Li$_2$CO$_3$-affiliative mechanism for air-accessible interface engineering of garnet electrolyte via facile liquid metal painting

Junwei Meng$^{1,2}$, Yang Zhang$^{1,2}$, Xuejun Zhou$^1$, Meng Lei$^1$ & Chilin Li$^{1,2}$

Garnet based solid-state batteries have the advantages of wide electrochemical window and good chemical stability. However, at Li-garnet interface, the poor interfacial wettability due to Li$_2$CO$_3$ passivation usually causes large resistance and unstable contact. Here, a Li$_2$CO$_3$-affiliative mechanism is proposed for air-accessible interface engineering of garnet electrolyte via facile liquid metal (LM) painting. The natural LM oxide skin enables a superior wettability of LM interlayer towards ceramic electrolyte and Li anode. Therein the removal of Li$_2$CO$_3$ passivation network is not necessary, in view of its delamination and fragmentation by LM penetration. This dissipation effect allows the lithiated LM nanodomains to serve as alternative Li-ion flux carriers at Li-garnet interface. This mechanism leads to an interfacial resistance as small as 5 $\Omega$ cm$^2$ even after exposing garnet in air for several days. The ultrastable Li plating and stripping across LM painted garnet can last for 9930 h with a small overpotential.
Lithium metal batteries (LMBs) are attracting more attentions due to their high energy densities, benefiting from lithium metal anode with low redox electrochemical potential and high theoretical specific capacity. Uncontrollable lithium dendrite growth would cause serious side reaction with organic liquid electrolyte (LE) and even lead to the dry up of electrolyte. The inferior cycling performance as well as the high safety risk (such as leakage and explosion) severely hinder the development and wide application of LMBs. The employment of solid-state electrolyte (SSE) is thought to be a promising solution to Li dendrite suppression due to its high Young’s modulus (e.g., ~150 GPa for garnet oxide ceramic) and chemical stability even at high temperature (e.g., up to 300 °C for garnet). Besides, many SSEs possess broader electrochemical window which can reach up to 5 V. Among current SSEs, polymer or hybrid electrolytes provide the advantages of flexibility and deformability but at a cost of relatively low ionic conductivity at room temperature (RT) (≤0.1 mS cm⁻¹). Inorganic ceramic SSEs not only provide high ionic conductivity (close to 1 mS cm⁻¹), but also are endowed with better nonflammability and moisture-resistance than sulfide/halide SSEs. The doped garnet-La₃Ga₅Zr₂O₁₂ (LLZO) SSE shows the anode stability advantage over other oxide SSEs, such as NASICON-LiₓAlₓTi₁₋ₓPO₄ and perovskite-Li₀.₃₂La₀.₅₆TiO₃, due to the lacking of redox active elements (e.g., Ti, Ge). Nevertheless, the interfacial problem between lithium metal and garnet electrolyte still exists in view of the potential passivation of ceramic grains by naturally formed Li₂CO₃, which results in poor wettability of LLZO surface by Li plating and large interfacial resistance. In order to modify the interface contact, some methods have been attempted to eliminate Li₂CO₃ (e.g., by carbothermal reaction, high-temperature calcination, or acid treatment) or construct lithiophilic interlayer (e.g., by depositing alloyforming metal, decorating Li⁺-conductive polymer, pasting soft graphite, or two-dimensional MoS₂). For the alloyable stage, some expensive installations and refined manipulation for thin film deposition (e.g., atomic layer deposition and chemical vapor deposition) are usually required in order to achieve compact planar contact. Although the facile addition of alloyable elements (e.g., Sn or graphite) into molten Li can also improve the wettability of anode on LLZO by tuning the surface tension and viscosity of molten lithium, high weight percent of blended alloy (e.g., blending 50% Sn or 70% graphite) is required for best wetting effect. In this case, the theoretical specific capacity of alloying anode would be significantly reduced compared with pristine Li anode.

Liquid metal (LM) gallium and gallium-based alloys have been widely used in the field of soft microfluidic electronics due to their low viscosity (2 mPa s), low toxicity, and negligible vapor pressure. Although the high surface tension of pure LM makes it difficult to wet substrates under oxygen-lean condition, the self-formed Ga₂O₃ skin in an oxygenated environment can lead to the lowering of effective surface tension. This oxide layer allows LM droplets to wet substrate surfaces and also stabilizes LM by preventing it from further oxidation. The Ga₂O₃ skin with a thickness of 0.5–3 nm behaves like an elastic membrane that can reform instantaneously when broken, therefore, enabling LM to be structurally self-stabilized under external multivariate conditions. This particular wetting behavior of LM with intrinsic Ga₂O₃ skin makes it an available painting material on substrate surface or penetrating material in grain boundaries (GBs).

