OPEN ACCESS OP Publishing | Songshan Lake Materials Laboratory

Mater. Futures 1 (2022) 045103 (10pp)

# Reinforced cathode-garnet interface for high-capacity all-solid-state batteries

# Chenxi Zheng<sup>1</sup>, Shijun Tang<sup>1</sup>, Fangmei Wen<sup>1</sup>, Jinxue Peng<sup>1</sup>, Wu Yang<sup>1</sup>, Zhongwei Lv<sup>1</sup>, Yongmin Wu<sup>2</sup>, Weiping Tang<sup>2</sup>, Zhengliang Gong<sup>1,\*</sup>, and Yong Yang<sup>1,3,\*</sup>

<sup>1</sup> College of Energy, Xiamen University, Xiamen 361102, People's Republic of China

<sup>2</sup> State Key Laboratory of Space Power-Sources Technology, Shanghai Institute of Space Power-Sources,

Shanghai 200245, People's Republic of China

<sup>3</sup> State Key Laboratory for Physical Chemistry of Solid Surface, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China

E-mail: zlgong@xmu.edu.cn and yyang@xmu.edu.cn

Received 24 October 2022, revised 4 November 2022 Accepted for publication 8 November 2022 Published 9 December 2022



### Abstract

Garnet-type solid-state electrolytes (SSEs) are particularly attractive in the construction of all-solid-state lithium (Li) batteries due to their high ionic conductivity, wide electrochemical window and remarkable (electro)chemical stability. However, the intractable issues of poor cathode/garnet interface and general low cathode loading hinder their practical application. Herein, we demonstrate the construction of a reinforced cathode/garnet interface by spark plasma sintering, via co-sintering  $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$  (LLZTO) electrolyte powder and LiCoO<sub>2</sub>/LLZTO composite cathode powder directly into a dense dual-layer with 5 wt% Li<sub>3</sub>BO<sub>3</sub> as sintering additive. The bulk composite cathode with LiCoO<sub>2</sub>/LLZTO cross-linked structure is firmly welded to the LLZTO layer, which optimizes both Li-ion and electron transport. Therefore, the one-step integrated sintering process implements an ultra-low cathode/garnet interfacial resistance of 3.9  $\Omega$  cm<sup>2</sup> (100 °C) and a high cathode loading up to 2.02 mAh cm<sup>-2</sup>. Moreover, the Li<sub>3</sub>BO<sub>3</sub> reinforced LiCoO<sub>2</sub>/LLZTO interface also effectively mitigates the strain/stress of  $LiCoO_2$ , which facilitates the achieving of superior cycling stability. The bulk-type LilLLZTOILiCoO<sub>2</sub>-LLZTO full cell with areal capacity of 0.73 mAh cm<sup>-2</sup> delivers capacity retention of 81.7% after 50 cycles at 100  $\mu$ A cm<sup>-2</sup>. Furthermore, we reveal that non-uniform Li plating/stripping leads to the formation of gaps and finally results in the separation of Li and LLZTO electrolyte during long-term cycling, which becomes the dominant capacity decay mechanism in high-capacity full cells. This work provides insight into the degradation of Li/SSE interface and a strategy to radically improve the electrochemical performance of garnet-based all-solid-state Li batteries.

Supplementary material for this article is available online

Keywords: garnet electrolyte, all-solid-state battery, high cathode loading, interface evolution, spark plasma sintering

\* Authors to whom any correspondence should be addressed.

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

#### Future perspectives

Garnet-type solid-state electrolytes demonstrate great potential to improve cell safety without employing organic liquid electrolytes and increase battery energy density with high-voltage cathodes and lithium (Li) metal anodes. However, the high interfacial impedance aroused by the poor interfacial contact and parasitic reactions remains a major challenge for high-performance bulk-type all-solid-state batteries (ASSBs). Future research into the interface engineering between garnet electrolytes and the electrodes will play a key role in the development of practical ASSBs. For Li/garnet interface, designing multifunctional flexible interlayers with excellent lithiophilicity and electronic insulativity is the key to enhancing the cycling stability and achieving high areal capacity. For cathode/garnet interface, advanced sintering methods such as spark plasma sintering have successfully attained intimate interface bonding. Further efforts can be made in developing bulk composite cathode with superior kinetics and stability to realize high rate performance and energy density.

#### 1. Introduction

Garnet-type solid-state electrolyte (SSE) is considered as a prospective candidate for building all-solid-state batteries (ASSBs) owing to its high ionic conductivity, wide electrochemical window and high stability against lithium (Li) metal and air [1-3], which enable it to fit high-voltage cathode materials and Li metal anode (3860 mAh  $g^{-1}$  and -3.040 V versus the standard hydrogen electrode) for higher energy density [4, 5]. However, the practical application of garnetbased ASSBs is restricted by the large interfacial resistance between the electrolytes and electrodes. Many attempts have been made to ameliorate the interfacial contact between the garnet SSE and Li anode, including introducing interface coatings (e.g. C, Mg, Al<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, LiF, Cu<sub>3</sub>N) [6-12], and removing the Li<sub>2</sub>CO<sub>3</sub> from the garnet by surface treatment (e.g. HCI, H<sub>3</sub>PO<sub>4</sub>, NH<sub>4</sub>F, H<sub>3</sub>BO<sub>3</sub>-HF) [13-16], which have effectively reduced the interfacial resistance and improved the performance of Li symmetric batteries. Nevertheless, building an intimate cathode/garnet SSE interface is still limited by the following challenges. (a) High-temperature sintering may give rise to unexpected side reactions between the cathode active material (CAM) and the electrolyte in the composite cathode, while low-temperature sintering leads to poor contact between CAM and the electrolyte, and between the composite cathode layer and the electrolyte layer [17-19]; (b) non-negligible volume change in CAM during cycling may cause particle fracture and interface delamination [20, 21]; (c) electrochemical reactions may occur between CAM and the electrolyte [22, 23]. All the above ultimately results in low cathode loading and poor cyclic performance of garnet-based ASSBs.

