

## Review

## Controlling the Dendrite Growth in Solid-State Electrolytes

He Liu, Xin-Bing Cheng, Jia-Qi Huang, Hong Yuan, Yang Lu, Chong Yan, Gao-Long Zhu, Rui Xu, Chen-Zi Zhao, Li-Peng Hou, Chuanxin He, Stefan Kaskel, and Qiang Zhang

ACS Energy Lett., **Just Accepted Manuscript** • DOI: 10.1021/acsenergylett.9b02660 • Publication Date (Web): 07 Feb 2020

Downloaded from pubs.acs.org on February 7, 2020

### Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

# Controlling the Dendrite Growth in Solid-State Electrolytes

He Liu,<sup>†,‡</sup> Xin-Bing Cheng,<sup>§</sup> Jia-Qi Huang,<sup>\*,†,‡</sup> Hong Yuan,<sup>†</sup> Yang Lu,<sup>§</sup> Chong Yan,<sup>†</sup> Gao-Long Zhu,<sup>§,⊥</sup> Rui Xu,<sup>†</sup> Chen-Zi Zhao,<sup>§</sup> Li-Peng Hou,<sup>§</sup> Chuanxin He,<sup>⊥</sup> Stefan Kaskel,<sup>#,+</sup> Qiang Zhang<sup>\*,§</sup>

<sup>†</sup> School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, China

<sup>‡</sup> Advanced Research Institute for Multidisciplinary Science, Beijing Institute of Technology, Beijing 100081, China

<sup>§</sup> Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P.R. China

<sup>⊥</sup> Shenzhen Key Laboratory of Functional Polymer, College of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen, 518000, China

<sup>#</sup> Department of Inorganic Chemistry, Dresden University of Technology, Bergstrasse 66, 01069 Dresden, Germany

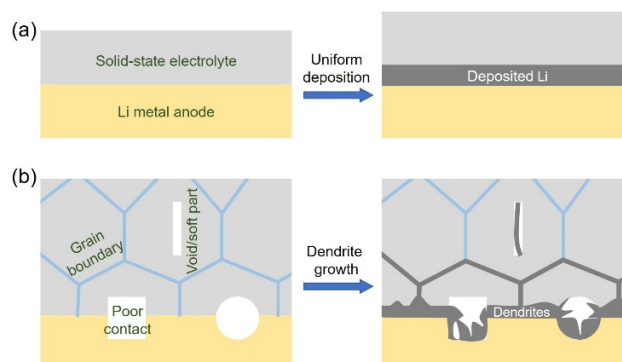
<sup>+</sup> Fraunhofer Institute for Material and Beam Technology Winterbergstraße 28, 01277 Dresden, Germany

**ABSTRACT:** Solid-state electrolytes (SSEs) are widely considered as an “enabler” to inhibit dendrite growth of lithium metal anodes for high-energy and highly safe next-generation batteries. However, recent studies demonstrated that lithium dendrites form in working SSEs. Theoretically, dendrite inhibition can be achieved in the perfect SSEs without any defect, while dendrite growth is extensively observed in the practical SSEs with poor interface stability, large grain boundaries, voids, and partial electronic conductivity. In this Focus Review, dendrite growth behaviors in SSEs, including polymer and inorganic electrolytes, are comprehensively summarized. The observed dendrite morphology in these SSEs, possible formation mechanisms, and some solutions are analyzed. The clear perspectives and some suggestions are also presented for the further development of SSEs in lithium metal batteries. This Focus Review intends to shed fresh light on the understanding of dendrite growth in SSEs, rational designs on the architecture and materials for SSEs matching lithium metal anode.

Lithium-ion batteries (LIBs) have revolutionized the portable electronic devices and electric vehicles. The goal of next-generation intelligentized electronic devices and long-range electric vehicles, however, call for advanced battery systems with higher energy density and safety as well as longer lifespan. Compared to the graphite anode in commercial LIBs, lithium (Li) metal anode, as the “Holy Grail” electrode, exhibits an ultrahigh theoretical specific capacity (3860 mAh g<sup>-1</sup>) and the lowest electrochemical potential (−3.04 V vs. the standard hydrogen electrode, graphite anode: 372 mAh g<sup>-1</sup> and 0.1 V).<sup>1,2</sup> Therefore, a higher energy density can be achieved by the multiplication of capacity and voltage when Li metal anode is adopted into a practical battery. However, Li metal batteries (LMBs) are long forsaken by practical devices due to the uncontrollable dendrite growth during repeated cycles, leading to reduced Coulombic efficiency, rapid capacity decay, poor lifespan, and severe safety hazards.<sup>3</sup>

The advances in electrode and electrolyte innovations facilitated by nanoscience and nanotechnology currently offer emerging opportunities to protect Li metal anode, such as composite Li electrode, artificial interfacial film, highly concentrated electrolyte (including local high-concentration electrolyte), solid-state electrolyte (SSE), and membrane coating, etc.<sup>4,5</sup> Among them, solid-state electrolyte with a high shear modulus is considered as an

effective “enabler” to inhibit dendrite growth.<sup>6–9</sup> In materials science, shear modulus, as one of several quantities for measuring the stiffness of materials, is defined as the ratio of shear stress to the shear strain. Additionally, the features of nonflammability, non-leakage, and high-oxidation voltage as well as low reduction voltage render SSE a promising choice to boost the high-energy-density and safety performance of cells.<sup>10–14</sup> Therefore, SSE is strongly believed as the ultimate remedy to solve the dendrite growth issues for the development of high-energy-density and highly safe LMBs (**Figure 1a**).



**Figure 1.** (a) Perfect SSEs without any defect are predicted to inhibit dendrite growth; (b) Inhomogeneous dendritic deposition is observed in practical SSEs.

However, things didn't work out the way researchers predicted. The shear modulus criterion proposed by Monroe and Newman is only intended for polymer electrolytes and SSE systems without any inhomogeneity and defeat. Dendrites are extensively observed in the SSE systems at the interface or along grain boundaries (GBs), voids, and other soft parts of SSEs (**Figure 1b**), even at a smaller current and capacity relative to the non-aqueous liquid electrolytes.<sup>15–17</sup> The critical current density, at which the short-circuit occurs by dendrite piercing, is  $0.05 - 0.9 \text{ mA cm}^{-2}$  for  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) and  $0.4 - 1.0 \text{ mA cm}^{-2}$  for  $\text{Li}_2\text{S-P}_2\text{S}_5$ , whereas it reaches  $3 - 10 \text{ mA cm}^{-2}$  for non-aqueous electrolytes at room temperature.<sup>15</sup> Seemingly, if the testing current density is larger than the critical current density of the SSE, short circuit induced by dendrite growth occurs more easily in SSE systems with inhomogeneities and defeats compared to their liquid counterparts, contradicting the prevailing knowledge that dendrites can be inhibited by SSEs with Li-ion transference number approaching 1.0 and shear modulus twice higher than that of Li metal (**Figure 2a**).<sup>18–21</sup> The detailed mechanism for dendrite formation in SSEs is not fully understood yet.<sup>22</sup> Nevertheless, it is clear that there are distinct mechanism differences for dendrite growth between SSEs and liquid electrolytes.<sup>23,24</sup> Hypotheses are proposed to illustrate the counterintuitive dendrite growth in SSEs, such as small packing density, low ionic conductivity at the GBs, tiny electronic conductivity of bulk electrolytes, random surface and bulk defects formed during SSE preparation, soft parts in the composite SSEs, and poor solid-solid interfacial contact between SSEs and Li metal.<sup>25</sup> The observation of Li metal penetration through SSEs indicates that a huge gap exists in revealing the relations between structural/chemical/mechanical evolution of SSE interfaces and electrochemistry of Li metal anode.<sup>26,27</sup> Deeply understanding the dendrite growth behaviors in SSEs is critically significant to realize a dendrite-free LMB with SSEs.<sup>28,29</sup>

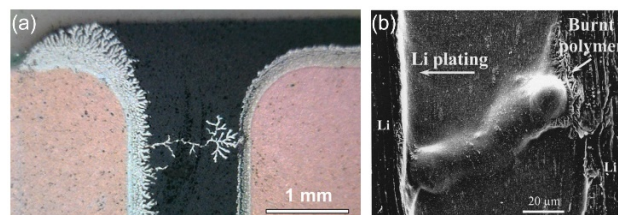
In this Focus Review, we summarize the dendrite growth behaviors in the polymer and inorganic SSEs. The observed dendrite growth in these SSEs, the possible mechanisms, and some solutions to suppress dendrite growth are analyzed. The clear perspectives and some suggested directions are also provided for the further development of SSEs in LMBs.

**Polymer electrolytes** Polymer electrolytes possess intermediate features between inorganic and non-aqueous electrolytes.<sup>30</sup> For instance, polymer electrolytes exhibit a high mechanical modulus relative to non-aqueous electrolytes and a superior flexibility compared with the fragile inorganic electrolytes. These features render polymer electrolytes as potential candidates for practical applications in the electric products.<sup>31,32</sup> The demonstration of polymer electrolytes has been well manifested by an electric vehicle, Autolib, in which the power source is provided by a LMB with a polymeric blend electrolyte composed of polyethylene oxide (PEO)/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).<sup>18</sup> The poly-

mer electrolyte in this product has to work at a temperature of  $40 - 70^\circ\text{C}$  to render a high ionic conductivity and uniform Li deposition/dissolution morphology.

