiley and Sons. (**c**) Cracks between LLZO SE and LCO cathode composite after cycling at 150 °C [25]. Reproduced from Liu et al. with permission. Copyright 2017 Elsevier. (**d**) The cross-sectional images of Li/LLZO interface after 10 cycles of lithium stripping at 25 °C (top) and 100 °C (bottom) [26]. Reproduced from Yonemoto et al. with permission. Copyright 2017 Elsevier. LCO, $LiCoO_2$; LLZO, Li-garnet-oxide $Li_7La_3Zr_2O_{12}$; NCA, Lithium nickel-cobalt-aluminum oxides; NCM, Lithium nickel-cobalt-manganese oxides; SE, solid electrolyte.

performance in SSBs. Although the design of a pure electrode with zero volume change can be challenging given the limited types of electrode materials, a net zero volume change can also be achieved by combining two active materials with opposite volume change behaviors during charge and discharge. For example, the combination of $LiCoO_2$ and NCM811 with a mass ratio of 45:55 exhibits small volume change [19]. Microstructure control of the composite electrodes is also important. Uniform distribution of active materials and SEs with small particle size and single-crystalline cathode active materials may help mitigate the reaction heterogeneity [32]. Although applying a huge stack pressure (tens of Megapascal) has been demonstrated to effectively suppress the mechanical instability in lithium thiophosphate-based SSBs, such a high pressure operation is unlikely appliable in real-world applications, mechanical reinforcing hosts or additives may be necessary for the electrode composites for low or no pressure operation [19,33].

A series of quantitative studies have been performed to understand the mechanical effect. Janek et al. [19] measured the electrode volume change based on the definition of partial molar volume. Meng et al. [34,35] investigated the effects of stack pressure during fabrication and testing on cycling stability, capacity retention, and rate performance of SSBs. Because the stress distribution in the electrodes and at the electrode/electrolyte interfaces can be highly heterogeneous, the mechanical failure of the electrodes is expected to be initiated and developed at some local positions. Future studies are needed to probe and quantify the heterogeneities of stress distribution in the electrode composites and at the interfaces. Existing studies on mechanical effect are mainly based on laboratory-scale SSBs where the SE is fixed at a particular position in the battery after pressing, whereas the SE can freely move in a pouch cell. The difference in the cell design (pelleted cell vs pouch cell) may lead to fundamentally different mechanical behaviors of the batteries using the same electrodes, especially in terms of the mechanical 'crosstalk' between the cathodes and the anodes.

(Electro)chemical instabilities

Reactions can occur between electrodes, electrolytes, and other components in the batteries. In some cases, the formation of reaction products is desirable. For example, the reduction of liquid electrolytes in LEBBs leads to the formation of solid electrolyte interphase, so-called SEI, which enables the successful utilization of graphite anodes [36]. Nevertheless, in many cases, the reactions will result in impedance rise in the batteries. For the purpose of discussing the effects of reactions on the interfacial behaviors, reactions in SSBs are divided into two categories: the reactions that occur during cell fabrication; and the reactions that occur during cell operation.

Garnet-oxide SEs have been reported to be unstable with the mainstream cathode materials, such as LCO, NCM, and Lithium nickel-cobalt-aluminum oxides (NCA), during high-temperature electrode fabrication process, as shown in Figure 2(a) [37]. Among these cathode materials, LCO shows better chemical stability with garnet-oxide SE LLZO than NCM and NCA. It would be fundamentally interesting to know which transition metal element(s) promote(s) the reactions of NCM and NCA with LLZO during sintering for future improvement of the chemical stability through composition optimization. Possible carbothermic reductions may also need to be considered if carbon is added to the cathode composites. Even though chemical reactions occur between electrodes and lithium thiophosphate SEs during cell fabrication, the reactions are expected to be less severe than those in the garnet-oxide-based SSBs where a high-temperature sintering process is usually needed to achieve intimate contacts between SEs and electrodes, particularly cathodes [38—40].

