

# Li<sub>2</sub>CO<sub>3</sub>: A Critical Issue for Developing Solid Garnet Batteries

Hanyu Huo,<sup>†,‡,⊥</sup> Jing Luo,<sup>⊥</sup> Venkataraman Thangadurai,<sup>§,¶</sup> Xiangxin Guo,<sup>\*,†</sup> Ce-Wen Nan,<sup>\*,||</sup> and Xueliang Sun<sup>\*,⊥,¶</sup>

<sup>†</sup>College of Physics, Qingdao University, Qingdao 266071, China

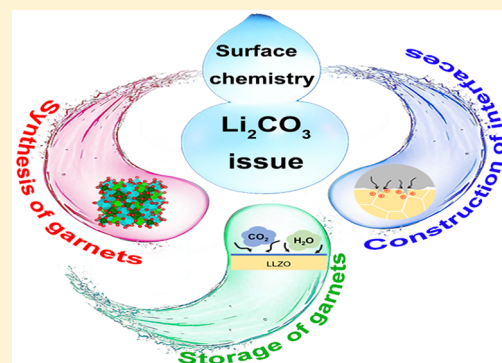
<sup>‡</sup>State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

<sup>§</sup>Department of Chemistry, University of Calgary, 2500 University Drive, Northwest Calgary, Alberta T2N 1N4, Canada

<sup>||</sup>School of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

<sup>⊥</sup>Department of Mechanical and Materials Engineering, University of Western Ontario, Ontario N6A 5B9, Canada

**ABSTRACT:** Solid garnet electrolytes are promising solid-state electrolytes because of their favorable ionic conductivity and high stability against Li metal anodes. However, their special surface chemistry greatly affects the practical applications whether in the form of garnet ceramic electrolytes (GCEs) or polymer/garnet electrolytes (PGEs). Even though large-scale production of garnet in an ambient atmosphere is possible, the passivated surface due to air exposure can lead to poor interfacial properties of GCEs with electrodes and low ionic conductivities of PGEs. Understanding the effects of air exposure on garnet structure stability, ion mobility, and interfacial configuration is crucial for better applications of solid garnet electrolytes. In this Perspective, we comprehensively recapitulate the reaction mechanisms and influencing factors of air-induced contaminations. Various surface engineering strategies tailoring garnet particles and/or pellets are reviewed. This Perspective provides insightful guidelines for better storage of garnet electrolytes and construction of solid garnet batteries with enhanced electrochemical performance.



The ever-increasing demands for high-energy-density energy storage strongly promote the development of next-generation lithium-ion batteries (LiBs). Solid-state batteries (SSBs) using high-voltage cathodes, solid-state electrolytes (SSEs), and Li metal anodes are expected to boost the energy density.<sup>1</sup> At the same time, the safety concerns intrinsic to the flammable liquid electrolytes can be eliminated by the replacement of nonflammable SSEs and the integration of SSBs.

As a key component in SSBs, various types of SSEs have been studied for decades. Among them, garnet-type electrolytes are highly promising due to their good chemical and electrochemical stability against Li metal and feasibility of mass production in air.<sup>2</sup> An ideal garnet structure has a general chemical formula of A<sub>3</sub>B<sub>2</sub>C<sub>3</sub>O<sub>12</sub>, where A (e.g., Ca, Mg, and Y), B (e.g., Ga, Fe, Al, and Ni), and C (e.g., Al, Si, and V) are eight-, six-, and four-oxygen-coordinated cation sites.<sup>3</sup> The availability of different coordination sites enables possibilities for different metal ion doping. Thangadurai et al. reported Li-stuffed garnets, Li<sub>3</sub>La<sub>3</sub>M<sub>2</sub>O<sub>12</sub> (M = Ta and Nb), as promising ion conductors in 2004, showing ionic conductivities in the magnitude of 10<sup>-6</sup> S cm<sup>-1</sup> at 25 °C.<sup>4</sup> Li<sub>3</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>

was found to be stable in contact with molten lithium, which is probably because of the weaker reducibility of Ta than other transition metals including Ti and Nb. Li<sub>3</sub>La<sub>3</sub>M<sub>2</sub>O<sub>12</sub> (M = Ta and Nb) were the first examples of fast Li<sup>+</sup> conductors possessing garnet structures and gave rise to further investigations of conductivity optimization by chemical substitutions and structural modifications.<sup>5</sup> In 2007, Murugan et al. proposed a new garnet-type solid electrolyte, Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO), showing an ionic conductivity of about 3 × 10<sup>-4</sup> S cm<sup>-1</sup> at 25 °C. The LLZO has a cubic crystal structure similar to that of Li<sub>3</sub>La<sub>3</sub>M<sub>2</sub>O<sub>12</sub>.<sup>6</sup> Geiger et al. further discovered that LLZO undergoes a phase transition between cubic and tetragonal phases in a temperature range of 100–150 °C, where the cubic phase exhibits a higher ionic conductivity than the tetragonal phase.<sup>7</sup> After a decade of intensive research, significant progress has been achieved based on LLZO electrolytes in terms of ionic conductivity

Received: November 4, 2019

Accepted: December 11, 2019

Published: December 11, 2019

improvement, structural characterization, and  $\text{Li}^+$  transport mechanism investigation. In most cases, the solid garnet electrolytes refer to LLZO-based electrolytes.<sup>8–10</sup>

PGEs are suitable for SSBs in electric vehicles and flexible electronics, while GCEs are more favorable for portable electronic devices.

Solid garnet electrolytes can be divided into two categories. One is the polymer/garnet composite electrolytes (PGEs), where garnet particles are uniformly dispersed in a polymer matrix as a flexible electrolyte membrane. The other is garnet ceramic electrolytes (GCEs), in which pure garnet composition is obtained by sintering at high temperatures. PGEs and GCEs show different typical advantages and drawbacks. PGEs generally stand out for their excellent flexibility to ensure good contact with electrodes, high mechanical strength in the form of a “polymer-in-ceramic” configuration to suppress Li dendrite growth,<sup>11</sup> and easy transition for manufacturing based on the matured LiB facilities. However, most PGEs are limited by the low ionic conductivity ( $<10^{-4} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ ) that hinders room-temperature applications. The electrochemical instability of polymer components at high voltages ultimately restricts the use of high-voltage cathodes.<sup>12</sup> In comparison, GCEs show much higher ionic conductivities and larger electrochemical windows than PGEs. Particularly, effective element doping (e.g., Ta and Nb) into LLZO can further enhance the room-temperature conductivity to over  $10^{-3} \text{ S cm}^{-1}$  because of the increased  $\text{Li}^+$  vacancies as hopping sites.<sup>13</sup> The high thermodynamic stability of GCEs can even enable applications in extreme environments such as aerospace. However, the mechanical stiffness and brittleness of GCEs not only cause interfacial problems with electrodes but also bring extra difficulties in battery fabrication. Nonetheless, PGEs and GCEs with distinct advantages are likely suitable for

different applications with different requirements. PGEs could be a good fit for SSBs in electric vehicles and flexible electronics, while GCEs could be more favorable for portable electronic devices. Further tuning their surface chemistries can potentially minimize the disadvantages for wider and more effective practice.

Surface chemistry of SSEs is directly related to the solid–solid interfacial properties and thus significantly affects the electrochemical performance of SSBs. Solid garnet electrolytes were initially believed to be chemically stable in ambient atmosphere, but recently, empirical and computational studies pointed out the harmful formation of  $\text{Li}_2\text{CO}_3$  in air upon reactions with moisture and  $\text{CO}_2$ . The influence of surface  $\text{Li}_2\text{CO}_3$  coverage on garnets has long been overlooked until the lithiophobic demonstration of the  $\text{Li}_2\text{CO}_3$  passivated garnets and the excellent lithiophilicity of pristine garnet surfaces.<sup>14</sup> The surface  $\text{Li}_2\text{CO}_3$  layer is also related to low ionic conductivity of PGEs and low density of GCEs. So far, various intermediate coatings have been proposed to enhance the interfacial wettability with molten Li but with little comparison between surface coatings and recovery of a pristine garnet surface in terms of interface stability, Li dendrite suppression, and cycling performance.

In this Perspective, we focus on the surface  $\text{Li}_2\text{CO}_3$  of garnet electrolytes toward GCEs/PGEs fabrication and interfacial construction. The air stability of garnet electrolytes and underlying fundamentals are discussed from reaction mechanisms to determining factors. Different surface engineering strategies are summarized, including rational component design, post-treatment, and efficient conversion. The influence of  $\text{Li}_2\text{CO}_3$  on both GCE/Li and GCE/cathode is discussed in detail. Answers to the following questions can be found in this Perspective as future design guidelines for garnet electrolytes. Can  $\text{Li}_2\text{CO}_3$  impurities occur inside of a dense garnet pellet? How is the growth of the  $\text{Li}_2\text{CO}_3$  layer upon aging? Should any intermediate layers be eliminated when the GCEs are intrinsically lithiophilic? Is a small amount