Polymer electrolytes are actually unable to completely inhibit the dendrite growth due to their relatively low modulus.<sup>20</sup> For instance, the elastic modulus of PEO-based electrolyte is approximately 2 – 3 orders of magnitude lower than that of metallic Li.<sup>33</sup> Besides, most polymer electrolytes need to be operated at elevated temperatures to enhance their low room-temperature ionic conductivity. This further reduces their elastic stiffness and increases the tendency of dendrite piercing through SSEs.<sup>34</sup>

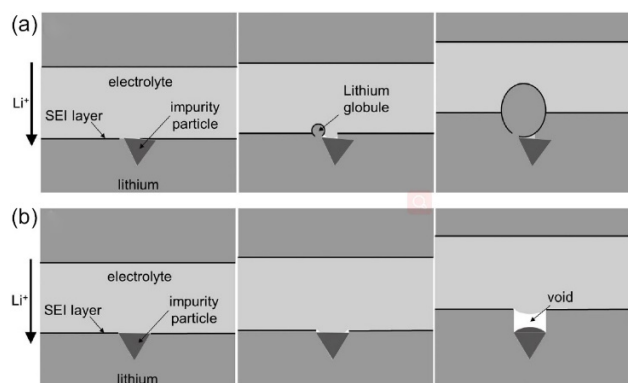
Li dendrite growth from metallic Li anode can easily transpire the soft polymer electrolytes due to their relatively low modulus, leading to cell short circuit and battery failure.<sup>35</sup> Even at a current density as low as  $50 \mu\text{A cm}^{-2}$ , short-circuiting behavior occurs in the PEO/LiTFSI electrolyte after 38 h polarizing.<sup>36</sup> Dollé and co-workers *in situ* observed Li polymer batteries by a scanning electron microscope. A Li morphology evolution from mossy to dendritic deposition with the increasing current density was confirmed. The dendrites grew outside the polymer and pushed away the Li and the polymer, giving rise to a complete delaminating between the electrode and the polymer electrolyte at specific spots, consequently deteriorating the cell performance (**Figure 2b**).<sup>37</sup>



**Figure 2.** (a) Optical micrograph showing Li dendrites growing along lithium phosphorus oxynitride (LiPON) interface between two Cu current collectors. (Reprinted with permission from Ref. 19.) (b) Scanning electron microscopy (SEM) image of a dendrite, just after it has crossed the polymer electrolyte. (Reprinted with permission from Ref. 37.)

Local surface inhomogeneities in SSEs play a critical role for the dendritic Li plating in Li/polymer batteries.<sup>36,38</sup> The impurity particles pre-located at the Li/SSE interface cause the irregular Li deposition (**Figure 3**).<sup>39</sup> The impurities are rich in oxygen and electronically insulating, preventing the direct reduction of Li metal on top of them. Instead, Li nucleation and plating are localized at the corner of the impurities due to the increasing local conductivity (**Figure 3a**). On the other hand, the inhomogeneous Li deposition leads to the generation of voids on the top of the impurities (**Figure 3b**). The Li/electrolyte interface near the impurities moves upward as the cycling continues, leaving behind the impurity particles at its original location. The degradation of polymer electrolytes caused by the side reactions on top of these impurities separates electrolytes from impurity surface, therefore

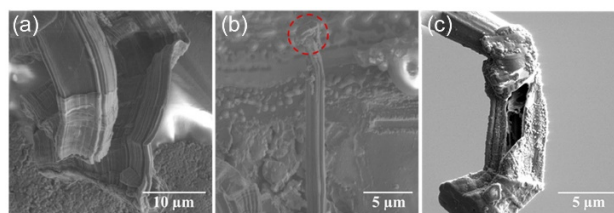
forming a void between them. The generated voids near the Li/electrolyte interface will in turn aggravate the growth of Li dendrites as discussed later.



**Figure 3.** Schematic illustrating the mechanism for (a) Li nucleation and growth at the edge of the impurity particle in a block copolymer electrolyte and (b) the generation of voids on the top of impurities. (Reprinted with permission from Ref. 39.)

Zaghib and co-workers conducted the morphological and chemical analyses of the dendrites in all-solid Li metal batteries with polyether-based polymer electrolytes and LiTFSI salts.<sup>40</sup> Two morphologies of mossy (Figure 4a) and hollow needles (Figure 4b, c) were observed. Notably, the dendrites herein are composed of  $\text{Li}_x\text{C}_y$ ,  $\text{Li}_2\text{O}$ , and  $\text{Li}_x\text{C}_y\text{O}_z$  rather than pure metallic Li as universally recognized. The carbide nature of the dendrites presents greater hardness than that of pure Li, thus showing the ability to perforate through the polymer electrolyte. However, this phenomenon is less observed in other literatures. These products may be highly system dependent, and do not necessarily represent the general composition of all Li dendrites in SSEs. The mechanism for the formation of hollow needles was also proposed: consumption of  $\text{Li}_x\text{C}_y$  in the initially formed dendrites by oxygen and carbon artifacts and  $\text{CO}_2$  degassing of the polymer during cycling.

Theoretical models have also been presented to evaluate the susceptibility of Li infiltration through polymer SSEs. A kinetic model was proposed incorporating the effects of surface tension and stresses at the interface to derive general criteria for stable Li deposition at solid-solid interfaces.<sup>41</sup> Two separate stable deposition regions in the stability diagram are depicted with different stability mechanisms: pressure-driven in SSEs with a high molar volume ratio and density-driven stability in SSEs with a low molar volume ratio. SSEs with a combination of high (low) molar volume and high (low) shear modulus are required for stable electrodeposition. However, polymer electrolytes generally have a high molar volume ratio but lower shear modulus than the critical value, leading to unstable Li deposition. As a result, material re-engineering at the working interfaces is strongly requested for stable Li deposition.



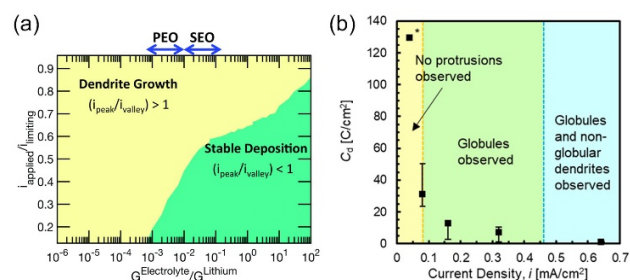
**Figure 4.** Dendrite growth in a Li metal battery with polyether-based polymer electrolytes. (Reprinted with permission from Ref. 40.) Dendrites observed *in situ* with (a) mossy and (b, c) hollow needle morphology.

The propensity of dendrite growth during electrodeposition in polymer-based batteries are strongly related to the applied current density.<sup>42</sup> A cation concentration gradient will be generated in the vicinity of Li anode surfaces at high current densities due to poor Li-ion mobility, leading to the formation of dendritic Li deposition. It is critically important to understand the competition between the dendrite growth induced by concentration/potential gradient and suppression rendered by mechanical stress. A phase map was constructed by Barai et al. to clearly depict the stable deposition regime by including the shear modulus of polymer and the applied current density (Figure 5a).<sup>43</sup> The tendency of dendritic deposition is determined by the actual current density, while high shear modulus of electrolytes renders operating the cell at a higher current without the rise of growing dendrites. The roles of the increased elastic modulus are summarized: (i) Higher compressive stress results in decreased exchange current density in the tips relative to that in the valley. (ii) If the electrolyte has a high shear modulus ( $G_{\text{Electrolyte}} > 10^{-3}G_{\text{Lithium}}$ ), the height of the dendritic tips can be largely reduced due to the plastic deformation of metallic Li. Besides, the yield strengths of polymer electrolyte and metallic Li anode severely affect dendrite propagation as well. The yield strength is defined as the stress at which a predetermined amount of permanent deformation occurs. The dendritic tips can be effectively stabilized by enhancing the electrolyte's yield strength, even when the polymer holds an elastic modulus two orders of magnitude lower relative to that of metallic Li.

Maslyn et al. experimentally obtained the current density at which the nonplanar electrodeposition initiates in symmetric Li-polymer-Li cells using the synchrotron X-ray tomography technique (Figure 5b).<sup>44</sup> The experimentally observed onset current density for nonuniform Li growth is around 20 times lower than the theoretical prediction values by Barai et al.<sup>43</sup> This is mainly induced by the presence of impurities in the current Li electrode, which act as the nucleation sites for the inhomogeneous Li deposition. The feature of deposited Li metal depends on the applied current density. Stable Li deposition without any dendrite can be achieved at a low current density below  $0.04 \text{ mA cm}^{-2}$  (yellow area). Globular protrusions are observed with increased current densities (green area,  $0.08 \leq i \leq 0.32 \text{ mA cm}^{-2}$ ). Both globular and dendritic



deposits are achieved (blue area) at a high current density of  $0.64 \text{ mA cm}^{-2}$ .



**Figure 5.** (a) A phase map depicting the stable Li deposition regime including the applied current and the shear modulus of polymer electrolyte. (Reprinted with permission from Ref. 43.) (b) Feature of observed Li protrusions with respect to the current density ( $i$ ). (Reprinted with permission from Ref. 44.)

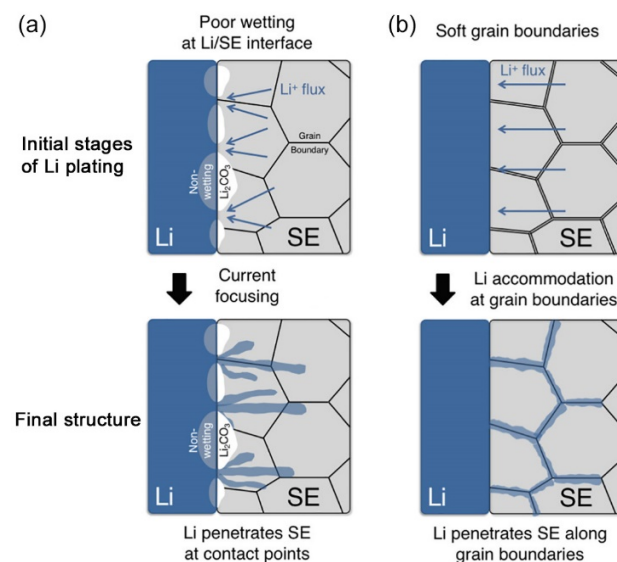
PEO-based polymer is one of the most frequently adopted polymer electrolytes due to its outstanding compatibility with lithium salts, high ionic conductivity, and good electrochemical stability.<sup>45</sup> The addition of inorganic fillers, organic compounds with low molecular weight, and cross-linked electrolytes are developed to improve the Li dendrite growth resistance in the PEO-based polymer electrolyte.<sup>46–48</sup> Some novel polymer electrolytes,<sup>47</sup> interface coating,<sup>49</sup> single-ion solid polymer electrolytes,<sup>50</sup> etc. are also proposed. As the polymer electrolytes especially at a high temperature indicate similar features to the non-aqueous electrolyte, some strategies to inhibit dendrite growth in the non-aqueous electrolytes can be implanted into the polymer electrolyte systems.