Unlike chemical stability, electrochemical stability refers to the stability of battery components under applied potentials. The electrochemical stability windows (ESWs) of both lithium thiophosphate-based and garnet-oxide SEs were believed to be very wide based on the cyclic voltammetry measurements of the Li/SE/inert electrode structure [10,41]. However, recent works suggest that the wide ESWs measured from the conventional measurements are a result of kinetic stabilization rather than intrinsic thermodynamic property [17]. A more reasonable way to approach the intrinsic ESWs of SEs is to add carbon into the SEs to make a Li/SE/SE-C cell (Figure 2(b)). The largely increased contact between SEs and carbon improves the reaction kinetics so that the decomposition reactions can be detected. The result measured from this modified cell can also reflect the behavior of SEs in a real battery, because in many cases the SEs will need to be mixed with electronic-conductive additives in the electrode composites. The ESW of $Li_{10}GeP_2S_{12}$ measured by this modified approach is only about 0.4 V, with the onset for the oxidation reaction being at 2.1 V and the reduction reaction starting at around 1.7 V. The results agree very well with first principles computation results (Figure 2(c)) [42,43]. Works from Janek et al. [44—46] Wagamaker et al. [47] and Ceder et al. [6,43] also demonstrated that the limited ESWs can be generalized to all thiophosphate-based SEs.

Thermodynamics suggests that LLZO is electrochemically stable from 0.05 V to 2.91 V [17,42], indicating the intrinsic instability between the LLZO and Li metal anode. The reductions of Zr and some dopants such as

Figure 2
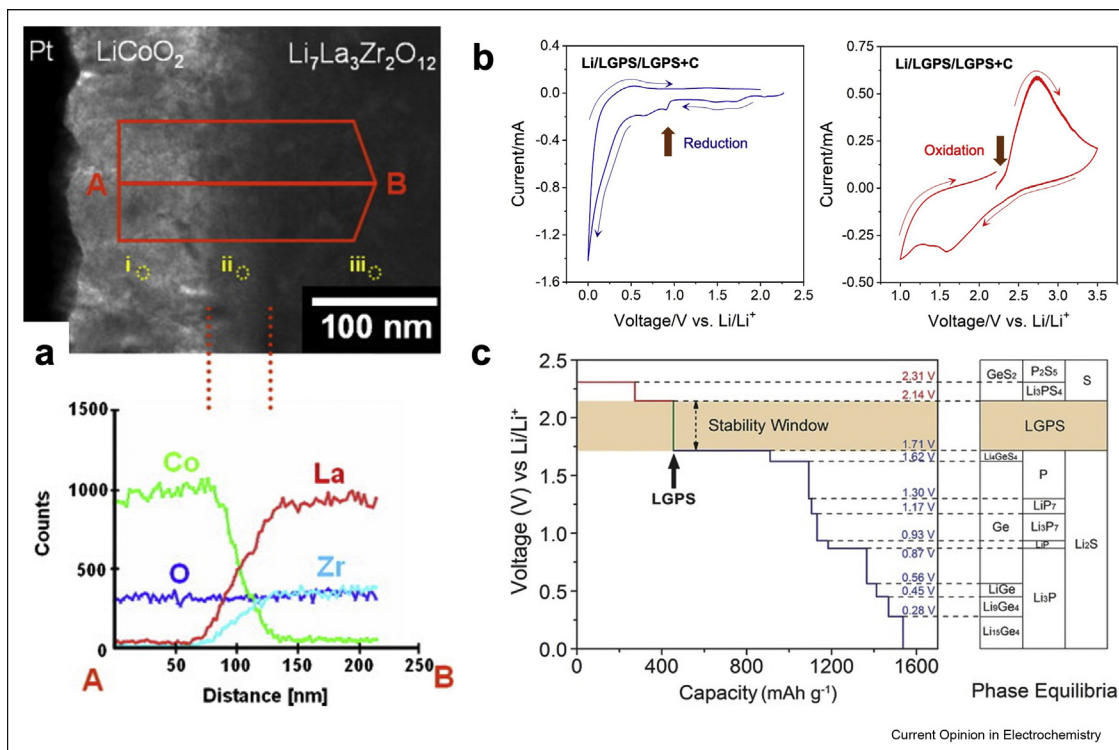
Illustrations of chemical and electrochemical instabilities. (**a**) The cross-sectional TEM image of LCO/LLZO interface and the EDS line profile from A to B. Interdiffusion of elements between LCO and LLZO occurs during the 973K-deposition of the thin-film LCO electrode [60]. Reproduced from Kim et al. with permission. Copyright 2011 Elsevier. (**b**) Cyclic voltammetry curves of Li/LGPS/LGPS-C in the voltage range of 0−2 V and 1−3.5 V versus Li$^+$/Li [61]. Reproduced from Han et al. with permission. Copyright 2015 John Wiley and Sons. (**c**) The voltage profile and phase equilibria of LGPS from first principles calculation [17]. Reproduced from Han et al. with permission. Copyright 2016 John Wiley and Sons. EDS, Energy dispersive spectroscopy; LCO, LiCoO$_2$; LGPS, Li$_{10}$GeP$_2$S$_{12}$; LLZO, Li-garnet-oxide Li$_7$La$_3$Zr$_2$O$_{12}$; TEM, Transmission electron microscopy.