Recent studies have made extensive efforts to reduce the resistance of the cathode/garnet SSE interface, where  $LiCoO_2$  (LCO) is extensively studied as CAM due to its high electronic conductivity, high thermal stability and similar thermal expansion coefficient to garnet SSEs [24–27]. Among them, three main approaches have been highlighted. (a) Depositing LCO on the garnet pellet directly to form a thin film [28–30]. However, the loading of the cathode film, which is typically

hundreds of nanometers thick, is extremely low. (b) Casting the composite cathode slurry on the top surface of garnet pellets followed by sintering [31–38]. To improve the contact of LCO and garnet, sintering additives such as Li<sub>3</sub>BO<sub>3</sub> (LBO) and its derivatives are added to the composite cathode slurry. Despite all this, most cells fabricated by this method still suffer from low operating current density and areal loading, which cannot meet the requirements of high-energy bulk-type Li batteries. (c) Co-sintering the electrolyte and the composite cathode into a dual-layer by simultaneous pressurization and heating, such as spark plasma sintering (SPS) [22, 39-41], and hot-press sintering [42]. The significant merit of the cosintering process is to construct a cathode/SSE interface directly from each specific powder rather than rigid pellets under applied pressure, which can easily attain tight interface bonding and high-capacity cathodes (>1 mAh  $cm^{-2}$ ). Generally, a lower sintering temperature ( $\sim$ 700 °C) is usually chosen to avert side reactions between LCO and garnet, yet leading to poor interfacial contact and high interfacial impedance. Moreover, degradation may occur at the LCO/garnet interface during electrochemical cycling [22], both resulting in poor cycling stability. Therefore, in terms of the state-of-the-art garnet-based ASSBs, there is still much scope for improvement to reach the desired target, and it remains a major challenge to enhance the stability of cathode/garnet interface.

Herein, we report a reinforced cathode/garnet interface constructed by the SPS method, which achieves an intimate contact between high-capacity cathode and garnet SSE. The electrolyte is composed of Li<sub>6.5</sub>La<sub>3</sub>Zr<sub>1.5</sub>Ta<sub>0.5</sub>O<sub>12</sub> (LLZTO) and LBO, and the composite cathode is composed of LCO, LLZTO and LBO (figure 1). LBO is served as a sintering additive with a room-temperature Li-ion conductivity of  $2 \times 10^{-6}$  S cm<sup>-1</sup> and melts at ~700 °C, which can wet the particles and accelerates the interdiffusion of atoms in liquid phase, beneficial to the enhancement of densification and Li<sup>+</sup> conductivity [43, 44]. Profiting from the SPS and LBO strategies, the composite cathode with conductive network structure is firmly bonded to the LLZTO layer, thereby reducing its interfacial impedance to as low as 3.9  $\Omega$  cm<sup>2</sup> at 100 °C. Thus, the bulk-type LilLLZTO/LCO-LLZTO ASSB with an areal loading of 0.73 mAh  $cm^{-2}$  exhibits superior cycling stability with a capacity retention of 81.7% after 50 cycles at 100  $\mu$ A cm<sup>-2</sup>. In addition, we reveal the evolution of LLZTO/electrode interfaces of full cells during cycling from multiple aspects and propose research directions to further improve the electrochemical performance of LLZTO-based ASSBs, laying an essential foundation for its future application.

#### 2. Methods

#### 2.1. Material synthesis

LLZTO and LBO were both synthesized via solid-state reaction methods. The starting materials of LLZTO, LiOH·H<sub>2</sub>O (99%, Aladdin), La<sub>2</sub>O<sub>3</sub> (99.99%, Aladdin), ZrO<sub>2</sub> (99.99%, Aladdin), Ta<sub>2</sub>O<sub>5</sub> (99.5%, Aladdin), were ball milled in



Figure 1. Schematic of the processes of the battery assembly.

stoichiometric amounts with 2-propanol as dispersant and 10 wt% excess LiOH·H<sub>2</sub>O was added to compensate for Li loss during subsequent sintering. The mixed powder was then dried and transferred to a muffle furnace for calcining at 900 °C for 12 h. The sintered powder was finally sieved into a uniform fine powder with a 200-mesh sieve. For LBO synthesis, LiOH·H<sub>2</sub>O (99%, Aladdin) and B<sub>2</sub>O<sub>3</sub> (98%, Aladdin) were mixed in a mole ratio of 6:1 and then calcined at 600 °C for 4 h.