**Inorganic electrolytes** Inorganic SSEs with a high mechanical strength and compactness are expected to inhibit the Li dendrite penetration through them.<sup>51</sup> Unfortunately, contrary to the general understanding, recent reports have indicated that Li dendrites form easily in inorganic SSEs.<sup>52</sup> Even worse, short-circuit initiates at a much lower current or cycling capacity in inorganic SSEs relative to liquid or polymer electrolytes.<sup>53,54</sup> The faster dendrite formation in inorganic SSEs is aggravated by two factors: (i) increased electric driving force due to the larger curvature at dendrite tips since it extends in the limited spaces in the SSEs (such as GBs, defects, voids, etc.);<sup>42</sup> (ii) less dendrite consumption resulting from the good chemical compatibility and unity transference number of ceramic SSEs.<sup>53</sup>

Based on the kinetic model proposed by Ahmad and Viswanathan, the SSEs for stable Li deposition needs to be with a combination of high (low) molar volume and high (low) shear modulus.<sup>41</sup> However, typical inorganic SSEs usually have a low molar volume ratio but a higher shear modulus than the critical one, which dissatisfies the criteria and results in unstable Li deposition. GBs in inorganic SSEs are confirmed as the preferential sites for Li dendrite growth considering their softening elastic property and low ionic conductivity compared to the bulk.<sup>55,56</sup> Chiang

and colleagues suggested an electrochemomechanical model of Li filled in the pre-existed defects to explain the observed Li infiltration through the single crystals.<sup>57</sup> In addition, the partial electronic conductivity of SSEs was considered as the origin for Li nucleation within the SSEs.<sup>15,58,59</sup> Furthermore, the high chemical stability and ionic transference number of inorganic SSEs result in less consumption of Li dendrites during cycling.<sup>53</sup> Therefore, dendrites are gravely aggravated and short-circuit the cells at low capacities.<sup>53</sup> These understandings can present novel insights into SSE designs in the high-energy-density and safe battery systems. In the following section, the forming scenarios of dendrite growth induced by poor-wettability and unstable electrode/electrolyte interface, grain boundary, void, and electronic conductivity of SSEs are introduced comprehensively.

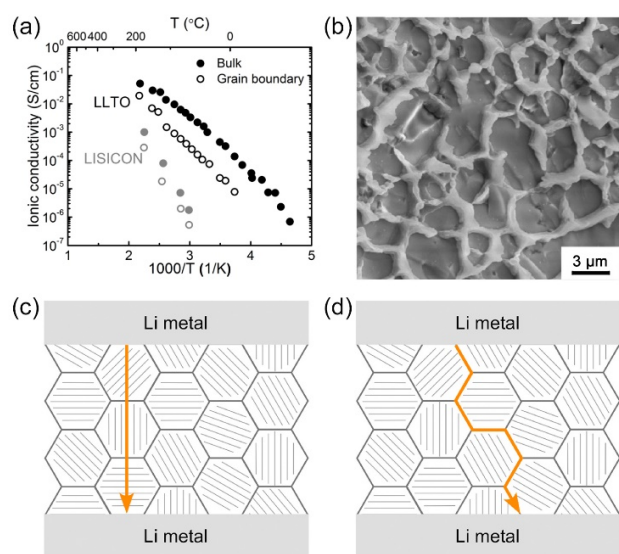
Many ceramic electrolytes, such as LLZO, have surface contaminants, including LiOH,  $\text{Li}_2\text{CO}_3$ , etc.<sup>60,61</sup> Li-ion diffusion rate in these contaminants is much slower compared to that in ceramic electrolytes. Li ions are forced to diffuse away from areas containing impurities and centralize on the confined contact points at Li/SSE interface. Therefore, the focusing current at these points leads to inhomogeneous distribution and deposition of Li, which eventually exacerbates the penetration of metallic dendrites into the SSEs. (Figure 6a).<sup>55</sup> In this case, cleaning the surface of SSEs<sup>60</sup> and coating with lithiophilic materials on SSE surface<sup>62</sup> are demonstrated to be effective in delaying the onset of Li infiltration even at a higher current density.



**Figure 6.** Potential microstructural contributions to dendritic Li deposition in SSEs. (Reprinted with permission from Ref. 55.) (a) The presence of surface contaminants leads to the current focusing in SSEs. (b) Li preferentially accumulates in the softer regions close to electrode/GB junction.

The GB is another site in inorganic SSEs for Li dendrite propagation. Significant softening in elastic properties near the GBs is proposed as the origin for dendrite growth

in these sites (Figure 6b).<sup>55</sup> The variations in atomic structure and density in the vicinity of GB plane lead to the decrease in the elastic modulus in this area.<sup>63</sup> Molecular dynamics simulations reveal that the shear modulus at GBs can be as high as 50% lower than that in the bulk regions. This inhomogeneous elastic property leads to deposited Li atom accumulation in softer regions near electrode/GB junctions during Li plating.<sup>26,64</sup> Consequently, locally stronger electric fields will be generated in the resulting Li protrusions, becoming the “hot spots” for the subsequent Li deposition. Consequently, the counterintuitive observation that soft Li metal penetrates ostensibly stiff inorganic SSEs could be rationalized by the existing GB “soft spots”.

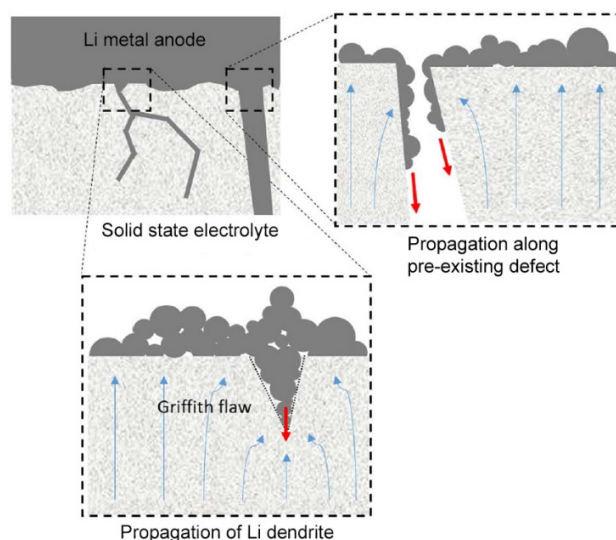


**Figure 7.** (a) Ionic conductivities at bulk and grain-boundary regions with respect to temperature in  $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_{2.94}$  (LLTO), and  $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$  (LISICON,  $x = 0.55$ ). (Reprinted with permission from Ref. 56.) (b) SEM image showing web-structure Li metal plating along the GBs in the bulk LLZO.<sup>64</sup> Schematic of Li metal (c) transgranular and (d) intergranular plating in polycrystalline LLZO SSEs. (Reprinted with permission from Ref. 64.)

Another driving force for Li dendrite growing along the GBs is the gap in the ionic conductivity between bulk and GB regions in SSEs. The bottleneck for achieving a high ionic conductivity in SSEs frequently lies in the significantly lower GB conductivity compared to the bulk (Figure 7a).<sup>56,65–69</sup> Molecular dynamics simulations predict that Li-ion mobility through the GBs is largely reduced, and Li-ion migration activation energy for all GBs are consistently higher relative to the bulk SSEs.<sup>65,68</sup> Ma et al. experimentally unraveled the atomic-scale reason for the low GB conductivity in  $(\text{Li}_x\text{La}_{2/3-x})\text{TiO}_3$ . A severe structural and chemical deviation is discovered at the GBs consisting of a Ti–O binary phase with a thickness of 2 – 3 unit cells. Such a structure is not favorable for Li<sup>+</sup> storage and transport, leading to the high GB resistance. This renders Li dendrites preferentially propagating along the GBs (Figure 7b-d).<sup>64,70</sup> Processing SSEs to achieve a high

fraction of low energy and compact boundaries can efficiently modify the GB conductivity and regulate dendrite growth behaviors. For example, modifying the SSEs by element doping,<sup>17,71,72</sup> carbon posttreatment,<sup>73</sup> sintering,<sup>74</sup> and hot-pressing,<sup>75</sup> as well as directly modifying the GBs with  $\text{Li}_2\text{CO}_3/\text{LiOH}$ <sup>76</sup> and additional Li<sup>77</sup> can improve the GB conductivity and the critical current density of SSEs.

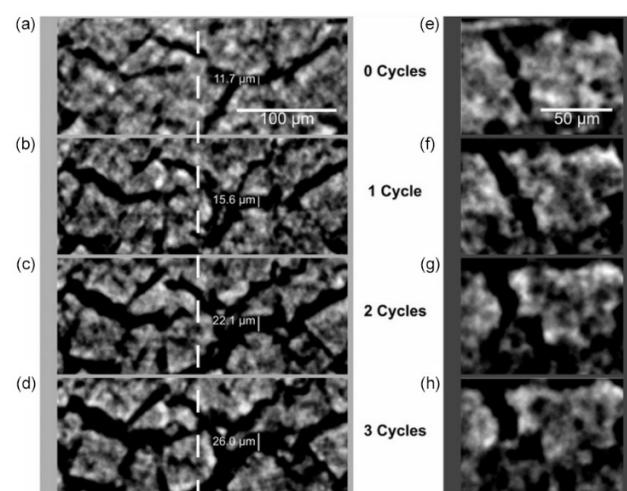
Pre-existed voids and cracks in inorganic SSEs or near the Li/SSE interface are also the suspicious spots to form Li dendrites. In an all-solid-state LMB with inorganic SSEs, a crack or void in the SSE near Li metal electrode can be easily penetrated by Li deposition due to the electric field amplification, inevitably forming dendrites in these sites.<sup>78,79</sup> Further insertion of Li into the cracks accompanies with the generation of pressure in SSEs (Figure 8).<sup>1</sup> The pressure in the cracks increases very rapidly, reaching up to 1 GPa within seconds even at normal charging rates. The high pressure will in return promote the propagation of cracks and release the pressure in the crack. However, the high pressure will be rebuilt rapidly in the longer crack, resulting in further crack extension. This process repeats until the crack reaches the cathode, finally short-circuiting the battery.<sup>80</sup>



**Figure 8.** Schematic of Li growth at the pre-existing interfacial defects (Griffith flaws: a crack will propagate when the reduction in potential energy that occurs due to crack growth is greater than or equal to the increase in surface energy due to the creation of new free surfaces) in SSEs and propagation of lithium along the pre-existed defects. Blue arrows represent the electric field lines and red arrows show the undesired Li metal growth into the bulk. (Reprinted with permission from Ref. 1.)