In this work, we propose a lithiophilic layer building strategy by brushing LM with excellent wetting behavior on garnet-based ceramic electrolyte surface to significantly reduce its interfacial resistance and assist the high reversibility of LMBs. This facile method does not require extra deposition equipment and exact (high) alloying content. The conformal oxide layer on LM enables a smooth brushing of LM paint on solid electrolyte surface, which can prevent garnet from further exposure to water and O₂ in air. In addition, LM can infiltrate into the GBs of garnet to a certain depth, leading to a better interface transition effect. On the other hand, lithiated LM layer can provide extra Li⁺ transport channels and its high affinity with Li₂CO₃ enables the bypassing of charge transport from Li₂CO₃ passivation layer. With the assistance of LM painting, the area-specific resistance (ASR) values of Li-garnet interface decrease to 5 Ω cm² at 60 °C. The Li/Li symmetric cells can cycle for at least 9930 h with small overvoltage values.

**Results**

**Wetting behavior of painted LM with naturally oxidized skin.** Herein, we choose Ta₂O₅ as doping agent for cubic garnet electrolyte in view of the structural stabilization and high ionic conductivity of LiₓLa₃AlₓZr₁₋ₓTa₉ₓO₁₂ (LLZT) electrolyte (Supplementary Figs. 1–3). The electrochemical impedance spectra (EIS) of Ag/garnet/Ag symmetric configuration were measured to obtain a RT ionic conductivity of LLZT of 4 × 10⁻⁴ S cm⁻¹ with an activation energy of 0.36 eV (Supplementary Fig. 4). Pristine garnet electrolyte with a lithiophobic surface from insulating Li₂O₂, causes poor wettability for lithium anode and therefore point contact between anode and electrolyte (Fig. 1a). There is a big gap that separates molten lithium from pristine garnet electrolyte surface (Supplementary Fig. 5). In contrast, with simple painting of gallium LM on garnet surface (marked as LM@LLZT under air, a highly lithiophilic and conformal interlayer is expected to be constructed due to the elastic Ga₂O₃ skin coverage on LM inclusions (Fig. 1b). Under oxygen-lean condition (e.g., in vacuum or argon), LM has low viscosity and high surface tension, and exists in the form of nearly spherical shape, which is hard to wet garnet substrate and shows a large contact angle more than 90° (Fig. 1c). After LM is exposed to air to generate an oxide layer, significantly reduced surface tension and improved viscosity endow LM with excellent wettability and paint behavior. After removing excess gallium metal, a dark film composed of residual elastic gallium oxide is well formed on garnet surface. The realistic photos at different stages are correspondingly provided as insets of Fig. 1c. To further certify the versatility of the unique painting behavior of LM, we dropped them on different substrates of Al₂O₃ plate, Cu foil and A₃ paper (Fig. 1d, e). The excellent spreadability is also observed for all the substrates when LM is operated under air with the formation of self-passivating Ga₂O₃ film. This stable pasting behavior is caused by surface-dispersed Van der Waals force of gallium oxide, which is favorable for the gap or void healing at anode-electrolyte interface. The scanning electron microscopy (SEM) images of LM@LLZT further certify the wetting behavior of surface-oxidized LM. Note that the Ga₂O₃ film enables a smooth and continuous coating on garnet grains (Fig. 1f and Supplementary Fig. 6), and the rough GBs are not discernable. From the view of cross-section images (Fig. 1g and Supplementary Fig. 7), LM with oxide skin totally wets the bumpiness zone and GBs at electrolyte surface without any gap exposure. Energy dispersive X-ray spectroscopy (EDS) mapping of LLZT proves the homogenous distribution of Ga element as consequence of favorable painting of LM (Supplementary Fig. 8).