#### 2.2. Fabrication of ASSBs

LCO-LLZTO/LLZTO half cells were sintered using a LABOX-212 SPS system. LCO (Canrd, China), LLZTO, LBO were mixed in a mass ratio of 50:50-x:x (x = 0, 2, 5, 10) as the composite cathode. LLZTO, LBO were mixed in a mass ratio of 100-x:x (x = 0, 2, 5, 10) as the electrolyte. The two powders were layered into a graphite mold with an inner diameter of 10 mm, and sintered at 80 MPa and 690 °C for 1 h at high vacuum. Then the LCO-LLZTO/LLZTO half cells were transferred to a tube furnace and annealed at 875 °C for 2 h in O<sub>2</sub> flow. The as-sintered pellets were firstly polished, where the LLZTO layers were about 800  $\mu$ m thick and the composite cathode layers were about 15–50  $\mu$ m thick according to different cathode areal loadings. Then Au thin film was sputtered on the composite cathode side served as current collector, and a thin graphite-based layer was coated on the electrolyte side to enhance the adhesion of Li foil anode [6]. The assembled full cells were sealed in a Swagelok cell and applied pressure of  $\sim 10$  kPa for further tests.

#### 2.3. Characterizations

The phase structure was analyzed by x-ray diffraction (XRD), using a Rigaku Ultima IV x-ray Diffractometer, which operated at 40 kV and 30 mA over the range of  $10 \sim 90^{\circ}$  ( $2\theta$ ) with Cu Ka radiation ( $\lambda = 1.5405$  Å). The microstructure and elemental distribution of samples were characterized using the SUPRA 55 scanning electron microscope (SEM) combined with energy dispersive spectrometer (EDS). Samples for EDS mapping were preprocessed by ion beam cutting. Raman spectra were recorded with a Horiba Scientific XploRA PLUS unit with a 532 nm excitation solid-state laser over a Raman Shift of 200 cm<sup>-1</sup>–1500 cm<sup>-1</sup>. The surface constitution of samples was examined using the Thermo Scientific K-Alpha x-ray Photoelectron Spectrometer (XPS) system. The Young's modulus of samples was measured using a Cypher ES Polymer Edition Atomic Force Microscope by scanning 256 points on an area of  $5 \times 5 \ \mu m^2$ .

#### 2.4. Electrochemical measurements

Galvanostatic charge and discharge tests of LilLLZTOILCO-LLZTO ASSBs were conducted between 3.0 and 4.05 V at different current density, and collected with a Land CT-2001A (Wuhan, China). The electrochemical impedance spectroscopy (EIS) tests were performed in an Auto Lab workstation, in the frequency range from 1 MHz to 0.01 Hz and with an amplitude of 10 mV. The full cells were charged to 4.05 V and held at 4.05 V for 12 h, then rest at open circuit voltage for 2 h before EIS testing.

#### 3. Results

As shown in figure S1, no discernible impurities are detected in the as-synthesized LLZTO and LBO by XRD, and the diffraction peaks of LLZTO are well indexed to cubic phase. Previous studies have reported that LCO and LLZTO would gradually set off a heat-induced reaction from 700 °C [18, 45], thus we selected 690 °C as the heating temperature. Owing to the relatively low temperature, the density of pellets can be improved by prolonging the dwell time, in contrast to that of other previous reports ( $\sim 10 \text{ min}$ ) [39, 41]. The Li-ion conductivity of the electrolyte pellets with various dwell time of 15 min, 30 min, 1 h, and 1.5 h were tested by EIS at room temperature (figure S2, table S1). The results indicate that the Li-ion conductivity increases with the prolongation of the dwell time within 1 h, and when the dwell time reaches 1.5 h, the excessive volatilization of Li leads to the formation of La2Zr2O7 impurity phase (figure S3), resulting in a slight decrease in ionic conductivity, and thus 1 h is selected as the dwell time.

During sintering above 600 °C, LCO in the composite cathode is reduced to CoO due to direct contact with graphite molds [25, 41, 46], but interestingly, this change can be reversed by annealing in O<sub>2</sub> flow, confirmed by both XRD, Raman spectroscopy, and XPS, as shown in figure 2. From XRD and Raman results (figures 2(a) and (b)), the patterns show explicitly that the CoO in the composite cathode is oxidized back to LCO after annealing. From XPS results (figure 2(c)), Co2p spectrum shows spin orbit splitting into



Figure 2. Characterization of the composite cathode. (a) XRD, (b) Raman, (c) XPS results of the composite cathode before (Cathode-B) and after annealing (Cathode-A).

 $2p_{1/2}$  (at the high binding energy) and  $2p_{3/2}$  (at the low binding energy) intensity peaks which contain the same chemical information. For the sample of composite cathode before annealing, the  $2p_{3/2}$  peak locates at 781.1 eV can be assigned to  $Co^{2+}$ , with a corresponding satellite peak at 786.8 eV, consistent with the previous report [47]. For the sample of composite cathode after annealing, the  $2p_{3/2}$  component can be well fitted into an intensive main peak at 779.4 eV assigned to  $Co^{3+}$  and a weak peak at 781.3 eV assigned to  $Co^{2+}$ , accompanied by a satellite peak at 788.4 eV [48], which indicates that most  $Co^{2+}$  is converted to  $Co^{3+}$ . By contrast, the cubic phase structure of LLZTO is well maintained during the sintering process, implying that LLZTO does not occur any chemical reaction with LCO or graphite at the current experimental conditions (figure S4).