Voids formed in Li metal near the electrolyte/electrode interface during cell operation are also propagation sites for Li dendrites. When Li metal is stripped above the critical current at which Li removal rate exceeds that Li can be replenished, voids form in the Li anode near the interface. In addition, stripping process firstly occurs to Li metal anode when it matches a Li-free cathode, such as

sulfur and oxygen. In this case, voids form on the Li metal close to the interface initially and accumulate in the following cycles.<sup>81</sup> Li plating initiates at the interface where Li metal contacts the SSEs to obtain Li ions and electrons simultaneously, and then grows unhindered along the voids. Therefore, Li deposition preferentially occurs at triple point where Li metal, SSE, and voids meet.<sup>82</sup> Irreversible pulverization of Li metal resulted from extended and interconnected cracks after long cycles further exacerbates the propagation of dendrites.<sup>83</sup> Additionally, voids near the interface deteriorates the interfacial contact between SSE and Li metal and elevates the local plating current density, leading to the formation of dendrites in the pre-generated voids.<sup>82</sup>



**Figure 9.** Synchrotron-based X-ray tomography monitoring voids expansion and Li evolution in a symmetric cell with  $\beta$ - $\text{Li}_3\text{PS}_4$  SSEs cycled at  $100 \mu\text{A cm}^{-2}$  at early stages of cycling. (Reprinted with permission from Ref. 84.)

It is important to reveal the relation between Li dendrite propagation and microstructure evolution of SSEs. Pylypenko and co-workers in-operando detected the Li dendrite growth in the voids and the void evolution during repeated cycles in a symmetric Li/ $\beta$ - $\text{Li}_3\text{PS}_4$ /Li cell by synchrotron-based X-ray tomography (Figure 9).<sup>84</sup> The expansion of voids as the cycling proceeds can be observed throughout the whole cell. This extension in void width resembles crack propagation caused by interactions between Li metal and voids in the  $\beta$ - $\text{Li}_3\text{PS}_4$  electrolyte. As a result, the void expansion can be assigned to the dendrite growth into the SSE bulk region. The continued dendrite growth after the void space is occupied will destroy the grains of  $\beta$ - $\text{Li}_3\text{PS}_4$ , further promoting Li dendrite propagation within the SSE and deteriorating the cell performance. Therefore, SSEs with connected pore regions aggravate dendrite growth and short circuit the cell at a lower critical current density relative to the samples with less interconnected pores.<sup>85</sup> Densifying SSEs and homogeneous Li metal/SSE interfaces with less voids and cracks are necessary to prevent dendrite growth in inorganic SSE systems.<sup>86</sup> Element doping,<sup>87,88</sup> interstitial filler,<sup>89</sup> and synthesis condition optimization<sup>75,85,90</sup> are effective

strategies to densify SSEs (relative density > 99%) and mitigate the dendrite growth.

Electronic conductivity is also a vital factor to affect the Li dendrite growth in SSEs.<sup>91,92</sup> The electronic conductivity of SSEs may give rise to Li metal growth directly within the bulk of SSEs, especially within the intrinsic GB/pores of the SSE, rather than uniaxial growth from Li/SSE interface to SSE.<sup>89</sup> Qi and colleagues investigated the Li dendrite formation and growth inside SSEs through a multiscale modeling by integrating density functional theory calculations and phase field simulations.<sup>59,93</sup> The lower band gap at surfaces (pores and cracks) compared to that in the bulk facilitates electron transport from Li metal to the surface. The trapped excess electrons on the surfaces allow isolated Li nucleation and accelerated Li dendrite growth.

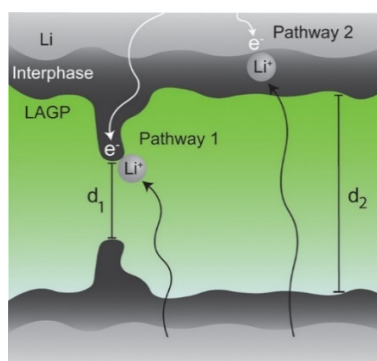
Han et al. compared the formation behaviors of Li dendrites in three representative SSEs (LLZO,  $\text{Li}_3\text{PS}_4$ , and LiPON) and found that ionic conductivity is also a possible reason for dendrite growth in SSE.<sup>15</sup> By comparing the relative density, shear modulus, interfacial resistance, and ionic conductivity of LLZO and LiPON, they predicted that LLZO should exhibit an approximate dendrite inhibition ability with that of LiPON. While in fact dendrites grow much severely in LLZO than that in LiPON. Therefore, some other parameters determine the tendency of dendrite growth. Instead, the critical current density of SSEs correlates well with their electronic conductivities. The LLZO and  $\text{Li}_2\text{S-P}_2\text{S}_5$  present electronic conductivities several orders of magnitude higher relative to that of LiPON, whereas the former two SSEs exhibit much lower critical current densities compared to LiPON. This is because the high electronic conductivity renders it easier for  $\text{Li}^+$  to receive electrons and directly generate Li dendrites within the SSEs. Consequently, the high electronic conductivity could potentially be the culprit of Li dendrite propagation in these SSEs. Additionally, the homogeneous and pore-free morphology of LiPON also contributes to its dendrite suppression capability.<sup>19</sup> This work provides another direction in regulating Li metal growth and indicates the need for lowering the electronic conductivity of SSEs in alleviating dendrite formation.

Unlike ceramic SSEs (such as LLZO,  $\text{Li}_3\text{OX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ),  $\text{LiBH}_4$ , etc.), another category of SSEs (including  $\text{Li}_7\text{P}_3\text{S}_{11}$  (LPS),  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS), and  $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{1.6}(\text{PO}_4)_3$  (LAGP), etc.) is not stable against Li metal anode.<sup>94-96</sup> (Electro)chemical reactions occur between Li metal anode and these electrolytes and the formed solid electrolyte interphase (SEI) will definitely transform the interfaces and affect the dendrite growth behaviors in SSEs.<sup>27,97</sup> LAGP is chemically and electrochemically active toward Li.<sup>98</sup> The chemically formed interphase between Li metal and LAGP before electrochemical reactions exhibits a mixed ionic and electronic conductivity with the electronic conductivity dominating.<sup>99</sup> This interface strongly affects the electrical properties, mechanical integrity, and thermal stability of SSEs. Two possible electrochemical reaction



pathways occur at this mixed-conducting interphase (Figure 10).<sup>97</sup> In pathway 1, LAGP is electrochemically reduced at the LAGP/interphase boundary by obtaining Li ions with electrons traversed the mixed-conducting interphase. Nonuniform Li deposition is accelerated thorough pathway 1 because of the decrease in the  $\text{Li}^+$  transport distance ( $d_1$  compared to  $d_2$ ) and thereby lowering the local ion conduction resistance. This shortened ion transport length will be amplified at higher currents due to the overall higher overpotential, resulting in severely inhomogenous plating morphology. Li deposition also occurs at the Li/LAGP interface as illustrated in pathway 2 (Figure 10). This reduction pathway will not cause the electrochemical formed interphase. The two pathways are in competition in this system depending on the operating current density.<sup>97</sup> The desired Li/electrolyte interphase needs to combine the features of high ionic conductivities, low electronic conductivities, and high chemical stability to suppress the formation of Li dendrites and realize the stable and safe solid-state batteries.

In short, the growth of Li dendrite in SSEs proceeds in two steps: dendrite nucleation and its subsequent propagation inside SSEs. The nucleation sites can be at the Li/electrolyte interface or inside the bulk SSEs depending on the surface chemistry and electronic conductivity of SSEs as well as the operating current density/capacity.<sup>2</sup> Once nucleation, Li dendrite tends to expand along the defects inside the SSEs, such as GBs, voids, and cracks, etc. The dendrite growth in SSEs follows different paths in different SSE systems and current densities/capacities. Once dendrites grow into a large diameter, giving rise to the concentrated mechanical stress between Li metal and SSEs and crack propagation even degradation of SSEs. Besides, some very thin and tiny dendrites grow and short-circuit the batteries before it can be detectable. In this case, the main driving force should be the enhanced local electrical field caused by the larger curvature at dendrite tips in the limited space of defects in SSEs.



**Figure 10.** Schematic illustrating possible reaction pathways and nonuniform evolution at Li/LAGP interphase with a mixed-conducting interphase. (Reprinted with permission from Ref. 97.)

**Summary and Outlook** SSEs are receiving great expectations, due to the nonflammability, non-leakage features, and high-oxidation voltage as well as low reduction volt-

age, which is hopeful to render highly safe and high-energy-density batteries. Their high mechanical modulus compared to the non-aqueous electrolytes is potential to inhibit dendrite growth of metallic Li as well. However, when SSEs match Li metal or other intercalation anodes even at moderate conditions, dendrite growth is observed between the interface of SSEs and anode, or inside the SSEs.

Li dendrites forms in polymer SSEs due to their relatively low modulus and surface impurities. Applied current density and pressure also affect the propensity of dendrite growth. In inorganic SSEs, dendrite growth can be contributed to the poor-wettability and unstable electrode/electrolyte interface, grain boundary, void, and electronic conductivity of SSEs. Theoretically, if SSEs are perfect without any defeat, dendrites cannot grow through SSEs, especially the rigid ceramics. However, it is quite difficult and nearly impossible to obtain a perfect electrolyte. To realize the large-scale application of fragile ceramic electrolytes, hybridizing of flexible polymer and rigid ceramic electrolytes is regarded as a promising route to obtain practical SSEs, where hard and soft components contribute in the composite SSEs synergetically.<sup>46</sup> Apparently, dendrite growth easily occurs in the soft part of the composite SSE. Therefore, for the future researches on SSEs matching Li metal anode, much more efforts are required to concentrate on the interfacial and bulk features of SSEs. Some suggested directions are presented herein.

(1) Detailed mechanisms of dendrite evolution in SSEs. Fundamental questions on the mechanisms depicting the dynamic processes of Li nucleation, propagation, interface migration, and crack evolution in SSE system still remain open. For example, how the surface chemistry and interfacial properties of SSEs affect the dynamic processes of Li dendrite growth? What's the influence of electric potential distribution at the dendrite tips and distribution of electronic and ionic transport channels in SSEs on the dendrite growth? These remained questions require further in-depth investigation.