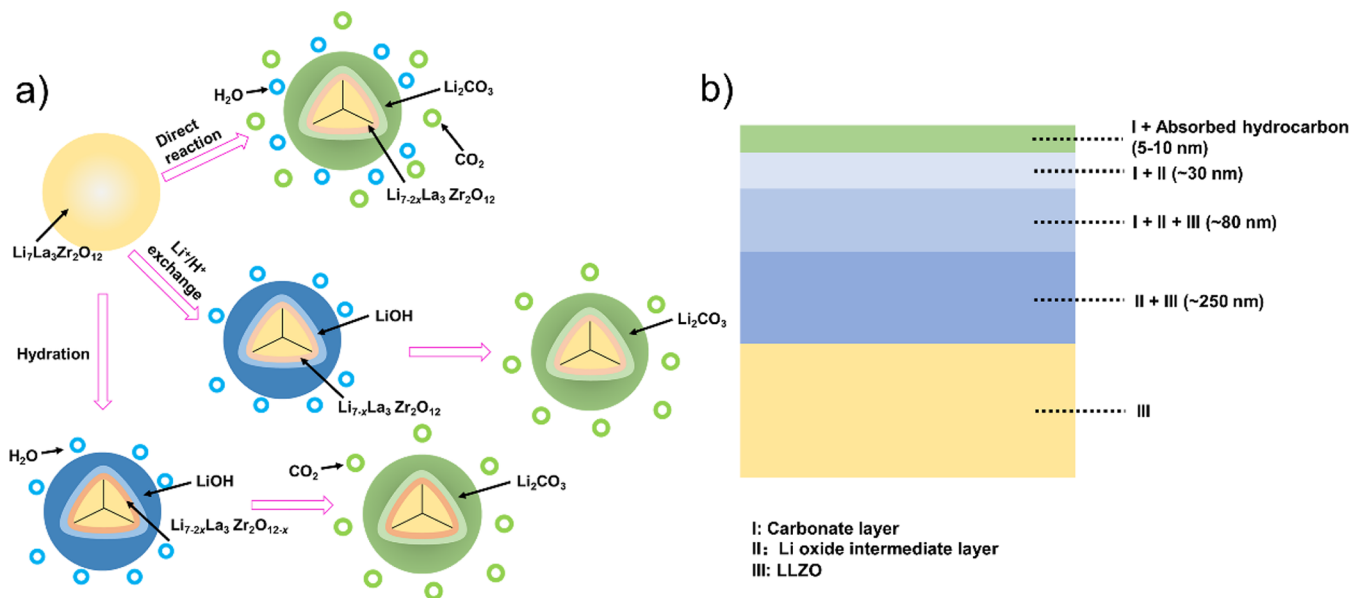
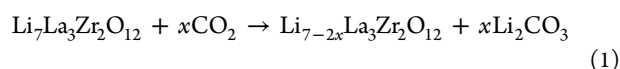


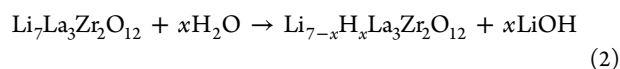
Figure 1. (a) Reaction pathways of garnet electrolytes with air (using LLZO, for example). (b) Schematic outlining the contamination layers on the surface of a garnet electrolyte; the compositions and layer thicknesses were characterized by XPS analysis and accompanied depth profiling. (Copyright Royal Society of Chemistry, reprinted with permission from ref 19.)

of liquid a good compromise for the cathode interface? On the basis of our recent progress and other valuable reports, we conclude several important design factors for constructing a robust garnet/electrode interface. Practical solid garnet batteries shall be realized in the near future depending on the in-depth understanding and precise control of garnet surface chemistry.

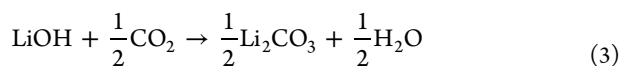
In fact, the  $\text{Li}_2\text{CO}_3$  contaminants can be difficult to avoid. The protonation might occur as early as during the cooling of garnet samples in the furnace after calcination.<sup>15</sup> Different pathways have been proposed to describe the reactions between air and garnet (Figure 1a). Some studies reported a single-step reaction pathway, where the garnet directly reacts with dry  $\text{CO}_2$  to form  $\text{Li}_2\text{CO}_3$  (eq 1, using LLZO as an example).<sup>16,17</sup>



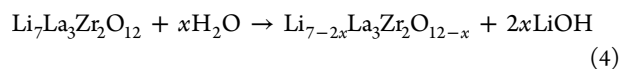
Although the direct reaction is a thermodynamically favorable route according to density functional theory (DFT) calculations, this reaction pathway is kinetically slow considering the negligible amount of  $\text{Li}_2\text{CO}_3$  formed on garnet samples after exposure in dry air. A more widely accepted reaction pathway includes two steps. First, the moisture in air reacts with LLZO to form  $\text{LiOH}$  by  $\text{Li}^+/\text{H}^+$  ion exchange (eq 2).<sup>14,18</sup>



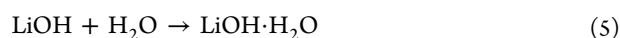
The  $\text{LiOH}$  subsequently reacts with  $\text{CO}_2$  to form  $\text{Li}_2\text{CO}_3$  on the surface of the garnet (eq 3).<sup>19</sup>



Spontaneous  $\text{Li}^+/\text{H}^+$  ion exchange was reported for various garnet oxides in aqueous solutions, such as  $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) and  $\text{Li}_7\text{La}_3\text{M}_2\text{O}_{12}$  ( $\text{M} = \text{Zr}, \text{Sn}$ ).<sup>20,21</sup> Such reactions do not change the cubic garnet structure but weaken the  $\text{Li}^+$  transport.<sup>22,23</sup> Alternatively, Cheng et al. reported the formation of Li-decent garnet and  $\text{LiOH}$  by hydration (eq 4), without  $\text{Li}^+/\text{H}^+$  ion exchange.<sup>24</sup>



However, Williams and Miller proposed that  $\text{LiOH}\cdot\text{H}_2\text{O}$  is a necessary intermediate and required precursor for the subsequent formation of  $\text{Li}_2\text{CO}_3$  after  $\text{Li}^+/\text{H}^+$  ion exchange (eq 5).



The amount of water should be sufficient to form a  $\text{LiOH}\cdot\text{H}_2\text{O}$  layer prior to or simultaneously with the  $\text{CO}_2$  reaction.<sup>25</sup> Although details of the sub- $\text{Li}_2\text{CO}_3$  surface chemistry and its related structural evolution remain unknown at the moment, the possible distributions of  $\text{LiOH}$  and  $\text{Li}_2\text{CO}_3$  in the contaminant layer are depicted in Figure 1b (LLZO samples exposed for up to 240 h in ambient air; relative humidity:  $\sim 50\%$ ).<sup>19,26</sup> Therefore, it is of great significance to develop in situ probing methods to understand the structural and chemical evolutions of the LLZO subsurface, thus promoting precise tuning of the surface properties by process designs.

On the basis of the fact that the grain boundaries and inner pores are more air-sensitive than the bulk, highly dense GCEs

(relative density:  $>99\%$ ) are expected to suppress  $\text{Li}_2\text{CO}_3$  generation inside of the ceramic pellets.<sup>16,27</sup> However, GCEs are difficult to densify. Even with high-temperature treatment over  $1000\text{ }^\circ\text{C}$  (at the risk of impurity formation by Li loss), it is difficult to achieve dense garnet ceramic pellets without the quality control of garnet powders. To obtain the green body before calcination, garnet powders are usually crushed by ball milling with a solvent (e.g., ethanol or isopropanol) and then dried in an oven. Such pretreatments often lead to a  $\text{Li}_2\text{CO}_3$  coating layer on the surface of garnet particles, but the surface  $\text{Li}_2\text{CO}_3$  contaminants are usually not taken into consideration because of the complete removal at high temperatures during calcination. In fact, the core-shell structure of garnet powders with a proton-rich garnet shell and a  $\text{Li}_2\text{CO}_3$  outer layer is opposed to the densification process due to the high surface reactivity.<sup>28</sup> In addition, an  $\text{Al}_2\text{O}_3$  crucible is commonly used as the container during the sintering process of garnet pellets. It was found that the pyrolytic  $\text{Li}_2\text{O}$  from  $\text{Li}_2\text{CO}_3$  can react with  $\text{Al}_2\text{O}_3$  at high temperatures, forming Li-Al-O impurities that hinder  $\text{Li}^+$  conduction.<sup>29</sup> Alternatively, fabrication of garnet pellets by the hot-pressing method is recommended because of the good control of powder quality and facile densification by high pressure.<sup>13</sup> The graphite mold instead of  $\text{Al}_2\text{O}_3$  crucible can avoid the formation of Al-containing impurities. The hot-pressed GCEs with a relative density over  $99.5\%$  show merged crystals. Fractured sections are mostly transgranular, evidencing the excellent grain boundary adhesion.<sup>30</sup> With little  $\text{Li}_2\text{CO}_3$  in the dense GCEs, a high ionic conductivity over  $10^{-3}\text{ S cm}^{-1}$  can be achieved at room temperature (RT).

Despite the efforts to simplify the garnet pellet fabrication by solid sintering at atmospheric pressure, the low relative density ( $<95\%$ ) and small grains with many grain boundaries could pose risks of reactions with air. Nevertheless, there are also conflicting reports about the effects of grain size on the air stability of LLZO. Cheng et al. pointed out that large-grained LLZO pellets can more easily form  $\text{Li}_2\text{CO}_3$  contaminants than the small-grained ones due to the distribution differences of Al and Li contents on the surface of Al-doped LLZO.<sup>16,31</sup> The higher Al and lower Li contents at small-grained sample surfaces lead to less  $\text{Li}_2\text{CO}_3$  formation upon air exposure, which is consistent with the experimental observations made by Janek et al.<sup>32</sup> In addition to the effects of materials microstructure, humidity and aging time are also key factors determining the amount of contaminants. Unlike artificially dense coating layers, the native  $\text{Li}_2\text{CO}_3$  layer is loose and susceptible to continuous  $\text{Li}^+/\text{H}^+$  ion exchange with humidity. The thickness of the  $\text{Li}_2\text{CO}_3$  layer on the LLZO pellet surface could increase from  $\sim 100\text{ nm}$  to  $\sim 1\text{ }\mu\text{m}$  by extending the aging time from 1 day to 6 months.<sup>16</sup>