As mentioned above, LBO was added as a sintering additive for SPS process, which has a great influence on the microstructure of sintered products. Figures S5(a) and (d) show the SEM images of the cross section of the sintered LCO-LLZTO/LLZTO half cells with 0 wt%, 2 wt%, 5 wt% and 10 wt% LBO, respectively. Figures S5(e)–(h) show the corresponding contact state of particles inside the composite cathode at high magnification, respectively. With the increase of LBO content, the voids between the composite cathode layer and the electrolyte layer and between the particles reduce accordingly, and the sintered density increases. When the LBO content reaches 5%, the LCO-LLZTO/LLZTO half cell achieves a fairly dense state, as shown in figure 3(a). An enlarged SEM image of the interface between the LCO composite cathode and the LLZTO electrolyte (red boxed area in figure 3(a)) is shown in figure 3(b), which shows a densified sintered structure and a well-welded interface. The EDS mappings of La, Zr, Co and B (figures 3(c)-(f)) demonstrate that the LLZTO and LCO are each connected into a conductive network, which are tightly cross-linked throughout the cathode, providing composite channels to facilitate Li-ion and electron transport. LBO is evenly scattered in the LCO-LLZTO/LLZTO half cell which boosts the cementing among particles to form a reinforced dual-layer structure and mitigate the strain/stress of LCO. The EDS line scan (figure 3(g)) shows the variation trends of elements in the direction perpendicular to the LLZTO/LCO interface (the inset in figure 3(g)), where a thin interfacial layer of about 320 nm think is formed, and no additional elements are detected in the bulk of LLZTO and LCO particles, implying that there is no obvious element diffusion or chemical reactions between the bulk of two particles. Furthermore, the electrolyte pellet with LBO exhibits a higher mechanical strength, as shown in the figure 3(h) and S6. The Young's modulus of the electrolyte pellet with 5% LBO is 6.5 GPa, while that without the additive is only 3.5 GPa. This also indicates that



**Figure 3.** Characterization of the LCO-LLZTO/LLZTO half cell with 5% LBO. (a) SEM image of the cross section. The yellow dotted line roughly marks the interface between the LCO-LLZTO composite cathode and the LLZTO electrolyte. (b) SEM image of the cross section after ion beam cutting and corresponding EDS mapping of (c) La, (d) Zr, (e) Co, (f) B. (g) EDS line scan across the LCO/LLZTO interphase, the inset shows its SEM image. (h) Young's modulus mapping of the electrolyte pellet with 5% LBO.

LBO enhances the compactness of the pellets, which conduces to improve Li-ion conductivity and restrains the growth of Li dendrite.

The optimal LBO content was explored by evaluating the impedance of the full cell. As shown in figure S7, the EIS spectra of LilLLZTOILCO-LLZTO ASSBs with different LBO contents at 100 °C all comprise four parts. The impedance value of the real axis intercept in the high frequency can be assigned to the resistance of LLZTO electrolyte ( $R_{LLZTO}$ ), the semicircle in the high-frequency region (1 MHz-150 Hz) represents the interfacial resistance between Li and LLZTO (RLi/LLZTO), the semicircle in the mid-frequency region (150 Hz-1 Hz) represents the interfacial resistance between composite cathode and LLZTO  $(R_{\text{LCO-LLZTO/LLZTO}})$ , and the diagonal line in the low frequency is related to the Warburg impedance attributed to the Li-ion diffusion process [31, 49]. The inserted equivalent circuit is used for simulating the electrical response of the full cells, wherein R is the resistance element, CPE is the constant phase element, W is the Warburg element. The fitting results of  $R_{LLZTO}$ ,  $R_{Li/LLZTO}$ , and  $R_{LCO-LLZTO/LLZTO}$  for the full cells with different LBO content are shown in table S2. It shows that each resistance component of the full cell with 5% LBO is the smallest. This can be attributed to the influences of sintering additive LBO. Wherein, moderate LBO can promote the densification, thus facilitate rapid ionic/electronic conduction. While excess addition is adverse to Li-ion transport due to the low Li-ion conductivity of LBO. Furthermore, the interfacial resistance between the cathode and LLZTO is as low as 3.9  $\Omega$  cm<sup>2</sup> (at 100 °C, 5% LBO), confirming that the SPS and sintering additive strategies are highly effective at improving the poor solid-solid contact between the garnet and the cathode.

We then selected LilLZTOILCO-LLZTO full cells with 5% LBO for electrochemical performance measurements due to their lower impedance. The full cells with different areal capacity are assembled and subjected to the galvanostatic charge–discharge test at 100 °C with a current density of 100  $\mu$ A cm<sup>-2</sup>. As shown in figure S8, the full cell with a high initial discharge areal capacity of 2.02 mAh cm<sup>-2</sup> shows poor cycling stability with a capacity retention of only 59.8% after 30 cycles. The charge–discharge profiles exhibit a large increase of the charge/discharge potential gap. Nevertheless, when the areal capacities of the full cells are decreased to 1.40 mAh cm<sup>-2</sup> and 0.73 mAh cm<sup>-2</sup>, the electrochemical performance is significantly improved (figures 4(a),



**Figure 4.** Electrochemical performance of LilLLZTOILCO-LLZTO full cells. (a) Cycling performance and (b) the charge–discharge profiles of the full cells at 100 °C. (c) EIS spectrum of the full cell underwent different cycle numbers at 100 °C. (d) The equivalent circuit model based on EIS spectrum and changing curves of  $R_{LLZTO}$ ,  $R_{Li/LLZTO}$  and  $R_{LCO-LLZTO/LLZTO}$  during cycling. (e) Cycling performance of the full cell with an areal capacity of 1.10 mAh cm<sup>-2</sup> at 60 °C.