(2) Facile characterization techniques. It is lacking powerful and facile characterization methods to track the detailed and in-depth interfacial evolution information of SSEs.<sup>100</sup> Due to the solid feature of SSEs, it is really hard to *in situ/operando* characterize the states of working SSEs. Currently, the frequently-applied tool to track the dendritic Li deposition in liquid electrolytes is optical and electron microscopy, yet it cannot provide the depth information of dendrite growth in SSEs.<sup>101</sup> Elaborate neutron measurements,<sup>15,52,102</sup> X-ray microtomography techniques,<sup>27,84,85,103</sup> and time-of-flight secondary-ion mass spectrometry<sup>53</sup> are always adopted to characterize SSEs. The *operando* or *in situ* microscopy and spectroscopy measurement techniques with higher spatial-temporal distribution and multidimensional resolution are required to obtain more detailed information on the working states



including morphology and chemistry of interface in SSEs.<sup>24</sup>

(3) Simulation methods. Interfacial stability between Li metal anodes and SSEs has been comprehensively investigated by ab initio molecular dynamics simulations.<sup>104</sup> Machine-learning techniques have also been proposed to computationally screen SSEs simultaneously with dendrite-suppression capability and high ionic conductivity.<sup>105</sup> While rare researches are conducted on the dendrite growth near the interface between SSEs and Li metal electrodes and inside the SSEs. Besides molecular dynamics simulations<sup>65,68</sup> and density functional theory calculations<sup>59</sup>, phase field simulations are also required to collaboratively predict the dendrite growth in SSEs.<sup>93</sup>

(4) Polymer/ceramic composite electrolytes. Recent researches on dendrite growth are mostly conducted in the single polymer or ceramic systems, while less are conducted based on the polymer/ceramic composite SSE, which is a quite promising electrolyte system in the future practical applications.<sup>106</sup> Information on structure and component distribution, ionic conduction paths, and Li deposition behavior is required for the design of an advanced composite SSEs.

(5) Implantation of dendrite-suppression strategies from the protection of Li metal anodes. Dendrite growth in the Li metal electrodes has been probed deeply. If Li deposits uniformly on the anode side regulated by Li metal anode itself, short-circuit by dendrite permeation will be largely relieved in SSEs. Li metal host and non-aqueous electrolyte wetting are promising methods to regulate Li deposition behaviors. Corporations with these strategies are helpful to realize a dendrite-free deposition behavior in SSE systems.

Li metal anode working with SSEs will be one of the ultimate solutions for the high-energy-density and highly safe battery systems. Future research efforts in this field need to be intelligently focused to achieve dendrite-free Li deposition at the Li/SSE interface and inside of SSEs. Exploiting facile tools to probe the structure and morphology evolution of the interfaces and SSEs at different time and space scales helps reveal the relations between SSE features, evolution of morphology dynamics, and electrochemical performance of Li metal anode. We hope that this Focus Review can shed new lights on the deep understanding of Li dendrite growth in SSE systems. It also helps rationally design the architectures and materials for SSEs matching Li metal anodes to open a new chapter in energy storage systems.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: jqhuang@bit.edu.cn (J.-Q.H.)  
zhang-qiang@mails.tsinghua.edu.cn (Q.Z.)

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

### Biographies

**He Liu** received her Ph.D. degree from Institute of Process Engineering, Chinese Academy of Sciences in 2017. Now she conducts her post-doctoral research in Jia-Qi Huang's group. Her current research interests mainly focus on the structure design of Li metal anode and solid-state electrolyte. Personal link: <http://orcid.org/0000-0003-1853-4732>

**Xin-Bing Cheng** received his B.Eng. (2012) from Tianjin University and Ph.D. (2017) degrees from Tsinghua University, China. He is a research assistant at Tsinghua University. His current research interests mainly focus on energy storage materials and devices. Personal link: <http://orcid.org/0000-0001-7567-1210>

**Jia-Qi Huang** received his B.Eng. (2007) and Ph.D. (2012) degrees from Tsinghua University, China. Now he is a professor in Beijing Institute of Technology. His research interests focus on synthetic approaches and application of nano-materials for rechargeable batteries, including Li-S batteries, Li metal anodes, etc. Personal link: <https://orcid.org/0000-0001-7394-9186>

**Hong Yuan** received his Ph.D. degree from Beijing Institute of Technology in 2017. Now he is an associate professor in Advanced Research Institute of Multidisciplinary Science in Beijing Institute of Technology. His research interests are focused on advanced Li-S batteries, Li-ion batteries and solid-state batteries. Personal link: <http://orcid.org/0000-0001-7565-2204>

**Yang Lu** completed his bachelor's degree in Tianjin University and Ph. D. degree in Shanghai Institute of Ceramics, Chinese Academy of Science. Now he is a postdoctoral researcher in Prof. Qiang Zhang's group in Tsinghua University. His current research focuses on solid-state electrolyte and their interfacial modifications. Personal link: <https://orcid.org/0000-0002-0946-7155>

**Chong Yan** gained his bachelor's and master's degrees from Henan Normal University and is currently a Ph.D. candidate at Beijing Institute of Technology. His current research focuses on the formation of electrode/electrolyte interface and the transport mechanism of Li<sup>+</sup> in solid-electrolyte interphase. Personal link: <https://orcid.org/0000-0001-9521-4981>

**Gao-Long Zhu** obtained his PhD from School of Physics in University of Electronic Science and Technology of China in 2018. He is now a post-doctor in Department of Chemical Engineering, Tsinghua University. His main areas of research address energy-storage materials, including solid electrolytes and separators. Personal link: <https://orcid.org/0000-0001-7860-5729>

**Rui Xu** received his B.Eng. in Chemical Engineering from Beijing Institute of Technology in 2017. He subsequently joined Prof. Jia-Qi Huang's group as a PhD student at Beijing Institute of Technology. His research interest is the interface design of stable lithium-metal batteries. Personal link: <https://orcid.org/0000-0001-6439-8706>

**Chen-Zi Zhao** obtained her B.Eng. from School of Materials Science and Engineering in Tsinghua University (2015). She is now a PhD candidate in Department of Chemical Engineering, Tsinghua University. Her main areas of research address energy-storage materials, including solid electrolytes and Li metal anodes. Personal link: <https://orcid.org/0000-0002-1794-3086>

**Li-Peng Hou** obtained his B.S. degree at Tianjin University in 2018. He is currently a Ph.D. student under the supervision of Prof. Qiang Zhang at the Department of Chemical Engineering, Tsinghua University. His research interests focus on Li metal batteries, especially the interface in Li-S batteries. Personal link: <https://orcid.org/0000-0002-9147-525X>

**Chuanxin He** is now the Assistant Dean of College of Chemistry and Environmental Engineering, Shenzhen University. His current research interesting is to design and synthesize novel nanostructure materials for fuel cells, water splitting and electrochemical reduction of carbon dioxide. Personal link: <https://orcid.org/0000-0002-2254-360X>

**Stefan Kaskel** became full professor for Inorganic Chemistry at Technical University Dresden in 2004. Since 2008 he is also working part time for Fraunhofer IWS, Dresden. His research interests are focused on porous and nanostructured materials for applications in energy storage, catalysis, batteries, and separation technologies. Personal link: <https://orcid.org/0000-0003-4572-0303>

**Qiang Zhang** is a full professor at Tsinghua University. His interests focus on energy materials (Li-metal anodes, Li-S batteries, and electrocatalysis). Currently, he is the associate editor of Journal of Energy Chemistry and advisory board of Matter, Advanced Functional Materials, EnergyChem, Energy Storage Mater, and so on. Personal link: <http://orcid.org/0000-0002-3929-1541>

## ACKNOWLEDGMENT

This work was supported by National Key Research and Development Program (2016YFA0202500 and 2016YFA0200102), National Natural Science Foundation of China (21676160, 21825501, 21805161, 21808121, and U1801257), and China Postdoctoral Science Foundation (2018M631480 and BX201700125).

## REFERENCES

- (1) Kerman, K.; Luntz, A.; Viswanathan, V.; Chiang, Y.-M.; Chen, Z. Review—Practical Challenges Hindering the Development of Solid State Li Ion Batteries. *J. Electrochem. Soc.* **2017**, *164*, A1731-A1744.
- (2) Famprikis, T.; Canepa, P.; Dawson, J. A.; Islam, M. S.; Masquelier, C. Fundamentals of Inorganic Solid-State Electrolytes for Batteries. *Nat. Mater.* **2019**, *18*, 1278-1291.
- (3) Zhang, X.-Q.; Zhao, C.-Z.; Huang, J.-Q.; Zhang, Q. Recent Advances in Energy Chemical Engineering of Next-Generation Lithium Batteries. *Engineering* **2018**, *4*, 831-847.
- (4) Zhao, C.-Z.; Duan, H.; Huang, J.-Q.; Zhang, J.; Zhang, Q.; Guo, Y.-G.; Wan, L.-J. Designing Solid-State Interfaces on Lithium-Metal Anodes: A Review. *Sci. China. Chem.* **2019**, *62*, 1286-1299.
- (5) Cheng, X.-B.; Zhang, R.; Zhao, C.-Z.; Zhang, Q. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* **2017**, *117*, 10403-10473.