When dipping LM@LLZT into molten lithium, fast lithiation can be achieved in merely 2 min (Fig. 2a), while molten lithium cannot wet the surface of pristine LLZT covered with an intrinsic lithiophobic skin (Supplementary Fig. 9). The garnet surface after lithiation shows a compact coverage of lithium with desired metallic luster. The improved wettability of Li metal toward LM-
The corresponding Ga$_2$O$_3$ peak is located at 531.9 eV\(^4\). The other SEM image of liquid metal painted garnet. Continuous morphology of interlayer is well preserved (Fig. 2b, c). Color turning from pristine dark (the color of gallium-oxide skin) and covers the entire surface of LM@LLZT within 5 min with the Li disc is heated at 200 °C, the molten Li spreads quickly (Fig. 1a). When a Li disc is heated at 200 °C, the molten Li spreads quickly and covers the entire surface of LM@LLZT within 5 min with the molten Li spreads quickly and covers the entire surface of LM@LLZT within 5 min with the wetting behavior of molten lithium on the surfaces of (a) unmodified garnet and (b) liquid metal painted garnet at 230 °C. Schematic of liquid metal on garnet surface in oxygen-lean atmosphere and air environment, as well as elastic gallium oxide residual on garnet surface. Inset: realistic wetting situation of liquid metal on garnet in corresponding environments. Wettability of liquid metal on different substrates (from left to right: Al$_2$O$_3$ plate, Cu foil, A$_4$ paper) under (d) argon and (e) air environments. f) Surface SEM image of liquid metal painted garnet. g) Cross-section SEM image of LM-wetted garnet.

Fig. 1 Wetting behavior of LM in air on garnet surface. Schematic of wetting behavior of molten lithium on the surfaces of (a) unmodified garnet and (b) liquid metal painted garnet at 230 °C. Schematic of liquid metal on garnet surface in oxygen-lean atmosphere and air environment, as well as elastic gallium oxide residual on garnet surface. Inset: realistic wetting situation of liquid metal on garnet in corresponding environments. Wettability of liquid metal on different substrates (from left to right: Al$_2$O$_3$ plate, Cu foil, A$_4$ paper) under (d) argon and (e) air environments. f) Surface SEM image of liquid metal painted garnet. g) Cross-section SEM image of LM-wetted garnet.

Li$_2$CO$_3$-affiliative mechanism via LM painting. Note that the good contact between LLZT and LM can be obtained even without intentional removal of the so-called passivated Li$_2$CO$_3$. There is a speculation that alloyable element (e.g., Zn) may react with Li$_2$CO$_3$ to create more Li vacancies in passivation layer for faster Li-ion transport at the interface zone\(^3\). However there is no strong evidence to support this prediction. Herein, we propose a Li$_2$CO$_3$-affiliative mechanism in which Li$_2$CO$_3$ on garnet surface is wetted and downsized by LM drops, and it is torn into Li$_2$CO$_3$ nanodomains by surrounding LM nanoparticles with similar nanoscale. The superior wettability can guarantee a homogeneous mixing of Li$_2$CO$_3$ and LM nanodomains. Therefore the separated Li$_2$CO$_3$ grains cannot form continuous passivation layer to retard Li-ion transport. Instead, the well-dispersed LM grains can serve as ion wires after lithiation to construct the alternative ion channels especially when they penetrate into continuous conductive network. To prove our hypothesis, we ground LM with Li$_2$CO$_3$ or garnet powder (Fig. 3a). Under the mechanical force during the mixing process in air, the shiny LM is pulverized into much smaller particles that blend with white Li$_2$CO$_3$ or light-yellow garnet powder. The resultant darkening stems from the higher-fraction oxidized regions of tearing LM grains by air or oxide powder. In contrast, the pristine LM still maintains its metal luster even after grinding in air in view of the self-limiting surface oxidation. These phenomena indicate the facile dispersion capability of LM when contacting with carbonate or ceramic powder. The strong Van der Waals’ force of self-formed gallium-oxide skin is responsible for its coverage on powder grains\(^3\). The XRD pattern of the mixture of LM and Li$_2$CO$_3$ (LM@Li$_2$CO$_3$) does not display the evident peaks ascribed to LM (Supplementary Fig. 14a), further indicating the attenuation of LM after dispersing and downsizing. The enrichment of gallium oxide does not cause the appearance of excess diffraction peaks due to its relatively poor crystallinity\(^3\) the Li$_2$CO$_3$ peak is found at 20.9 eV for Ga 3d as expected, and it is more intensive than that of Ga metal at 19.5 eV, which is conformally coated by the former\(^3\). For O 1s spectrum, the corresponding Ga$_2$O$_3$ peak is located at 531.9 eV\(^4\) the other peaks due to its relatively poor crystallinity\(^3\). The pronounced
peaks of Li₂CO₃ are still preserved after mixing with LM, considering the mechanical robustness of well-crystallized Li₂CO₃. Similarly, the mixing of LM with LLZT (LM@LLZT) also causes the weakening and elimination of LM diffraction peaks (Supplementary Fig. 16). The cubic phase structure of LLZT is not destroyed after mixing with LM.