(b) and S9). Both cells show initial coulombic efficiencies of about 80%, and the coulombic efficiencies rapidly increase to ~97.5% in the third cycle, then slightly increase to ~98.5% during the following cycles. It also shows that the cell with lower areal capacity exhibits superior cycling stability. As for the cell with areal capacity of 1.40 mAh cm<sup>-2</sup>, fast capacity decay is observed with a low capacity retention of 66.7% after 50 cycles. While for the cell with areal

capacity of 0.73 mAh cm<sup>-2</sup>, the cycling stability is greatly improved. It still delivers a high capacity of 0.60 mAh cm<sup>-2</sup> with a capacity retention of 81.7% after 50 cycles. Operando EIS was employed to investigate the fading mechanism of the LilLLZTOILCO-LLZTO full cell. Figure 4(c) shows the EIS spectra of the battery with a capacity of 1.40 mAh cm<sup>-2</sup> underwent different cycle numbers. It shows that the impedance steadily increasing throughout the cycling



**Figure 5.** Cross-sectional SEM images of LLZTO/anode and LLZTO/cathode interfaces with different cycling condition. LLZTO/anode interface (a) before cycling, (b) after 30 cycles, and (c) after cell failed at 130 cycles. (d) LLZTO/cathode interface and the magnified composite cathode after cell failed. The yellow dotted line roughly marks the LLZTO/cathode interface.

process, corresponding to the continuous increase in polarization. Figure 4(d) displays the value of  $R_{LLZTO}$ ,  $R_{Li/LLZTO}$ , and  $R_{\text{LCO-LLZTO/LLZTO}}$  by fitting the impedance data. It shows that only  $R_{\text{Li/LLZTO}}$  of the three resistance components apparently increases as the galvanostatic cycle progresses, which is related to the acute deterioration of the Li/LLZTO interface. Conversely, the largely stable  $R_{LCO-LLZTO/LLZTO}$  is because, firstly, the interface formed by integrated sintering is inherently more stable than that formed by attaching, and secondly, the charge cut-off voltage of 4.05 V sufficiently limits the volume change of LCO to prevent structural collapse. Therefore, the main reason for the performance decay of full cells is presumably the incremental impedance of the Li/LLZTO interface. Moreover, in practice, the batteries usually need to operate at a lower temperature, so the electrochemical performances of the LilLLZTOILCO-LLZTO full cells at 60 °C were also investigated. As shown in figure 4(e), the cell still exhibits stable cycling for more than 100 cycles at a current density of 50  $\mu$ A cm<sup>-2</sup> with an initial discharge capacity of 1.1 mAh cm<sup>-2</sup>. The coulombic efficiency of the cell gradually increases from 71% to 99% in the first 15 cycles and then remains stable. After 50 cycles, the cell reveals a substantial capacity loss, with a retention rate of 60.2%. The reason is that lower temperature results in worse mass transfer kinetics of Li metal, making it less prone to creep to fill the voids at the Li/LLZTO interface. Meanwhile, the conduction of Li ions inside the cell is also retarded, eventually leading to worse electrochemical performance than that at 100  $^{\circ}$ C.

To further explore the evolution of electrode/electrolyte interfaces of the cell during cycling, we performed exsitu SEM tests on the same batch of high-capacity cells  $(\sim 1 \text{ mAh cm}^{-2})$  with different cycle numbers at 60 °C. For LLZTO/anode interface, the Li metal exhibits intimate contact with the LLZTO electrolyte prior to cycling (figure 5(a)). After 30 cycles, as shown in figure 5(b), there are several gaps between Li and LLZTO electrolyte, triggered by the accumulated stress due to the persistent uneven Li plating/stripping at the Li/LLZTO interface. The loss in the interface contact would accelerate the generation of an uneven electric field, causing the continuous deterioration of the Li/LLZTO interface. After 130 cycles, the Li/LLZTO interface shows severe degradation with the formation of large voids and the cell fails (figure 5(c)). In comparison, there is no obvious change observed for the LCO/LLZTO interface, which is still in intimate contact even after 130 cycles (figure 5(d)). The composite cathode layer maintains a dense state as well, where most particles show no obvious fractures (the inset of figure 5(d)). Besides, no impurity is generated in the composite cathode

Reference	Cathode	Temp. (°C)	Current density $(\mu A \text{ cm}^{-2})$	Areal capacity $(mAh cm^{-2})$	Voltage range (V)	No. of cycles (Capacity retention)
[29]	LCO (Al <sub>2</sub> O <sub>3</sub> interlayer)	NR	3.85 (0.1 C)	~0.039	2.5-4.2	100 (~85%)
[31]	LCO-LLZO-	25 100	5.75	0.094	3.0-4.05	100 (~94%) 40 (63 2%)
[32]	LCO-LLZO- Al <sub>2</sub> O <sub>3</sub>	100	38.4	0.116	2.8–4.2	40 (03.2 <i>%</i> ) 16 (92%)
[33]	LCO-Li <sub>2</sub> BO <sub>2</sub> - In <sub>2</sub> O <sub>5</sub> Sn	80	14 (0.1 C)	~0.14	3.0-4.5	25 (55%)
[36]	LCO-LBO- In <sub>2</sub> O <sub>5</sub> Sn	RT	5	0.056	2.8-4.3	6 (87%)
[37]	LCO-LBO- In <sub>2(1-x)</sub> Sn <sub>2x</sub> O <sub>3</sub>	80	15 (0.08 C)	~0.188	2.8-4.3	20 (86%)
[38]	LCO-LLZO	80	4.2	0.086	3.0-4.05	14 (97.5%)
[42]	LCO-LLZO- Li <sub>2.985</sub> B <sub>0.005</sub> OCl	90	~4.8 (0.05 C)	0.096	3.0-4.1	50 (~64%)
This work	LCO-LLZO-	100	100	1.40	3.0-4.05	50 (66.7%)
	LBO		100	0.73		50 (81.7%)
			100	0.49		50 (92.3%)