- (6) Xu, H.; Chien, P.-H.; Shi, J.; Li, Y.; Wu, N.; Liu, Y.; Hu, Y.-Y.; Goodenough, J. B. High-Performance All-Solid-State Batteries Enabled by Salt Bonding to Perovskite in Poly(ethylene oxide). *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 18815.
- (7) Zeng, X.-X.; Yin, Y.-X.; Li, N.-W.; Du, W.-C.; Guo, Y.-G.; Wan, L.-J. Reshaping Lithium Plating/Stripping Behavior via Bifunctional Polymer Electrolyte for Room-Temperature Solid Li Metal Batteries. *J. Am. Chem. Soc.* **2016**, *138*, 15825-15828.
- (8) Hou, L.-P.; Yuan, H.; Zhao, C.-Z.; Xu, L.; Zhu, G.-L.; Nan, H.-X.; Cheng, X.-B.; Liu, Q.-B.; He, C.-X.; Huang, J.-Q.; Zhang, Q. Improved Interfacial Electronic Contacts Powering High Sulfur Utilization in All-Solid-State Lithium-Sulfur Batteries. *Energy Storage Mater.* **2020**, *25*, 436-442.
- (9) Cheng, X.-B.; Zhao, C.-Z.; Yao, Y.-X.; Liu, H.; Zhang, Q. Recent Advances in Energy Chemistry between Solid-State Electrolyte and Safe Lithium-Metal Anodes. *Chem* **2019**, *5*, 74-96.
- (10) Samson, A. J.; Hofstetter, K.; Bag, S.; Thangadurai, V. A Bird's-Eye View of Li-Stuffed Garnet-Type  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Ceramic electrolytes for Advanced All-Solid-State Li Batteries. *Energy Environ. Sci.* **2019**, *12*, 2957-2975.
- (11) Cortes, F. J. Q.; Lewis, J. A.; Tippens, J.; Marchese, T. S.; McDowell, M. T. How Metallic Protection Layers Extend the Lifetime of NASICON-Based Solid-State Lithium Batteries. *J. Electrochem. Soc.* **2020**, *167*, 050502.
- (12) Sun, N.; Liu, Q.; Cao, Y.; Lou, S.; Ge, M.; Xiao, X.; Lee, W.-K.; Gao, Y.; Yin, G.; Wang, J.; Sun, X. Anisotropically Electrochemo-Mechanical Evolution in Solid-State Batteries and Interfacial Tailored Strategy. *Angew. Chem. Int. Ed.* **2019**, *58*, 18647-18653.
- (13) Zhao, C.-Z.; Chen, P.-Y.; Zhang, R.; Chen, X.; Li, B.-Q.; Zhang, X.-Q.; Cheng, X.-B.; Zhang, Q. An Ion Redistributor for Dendrite-Free Lithium Metal Anodes. *Sci. Adv.* **2018**, *4*, eaat3446.
- (14) Sun, Y.-Z.; Huang, J.-Q.; Zhao, C.-Z.; Zhang, Q. A Review of Solid Electrolytes for Safe Lithium-Sulfur Batteries. *Sci. China. Chem.* **2017**, *60*, 1508-1526.
- (15) Han, F.; Westover, A. S.; Yue, J.; Fan, X.; Wang, F.; Chi, M.; Leonard, D. N.; Dudney, N. J.; Wang, H.; Wang, C. High Electronic Conductivity as the Origin of Lithium Dendrite Formation within Solid Electrolytes. *Nat. Energy* **2019**, *4*, 187-196.
- (16) Li, G.; Monroe, C. W. Dendrite Nucleation in Lithium-Conductive Ceramics. *Phys. Chem. Chem. Phys.* **2019**, *21*, 20354-20359.
- (17) Suzuki, Y.; Kami, K.; Watanabe, K.; Watanabe, A.; Saito, N.; Ohnishi, T.; Takada, K.; Sudo, R.; Imanishi, N. Transparent Cubic Garnet-Type Solid Electrolyte of  $\text{Al}_2\text{O}_3$ -Doped  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ . *Solid State Ionics* **2015**, *278*, 172-176.
- (18) Zhang, H.; Li, C.; Piszcz, M.; Coya, E.; Rojo, T.; Rodriguez-Martinez, L. M.; Armand, M.; Zhou, Z. Single Lithium-Ion Conducting Solid Polymer Electrolytes: Advances and Perspectives. *Chem. Soc. Rev.* **2017**, *46*, 797-815.
- (19) Westover, A. S.; Dudney, N. J.; Sacci, R. L.; Kalnaus, S. Deposition and Confinement of Li Metal along an Artificial LiPON-LiPON Interface. *ACS Energy Lett.* **2019**, *4*, 651-655.
- (20) Monroe, C.; Newman, J. The Impact of Elastic Deformation on Deposition Kinetics at Lithium/Polymer Interfaces. *J. Electrochem. Soc.* **2005**, *152*, A396-A404.
- (21) Wood, K. N.; Noked, M.; Dasgupta, N. P. Lithium Metal Anodes: Toward an Improved Understanding of Coupled Morphological, Electrochemical, and Mechanical Behavior. *ACS Energy Lett.* **2017**, *2*, 664-672.
- (22) Ma, J.; Chen, B.; Wang, L.; Cui, G. Progress and Prospect on Failure Mechanisms of Solid-State Lithium Batteries. *J. Power Sources* **2018**, *392*, 94-115.
- (23) Albertus, P.; Babinec, S.; Litzelman, S.; Newman, A. Status and Challenges in Enabling the Lithium Metal Electrode for High-Energy and Low-Cost Rechargeable Batteries. *Nat. Energy* **2018**, *3*, 16-21.

- (24) Krauskopf, T.; Dippel, R.; Hartmann, H.; Peppler, K.; Mogwitz, B.; Richter, F. H.; Zeier, W. G.; Janek, J. Lithium-Metal Growth Kinetics on LLZO Garnet-Type Solid Electrolytes. *Joule* **2019**, *3*, 2030-2049.
- (25) Luo, C.; Ji, X.; Chen, J.; Gaskell, K. J.; He, X.; Liang, Y.; Jiang, J.; Wang, C. Solid-State Electrolyte Anchored with a Carboxylated Azo Compound for All-Solid-State Lithium Batteries. *Angew. Chem. Int. Ed.* **2018**, *57*, 8567-8571.
- (26) Lewis, J. A.; Tippens, J.; Cortes, F. J. Q.; McDowell, M. T. Chemo-Mechanical Challenges in Solid-State Batteries. *Trends in Chemistry* **2019**, *1*, 845-857.
- (27) Tippens, J.; Miers, J. C.; Afshar, A.; Lewis, J. A.; Cortes, F. J. Q.; Qiao, H.; Marchese, T. S.; Di Leo, C. V.; Saldana, C.; McDowell, M. T. Visualizing Chemomechanical Degradation of a Solid-State Battery Electrolyte. *ACS Energy Lett.* **2019**, *4*, 1475-1483.
- (28) Liu, M.; Cheng, Z.; Ganapathy, S.; Wang, C.; Haverkate, L. A.; Tułodziecki, M.; Unnikrishnan, S.; Wagemaker, M. Tandem Interface and Bulk Li-Ion Transport in a Hybrid Solid Electrolyte with Microsized Active Filler. *ACS Energy Lett.* **2019**, *4*, 2336-2342.
- (29) Yu, J.; Wang, C.; Li, S.; Liu, N.; Zhu, J.; Lu, Z. Li<sup>+</sup>-Containing, Continuous Silica Nanofibers for High Li<sup>+</sup> Conductivity in Composite Polymer Electrolyte. *Small* **2019**, *15*, 1902729.
- (30) Zhao, C.; Liang, J.; Zhao, Y.; Luo, J.; Sun, Q.; Liu, Y.; Lin, X.; Yang, X.; Huang, H.; Zhang, L.; Zhao, S.; Lu, S.; Sun, X. Engineering a "Nanonet"-Reinforced Polymer Electrolyte for Long-Life Li-O<sub>2</sub> Batteries. *J. Mater. Chem. A* **2019**, *7*, 24947-24952.
- (31) Wu, H.; Xu, Y.; Ren, X.; Liu, B.; Engelhard, M. H.; Ding, M. S.; El-Khoury, P. Z.; Zhang, L.; Li, Q.; Xu, K.; Wang, C.; Zhang, J.-G.; Xu, W. Polymer-in-"Quasi-Ionic Liquid" Electrolytes for High-Voltage Lithium Metal Batteries. *Adv. Energy Mater.* **2019**, *9*, 1902108.
- (32) Wang, C.; Wang, T.; Wang, L.; Hu, Z.; Cui, Z.; Li, J.; Dong, S.; Zhou, X.; Cui, G. Differentiated Lithium Salt Design for Multilayered PEO Electrolyte Enables a High-Voltage Solid-State Lithium Metal Battery. *Adv. Sci.* **2019**, *6*, 1901036.
- (33) Harry, K. J.; Higa, K.; Srinivasan, V.; Balsara, N. P. Influence of Electrolyte Modulus on the Local Current Density at a Dendrite Tip on a Lithium Metal Electrode. *J. Electrochem. Soc.* **2016**, *163*, A2216-A2224.
- (34) Geng, H. Z.; Rosen, R.; Zheng, B.; Shimoda, H.; Fleming, L.; Liu, J.; Zhou, O. Fabrication and Properties of Composites of Poly(ethylene oxide) and Functionalized Carbon Nanotubes. *Adv. Mater.* **2002**, *14*, 1387-1390.
- (35) Rosso, M.; Brissot, C.; Teyssot, A.; Dollé, M.; Sannier, L.; Tarascon, J.-M.; Bouchet, R.; Lascaud, S. Dendrite Short-Circuit and Fuse Effect on Li/Polymer/Li Cells. *Electrochim. Acta* **2006**, *51*, 5334-5340.
- (36) Brissot, C.; Rosso, M.; Chazalviel, J. N.; Lascaud, S. Dendritic Growth Mechanisms in Lithium/Polymer Cells. *J. Power Sources* **1999**, *81-82*, 925-929.
- (37) Dollé, M.; Sannier, L.; Beaudoin, B.; Trentin, M.; Tarascon, J.-M. Live Scanning Electron Microscope Observations of Dendritic Growth in Lithium/Polymer Cells. *Electrochem. Solid-State Lett.* **2002**, *5*, A286-A289.
- (38) Rosso, M.; Gobron, T.; Brissot, C.; Chazalviel, J. N.; Lascaud, S. Onset of Dendritic Growth in Lithium/Polymer Cells. *J. Power Sources* **2001**, *97-98*, 804-806.
- (39) Harry, K. J.; Liao, X.; Parkinson, D. Y.; Minor, A. M.; Balsara, N. P. Electrochemical Deposition and Stripping Behavior of Lithium Metal across a Rigid Block Copolymer Electrolyte Membrane. *J. Electrochem. Soc.* **2015**, *162*, A2699-A2706.
- (40) Golozar, M.; Hovington, P.; Paoletta, A.; Bessette, S.; Lagacé, M.; Bouchard, P.; Demers, H.; Gauvin, R.; Zaghib, K. In Situ Scanning Electron Microscopy Detection of Carbide Nature of Dendrites in Li-Polymer Batteries. *Nano Lett.* **2018**, *18*, 7583-7589.
- (41) Ahmad, Z.; Viswanathan, V. Stability of Electrodeposition at Solid-Solid Interfaces and Implications for Metal Anodes. *Phys. Rev. Lett.* **2017**, *119*, 056003.
- (42) Raj, R.; Wolfenstine, J. Current Limit Diagrams for Dendrite Formation in Solid-State Electrolytes for Li-Ion Batteries. *J. Power Sources* **2017**, *343*, 119-126.
- (43) Barai, P.; Higa, K.; Srinivasan, V. Lithium Dendrite Growth Mechanisms in Polymer Electrolytes and Prevention Strategies. *Phys. Chem. Chem. Phys.* **2017**, *19*, 20493-20505.
- (44) Maslyn, J. A.; Loo, W. S.; McEntush, K. D.; Oh, H. J.; Harry, K. J.; Parkinson, D. Y.; Balsara, N. P. Growth of Lithium Dendrites and Globules through a Solid Block Copolymer Electrolyte as a Function of Current Density. *J. Phys. Chem. C* **2018**, *122*, 26797-26804.
- (45) Xue, Z.; He, D.; Xie, X. Poly(ethylene oxide)-based electrolytes for lithium-ion batteries. *J. Mater. Chem. A* **2015**, *3*, 19218-19253.
- (46) Liu, Y.; Xu, B.; Zhang, W.; Li, L.; Lin, Y.; Nan, C. Composition Modulation and Structure Design of Inorganic-in-Polymer Composite Solid Electrolytes for Advanced Lithium Batteries. *Small* **2019**, *15*, 1902813.
- (47) Zhang, X.; Wang, S.; Xue, C.; Xin, C.; Lin, Y.; Shen, Y.; Li, L.; Nan, C.-W. Self-Suppression of Lithium Dendrite in All-Solid-State Lithium Metal Batteries with Poly(vinylidene difluoride)-Based Solid Electrolytes. *Adv. Mater.* **2019**, *31*, 1806082.
- (48) Zhao, C.-Z.; Zhang, X.-Q.; Cheng, X.-B.; Zhang, R.; Xu, R.; Chen, P.-Y.; Peng, H.-J.; Huang, J.-Q.; Zhang, Q. An Anion-Immobilized Composite Electrolyte for Dendrite-Free Lithium Metal Anodes. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 11069.
- (49) Fan, Z.; Ding, B.; Zhang, T.; Lin, Q.; Malgras, V.; Wang, J.; Dou, H.; Zhang, X.; Yamauchi, Y. Solid/Solid Interfacial Architecturing of Solid Polymer Electrolyte-Based All-Solid-State Lithium-Sulfur Batteries by Atomic Layer Deposition. *Small* **2019**, *15*, 1903952.
- (50) Cao, C.; Li, Y.; Chen, S.; Peng, C.; Li, Z.; Tang, L.; Feng, Y.; Feng, W. Electrolyte-Solvent-Modified Alternating Copolymer as a Single-Ion Solid Polymer Electrolyte for High-Performance Lithium Metal Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 35683-35692.
- (51) Xie, H.; Bao, Y.; Cheng, J.; Wang, C.; Hitz, E. M.; Yang, C.; Liang, Z.; Zhou, Y.; He, S.; Li, T.; Hu, L. Flexible Garnet Solid-State Electrolyte Membranes Enabled by Tile-and-Grout Design. *ACS Energy Lett.* **2019**, *4*, 2668-2674.
- (52) Li, Q.; Yi, T.; Wang, X.; Pan, H.; Quan, B.; Liang, T.; Guo, X.; Yu, X.; Wang, H.; Huang, X.; Chen, L.; Li, H. In-Situ Visualization of Lithium Plating in All-Solid-State Lithium-Metal Battery. *Nano Energy* **2019**, *63*, 103895.
- (53) Wang, S.; Xu, H.; Li, W.; Dolocan, A.; Manthiram, A. Interfacial Chemistry in Solid-State Batteries: Formation of Interphase and Its Consequences. *J. Am. Chem. Soc.* **2018**, *140*, 250-257.
- (54) Han, F.; Yue, J.; Zhu, X.; Wang, C. Suppressing Li Dendrite Formation in Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> Solid Electrolyte by LiI Incorporation. *Adv. Energy Mater.* **2018**, *8*, 1703644.
- (55) Yu, S.; Siegel, D. J. Grain Boundary Softening: A Potential Mechanism for Lithium Metal Penetration through Stiff Solid Electrolytes. *ACS Appl. Mater. Interfaces* **2018**, *10*, 38151-38158.
- (56) Bachman, J. C.; Muy, S.; Grimaud, A.; Chang, H.-H.; Pour, N.; Lux, S. F.; Paschos, O.; Maglia, F.; Lupart, S.; Lamp, P.; Giordano, L.; Shao-Horn, Y. Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction. *Chem. Rev.* **2016**, *116*, 140-162.