Nb and Al have been reported when LLZO is in contact with Li [17,48]. However, owing to the limited thermodynamics driving force (~ 0.05 eV), the interface between LLZO and Li is expected to be easily stabilized by kinetics, and LLZO is by far one of the most stable SEs with Li metal [49]. In addition to the electrochemical decomposition of the SE itself, the electrochemical reactions can also be facilitated by other components in SSBs such as electrode active material and carbon additives [50]. A recent report demonstrated that carbon additives can lead to detrimental effects on the interfaces owing to the accelerated decomposition reactions within the electrode composites [51].

Based on the previous discussion, the extent of reactions depends on kinetics, and the exact magnitude of interfacial resistance caused by the reactions depends on the properties of the reaction products, namely, interphases. Four classes of interphases can be formed within SSBs owing to the reactions: (i) ionically conducting but electronically insulating interphase; (ii) ionically insulating and electronically insulating interphase; (iii) electronically conducting interphase; and (iv) redox-active interphase [17,46,52]. The first case is essentially the same as the formation of the SEI in LEBBs and is mostly desired. The formation of insulating interphases will lead to the interfacial resistance. Even though the electronically conducting interphase itself will not increase the interfacial resistance unless it is also ionically insulating, the formation of electronically conducting product in the interphase will promote the continuous decomposition of SEs, leading to impedance rise of the cell [44]. Forming a redox-active interphase is expected to result in interfacial degradation if the lithiation/delithiation of the interphase is accompanied by a large volume change, although more detailed studies are needed to quantify this effect.

For thiophosphate-based SSBs, coating on electrode active materials is an effective way to improve both chemical and electrochemical stability [53,54]. Nevertheless, the coating on active materials cannot prevent the reactions at the interface between SEs and carbon, and future works are needed to study the effect of reactions of other components such as polymeric binders and reinforcing phases on the interfacial behavior. For

garnet-oxide-based SSBs, lowering the sintering temperature, for example, by cold sintering [55], liquid precursor deposition [56], and aerosol deposition [57], is the key to mitigate the effect of reactions. Although it is not possible to change the intrinsic electrochemical stability of SEs, the properties of the interphases can be adjusted by tuning the composition of the SEs [58]. Using multiple electrolytes into one battery may be necessary for future SSB development by taking advantage of the stability of different SEs with various voltage ranges [59].
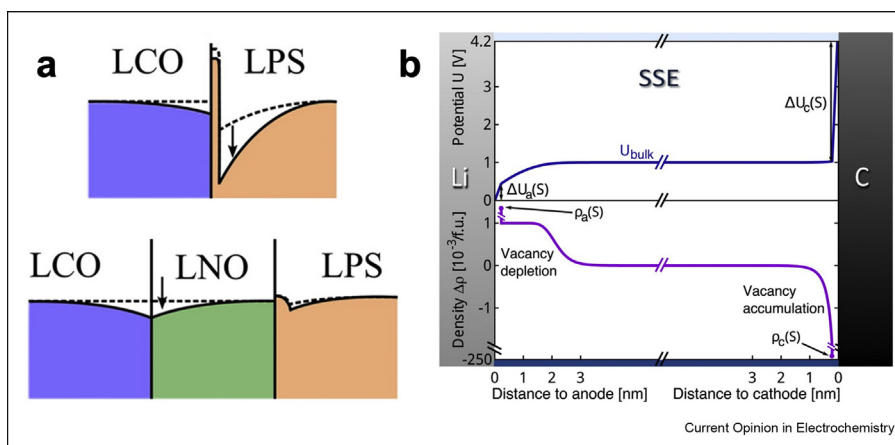
Space charge layer formation

The difference in the electrochemical potential of SEs and electrodes will also lead to the formation of space charge layer at the interface [62–64]. Unlike in the liquid electrolytes where the potential gradient can be compensated by multiple charge carriers such as anions and solvent dipoles, the space charge layer formation in SSBs is solely based on the diffusion of Li ions (interstitials or vacancies), and therefore, a sharp concentration gradient is expected in SSBs [5]. Figure 3(a) shows the depletion of lithium ions in the lithium thiophosphate SE at the interface between the thiophosphate-based SE and LCO cathode. The space charge layer formed in SSBs varies significantly with different electrode/electrolyte combinations [65,66] and with the state of charge for a particular combination of the electrode and electrolyte [67]. A work from Luntz et al. highlighted that the formation of space charge layer will lead to a higher resistance at the cathode/SE interface than at the Li/SE interface (Figure 3(b)) owing to the greater potential difference [5].