 Table 1. Electrochemical performance of Li/LLZO/LCO ASSBs reported in the past decade (NR: not reported, RT: room temperature, electrolyte materials are all represented by LLZO).

after 130 cycles, validated by the XRD pattern (figure S10). These results indicate that the electrochemical reaction and the resultant volume change are uniform throughout the composite cathode, and the SPS process builds a durable SSE/cathode interface that keep unchanged and intact in structure during long-term cycling. Hence, it can be concluded that the performance degradation of the bulk-type LilLLZTOILCO-LLZTO ASSBs is primarily due to the continuous deterioration of the Li/LLZTO interface. Based on the previous electrochemical results (figures S8, 4(a)), generally, lowering the areal Li plating/stripping capacity could alleviate the deterioration of the Li/LLZTO interface, thus improving the cycling stability the ASSBs. To investigate the effects of cathode areal capacity on the electrochemical performance of LilLLZTOILCO-LLZTO ASSBs, we decreased the areal capacity to 0.49 mAh cm<sup>-2</sup>. As expected, the cycling stability is significantly enhanced. It shows that the capacity retention is high up to 92.3% after 50 cycles (figure S11(a)). And the Li metal anode still maintains intimate contact with LLZTO electrolyte (figure S11(b)). The difference in behavior of the Li/LLZTO interface demonstrates the effectiveness of the low cathode capacity in lessening the contact loss between Li anode and LLZTO electrolyte, which forcefully proves that the stability of the Li/LLZTO interface plays a vital role in the cycling stability of the bulk-type LilLLZTOILCO-LLZTO ASSBs with high areal capacities.

To date, various works have been reported to construct LLZO-based ASSBs, as shown in table 1. It is obvious that the LilLLZTOILCO-LLZTO full cell in this work demonstrates outstanding operating current density, areal capacity, and cycling stability. For pursuing better electrochemical performance, subsequent research endeavors can be made in improving the mechanical stability of a Li/LLZO interface during repeated high-capacity (>3 mAh cm<sup>-2</sup>) Li

plating/stripping process, for example, combining 3D interface construction and multifunctional interlayers, and then adapting it to ASSB systems, thereby achieving high capacity and extended cycling.

#### 4. Conclusion

In summary, a solid and durable cathode/garnet interface is successfully constructed by low temperature densification strategy using the SPS method with LBO as sintering additive. The intimate LCO-LLZTO/LLZTO interface and the cross-linked structure of the composite cathode are efficiently constructed and provide unimpeded ionic/electronic conducting pathways, ensuring high electrochemical activity under high areal capacity. As a consequence, the initial LCO-LLZTO/LLZTO interfacial impedance  $R_{\text{LCO-LLZTO/LLZTO}}$  is remarkably reduced to 3.9  $\Omega$  cm<sup>2</sup> (100 °C), and the areal capacity is high up to 2.02 mAh  $cm^{-2}$ . EIS and SEM analyses reveal that the capacity decay of the bulk-type LilLLZTOILCO-LLZTO ASSBs is mainly attributed to the degradation of the Li/LLZTO interface induced by the uneven Li plating/stripping, which results in interfacial contact loss and continuous increase in interfacial impedance, while the LCO/LLZTO interface possesses high stability, and maintains intimate contact and extremely low interfacial impedance even after long-term operation. The deterioration of the Li/LLZTO interface can be mitigated via decreasing the areal capacity of Li plating/stripping. The LilLLZTO/LCO-LLZTO full cells with areal capacities of 0.73 mAh cm<sup>-2</sup> and 0.49 mAh cm<sup>-2</sup> exhibit superior cycling stability with capacity retention of 81.7% and 92.3% after 50 cycles, respectively. Overall, our investigation proposes a promising methodology to address the key challenge of a cathode/LLZTO interface and provides guidance for future development of high-capacity garnetbased ASSBs.

#### Acknowledgments

This work was supported by the National Key R&D Program of China (Grant No. 2021YFB2401800), the National Natural Science Foundation of China (Grants Nos. 21875196, 22279108, 21935009 and 22021001) and the Fundamental Research Funds for Xiamen University (No. 20720202019).

## **Conflict of interest**

The authors declare no conflict of interest.

### **ORCID iDs**

Chenxi Zheng b https://orcid.org/0000-0002-9627-3059 Shijun Tang b https://orcid.org/0000-0002-1943-1922 Zhengliang Gong b https://orcid.org/0000-0003-4671-4044 Yong Yang b https://orcid.org/0000-0002-9928-7165