- (57) Porz, L.; Swamy, T.; Sheldon, B. W.; Rettenwander, D.; Frömling, T.; Thaman, H. L.; Berendts, S.; Uecker, R.; Carter, W. C.; Chiang, Y.-M. Mechanism of Lithium Metal Penetration through Inorganic Solid Electrolytes. *Adv. Energy Mater.* **2017**, *7*, 1701003.
- (58) Aguesse, F.; Manalastas, W.; Buannic, L.; Lopez del Amo, J. M.; Singh, G.; Llordés, A.; Kilner, J. Investigating the Dendritic Growth during Full Cell Cycling of Garnet Electrolyte in Direct Contact with Li Metal. *ACS Appl. Mater. Interfaces* **2017**, *9*, 3808–3816.
- (59) Tian, H.-K.; Xu, B.; Qi, Y. Computational Study of Lithium Nucleation Tendency in  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) and Rational Design of Interlayer Materials to Prevent Lithium Dendrites. *J. Power Sources* **2018**, *392*, 79–86.
- (60) Sharafi, A.; Kazyak, E.; Davis, A. L.; Yu, S.; Thompson, T.; Siegel, D. J.; Dasgupta, N. P.; Sakamoto, J. Surface Chemistry Mechanism of Ultra-Low Interfacial Resistance in the Solid-State Electrolyte  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ . *Chem. Mater.* **2017**, *29*, 7961–7968.
- (61) Sharafi, A.; Yu, S.; Naguib, M.; Lee, M.; Ma, C.; Meyer, H. M.; Nanda, J.; Chi, M.; Siegel, D. J.; Sakamoto, J. Impact of Air Exposure and Surface Chemistry on Li- $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Interfacial Resistance. *J. Mater. Chem. A* **2017**, *5*, 13475–13487.
- (62) Han, X.; Gong, Y.; Fu, K.; He, X.; Hitz, G. T.; Dai, J.; Pearse, A.; Liu, B.; Wang, H.; Rubloff, G.; Mo, Y.; Thangadurai, V.; Wachsman, E. D.; Hu, L. Negating Interfacial Impedance in Garnet-based Solid-State Li Metal Batteries. *Nat. Mater.* **2016**, *16*, 572.
- (63) Adams, J. B.; Wolfer, W. G.; Foiles, S. M. Elastic Properties of Grain Boundaries in Copper and Their Relationship to Bulk Elastic Constants. *Phys. Rev. B* **1989**, *40*, 9479–9484.
- (64) Cheng, E. J.; Sharafi, A.; Sakamoto, J. Intergranular Li Metal Propagation through Polycrystalline  $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$  Ceramic Electrolyte. *Electrochim. Acta* **2017**, *223*, 85–91.
- (65) Yu, S.; Siegel, D. J. Grain Boundary Contributions to Li-Ion Transport in the Solid Electrolyte  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO). *Chem. Mater.* **2017**, *29*, 9639–9647.
- (66) Inaguma, Y.; Liquan, C.; Itoh, M.; Nakamura, T.; Uchida, T.; Ikuta, H.; Wakihara, M. High Ionic Conductivity in Lithium Lanthanum Titanate. *Solid State Commun.* **1993**, *86*, 689–693.
- (67) Bruce, P. G.; West, A. R. The A-C Conductivity of Polycrystalline LISICON,  $\text{Li}_{1+x}\text{Zn}_{1-x}\text{GeO}_4$ , and a Model for Intergranular Constriction Resistances. *J. Electrochem. Soc.* **1983**, *130*, 662–669.
- (68) Dawson, J. A.; Canepa, P.; Famprikis, T.; Masquelier, C.; Islam, M. S. Atomic-Scale Influence of Grain Boundaries on Li-Ion Conduction in Solid Electrolytes for All-Solid-State Batteries. *J. Am. Chem. Soc.* **2018**, *140*, 362–368.
- (69) Yu, C.; Ganapathy, S.; van Eck, E. R. H.; van Eijck, L.; de Klerk, N.; Kelder, E. M.; Wagemaker, M. Investigation of Li-Ion Transport in  $\text{Li}_7\text{P}_3\text{S}_{11}$  and Solid-State Lithium Batteries. *J. Energy Chem.* **2019**, *38*, 1–7.
- (70) Ren, Y.; Shen, Y.; Lin, Y.; Nan, C.-W. Direct Observation of Lithium Dendrites Inside Garnet-Type Lithium-Ion Solid Electrolyte. *Electrochem. Commun.* **2015**, *57*, 27–30.
- (71) Pesci, F. M.; Brugge, R. H.; Hekselman, A. K. O.; Cavallaro, A.; Chater, R. J.; Aguadero, A. Elucidating the Role of Dopants in the Critical Current Density for Dendrite Formation in Garnet Electrolytes. *J. Mater. Chem. A* **2018**, *6*, 19817–19827.
- (72) Im, C.; Park, D.; Kim, H.; Lee, J. Al-Incorporation into  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Solid Electrolyte Keeping Stabilized Cubic Phase for All-Solid-State Li Batteries. *J. Energy Chem.* **2018**, *27*, 1501–1508.
- (73) Li, Y.; Chen, X.; Dolocan, A.; Cui, Z.; Xin, S.; Xue, L.; Xu, H.; Park, K.; Goodenough, J. B. Garnet Electrolyte with an Ultralow Interfacial Resistance for Li-Metal Batteries. *J. Am. Chem. Soc.* **2018**, *140*, 6448–6455.
- (74) Ban, C. W.; Choi, G. M. The Effect of Sintering on the Grain Boundary Conductivity of Lithium Lanthanum Titanates. *Solid State Ionics* **2001**, *140*, 285–292.
- (75) David, I. N.; Thompson, T.; Wolfenstine, J.; Allen, J. L.; Sakamoto, J. Microstructure and Li-Ion Conductivity of Hot-Pressed Cubic  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ . *J. Am. Ceram. Soc.* **2015**, *98*, 1209–1214.
- (76) Hongahally Basappa, R.; Ito, T.; Morimura, T.; Bekarevich, R.; Mitsuishi, K.; Yamada, H. Grain Boundary Modification to Suppress Lithium Penetration through Garnet-Type Solid Electrolyte. *J. Power Sources* **2017**, *363*, 145–152.
- (77) Chung, H.; Kang, B. Increase in Grain Boundary Ionic Conductivity of  $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$  by Adding Excess Lithium. *Solid State Ionics* **2014**, *263*, 125–130.
- (78) Krauskopf, T.; Mogwitz, B.; Rosenbach, C.; Zeier, W. G.; Janek, J. Diffusion Limitation of Lithium Metal and Li-Mg Alloy Anodes on LLZO Type Solid Electrolytes as a Function of Temperature and Pressure. *Adv. Energy Mater.* **2019**, *9*, 1902568.
- (79) Swamy, T.; Park, R.; Sheldon, B. W.; Rettenwander, D.; Porz, L.; Berendts, S.; Uecker, R.; Carter, W. C.; Chiang, Y.-M. Lithium Metal Penetration Induced by Electrodeposition through Solid Electrolytes: Example in Single-Crystal  $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$  Garnet. *J. Electrochem. Soc.* **2018**, *165*, A3648–A3655.
- (80) Klinsmann, M.; Hildebrand, F. E.; Ganzer, M.; McMeeking, R. M. Dendritic Cracking in Solid Electrolytes Driven by Lithium Insertion. *J. Power Sources* **2019**, *442*, 227226.
- (81) Liu, H.; Cheng, X.-B.; Xu, R.; Zhang, X.-Q.; Yan, C.; Huang, J.-Q.; Zhang, Q. Plating/Stripping Behavior of Actual Lithium Metal Anode. *Adv. Energy Mater.* **2019**, *9*, 1902254.
- (82) Kasemchainan, J.; Zekoll, S.; Spencer Jolly, D.; Ning, Z.; Hartley, G. O.; Marrow, J.; Bruce, P. G. Critical Stripping Current Leads to Dendrite Formation on Plating in Lithium Anode Solid Electrolyte Cells. *Nat. Mater.* **2019**, *18*, 1105–1111.
- (83) Lu, Y.; Huang, X.; Song, Z.; Rui, K.; Wang, Q.; Gu, S.; Yang, J.; Xiu, T.; Badding, M. E.; Wen, Z. Highly Stable Garnet Solid Electrolyte based Li-S Battery with Modified Anodic and Cathodic Interfaces. *Energy Storage Mater.* **2018**, *15*, 282–290.
- (84) Seitzman, N.; Guthrey, H.; Sulas, D. B.; Platt, H. A. S.; Al-Jassim, M.; Pylypenko, S. Toward All-Solid-State Lithium Batteries: Three-Dimensional Visualization of Lithium Migration in  $\beta\text{-Li}_3\text{PS}_4$  Ceramic Electrolyte. *J. Electrochem. Soc.* **2018**, *165*, A3732–A3737.
- (85) Shen, F.; Dixit, M. B.; Xiao, X.; Hatzell, K. B. Effect of Pore Connectivity on Li Dendrite Propagation within LLZO Electrolytes Observed with Synchrotron X-ray Tomography. *ACS Energy Lett.* **2018**, *3*, 1056–1061.
- (86) Lu, Y.; Huang, X.; Ruan, Y.; Wang, Q.; Kun, R.; Yang, J.; Wen, Z. An in situ Element Permeation Constructed High Endurance Li-LLZO Interface at High Current Densities. *J. Mater. Chem. A* **2018**, *6*, 18853–18858.
- (87) Ren, Y.; Shen, Y.; Lin, Y.; Nan, C.-W. Microstructure Manipulation for Enhancing the Resistance of Garnet-Type Solid Electrolytes to “Short Circuit” by Li Metal Anodes. *ACS Appl. Mater. Interfaces* **2019**, *11*, 5928–5937.
- (88) Sudo, R.; Nakata, Y.; Ishiguro, K.; Matsui, M.; Hirano, A.; Takeda, Y.; Yamamoto, O.; Imanishi, N. Interface Behavior Between Garnet-Type Lithium-Conducting Solid Electrolyte and Lithium meMal. *Solid State Ionics* **2014**, *262*, 151–154.
- (89) Mo, F.; Ruan, J.; Sun, S.; Lian, Z.; Yang, S.; Yue, X.; Song, Y.; Zhou, Y.-N.; Fang, F.; Sun, G.; Peng, S.; Sun, D. Inside or Outside: Origin of Lithium Dendrite Formation of All Solid-State Electrolytes. *Adv. Energy Mater.* **2019**, *9*, 1902123.
- (90) Huang, X.; Lu, Y.; Song, Z.; Rui, K.; Wang, Q.; Xiu, T.; Badding, M. E.; Wen, Z. Manipulating  $\text{Li}_2\text{O}$  Atmosphere for Sintering Dense  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Solid Electrolyte. *Energy Storage Mater.* **2019**, *22*, 207–217.