To further explore this fascinating wetting phenomenon of LM with Li₂CO₃ powder, transmission electron microscopy (TEM) was resorted to. Fig. 3b discloses the excellent mutual miscibility between LM and Li₂CO₃ nanodomains, and there is no serious phase segregation observed. Under high resolution (Fig. 3c, d), we clearly observe the homogenous distribution of LM and Li₂CO₃ nanoparticles with comparable sizes as small as 3–5 nm. The LM particles are discerned from the darker spots, while the Li₂CO₃ ones are the crystallized domains with typical lattice fringes corresponding to (311), (020), (−112) planes with d-spacings of 0.187, 0.249, 0.262 nm, respectively (Supplementary Fig. 17). In view of the actual interface with excess LM modification compared with the amount of naturally formed Li₂CO₃, we also intentionally blended higher-fraction LM with Li₂CO₃ to see the microscopic distribution of mixture. As shown in Fig. 3e–g, some big drop-like spheres of LM are still residual without undergoing

Fig. 2 Improved wetting behavior of Li anode on LM-painted garnet. a Photos taken with time showing the lithiation process of LM-wetted garnet and photo of lithiated anode tightly adhered on garnet surface after 2 min. b SEM image of lithiated interface with liquid metal painting between Li and LLZT and (c) its enlarged SEM image to disclose the compact interface. Cross-section SEM images of interfaces between Li and liquid metal painted garnet after (d) Li plating and (e) stripping based on an area capacity of 1 mAh cm⁻². XPS spectra of LM-decorated garnet surface exhibiting (f) Ga 3d and (g) O 1s spectra before and after lithiation.
the fragmentation due to the insufficiency of carbonate. However, their oxidation surface still has good affilative ability toward surrounding Li$_2$CO$_3$, leading to the appearance of Li$_2$CO$_3$ moieties anchored on LM sphere surface. A part of Ga$_2$O$_3$ skins are likely peeled off and enter into the Li$_2$CO$_3$ network to form the mutual mixture. This would result in the interaction reinforcement at Li$_2$CO$_3$-LM interface as indicated from the firm attachment of LM to the Li$_2$CO$_3$-covered LLZT surface even after Li plating and stripping. The scanning transmission electron microscopy (STEM) image and corresponding EDS mapping images of C, O, Ga elements (Fig. 3h) disclose the similar spatial distributions of carbonate and LM components, further confirming the uniform...
Solid-state cells benefiting from superior LM wettability. To characterize the electrochemical benefit from this strategy, lithium symmetric cells were assembled with the LM-painted LLZT (marked as Li|LM@LLZT|Li) and unmodified garnet (marked as Li|LLZT|Li) as solid electrolytes, respectively. The EIS of Li/Li symmetric cells was performed to evaluate the interface situation. The interfacial ASR values of symmetric cells are significantly decreased from 1.75 × 104 to 19.5 mΩ cm2 at RT, and from 272 to 5 Ω cm2 at 60 °C after LM painting on both the sides of garnet (Fig. 4a, b). The ASR values are estimated based on the equivalent circuit in the insets of Fig. 4a, b, which shows good fitting effect. Therein \( R_Ω \), \( R_{opt} \), and \( R_{surf} \) denote the ASRs for garnet, interface transfer, and surface reaction, respectively. \( CPE_{int} \) and \( CPE_{surf} \) denote the constant phase elements paralleled with \( R_{int} \) and \( R_{surf} \), respectively. The corresponding characteristic time constants (\( \tau \) and capacitance values (\( C \)) are listed in Supplementary Table 1. C and \( \tau \) can be expressed by \( (R^{−1}nCPE)^{1/n} \) and RC, where \( n \) is CPE exponent. The capacitance values referring to interfacial transport are in the range of \( 10^{−9}−10^{−7} \) F cm−2, while those referring to surface reaction are in the range of \( 10^{−7}−10^{−5} \) F cm−2. The discrepancy of capacitance range depending on different process is in accordance with the precious report by Irvine et al. After LM painting, the relaxation time is shortened no matter for the interfacial or surface process, also indicating an improved electrochemical kinetics. Both the ASR values of Li|LM@LLZT|Li at RT and 60 °C are smaller than most of reported values even if the garnet pellets we used have been intentionally exposed to air for several days (Supplementary Table 2). These comparisons demonstrate the superiority of this facile painting strategy.