#### References

- Zhao N, Khokhar W, Bi Z, Shi C, Guo X, Fan L Z and Nan C W 2019 Solid garnet batteries *Joule* 3 1190–9
- [2] Manthiram A, Yu X and Wang S 2017 Lithium battery chemistries enabled by solid-state electrolytes *Nat. Rev. Mater.* 2 16103
- [3] Gao Y, Sun S, Zhang X, Liu Y, Hu J, Huang Z, Gao M and Pan H 2021 Amorphous dual-layer coating: enabling high Li-ion conductivity of non-sintered garnet-type solid electrolyte Adv. Funct. Mater. 31 2009692
- [4] Xu W, Wang J, Ding F, Chen X, Nasybulin E, Zhang Y and Zhang J G 2014 Lithium metal anodes for rechargeable batteries *Energy Environ. Sci.* 7 513–37
- [5] Murugan R, Thangadurai V and Weppner W 2007 Fast lithium ion conduction in garnet-type Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> Angew. Chem., Int. Ed. 46 7778–81
- [6] Shao Y *et al* 2018 Drawing a soft interface: an effective interfacial modification strategy for garnet-type solid-state Li batteries ACS Energy Lett. 3 1212–8
- [7] Fu K K, Gong Y, Fu Z, Xie H, Yao Y, Liu B, Carter M, Wachsman E and Hu L 2017 Transient behavior of the metal interface in lithium metal-garnet batteries *Angew*. *Chem., Int. Ed.* 56 14942–7
- [8] Han X *et al* 2017 Negating interfacial impedance in garnet-based solid-state Li metal batteries *Nat. Mater.* 16 572–9
- [9] Huang Y, Chen B, Duan J, Yang F, Wang T, Wang Z, Yang W, Hu C, Luo W and Huang Y 2020 Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>): an interface enabler for solid-state lithium metal batteries *Angew. Chem., Int. Ed.* **59** 3699–704
- [10] Tang S, Chen G, Ren F, Wang H, Yang W, Zheng C, Gong Z and Yang Y 2021 Modifying an ultrathin insulating layer to suppress lithium dendrite formation within garnet solid electrolytes J. Mater. Chem. A 9 3576–83
- [11] Lee S, Lee K S, Kim S, Yoon K, Han S, Lee M H, Ko Y, Noh J H, Kim W and Kang K 2022 Design of a lithiophilic and electron-blocking interlayer for dendrite-free lithium-metal solid-state batteries *Sci. Adv.* 8 eabg0153
- [12] Huo H, Chen Y, Li R, Zhao N, Luo J, Pereira da Silva J G, Mücke R, Kaghazchi P, Guo X and Sun X 2020 Design

of a mixed conductive garnet/Li interface for dendrite-free solid lithium metal batteries *Energy Environ. Sci.* **13** 127–34

- [13] Huo H, Chen Y, Zhao N, Lin X, Luo J, Yang X, Liu Y, Guo X and Sun X 2019 *In-situ* formed Li<sub>2</sub>CO<sub>3</sub>-free garnet/Li interface by rapid acid treatment for dendrite-free solid-state batteries *Nano Energy* 61 119–25
- [14] Ruan Y, Lu Y, Huang X, Su J, Sun C, Jin J and Wen Z 2019 Acid induced conversion towards a robust and lithiophilic interface for Li–Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> solid-state batteries *J. Mater. Chem.* A 7 14565–74
- [15] Duan H et al 2020 Building an air stable and lithium deposition regulable garnet interface from moderate-temperature conversion chemistry Angew. Chem., Int. Ed. 59 12069–75
- [16] Cai M, Jin J, Xiu T, Song Z, Badding M E and Wen Z 2022 In-situ constructed lithium-salt lithiophilic layer inducing bi-functional interphase for stable LLZO/Li interface Energy Storage Mater. 47 61–69
- [17] Park K, Yu B C, Jung J W, Li Y, Zhou W, Gao H, Son S and Goodenough J B 2016 Electrochemical nature of the cathode interface for a solid-state lithium-ion battery: interface between LiCoO<sub>2</sub> and garnet-Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> Chem. Mater. 28 8051–9
- [18] Ren Y, Liu T, Shen Y, Lin Y and Nan C W 2016 Chemical compatibility between garnet-like solid state electrolyte Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Ta<sub>0.25</sub>O<sub>12</sub> and major commercial lithium battery cathode materials *J. Materiomics* 2 256–64
- [19] Yu C Y, Choi J, Han J, Lee E and Kim J-H 2022 Phase stability of garnet solid-electrolyte interfacing with various cathodes in all solid-state batteries *J. Electrochem. Soc.* 169 020520
- [20] Zhang L, Zhuang Q, Zheng R, Wang Z, Sun H, Arandiyan H, Wang Y, Liu Y and Shao Z 2022 Recent advances of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>-based solid-state lithium batteries towards high energy density *Energy Storage Mater*. 49 299–338
- [21] Mücke R, Finsterbusch M, Kaghazchi P, Fattakhova-Rohlfing D and Guillon O 2021 Modelling electro-chemical induced stresses in all-solid-state batteries: anisotropy effects in cathodes and cell design optimisation *J. Power Sources* 489 229430
- [22] Ihrig M et al 2022 Study of LiCoO<sub>2</sub>/Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>: taInterface degradation in all-solid-state lithium batteries ACS Appl. Mater. Interfaces 14 11288–99
- [23] Zhu Y, He X and Mo Y 2016 First principles study on electrochemical and chemical stability of solid electrolyte–electrode interfaces in all-solid-state Li-ion batteries J. Mater. Chem. A 4 3253–66
- [24] Menetrier M, Saadoune I, Levasseur S and Delmas C 1999 The insulator-metal transition upon lithium deintercalation from LiCoO<sub>2</sub>: electronic properties and <sup>7</sup>Li NMR study J. Mater. Chem. 9 1135–40
- [25] Antolini E and Ferretti M 1995 Synthesis and thermal stability of LiCoO<sub>2</sub> J. Solid State Chem. 117 1–7
- [26] Hubaud A A, Schroeder D J, Ingram B J, Okasinski J S and Vaughey J T 2015 Thermal expansion in the garnet-type solid electrolyte (Li<sub>7-x</sub>Al<sub>x/3</sub>)La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> as a function of Al content J. Alloys Compd. 644 804–7
- [27] Cheng E J, Taylor N J, Wolfenstine J and Sakamoto J 2018 Elastic properties of lithium cobalt oxide (LiCoO<sub>2</sub>) J. Asian Ceram. Soc. 5 113–7
- [28] Sastre J, Chen X, Aribia A, Tiwari A N and Romanyuk Y E 2020 Fast charge transfer across the Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> solid electrolyte/LiCoO<sub>2</sub> cathode interface enabled by an interphase-engineered all-thin-film architecture ACS Appl. Mater. Interfaces 12 36196–207
- [29] Ren Y and Wachsman E D 2022 All solid-state Li/LLZO/LCO battery enabled by alumina interfacial coating J. *Electrochem. Soc.* 169 040529