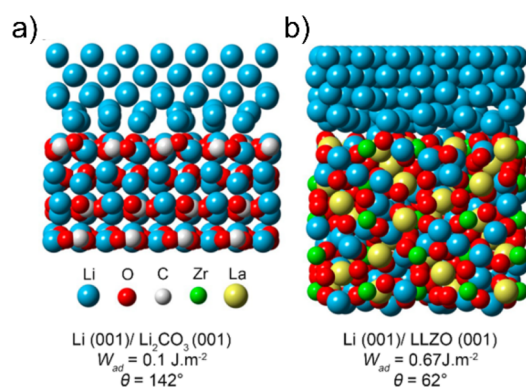
The formation of  $\text{Li}_2\text{CO}_3$  is harmful to GCEs in terms of both ionic conductivity and interfacial contact. Since  $\text{Li}_2\text{CO}_3$  preferentially forms along the grain boundaries because of the high interfacial energy,<sup>33</sup> the ultralow ionic conductivity ( $\sim 10^{-8}\text{ S cm}^{-1}$  at  $200\text{ }^\circ\text{C}$ ) of  $\text{Li}_2\text{CO}_3$  severely hinders  $\text{Li}^+$  mobility across grain boundaries and thus decreases the overall ionic conductivity.<sup>34</sup> Duan and Liu et al. reported an obvious drop in ionic conductivity of the Al-doped LLZO (relative density:  $89\%$ ) from  $1.81 \times 10^{-4}$  to  $2.39 \times 10^{-5}\text{ S cm}^{-1}$  after 3 month of air exposure.<sup>27</sup> Considering the GCE/Li interface, the area-specific resistance (ASR) needs to be smaller than  $100\text{ }\Omega\text{ cm}^2$  to achieve comparable electrochemical performance to traditional liquid-based LiBs.<sup>35</sup> Due



to the lithophobic nature and low conductivity of  $\text{Li}_2\text{CO}_3$ , even a thin  $\text{Li}_2\text{CO}_3$  layer of 10–100 nm can increase the interfacial resistance by an order of magnitude.<sup>24</sup> The large interfacial resistance ( $>1000 \Omega \text{ cm}^2$ ) and poor interfacial contact often lead to Li dendrite growth and rapid capacity decay of SSBs. Moreover, the presence of  $\text{Li}_2\text{CO}_3$  can also interrupt the cathode/GCE interface due to its reaction with conductive carbon above 3.2 V (eq 6), causing a deteriorated interface at the cathode side.<sup>36</sup>



Acknowledging that the large interfacial resistance originated from the  $\text{Li}_2\text{CO}_3$  contaminant, some recent studies focus on constructing a  $\text{Li}_2\text{CO}_3$ -free interface for Li anodes. A  $\text{Li}_2\text{CO}_3$ -free garnet surface is proved to be lithophilic, rendering good wettability with molten Li. Sakamoto et al. first quantified the relationships between different interfacial chemistries and Li wettability.<sup>14</sup> The large contact angles of Li with  $\text{Li}_2\text{CO}_3$  and LiOH are calculated by DFT as 142 and 125°, respectively, demonstrating poor wettability. The contact angle of 62° between  $\text{Li}_2\text{CO}_3$ -free LLZO and Li indicates intrinsic lithophilicity of garnet electrolytes (Figure 2). Guo et al. later experimentally observed the excellent



**Figure 2.** Calculated work of adhesion ( $W_{\text{ad}}$ ), contact angle ( $\theta$ ), and atomic structure for the (a) Li/ $\text{Li}_2\text{CO}_3$  and (b) Li/LLZO interfaces. (Copyright American Chemical Society, reprinted with permission from ref 14.)

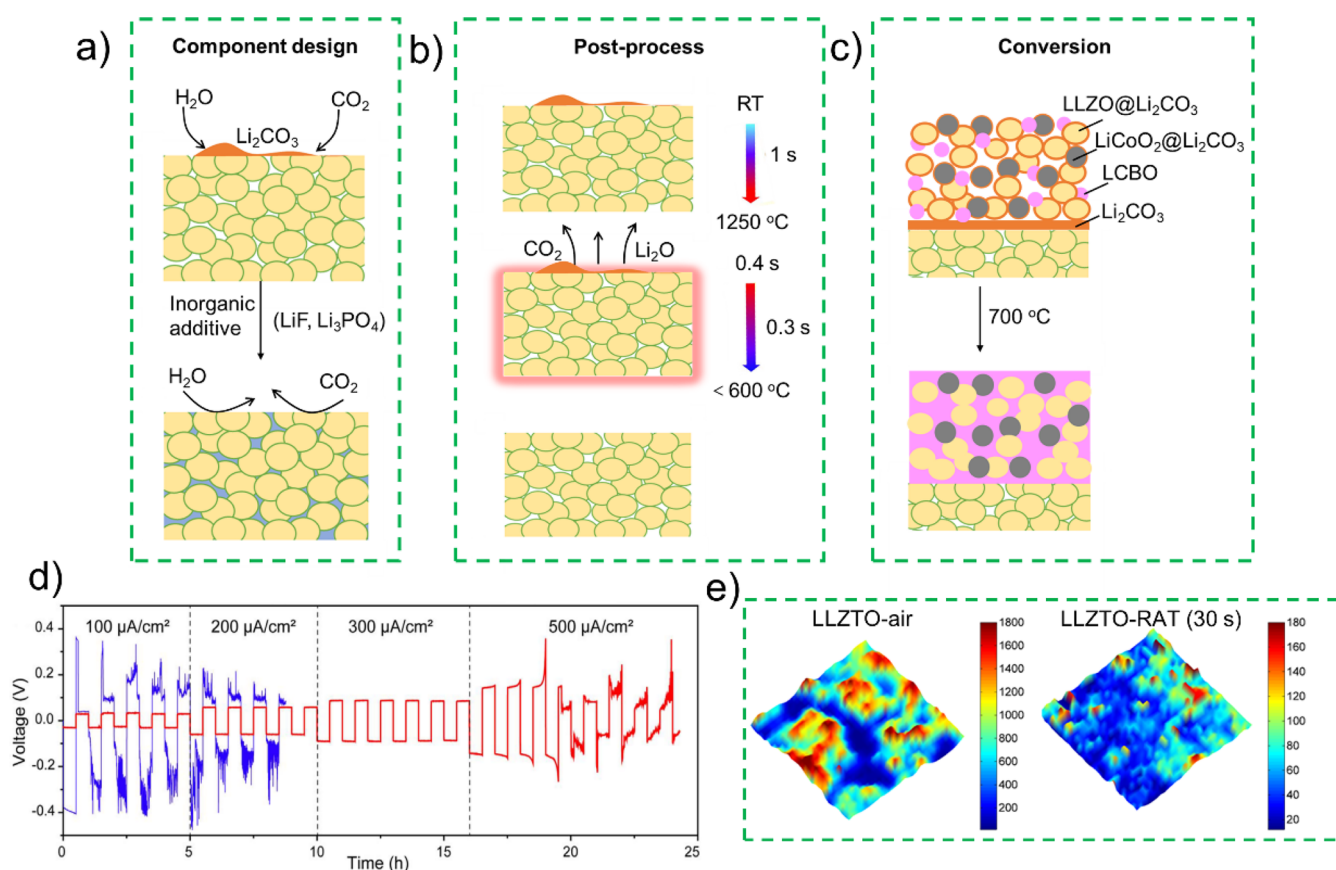
wettability between LLZO and Li.<sup>37</sup> Ga-, Al-, and Ta-doped LLZO electrolytes show similarly small contact angles of 56, 59.5, and 65°, respectively, in the absence of surface contaminants. Therefore,  $\text{Li}_2\text{CO}_3$ -free garnet electrolytes are generally considered lithophilic despite of element doping. In addition, the theoretical ASR of the GCE/Li interface is as low as  $0.01 \Omega \text{ cm}^2$ .<sup>38</sup> The activation energy ( $E_a$ ) of the GCE/Li interface is 0.33 eV, which is close to the  $E_a$  of the LLZO bulk ionic conductivity.<sup>24,39</sup> The low  $E_a$  is beneficial for the  $\text{Li}^+$  rapid migration across the interface at an elevated current density. Therefore, removal of surface  $\text{Li}_2\text{CO}_3$  contaminants is an excellent strategy to address the interfacial contact issue with Li metal anodes in SSBs.

Figure 3 summarizes the different surface engineering strategies to achieve a  $\text{Li}_2\text{CO}_3$ -free garnet/electrode interface. For the Li anode interface, one strategy is introduction of inorganic additives (e.g., LiF and  $\text{Li}_3\text{PO}_4$ ) into the GCE pellets to prevent the formation of  $\text{Li}_2\text{CO}_3$  (Figure 3a).<sup>40,41</sup> These additives are mixed with garnet powder and do not change the garnet structure after calcination. Zhou and

Goodenough et al. reported that adding 2 wt % LiF into Ta-doped LLZO (LLZTO) can effectively suppress the  $\text{Li}_2\text{CO}_3$  formation because of the excellent hydrophobicity of LiF with a strong ionic bonding. As a result, the LLZTO/Li interfacial resistance decreased from 1260 to  $345 \Omega \text{ cm}^2$  at 25 °C.<sup>40</sup> However, it is difficult to select a hydrophobic inorganic additive that does not interrupt the garnet structure nor lower the ionic conductivity. Machine learning and automated reaction screening may be a direction to guide the rational selection of additives before doping experiments in the future.