Although a large amount of theoretical works have been reported to study space charge layer formation, experimental studies are quite limited. The low-voltage slope during initial charge was considered as an evidence for the space charge layer formation [53,62–64,68,69]. Coating electronic-insulating but ionic-conducting oxides (e.g. $LiNbO_3$) has been demonstrated as an effective approach to suppress the low-voltage slopes and improve the rate performance. Concentration gradient at the interface has been observed by TEM [70,71]. However, because many SEs are not stable at the voltage of the electrodes, it is still an open question whether the low-voltage slope and the concentration gradient at the interface are also related to the electrochemical reactions of SEs, and for the same reason, it is not possible to separate the contributions from space charge layer formation and electrochemical decomposition. As a result, whether the formation of space charge layer can lead to significant effect on the interfacial resistance is still under debate [65]. Further experimental research is still needed to understand the exact contribution of space charge layer formation to the interfacial resistance. Utilization of electrochemical stable SEs such as LLZO or phosphate-based SEs as the model SE may be considered to isolate the effect from (electro)chemical instabilities.

Discussion

Although mechanical instability, (electro)chemical instabilities, and space charge layer formation each contribute to the interfacial resistance of a SSB based on distinct mechanisms, we would like to emphasize that these effects are strongly coupled in an operating

Figure 3

Illustrations of space charge layer formation. (**a**) Schematic illustration of space charge layer formation (high-interfacial lithium concentration in the SE) between LCO and LPS at the initial stage of charge (top). The LNO interlayer can significantly suppress the concentration gradient (bottom) [64]. Reproduced from Haruyama et al. with permission. Copyright 2014 American Chemical Society. (**b**) One-dimensional model of potential drop and mobile charge density distribution between the cathode and anode for a Li|SE|C battery where 'C' means the cathode [5]. Reproduced from Luntz et al. with permission. Copyright 2015 American Chemical Society. LCO, $LiCoO_2$; LNO, $LiNiO_2$; LPS, Lithium thiophosphate-based solid electrolyte; SE, solid electrolyte.

battery. The charge/discharge of a SSB will lead to the volume change of electrode active materials. The stress/strain generated owing to the volume change can lead to mechanical degradation such as contact loss and crack formation. At different states of charge, the thermodynamic (electro)chemical stabilities between electrodes and electrolytes also change. The changing potential of electrodes will alter the space charge layer formed at the electrode/electrolyte interface. In addition to the simultaneous occurrence of these effects, interfacial degradation caused by one effect may accelerate the degradations by others. For example, the nonuniform and dynamic formation of interphases owing to (electro)chemical instabilities will promote mechanical degradation and also change the space charge layer.

Summary and perspectives

We review the effects of mechanical instability, chemical instability, electrochemical instability, and space charge layer formation on the interfacial resistances in solid-state batteries. We hope to have conveyed the message that the resulting interfacial resistance of a SSB arises from a coupled effect. Separating the effect from each factor is very difficult, but identifying the dominant source, which can be performed by establishing the correlation between each factor and the observed interfacial resistance, is important for future development of high-performance SSBs.

A major challenge for studying the interfaces in SSBs is that the interfaces are usually buried in the battery. We hope that this short review can call for future development of *in-situ*, nondestructive, and high-penetration-depth techniques to characterize the interfaces. Although replacing liquid electrolytes with rigid, single-ion conducting SEs leads to several unique interfacial challenges in terms of mechanical instability and space charge layer formation, the utilization of SEs also eliminates the concentration polarization and desolvation processes which are the major kinetic limitations in the LEBBs. Because SSBs with a much higher rate performance than the LEBBs have been developed [11], in our opinion, 'solidifying' the electrolyte is overall favorable for high-rate performance. With more efforts into understanding and addressing the interfacial challenges in SSBs, we are optimistic to see SSBs as a viable technology for high-power energy storage in the near future.

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Declaration of competing interest

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.

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