The symmetric Li|LM@LLZT|Li cells can achieve an ultralong Li plating/stripping cycling for at least 9930 h (4965 cycles) at 60 °C with an ultra-small overpotential from ~10 to 10 mA m−2, as well as from ~33 to 33 mV at RT at a current density of 0.2 mA cm−2 based on an areal capacity of 0.2 mA h cm−2 (Fig. 4c). The symmetric cell at RT can be steadily cycled for at least 2000 h. Note that the Li plating and stripping curves of symmetric cells are quite flat and smooth during the early cycling and after long-term cycling (insets of Fig. 4c), indicating the elimination of nucleation overpotential as a consequence of facile charge transport across lithiated LM. In all-solid-state architecture, there is no extra accumulation of solid electrolyte interface from side reaction to cause larger nucleation resistance and overpotential. The modification of impedance and cycling performance also benefits from the prior Li melting step (230 °C for 5 min) for better interface contact. Note that the symmetric cell even without Li melting pretreatment can also cycle for a long time over 750 h, but at a cost of unstable polarization activation process during early cycling (Supplementary Fig. 19). After activation, the overpotential is quite stable and is still small (from ~20 to 20 mV) at 60 °C, benefiting from the construction of mixed conductive network induced by electrochemical lithiation of LM interlayer. In contrast, the symmetric cell with unmodified garnet reaches to the short circuit stage quickly after merely several hours (Supplementary Fig. 20). Before short circuit, the overpotential is also large and asymmetric between plating and stripping (with a gap of ~1.3 V) even at a smaller current density of 0.1 mA cm−2. The appearance of tip phenomenon in voltage profiles is caused by the poor interface contact. For the LM-modified symmetric cell, stable rate performance is recorded with the increase of current density from 0.05 to 1.2 mA cm−2 as shown in Fig. 4d. The corresponding voltage profiles do not undergo serious degradation, and they are roughly flat even at much higher current density exceeding 1 mA cm−2. Even when reaching to 1 mA cm−2, the overpotential is still controlled between ~28 and 28 mV (Fig. 4e). This low plateau overpotential does not increase remarkably and can last for at least 150 h during the following cycling. A high critical current density (CCD, defined as the highest applied current density that the solid-state electrolyte can endure the lithium dendrite penetration) value up to 1.7 mA cm−2 can be reached for the LM improved symmetric cell (Fig. 4g), while the CCD value for unmodified cell is much smaller (0.3 mA cm−2) even with the assistance of LE wetting (Fig. 4f). This high CCD value in this work is superior to most of the literature reports (e.g., 0.5 mA cm−2 for Sn film alloying, 0.8 mA cm−2 for H2PO4 modification, 1 mA cm−2 for Li-graphite anode), indicating an excellent defense capability of LM interlayer against Li dendrite growth.20,29,48 As suggested by Flachers et al.,46 CCD is highly related to the conditions of interface wetting, pressure, and temperature. The obtained high CCD value also confirms the perfect Li wetting and agrees with the significantly reduced ASR values at the fixed conditions without externally applied pressure and high temperature.