Another strategy is based on post-treatment to remove the formed  $\text{Li}_2\text{CO}_3$ . Common practices include mechanical polishing under an inert atmosphere and high-temperature treatment. However, mechanical polishing cannot completely remove the  $\text{Li}_2\text{CO}_3$  (especially those buried along grain boundaries) and may bring additional contaminations from the polishing paper. As for high-temperature treatments, annealing over 750 °C is required for complete removal of the  $\text{Li}_2\text{CO}_3$  and LiOH contaminants in forms of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .<sup>42</sup> A main drawback is the possible Li loss due to  $\text{Li}_2\text{O}$  evaporation at 600 °C, which can lead to impurity phase formation and poor  $\text{Li}^+$  conductivity.<sup>43</sup> When Guo et al. calcined the LLZO pellets at 900 °C in air for 24 h to remove  $\text{Li}_2\text{CO}_3$ , subsequent polishing was still required to avoid side effects from the Li-deficient impurity coatings.<sup>37</sup> It is favorable to develop an annealing method at lower temperatures that prevents Li loss while maintaining the cleaning effect. Goodenough et al. introduced carbon to react with  $\text{Li}_2\text{CO}_3$  in Ar at 700 °C, which perfectly eliminated  $\text{Li}_2\text{CO}_3$  contaminants for a lithophilic surface.<sup>36</sup> Dasgupta and Sakamoto combined wet polishing and annealing at 500 °C to achieve an intrinsic GCE surface with an interfacial resistance as low as  $2 \Omega \text{ cm}^2$  at RT.<sup>14</sup> Recently, Cheng et al. reported that heating LLZO at 250 °C under an inert atmosphere can reverse the surface degradation caused by air exposure and obtain a lowered interfacial resistance of  $178 \Omega \cdot \text{cm}^2$ .<sup>44</sup> The Li components of  $\text{Li}_2\text{CO}_3$  were able to recover back into the LLZO structure together with reversed  $\text{Li}^+/\text{H}^+$  ion exchange, given that these reverse reactions occurred more readily on the outer surface than at the subsurface. Feasible recovery of a  $\text{Li}_2\text{CO}_3$ -free lithophilic interface at low temperatures may simplify the manufacturing processes by less stringent moisture and  $\text{CO}_2$  controls. However, the origin of the lithophilic interface retrieved by thermal treatments remains a pending question. Ingenious characterizations and computational simulations are needed to trace the conversions between  $\text{Li}_2\text{O}$  and LiOH/ $\text{Li}_2\text{CO}_3$ .

Conventional thermal treatments using a furnace usually require several hours to ramp the temperature, which is time-consuming and energy-inefficient for practical battery manufacturing. Hu et al. demonstrated a novel thermal pulsing technique for rapid surface processing, which can clean the garnet surface contaminations in less than 2 s (Figure 3b).<sup>45</sup> The LLZO pellets were placed on top of a carbon-felt heater in an argon-filled glovebox, and the carbon felt strip was rapidly powered through Joule heating. The LLZO pellets were rapidly heated up from RT to 1250 °C in about 1 s, held at the temperature for about 0.4 s, and quenched in 0.3 s. The thermal pulsing treatment can effectively remove the  $\text{Li}_2\text{CO}_3$  impurity, leading to an increased critical current density from 0.1 to  $0.5 \text{ mA cm}^{-2}$  at 25 °C (Figure 3d). This approach is also suitable for garnet powders to minimize Li loss. In addition to the decomposition



**Figure 3.** Schematics of novel strategies of surface engineering to eliminate  $\text{Li}_2\text{CO}_3$  contaminants by (a) inorganic additives, (b) rapid thermal treatment, and (c) conversion reactions. (d) Voltage profiles of the Li symmetric cells cycled at different current densities. The blue curve is the cell with the untreated garnet, and the red curve is the cell with the thermal pulse-treated garnet. (Copyright Elsevier, reprinted with permission from ref 45.) (e) Raman mappings of the aged LLZTO pellet and LLZTO after rapid acid treatment (Copyright Elsevier, reprinted with permission from ref 30.)

of  $\text{Li}_2\text{CO}_3$  at high temperatures, Guo et al. proposed rapid acid treatment to chemically etch the  $\text{Li}_2\text{CO}_3$  passivation layer.<sup>30</sup> Even after aging the LLZTO pellets in air for 1 month, merely 30 s of HCl (1 M) treatment is enough to clean the surface  $\text{Li}_2\text{CO}_3$  without damaging the bulk pellets (Figure 3e).

A  $\text{Li}_2\text{CO}_3$ -free GCE surface solves the contact issue with Li metal anodes, but other challenges (e.g., high rate performance) remain unsettled. The interfacial resistance of a  $\text{Li}_2\text{CO}_3$ -free interface is comparable to that using various intermediate layers. However, at high current densities above  $1.0\text{ mA cm}^{-2}$ , short circuit due to metallic Li penetration still occurs. Various recent studies have tried to understand the relevant mechanisms and seek possible solutions. Han et al. revealed that the residual electronic conductivity of LLZO ceramic is the origin of dendrite formation in SSBs using neutron depth profiling (NDP).<sup>46</sup> The study by Guo et al. agrees that the injection of electrons could cause precipitation of metallic Li in polycrystalline garnets.<sup>47</sup> Therefore, an ionic conductive but electronic insulating intermediate layer is required at the GCE/Li interface to achieve comprehensive functionalities of preventing  $\text{Li}_2\text{CO}_3$  contaminant regeneration, blocking electron injection, and suppressing Li dendrite growth.

In addition to constructing a favorable initial GCE/Li interface, the interfacial stability is highly important because of the constantly changing interface upon plating and stripping of Li metal during repeated charge/discharge cycles. The

inflexible GCEs could easily detach from the fluctuating volume of Li metal and create hot spots for Li dendrite growth. Inspired by the three-dimensional Li metal anodes in liquid electrolytes, Hu et al. proposed a garnet-based bilayer structure with a dense layer as the separator and a porous extension layer accommodating Li metal to alleviate the volumetric influence.<sup>48</sup> As illustrated in Figure 4, an ideal GCE/Li interface should lead to a small interfacial resistance, high ionic conductivity, negligible electronic conductivity, and mechanical stability during electrochemical cycles.

$\text{Li}_2\text{CO}_3$  is commonly formed on the surface of lithiated cathode materials after air exposure. However, the effects of the  $\text{Li}_2\text{CO}_3$  layer on the electrochemical performance of cathodes are still elusive. On the one hand, the low ionic and electronic conductivities of the  $\text{Li}_2\text{CO}_3$  layer can hinder the ion/electron transport between cathode particles, thus decreasing the capacity and hindering the rate performance.<sup>49</sup> On the other hand,  $\text{Li}_2\text{CO}_3$  coatings were demonstrated as an artificial cathode–electrolyte interphase (CEI) for impeding the formation of unstable native CEIs and preserving the capacity retention.<sup>50</sup> Therefore, comprehensive assessments are required for different electrolytes and cathode materials.

The cathode/garnet interface in SSBs is currently less investigated compared to the Li/garnet interface. Not only intimate interfacial contacts but also high ionic and electronic conductivities are required for the cathode/SSE composites to achieve complete electrochemical reactions. Some attempts

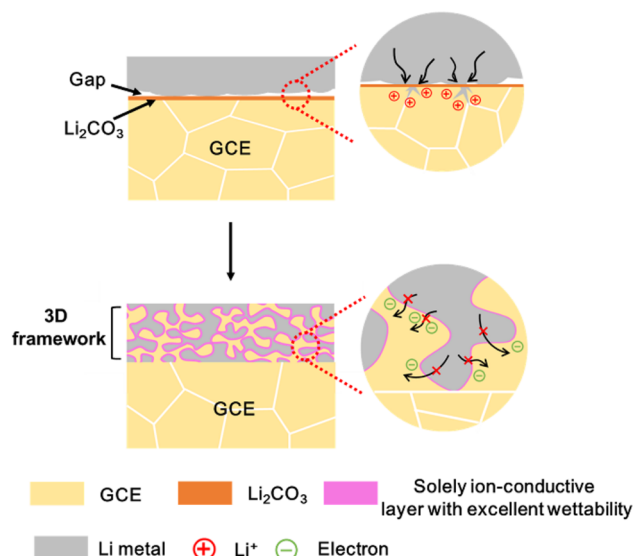


Figure 4. Schematic of an excellent garnet/Li interface for Li dendrite suppression.

have been made to minimize the interfacial resistance based on thin-film cathodes.<sup>39,51</sup> For example, Shingo Ohta et al. coated the LiCoO<sub>2</sub> (LCO) cathode on the surface of Nb-doped LLZO by pulsed laser deposition.<sup>39</sup> The ASR at the cathode interface was 170 Ω cm<sup>2</sup> after charging to 3.95 V vs Li<sup>+</sup>/Li, which is comparable to the liquid-based batteries. It is believed that Li<sub>2</sub>CO<sub>3</sub> removal can further decrease the cathode/garnet interfacial resistance.

To increase the cathode loading for practical application, co-sintering is a common approach to enhance interfacial contact. LCO is a favorable cathode material to co-sinter with garnet particles and sintering additives (e.g., Li<sub>3</sub>BO<sub>3</sub>) because the high electronic conductivity of LCO enables fast lithiation/delithiation without extra electronic conductive additives. However, the undesired surface Li<sub>2</sub>CO<sub>3</sub> on the garnet electrolyte and LCO not only impedes the Li<sup>+</sup> transportation in composite cathodes but also decreases the wettability between garnet/LCO and sintering additives. The partial contact of LCO and garnet due to incomplete coverage leads to severe side reactions between each other during sintering at high temperature, thus the low capacity of the all-solid-state garnet batteries. Han et al. proposed an innovative approach to address the Li<sub>2</sub>CO<sub>3</sub> issue by introducing a low-

Garnet electrolytes are not stable with conventional carbonate-based liquid electrolytes due to Li<sup>+</sup>/H<sup>+</sup> exchange. The decomposition of liquid electrolytes may lead to capacity fading of the batteries.

melting-point Li<sub>2.3</sub>C<sub>0.7</sub>B<sub>0.3</sub>O<sub>3</sub> intermediate phase (Figure 3c). The Li<sub>2.3</sub>C<sub>0.7</sub>B<sub>0.3</sub>O<sub>3</sub> can react with Li<sub>2</sub>CO<sub>3</sub> to form Li<sub>2.3-x</sub>C<sub>0.7+x</sub>B<sub>0.3-x</sub>O<sub>3</sub> (LCBO), which shows a higher Li<sup>+</sup> conductivity than that of Li<sub>2</sub>CO<sub>3</sub> by several orders of magnitude and even higher than that of the traditional Li<sub>3</sub>BO<sub>3</sub> additive. The thermal soldered LCO and LLZO by LCBO showed uniform distribution with a strong wetting property at the cathode interface. The interphase-engineered all-ceramic LCO/LLZO/Li cell delivered a stable capacity of 83 mAh g<sup>-1</sup> after 100 cycles under 0.05 C at 25 °C. Conversion of the Li<sub>2</sub>CO<sub>3</sub> layer during co-sintering is proved to be effective for addressing the cathode interface issue. Higher ionic/electronic conductivities of the sintered interface at RT are expected to deliver better electrochemical performance for all-ceramic garnet batteries. Seeking other suitable sintering additives shall be an ongoing direction.