- [30] Kato T, Hamanaka T, Yamamoto K, Hirayama T, Sagane F, Motoyama M and Iriyama Y 2014 *In-situ* Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>/ LiCoO<sub>2</sub> interface modification for advanced all-solid-state battery J. Power Sources 260 292–8
- [31] Han F, Yue J, Chen C, Zhao N, Fan X, Ma Z, Gao T, Wang F, Guo X and Wang C 2018 Interphase engineering enabled all-ceramic lithium battery *Joule* 2 497–508
- [32] Guo H, Shen F, Guo W, Zeng D, Yin Y and Han X 2021 LiCoO<sub>2</sub>/Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Nb<sub>0.25</sub>O<sub>12</sub> interface modification enables all-solid-state battery *Mater. Lett.* **301** 130302
- [33] Balasubramaniam R, Nam C W, Aravindan V, Eum D, Kang K and Lee Y S 2021 Interfacial engineering in a cathode composite based on garnet-type solid-state Li-Ion battery with high voltage cycling *ChemElectroChem* 8 570–6
- [34] Tsai C-L et al 2019 A garnet structure-based all-solid-state Li battery without interface modification: resolving incompatibility issues on positive electrodes Sustain. Energy Fuels 3 280–91
- [35] Liu T, Zhang Y, Zhang X, Wang L, Zhao S X, Lin Y H, Shen Y, Luo J, Li L and Nan C W 2018 Enhanced electrochemical performance of bulk type oxide ceramic lithium batteries enabled by interface modification *J. Mater. Chem.* A 6 4649–57
- [36] Liu T, Ren Y, Shen Y, Zhao S X, Lin Y and Nan C W 2016 Achieving high capacity in bulk-type solid-state lithium ion battery based on Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Ta<sub>0.25</sub>O<sub>12</sub> electrolyte: interfacial resistance J. Power Sources **324** 349–57
- [37] Liu T, Zhang Y, Chen R, Zhao S X, Lin Y, Nan C W and Shen Y 2017 Non-successive degradation in bulk-type all-solid-state lithium battery with rigid interfacial contact *Electrochem. Commun.* 79 1–4
- [38] Kim K J and Rupp J L M 2020 All ceramic cathode composite design and manufacturing towards low interfacial resistance for garnet-based solid-state lithium batteries *Energy Environ. Sci.* 13 4930–45
- [39] Ihrig M et al 2021 Low temperature sintering of fully inorganic all-solid-state batteries—impact of interfaces on full cell performance J. Power Sources 482 228905

- [40] Bram M et al 2020 Application of electric current-assisted sintering techniques for the processing of advanced materials Adv. Eng. Mater. 22 2000051
- [41] Laptev A M, Zheng H, Bram M, Finsterbusch M and Guillon O 2019 High-pressure field assisted sintering of half-cell for all-solid-state battery *Mater. Lett.* 247 155–8
- [42] Feng W, Lai Z, Dong X, Li P, Wang Y and Xia Y 2020 Garnet-based all-ceramic lithium battery enabled by Li<sub>2985</sub>B<sub>0005</sub>OCl solder *iScience* 23 101071
- [43] Il'ina E, Pershina S, Antonov B and Pankratov A 2021 Impact of Li<sub>3</sub>BO<sub>3</sub> Addition on solid electrode-solid electrolyte interface in all-solid-state batteries *Materials* 14 7099
- [44] Han X et al 2021 All solid thick oxide cathodes based on low temperature sintering for high energy solid batteries Energy Environ. Sci. 14 5044–56
- [45] Kim K H, Iriyama Y, Yamamoto K, Kumazaki S, Asaka T, Tanabe K, Fisher C A J, Hirayama T, Murugan R and Ogumi Z 2011 Characterization of the interface between LiCoO<sub>2</sub> and Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> in an all-solid-state rechargeable lithium battery J. Power Sources 196 764–7
- [46] Takahara H, Takeuchi T, Tabuchi M, Kageyama H, Kobayashi Y, Kurisu Y, Kondo S and Kanno R 2004 All-solid-state lithium secondary battery using oxysulfide glass—addition and coating of carbon to positive electrode *J. Electrochem. Soc.* 151 A1539–44
- [47] Carson G A, Nassir M H and Langell M A 1996 Epitaxial growth of Co<sub>3</sub>O<sub>4</sub> on CoO (100) J. Vac. Sci. Technol. A 14 1637–42
- [48] Xu J, Wu J, Luo L, Chen X, Qin H, Dravid V, Mi S and Jia C 2015 Co<sub>3</sub>O<sub>4</sub> nanocubes homogeneously assembled on few-layer graphene for high energy density lithium-ion batteries J. Power Sources 274 816–22
- [49] Ohta S, Kobayashi T, Seki J and Asaoka T 2012 Electrochemical performance of an all-solid-state lithium ion battery with garnet-type oxide electrolyte *J. Power Sources* 202 332–5