- (91) Song, Y.; Yang, L.; Zhao, W.; Wang, Z.; Zhao, Y.; Wang, Z.; Zhao, Q.; Liu, H.; Pan, F. Revealing the Short-Circuiting Mechanism of Garnet-Based Solid-State Electrolyte. *Adv. Energy Mater.* **2019**, *9*, 1900671.
- (92) Cheng, X.-B.; Yan, C.; Zhang, X.-Q.; Liu, H.; Zhang, Q. Electronic and Ionic Channels in Working Interfaces of Lithium Metal Anodes. *ACS Energy Lett.* **2018**, *3*, 1564-1570.
- (93) Tian, H.-K.; Liu, Z.; Ji, Y.; Chen, L.-Q.; Qi, Y. Interfacial Electronic Properties Dictate Li Dendrite Growth in Solid Electrolytes. *Chem. Mater.* **2019**, *31*, 7351-7359.
- (94) Wenzel, S.; Leichtweiss, T.; Krüger, D.; Sann, J.; Janek, J. Interphase Formation on Lithium Solid Electrolytes—An in situ Approach to Study Interfacial Reactions by Photoelectron Spectroscopy. *Solid State Ionics* **2015**, *278*, 98-105.
- (95) Pervez, S. A.; Cambaz, M. A.; Thangadurai, V.; Fichtner, M. Interface in Solid-State Lithium Battery: Challenges, Progress, and Outlook. *ACS Appl. Mater. Interfaces* **2019**, *11*, 22029-22050.
- (96) Chen, S.; Xie, D.; Liu, G.; Mwizerwa, J. P.; Zhang, Q.; Zhao, Y.; Xu, X.; Yao, X. Sulfide Solid Electrolytes for All-Solid-State Lithium Batteries: Structure, Conductivity, Stability and Application. *Energy Storage Mater.* **2018**, *14*, 58-74.
- (97) Lewis, J. A.; Cortes, F. J. Q.; Boebinger, M. G.; Tippens, J.; Marchese, T. S.; Kondekar, N.; Liu, X.; Chi, M.; McDowell, M. T. Interphase Morphology between a Solid-State Electrolyte and Lithium Controls Cell Failure. *ACS Energy Lett.* **2019**, *4*, 591-599.
- (98) Wang, S.; Wang, J.; Liu, J.; Song, H.; Liu, Y.; Wang, P.; He, P.; Xu, J.; Zhou, H. Ultra-Fine Surface Solid-State Electrolytes for Long Cycle Life All-Solid-State Lithium-Air Batteries. *J. Mater. Chem. A* **2018**, *6*, 21248-21254.
- (99) Chung, H.; Kang, B. Mechanical and Thermal Failure Induced by Contact between a  $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$  Solid Electrolyte and Li Metal in an All Solid-State Li Cell. *Chem. Mater.* **2017**, *29*, 8611-8619.
- (100) Zhang, C.; Feng, Y.; Han, Z.; Gao, S.; Wang, M.; Wang, P. Electrochemical and Structural Analysis in All-Solid-State Lithium Batteries by Analytical Electron Microscopy: Progress and Perspectives. *Adv. Mater.* **2019**, *31*, 1903747.
- (101) Shen, Z.; Zhang, W.; Zhu, G.; Huang, Y.; Feng, Q.; Lu, Y. Design Principles of the Anode-Electrolyte Interface for All Solid-State Lithium Metal Batteries. *Small Methods* **2019**, *3*, 1900592.
- (102) Wang, C.; Gong, Y.; Dai, J.; Zhang, L.; Xie, H.; Pastel, G.; Liu, B.; Wachsman, E.; Wang, H.; Hu, L. In Situ Neutron Depth Profiling of Lithium Metal-Garnet Interfaces for Solid State Batteries. *J. Am. Chem. Soc.* **2017**, *139*, 14257-14264.
- (103) Harry, K. J.; Hallinan, D. T.; Parkinson, D. Y.; MacDowell, A. A.; Balsara, N. P. Detection of Subsurface Structures Underneath Dendrites Formed on Cycled Lithium Metal Electrodes. *Nat. Mater.* **2013**, *13*, 69-73.
- (104) Nolan, A. M.; Zhu, Y.; He, X.; Bai, Q.; Mo, Y. Computation-Accelerated Design of Materials and Interfaces for All-Solid-State Lithium-Ion Batteries. *Joule* **2018**, *2*, 2016-2046.
- (105) Ahmad, Z.; Xie, T.; Maheshwari, C.; Grossman, J. C.; Viswanathan, V. Machine Learning Enabled Computational Screening of Inorganic Solid Electrolytes for Suppression of Dendrite Formation in Lithium Metal Anodes. *ACS Cent. Sci.* **2018**, *4*, 996-1006.
- (106) Huo, H.; Chen, Y.; Luo, J.; Yang, X.; Guo, X.; Sun, X. Rational Design of Hierarchical “Ceramic-in-Polymer” and “Polymer-in-Ceramic” Electrolytes for Dendrite-Free Solid-State Batteries. *Adv. Energy Mater.* **2019**, *9*, 1804004.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

**Highlighted quotes**

Seemingly, short-circuit induced by Li dendrites is more easily formed in SSE systems compared to their liquid counterparts, contradicting the prevailing knowledge of dendrites that can be inhibited by SSEs with Li-ion transference number approaching 1.0 and shear modulus twice higher than that of Li metal.

Li dendrite growth from metallic Li anode can easily transpierce soft polymer electrolytes due to their relatively low modulus, leading to cell short circuit and battery failure.

Dendrite growth in inorganic SSEs can be induced by poor-wettability and unstable electrode/electrolyte interface, grain boundary, void, and electronic conductivity of SSEs.

Table of Contents