As a transition period from liquid batteries to all-solid-state batteries, a small amount of liquid is generally added to wet the interface between the cathode and garnet to demonstrate a working battery. Various liquids have been reported, including liquid electrolytes, ionic liquids, and low-melting-point plasticizers. The LiFePO<sub>4</sub>/LLZTO/Li cell with an interfacial wetted cathode interface can deliver a high specific capacity of 142.7 mAh g<sup>-1</sup> at 0.1 C and a high capacity retention of 82.1% after 150 cycles at RT.<sup>30</sup> However, Xu et al. reported that LLZO is not stable with the conventional carbonate-based liquid electrolytes due to Li<sup>+</sup>/H<sup>+</sup> exchange.<sup>52</sup> They further pointed out that the decomposition of liquid electrolytes may lead to the capacity fading of the batteries, while the superbase *n*-BuLi can effectively stabilize the LLZO/liquid electrolyte interface. Further understanding of the underlying interfacial reaction mechanisms is required, especially during the development of solid/liquid hybrid batteries.

The development of organic/inorganic hybrid solid-state membranes is highly dependent on the choice and properties

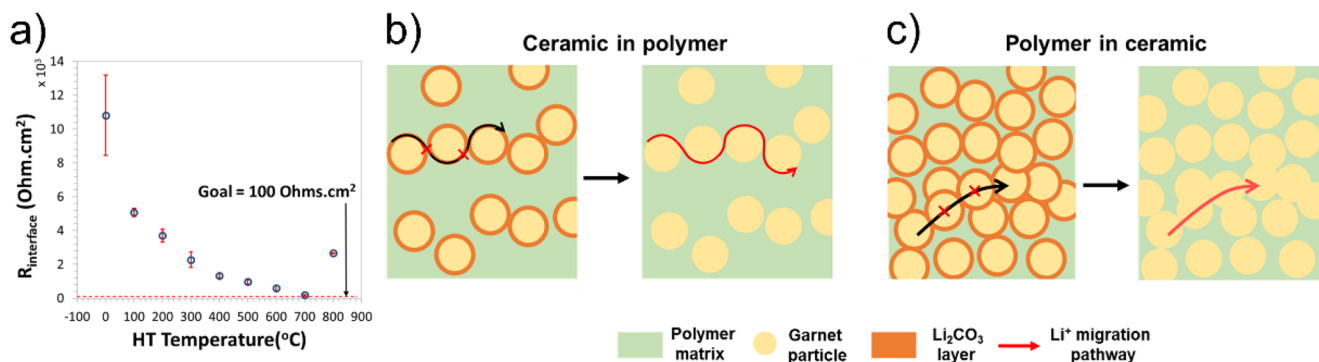


Figure 5. (a) Effect of Li<sub>2</sub>CO<sub>3</sub> on the interfacial resistance between PEO-LiTFSI and LLZTO at 30 °C. (Copyright Electrochemical Society, reprinted with permission from ref 56.) Schematics presenting (b) highly conductive interfacial pathways in “ceramic-in-polymer” PGEs and (c) highly conductive garnet bulk pathways in “polymer-in-ceramic” PGEs by removing surface Li<sub>2</sub>CO<sub>3</sub> of the garnet particles.



of fillers, where conductive electrolyte fillers are relatively attractive. A practical hybrid electrolyte should meet the following requirements: (1) ionic conductivity above  $10^{-4}$  S  $\text{cm}^{-2}$  at RT, (2) a large electrochemical window over 5 V, (3) a stable and robust interface between SSEs and electrodes for smooth  $\text{Li}^+$  transport, and (4) be mechanically strong to suppress Li dendrite proliferation.<sup>12</sup> Rationally designed PGEs can take advantage of the merits of both polymer electrolytes and garnet-type SSEs. An appropriate proportion of garnet particles can decrease the crystallinity by interrupting the polymer chains for enhanced ionic conductivity while maintaining the mechanical strength for lithium dendrite suppression. Various polymers have been studied as the matrix for PGEs, including poly(ethylene oxide) (PEO),<sup>53</sup> poly(vinylidene fluoride) (PVDF),<sup>54</sup> and poly(propylene carbonate) (PPC).<sup>55</sup>

Garnet powders are more sensitive to moist air than the dense GCE pellets. However, the polymer matrix can resist  $\text{Li}_2\text{CO}_3$  formation at the PGEs/electrode interfaces. The flexible polymers can also achieve good interfacial contact with low resistance. Therefore, the presence of  $\text{Li}_2\text{CO}_3$  mainly affects the  $\text{Li}^+$  conduction within the PGEs. Sakamoto et al. studied ionic transport through the PEO-LiTFSI/LLZTO interface with the effect of  $\text{Li}_2\text{CO}_3$ .<sup>56</sup> The untreated LLZTO pellets showed interfacial ASR over  $10 \text{ k}\Omega \text{ cm}^2$  at  $30^\circ\text{C}$  due to the  $\text{Li}_2\text{CO}_3$  surface layer as a barrier of charge transfer between PEO-LiTFSI and LLZTO (Figure 5a). The uncontrollable initial thickness of the  $\text{Li}_2\text{CO}_3$  layer also led to the large ASR variability ( $2.38 \text{ k}\Omega \text{ cm}^2$ ) for the untreated LLZTO samples. It was observed that the higher the heat-treatment temperature, the lower the interfacial ASR of the cell. The lowest interfacial ASR ( $180 \Omega \text{ cm}^2$ ) was achieved by a heat treatment of  $700^\circ\text{C}$ , which is close to the decomposition temperature of  $\text{Li}_2\text{CO}_3$ . It indicates that a  $\text{Li}_2\text{CO}_3$ -free polymer/garnet interface has faster  $\text{Li}^+$  transportation capability. The ionic conductivity of PGEs can be increased if the  $\text{Li}_2\text{CO}_3$  layers are removed from the surface of garnet particles.

In fact, the  $\text{Li}^+$  conductive mechanism in PGEs is much more complicated than that of the simple model, where PEO-LiTFSI is coated on the LLZTO pellets. The introduction of garnet particles into polymers can result in various interactions among garnet, Li salt, and the polymer matrix, such as dissolution improvement of Li salt, crystallinity decrease of the polymer, and acid–base interactions between each other.<sup>54</sup> Identifying the  $\text{Li}^+$  migration pathways can not only be beneficial for understanding the effect of  $\text{Li}_2\text{CO}_3$  but also guide the rational design of advanced PGEs with excellent ionic conductivity. In general, there are three  $\text{Li}^+$  conductive pathways in PGEs, including the polymer, polymer/garnet interface, and garnet bulk. The different  $\text{Li}^+$  migration pathways can be changed or show a synergistic effect when various amounts of garnet particles are introduced into the PGEs. It is generally acknowledged that the  $\text{Li}^+$  is mainly transported in the polymer phase when the content of garnets is low in polymer-rich PGEs, while  $\text{Li}^+$  mainly migrates in the garnet bulk when a large content of garnets makes up ceramic-rich PGEs. The controversy focuses on the polymer/garnet interfacial conduction. Many groups reported the ionic conductivity threshold of PGEs based on nonconductive fillers (e.g.,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ) or conductive electrolyte fillers (e.g., LLZO).<sup>57,58</sup> They attributed the optimized conductivity to the highly conductive interfacial conduction beneficial from

the percolation effect. The interfacial conduction has some positive effects on the ionic conductivity. For example, the LLZTO with smaller size or nanofiber shape exhibited higher ionic conductivity due to the increased interfaces between LLZTO and PEO.<sup>58,59</sup> The finite-element simulations also confirmed the possibility of  $\text{Li}^+$  transport at the interface.<sup>60</sup> However, some researchers argued that the continuous interfacial pathway, as the key factor of the percolation effect, is hard to construct, considering the tendency of filler agglomeration in PGEs; even if the continuous interfacial pathway is formed, the connected garnet particles can also conduct  $\text{Li}^+$  from the bulk pathway. Li nuclear magnetic resonance (NMR) further indicated a preferential  $\text{Li}^+$  pathway through the ceramic phase in a PEO/LLZO-based PGE rather than the PEO/LLZO interface.<sup>61</sup>

Figure 5b,c shows the possible effects of  $\text{Li}_2\text{CO}_3$  on the PGEs. Due to its much lower ionic conductivity compared with that of the garnet electrolyte,  $\text{Li}_2\text{CO}_3$  may hinder the  $\text{Li}^+$  rapid migration along the polymer/garnet interface in the “ceramic-in-polymer” PGEs, while  $\text{Li}_2\text{CO}_3$  may impede the  $\text{Li}^+$  conduction through garnet bulk in “polymer-in-ceramic” PGEs. Further investigation by advanced characterization techniques is required, such as NMR, neutron diffraction, and STXM (synchrotron scanning transmission X-ray microscopy). To remove the  $\text{Li}_2\text{CO}_3$  on the surface of garnet particles, traditional high-temperature treatments show little effect due to the  $\text{Li}_2\text{CO}_3$  formation again during natural cooling. The rapid thermal pulse method (Figure 3b) is recommended because the rapid cleaning process prevents the garnet phase decomposition and  $\text{Li}_2\text{CO}_3$  formation again. The PGEs using LLZO fillers with or without  $\text{Li}_2\text{CO}_3$  should be assessed in terms of the ionic conductivity, electrochemical window,  $\text{Li}^+$  transference number, and capability of  $\text{Li}^+$  dendrite suppression. It is highly expected that something new will be obtained in the near future.

Interference of  $\text{Li}_2\text{CO}_3$  at the polymer/garnet interface makes the  $\text{Li}^+$  conduction mechanism in PGEs much more complicated, where advanced characterization techniques are required for further investigation.

Solid garnet batteries are very promising for next-generation energy storage systems due to the enhancement of energy density and guarantee of safety. However, various critical issues have hindered their commercialization, such as Li dendrite growth, high interfacial resistance, and poor rate performance. The mechanisms behind are complex and require special assessments. Formation of surface  $\text{Li}_2\text{CO}_3$  due air exposure is reported as a common impurity coating on the garnet electrolytes. Its effects on solid garnet batteries have been discussed in detail in this Perspective from electrolyte fabrication to interface construction. Here, we provide our perspectives regarding the  $\text{Li}_2\text{CO}_3$  issue for better constructing solid garnet batteries (Figure 6):

- (1) In order to improve the air stability and suppress the  $\text{Li}_2\text{CO}_3$  formation, abundant experiences can be learned from sulfide electrolytes. In fact, sulfide electrolytes are much more air-sensitive compared with garnet electrolytes. However, their air stability can be greatly

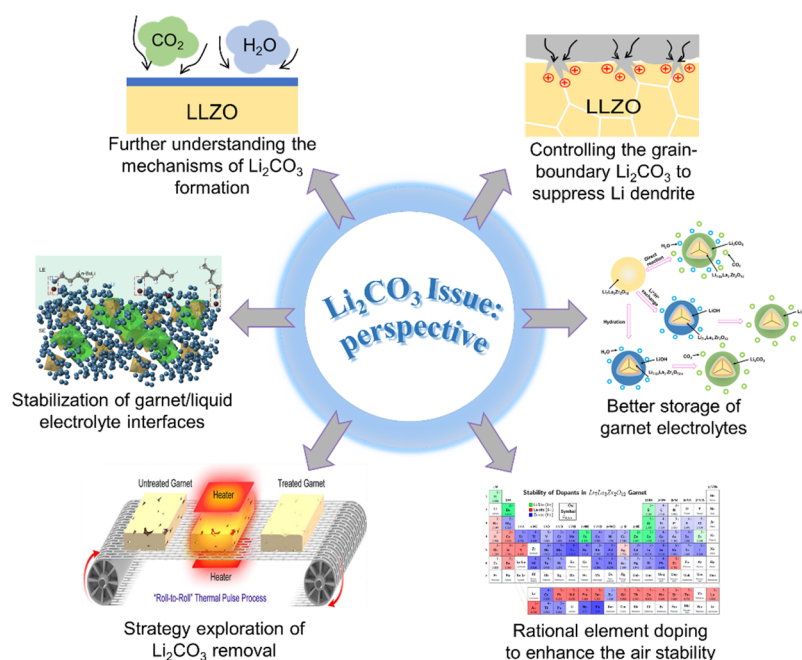


Figure 6. Perspectives of developing solid garnet batteries based on the  $\text{Li}_2\text{CO}_3$  issue. (Copyright Elsevier, reprinted with permission from ref 45; Copyright American Chemical Society, reprinted with permission from refs 52 and 63.)

improved by rational element doping based on the hard and soft acids and bases theory. It is highly expected that element doping can also enhance the air stability of garnet electrolytes and suppress the formation of  $\text{Li}_2\text{CO}_3$ . Further understanding the reaction mechanisms and finding targeted strategies are critically important for rational selection of doping elements.<sup>62</sup> Machine learning and automated reaction screening may be a direction to guide the element selection before doping experiments in the future.

- (2) The first step of  $\text{Li}_2\text{CO}_3$  formation is the reaction between  $\text{H}_2\text{O}$  and garnet electrolytes by  $\text{Li}^+/\text{H}^+$  exchange. Therefore, controlling the moisture content to a low level is important for storing garnet electrolytes. A dry room or a glovebox is usually used to store garnet electrolytes. However, the  $\text{Li}_2\text{CO}_3$  still gradually forms on the surface of garnet electrolytes due to the inevitable  $\text{H}_2\text{O}$  in the dry room or volatile organic electrolytes in the glovebox. Surface polishing in an inert atmosphere may be required before the use of GCEs. Some weak acids can be added during ball milling of garnet powder to protect it against air corrosion.
- (3) The high electronic conductivity of GCEs was reported as the origin of Li dendrite proliferation.<sup>46</sup> The grain boundaries as inner defect sites can easily trap electrons compared to the garnet bulk, thus guiding the isolated Li nucleation inside of the GCEs and proliferation along the grain boundaries. On the other hand,  $\text{Li}_2\text{CO}_3$  preferentially forms along the grain boundaries upon air exposure. It is generally acknowledged that the grain-boundary  $\text{Li}_2\text{CO}_3$  leads to the decreased ionic conductivity of GCEs due to its ultralow ionic conductivity. However,  $\text{Li}_2\text{CO}_3$  is also an electronic insulator. Whether the grain-boundary  $\text{Li}_2\text{CO}_3$  can suppress the Li dendrite nucleation inside of the GCEs is an interesting question. Precisely controlled

growth of grain-boundary  $\text{Li}_2\text{CO}_3$  could be a promising approach to achieve both high ionic conductivity and excellent capability of Li dendrite suppression for the GCEs.

- (4) Recent publications indicate that the interface kinetics and its morphological stability during cycling can affect the Li dendrite growth and not only the interfacial wettability at an initial stage.<sup>63,64</sup> Although both  $\text{Li}_2\text{CO}_3$ -free garnet/Li interfaces and garnet/Li interfaces with lithiophilic coatings (e.g.,  $\text{Al}_2\text{O}_3$ , Si, and Sn) show similarly low interfacial resistances before cycling, the different effects on long-term interface stability upon repeated cycling remain unclear. Operando techniques are helpful for studying the relationship between the interface evolution and dendrite growth during cycling, such as in-operando electrochemical impedance spectroscopy (EIS) and in-operando scanning electron microscope (SEM). In addition, combining surface coating of an ion-conductive but electronic-insulating layer with surface  $\text{Li}_2\text{CO}_3$  removal may be a promising strategy to realize excellent interfacial stability and Li dendrite suppression.
- (5) The stability between garnet electrolytes and various liquid electrolytes should be studied in detail because a small amount of liquid electrolyte is usually added to wet the garnet/cathode interfaces. It may be a complex chain reaction from the  $\text{Li}^+/\text{H}^+$  exchange to the decomposition of liquid electrolytes.<sup>52</sup> For the solid/liquid hybrid cells, a balance between the decrease of the liquid content as much as possible and feasible electrochemical performance remains challenging. More studies are expected to pave the way for all-solid-state batteries.
- (6) Studies on the  $\text{Li}^+$  conduction mechanism in PGEs are important for PGE designs. However, the polymer/garnet interface as a highly conductive  $\text{Li}^+$  migration pathway by a percolation effect remains controversial.



The interference of the  $\text{Li}_2\text{CO}_3$  passivation layer at the interface makes the  $\text{Li}^+$  conduction mechanism much more complicated. Advanced characterization techniques such as NMR, neutron diffraction, and STXM are powerful tools to investigate the interfacial  $\text{Li}^+$  transport. It is believed that a  $\text{Li}_2\text{CO}_3$ -free polymer/garnet interface can enhance the ionic conductivity to some extent. In addition, the essential electrochemical properties need to be revisited when  $\text{Li}_2\text{CO}_3$  is removed in the PGEs, including the electrochemical window and  $\text{Li}^+$  transference number.

## AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: [xxguo@qdu.edu.cn](mailto:xxguo@qdu.edu.cn).

\*E-mail: [cwnan@mail.tsinghua.edu.cn](mailto:cwnan@mail.tsinghua.edu.cn).

\*E-mail: [xsun9@uwo.ca](mailto:xsun9@uwo.ca).

### ORCID

Venkataraman Thangadurai: 0000-0001-6256-6307

Xueliang Sun: 0000-0003-0374-1245

### Notes

The authors declare no competing financial interest.

### Biographies

**Hanyu Huo** obtained his B.E. at Shandong University in 2015. He is currently a Ph.D. candidate under the supervision of Prof. Xiangxin Guo and Prof. Xueliang (Andy) Sun. His research interests focus on solid-state batteries and Li metal batteries. He received the CAS Presidential Scholarship (Excellence Award) in 2019.

**Jing Luo** received her M.S. degree from National Taiwan University (Taiwan) in 2016. She is now pursuing her Ph.D. degree in Prof. Xueliang (Andy) Sun's group at the University of Western Ontario, Canada. Her current research interests focus on atomic layer deposition in the application of Li-ion batteries and polymer-based solid-state batteries.

**Venkataraman Thangadurai** is a full professor of chemistry at the University of Calgary, Canada. He is a Fellow of the Royal Society of Chemistry, United Kingdom. In 2016, he received the prestigious Keith Laidler Award from the Canadian Society of Chemistry. He has published over 180 papers in refereed journals.

**Xiangxin Guo** is currently a full professor at the College of Physics, Qingdao University under the funding of the "Taishan Scholars Program". His research focuses on solid garnet batteries, metal-air batteries, and heterostructure-based solid-state ionic devices.

**Ce-Wen Nan** is a professor in the Department of Materials Science and Engineering, Tsinghua University. Prof. Nan's research focuses on functional materials, including multiferroic magnetoelectric materials, thermoelectric oxides, functional polymer-based composites, and solid-state electrolytes.

**Xueliang (Andy) Sun** is a Canada Research Chair in Development of Nanomaterials for Clean Energy, Fellow of the Royal Society of Canada and Canadian Academy of Engineering, and Full Professor at the University of Western Ontario, Canada. His current research interests focus on advanced materials for electrochemical energy storage and conversion.

## ACKNOWLEDGMENTS

The authors would like to thank the National Key R&D Program of China (Grant No. 2018YFB0104300), the National Natural Science Foundation of China (Grant No.

51771222, 51532002), the Project of Qingdao Leading talents in Entrepreneurship and innovation "Taishan Scholars Program", the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Research Chair Program (CRC), and the University of Western Ontario.

## REFERENCES

- (1) Sun, C.; Liu, J.; Gong, Y.; Wilkinson, D. P.; Zhang, J. Recent advances in all-solid-state rechargeable lithium batteries. *Nano Energy* **2017**, *33*, 363–386.
- (2) Zhao, N.; Khokhar, W.; Bi, Z.; Shi, C.; Guo, X.; Fan, L.-Z.; Nan, C.-W. Solid Garnet Batteries. *Joule* **2019**, *3* (5), 1190–1199.
- (3) Thangadurai, V.; Pinzaru, D.; Narayanan, S.; Baral, A. K. Fast Solid-State Li Ion Conducting Garnet-Type Structure Metal Oxides for Energy Storage. *J. Phys. Chem. Lett.* **2015**, *6* (2), 292–9.
- (4) Thangadurai, V.; Adams, S.; Weppner, W. Crystal structure revision and identification of  $\text{Li}^+$ -ion migration pathways in the garnet-like  $\text{Li}_3\text{La}_3\text{M}_2\text{O}_{12}$  (M= Nb, Ta) oxides. *Chem. Mater.* **2004**, *16* (16), 2998–3006.
- (5) Thangadurai, V.; Weppner, W.  $\text{Li}_6\text{AlLa}_2\text{Nb}_2\text{O}_{12}$  (A= Ca, Sr, Ba): A New Class of Fast Lithium Ion Conductors with Garnet-Like Structure. *J. Am. Ceram. Soc.* **2005**, *88* (2), 411–418.
- (6) Murugan, R.; Thangadurai, V.; Weppner, W. Fast lithium ion conduction in garnet-type  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ . *Angew. Chem., Int. Ed.* **2007**, *46* (41), 7778–81.
- (7) Geiger, C. A.; Alekseev, E.; Lazic, B.; Fisch, M.; Armbruster, T.; Langner, R.; Fechtelkord, M.; Kim, N.; Pettke, T.; Weppner, W. Crystal chemistry and stability of " $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ " garnet: a fast lithium-ion conductor. *Inorg. Chem.* **2011**, *50* (3), 1089–1097.
- (8) 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* (10), 2957–2975.
- (9) Ramakumar, S.; Deviannapoorani, C.; Dhivya, L.; Shankar, L. S.; Murugan, R. Lithium garnets: synthesis, structure,  $\text{Li}^+$  conductivity,  $\text{Li}^+$  dynamics and applications. *Prog. Mater. Sci.* **2017**, *88*, 325–411.
- (10) Hofstetter, K.; Samson, A. J.; Narayanan, S.; Thangadurai, V. Present understanding of the stability of Li-stuffed garnets with moisture, carbon dioxide, and metallic lithium. *J. Power Sources* **2018**, *390*, 297–312.
- (11) 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.
- (12) Zhou, D.; Shanmukaraj, D.; Tkacheva, A.; Armand, M.; Wang, G. Polymer Electrolytes for Lithium-Based Batteries: Advances and Prospects. *Chem.* **2019**, *5* (9), 2326–2352.
- (13) Du, F.; Zhao, N.; Li, Y.; Chen, C.; Liu, Z.; Guo, X. All solid state lithium batteries based on lamellar garnet-type ceramic electrolytes. *J. Power Sources* **2015**, *300*, 24–28.
- (14) 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* (18), 7961–7968.
- (15) Wagner, R.; Rettenwander, D.; Redhammer, G. J.; Tippelt, G.; Sabathi, G.; Musso, M. E.; Stanje, B.; Wilkening, M.; Suard, E.; Amthauer, G. Synthesis, Crystal Structure, and Stability of Cubic  $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Bi}_x\text{O}_{12}$ . *Inorg. Chem.* **2016**, *55* (23), 12211–12219.
- (16) Cheng, L.; Wu, C. H.; Jarry, A.; Chen, W.; Ye, Y.; Zhu, J.; Kostecki, R.; Persson, K.; Guo, J.; Salmeron, M.; Chen, G.; Doeff, M. Interrelationships among Grain Size, Surface Composition, Air Stability, and Interfacial Resistance of Al-Substituted  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Solid Electrolytes. *ACS Appl. Mater. Interfaces* **2015**, *7* (32), 17649–55.
- (17) Truong, L.; Howard, M.; Clemens, O.; Knight, K. S.; Slater, P. R.; Thangadurai, V. Facile proton conduction in  $\text{H}^+/\text{Li}^+$  ion-

exchanged garnet-type fast Li-ion conducting  $\text{Li}_3\text{La}_3\text{Nb}_2\text{O}_{12}$ . *J. Mater. Chem. A* **2013**, *1* (43), 13469.

(18) Ma, C.; Rangasamy, E.; Liang, C.; Sakamoto, J.; More, K. L.; Chi, M. Excellent stability of a lithium-ion-conducting solid electrolyte upon reversible  $\text{H}^+/\text{Li}^+$  exchange in aqueous solutions. *Angew. Chem., Int. Ed.* **2015**, *54* (1), 129–33.

(19) 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  $\text{Li}-\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  interfacial resistance. *J. Mater. Chem. A* **2017**, *5* (26), 13475–13487.

(20) Truong, L.; Thangadurai, V. Soft-Chemistry of Garnet-Type  $\text{Li}_{5-x}\text{Ba}_x\text{La}_{3-x}\text{Nb}_2\text{O}_{12}$  ( $x=0, 0.5, 1$ ): Reversible  $\text{H}^+\leftrightarrow\text{Li}^+$  Ion-Exchange Reaction and Their X-ray,  $^7\text{Li}$  MAS NMR, IR, and AC Impedance Spectroscopy Characterization. *Chem. Mater.* **2011**, *23* (17), 3970–3977.

(21) Truong, L.; Thangadurai, V. First total  $\text{H}^+/\text{Li}^+$  ion exchange in garnet-type  $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$  using organic acids and studies on the effect of Li stuffing. *Inorg. Chem.* **2012**, *51* (3), 1222–1224.

(22) Liu, C.; Rui, K.; Shen, C.; Badding, M. E.; Zhang, G.; Wen, Z. Reversible ion exchange and structural stability of garnet-type Nb-doped  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  in water for applications in lithium batteries. *J. Power Sources* **2015**, *282*, 286–293.

(23) Howard, M.; Clemens, O.; Kendrick, E.; Knight, K.; Apperley, D.; Anderson, P.; Slater, P. Effect of Ga incorporation on the structure and Li ion conductivity of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ . *Dalton Transactions* **2012**, *41* (39), 12048–12053.

(24) Cheng, L.; Crumlin, E. J.; Chen, W.; Qiao, R.; Hou, H.; Franz Lux, S.; Zorba, V.; Russo, R.; Kostecki, R.; Liu, Z.; Persson, K.; Yang, W.; Cabana, J.; Richardson, T.; Chen, G.; Doeff, M. The origin of high electrolyte-electrode interfacial resistances in lithium cells containing garnet type solid electrolytes. *Phys. Chem. Chem. Phys.* **2014**, *16* (34), 18294–300.

(25) Pinzaru, D.; Thangadurai, V. Synthesis, Structure and Li Ion Conductivity of Garnet-like  $\text{Li}_{5+2x}\text{La}_3\text{Nb}_{2-x}\text{Sm}_x\text{O}_{12}$  ( $0 \leq x \leq 0.7$ ). *J. Electrochem. Soc.* **2014**, *161* (14), A2060–A2067.

(26) Xia, W.; Xu, B.; Duan, H.; Tang, X.; Guo, Y.; Kang, H.; Li, H.; Liu, H. Reaction mechanisms of lithium garnet pellets in ambient air: The effect of humidity and  $\text{CO}_2$ . *J. Am. Ceram. Soc.* **2017**, *100* (7), 2832–2839.

(27) Xia, W.; Xu, B.; Duan, H.; Guo, Y.; Kang, H.; Li, H.; Liu, H. Ionic Conductivity and Air Stability of Al-Doped  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Sintered in Alumina and Pt Crucibles. *ACS Appl. Mater. Interfaces* **2016**, *8* (8), 5335–42.

(28) Aguesse, F.; López del Amo, J. M.; Roddatis, V.; Aguadero, A.; Kilner, J. A. Enhancement of the grain boundary conductivity in ceramic  $\text{Li}_{0.34}\text{La}_{0.55}\text{TiO}_3$  electrolytes in a moisture-free processing environment. *Adv. Mater. Interfaces* **2014**, *1* (7), 1300143.

(29) Lan, W. Investigation of  $\text{Al}_2\text{O}_3$  Crucible Contamination induced by extra  $\text{Li}_2\text{CO}_3$  during  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Solid Electrolyte Sintering process. *Int. J. Electrochem. Sci.* **2019**, 9695–9703.

(30) Huo, H.; Chen, Y.; Zhao, N.; Lin, X.; Luo, J.; Yang, X.; Liu, Y.; Guo, X.; Sun, X. In-situ formed  $\text{Li}_2\text{CO}_3$ -free garnet/Li interface by rapid acid treatment for dendrite-free solid-state batteries. *Nano Energy* **2019**, *61*, 119–125.

(31) Cheng, L.; Chen, W.; Kunz, M.; Persson, K.; Tamura, N.; Chen, G.; Doeff, M. Effect of surface microstructure on electrochemical performance of garnet solid electrolytes. *ACS Appl. Mater. Interfaces* **2015**, *7* (3), 2073–81.

(32) Buschmann, H.; Berendts, S.; Mogwitz, B.; Janek, J. Lithium metal electrode kinetics and ionic conductivity of the solid lithium ion conductors “ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ” and  $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12}$  with garnet-type structure. *J. Power Sources* **2012**, *206*, 236–244.

(33) 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.

(34) Dissanayake, M.; Mellander, B.-E. Phase diagram and electrical conductivity of the  $\text{Li}_2\text{SO}_4\text{-Li}_2\text{CO}_3$  system. *Solid State Ionics* **1986**, *21* (4), 279–285.

(35) Christensen, J.; Albertus, P.; Sanchez-Carrera, R. S.; Lohmann, T.; Kozinsky, B.; Liedtke, R.; Ahmed, J.; Kojic, A. A critical review of Li/air batteries. *J. Electrochem. Soc.* **2011**, *159* (2), R1–R30.

(36) 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* (20), 6448–6455.

(37) Wu, J.-F.; Pu, B.-W.; Wang, D.; Shi, S.-Q.; Zhao, N.; Guo, X.; Guo, X. In Situ Formed Shields Enabling  $\text{Li}_2\text{CO}_3$ -Free Solid Electrolytes: A New Route to Uncover the Intrinsic Lithiophilicity of Garnet Electrolytes for Dendrite-Free Li-Metal Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11* (1), 898–905.

(38) Gao, J.; Guo, X.; Li, Y.; Ma, Z.; Guo, X.; Li, H.; Zhu, Y.; Zhou, W. The Ab Initio Calculations on the Areal Specific Resistance of Li-Metal/ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Interphase. *Adv. Theory and Simulations* **2019**, 1900028.

(39) Ohta, S.; Kobayashi, T.; Seki, J.; Asaoka, T. Electrochemical performance of an all-solid-state lithium ion battery with garnet-type oxide electrolyte. *J. Power Sources* **2012**, *202*, 332–335.

(40) Li, Y.; Xu, B.; Xu, H.; Duan, H.; Lu, X.; Xin, S.; Zhou, W.; Xue, L.; Fu, G.; Manthiram, A.; Goodenough, J. B. Hybrid Polymer/Garnet Electrolyte with a Small Interfacial Resistance for Lithium-Ion Batteries. *Angew. Chem., Int. Ed.* **2017**, *56* (3), 753–756.

(41) Xu, B.; Li, W.; Duan, H.; Wang, H.; Guo, Y.; Li, H.; Liu, H.  $\text{Li}_3\text{PO}_4$ -added garnet-type  $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$  for Li-dendrite suppression. *J. Power Sources* **2017**, *354*, 68–73.

(42) Rao, R. P.; Gu, W.; Sharma, N.; Peterson, V. K.; Avdeev, M.; Adams, S. In Situ Neutron Diffraction Monitoring of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Formation: Toward a Rational Synthesis of Garnet Solid Electrolytes. *Chem. Mater.* **2015**, *27* (8), 2903–2910.

(43) Nyman, M.; Alam, T. M.; McIntyre, S. K.; Bleier, G. C.; Ingersoll, D. Alternative Approach to Increasing Li Mobility in Li-La-Nb/Ta Garnet Electrolytes. *Chem. Mater.* **2010**, *22* (19), 5401–5410.

(44) Cheng, L.; Liu, M.; Mehta, A.; Xin, H.; Lin, F.; Persson, K.; Chen, G.; Crumlin, E. J.; Doeff, M. Garnet Electrolyte Surface Degradation and Recovery. *ACS Appl. Energy Mater.* **2018**, *1* (12), 7244–7252.

(45) Wang, C. W.; Xie, H.; Ping, W. W.; Dai, J. Q.; Feng, G. L.; Yao, Y. G.; He, S. M.; Weaver, J.; Wang, H.; Gaskell, K.; Hu, L. B. A general, highly efficient, high temperature thermal pulse toward high performance solid state electrolyte. *Energy Storage Materials* **2019**, *17*, 234–241.

(46) Han, F. D.; Westover, A. S.; Yue, J.; Fan, X. L.; Wang, F.; Chi, M. F.; Leonard, D. N.; Dudney, N.; Wang, H.; Wang, C. S. High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes. *Nature Energy* **2019**, *4* (3), 187–196.

(47) Xie, X.; Xing, J.; Hu, D.; Gu, H.; Chen, C.; Guo, X. Lithium Expulsion from the Solid-State Electrolyte  $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$  by Controlled Electron Injection in a SEM. *ACS Appl. Mater. Interfaces* **2018**, *10* (6), 5978–5983.

(48) Liu, B.; Zhang, L.; Xu, S.; McOwen, D. W.; Gong, Y.; Yang, C.; Pastel, G. R.; Xie, H.; Fu, K.; Dai, J.; Chen, C.; Wachsman, E. D.; Hu, L. 3D lithium metal anodes hosted in asymmetric garnet frameworks toward high energy density batteries. *Energy Storage Materials* **2018**, *14*, 376–382.

(49) Nohma, T.; Kurokawa, H.; Uehara, M.; Takahashi, M.; Nishio, K.; Saito, T. Electrochemical characteristics of  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$  as a positive material for lithium secondary batteries. *J. Power Sources* **1995**, *54* (2), 522–524.

(50) Guo, J.; Cai, Y.; Zhang, S.; Chen, S.; Zhang, F. Core-Shell Structured  $\text{o-LiMnO}_2@(\text{Li}_2\text{CO}_3)$  Nanosheet Array Cathode for High-Performance, Wide-Temperature-Tolerance Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2016**, *8* (25), 16116–24.

(51) Kim, K. H.; Iriyama, Y.; Yamamoto, K.; Kumazaki, S.; Asaka, T.; Tanabe, K.; Fisher, C. A.; Hirayama, T.; Murugan, R.; Ogumi, Z. Characterization of the interface between  $\text{LiCoO}_2$  and  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  in an all-solid-state rechargeable lithium battery. *J. Power Sources* **2011**, *196* (2), 764–767.

(52) Xu, B.; Duan, H.; Liu, H.; Wang, C. A.; Zhong, S. Stabilization of Garnet/Liquid Electrolyte Interface Using Superbase Additives for Hybrid Li Batteries. *ACS Appl. Mater. Interfaces* **2017**, *9* (25), 21077–21082.

(53) Huo, H.; Zhao, N.; Sun, J.; Du, F.; Li, Y.; Guo, X. Composite electrolytes of polyethylene oxides/garnets interfacially wetted by ionic liquid for room-temperature solid-state lithium battery. *J. Power Sources* **2017**, *372*, 1–7.

(54) Zhang, X.; Liu, T.; Zhang, S.; Huang, X.; Xu, B.; Lin, Y.; Xu, B.; Li, L.; Nan, C. W.; Shen, Y. Synergistic Coupling between  $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$  and Poly(vinylidene fluoride) Induces High Ionic Conductivity, Mechanical Strength, and Thermal Stability of Solid Composite Electrolytes. *J. Am. Chem. Soc.* **2017**, *139* (39), 13779–13785.

(55) Huo, H.; Sun, J.; Chen, C.; Meng, X.; He, M.; Zhao, N.; Guo, X. Flexible interfaces between Si anodes and composite electrolytes consisting of poly(propylene carbonates) and garnets for solid-state batteries. *J. Power Sources* **2018**, *383*, 150–156.

(56) Gupta, A.; Sakamoto, J. Controlling Ionic Transport through the PEO-LiTFSI/LLZTO Interface. *Electrochem. Soc. Interface* **2019**, *28* (2), 63–69.

(57) Nan, C. W.; Fan, L.; Lin, Y.; Cai, Q. Enhanced ionic conductivity of polymer electrolytes containing nanocomposite  $\text{SiO}_2$  particles. *Phys. Rev. Lett.* **2003**, *91* (26), 266104.

(58) Zhang, J.; Zhao, N.; Zhang, M.; Li, Y.; Chu, P. K.; Guo, X.; Di, Z.; Wang, X.; Li, H. Flexible and ion-conducting membrane electrolytes for solid-state lithium batteries: Dispersion of garnet nanoparticles in insulating polyethylene oxide. *Nano Energy* **2016**, *28*, 447–454.

(59) Fu, K. K.; Gong, Y.; Dai, J.; Gong, A.; Han, X.; Yao, Y.; Wang, C.; Wang, Y.; Chen, Y.; Yan, C.; et al. Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (26), 7094–7099.

(60) Kalnaus, S.; Sabau, A. S.; Tenhaeff, W. E.; Dudney, N. J.; Daniel, C. Design of composite polymer electrolytes for Li ion batteries based on mechanical stability criteria. *J. Power Sources* **2012**, *201*, 280–287.

(61) Zheng, J.; Tang, M.; Hu, Y. Y. Lithium Ion Pathway within  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ -Polyethylene Oxide Composite Electrolytes. *Angew. Chem., Int. Ed.* **2016**, *55* (40), 12538–42.

(62) Miara, L. J.; Richards, W. D.; Wang, Y. E.; Ceder, G. First-Principles Studies on Cation Dopants and Electrolyte/Cathode Interphases for Lithium Garnets. *Chem. Mater.* **2015**, *27* (11), 4040–4047.

(63) Krauskopf, T.; Hartmann, H.; Zeier, W. G.; Janek, J. Toward a Fundamental Understanding of the Lithium Metal Anode in Solid-State Batteries—An Electrochemo-Mechanical Study on the Garnet-Type Solid Electrolyte  $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ . *ACS Appl. Mater. Interfaces* **2019**, *11* (15), 14463–14477.

(64) 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* (8), 2030–2049.