Since the symmetric cell architecture employs excess Li, it is not suitable to evaluate the accurate utilization ratio of anode as well as accumulation degree of dendritic Li or dead Li in GBs. To further explore the dendrite suppression effect modulated by LM painting, we also performed the asymmetric cells, which were not often used to estimate the Li plating behavior. Herein the carbon-coated Al foil (denoted as C@Al) is used as the nonlithium electrode. The asymmetric cell with solid electrolyte painted by LM is denoted as Li|LM@LLZT|C@Al, while the control cell with extra LE dropped on the anode side of garnet is denoted as Li|LE@LLZT|C@Al. Benefiting from the excellent wettability of LM and its dissipation effect on passive Li2CO3, the lithiated interphase layer allows a uniform Li+ flux from bulk electrolyte to anode, thus resulting in a high utilization ratio of Li (Fig. 5a). In contrast, for control cell, the dendrites are expected to initiate at interface and grow inside garnet due to the uneven Li+ flux frustrated by continuous Li2CO3, causing a low utilization ratio of Li even with LE addition (Supplementary Fig. 21). The coulombic efficiencies (CEs) for Li|LM@LLZT|C@Al are well stabilized at the high values close to 100% for at least 100 cycles after early activation (Fig. 5b), while the Li|LE@LLZT|C@Al cell can only run for <20 cycles with a smaller CE value of ~90% before failure. The former cell has a much smaller voltage hysteresis (e.g., 70 mV
Fig. 4 Electrochemistry of Li/Li symmetric cells based on LM-wetted garnet. Electrochemical impedance spectra of Li|LM@LLZT|Li symmetric cells at (a) room temperature and (b) 60 °C. Insets: corresponding impedance spectra of Li|LLZT|Li symmetric cells without any modification. c Long-term performance of Li|LM@LLZT|Li symmetric cells at 0.2 mA cm$^{-2}$ at room temperature and 60 °C. Insets: corresponding voltage profiles at different cycling stages. d Rate performance of Li|LM@LLZT|Li symmetric cell from 0.05 to 1.2 mA cm$^{-2}$. e Li plating-stripping performance Li|LM@LLZT|Li symmetric cell at a high current density of 1 mA cm$^{-2}$. Critical current density measurement of Li/Li symmetric cells based on (f) unmodified garnet (with 10 μL of liquid electrolyte adding) and based on (g) liquid metal painted garnet.
in the 10th cycle) than that (325 mV) for the latter cell in the same cycling stages (Fig. 5c). The voltage hysteresis after LM painting is preserved at a low value without serious fluctuation during the whole cycling process (Fig. 5d). For unmodified cell, the voltage hysteresis increases rapidly after ten cycles. These results further confirm the improved reversibility and kinetics of Li plating through the stable LM interlayer, leading to the alleviations of active Li roughening and dead Li formation.

Interface reactions between lithiated LM components and LLZT were also studied (based on first-principle computations)\textsuperscript{49,50}. The interface is considered as a pseudo-binary structure of lithiated interphase and garnet and the most stable phase equilibria based on thermodynamic driving forces is determined. Lithiated interphase (e.g., main components Li\textsubscript{3}Ga\textsubscript{2}, Li\textsubscript{2}Ga\textsubscript{3}, and LiGaO\textsubscript{2}) shows better chemical stability with garnet (than Li metal) with a minor reaction energy more than −15 meV/atom (Fig. 5e), which is higher than that of Li-LLZT and much higher than previously reported values (e.g., −40 to −90 meV/atom for Si-garnet, −24.78 to −62 meV/atom for Al-garnet, −20 to −100 meV/atom for Li\textsubscript{x}C-garnet)\textsuperscript{21,29,51}. Therefore the side reaction between lithiated LM and LLZT is greatly mitigated. The mutual reaction energy shows the similar trend (Fig. 5f) and this moderate mutual reaction might assist the wetting of LM-alloyed anode with garnet surface (especially for Li\textsubscript{2}Ga component). Since the wettability of molten lithium on Li\textsubscript{2}CO\textsubscript{3}-free garnet is not bad\textsuperscript{52}, the much more negative mutual reaction energy (than −10.54 to −10.61 meV/atom for Li-garnet in Supplementary Table 3a) may be not necessary. The higher minor reaction energy of lithiated interphases than pure Li would not cause serious interface passivation and be favorable for the endurance in terms of long cycling, high current density, and large area capacity of symmetric cells. We also considered the potentiality of reaction between other possible component (e.g., LiGa, Li\textsubscript{2}Ga\textsubscript{7}, Li\textsubscript{5}Ga\textsubscript{4} undetectable from XRD of lithiated LM) or trace phase (LiGa\textsubscript{5}O\textsubscript{8}) and garnet electrolyte. There is no probable reaction occurring between LiGa or Li\textsubscript{2}Ga\textsubscript{7} and ceramic, while Li\textsubscript{5}Ga\textsubscript{4} has a low reactivity based on its reaction energy of −6 meV/atom with garnet ( Supplementary Table 3d), which is higher than the decomposition energy of Li\textsubscript{2}CO\textsubscript{3}}.
The trace LiGa2O4 phase shows the more negative reaction energy values (Supplementary Table 3f) comparable with those for Al and graphite29,51, and its possible reaction products are still stable Li2GaO4 and LiGa2O3 phases (no reaction between Li2GaO4 and garnet). Therefore the Li-Ga-O interphases would not passivate the interface with LLZT.

LM-painted garnet is expected to drive the solid-state LMBs with better kinetic performance. The Li[LiM@LLZT]PEO@LiFePO4 cell contains LiFePO4 cathode composited with polyethylene oxide (PEO) and lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) salt as Li-ion wire (Fig. 6a). The interfacial resistance of full cell including both the contributions of anode and cathode interfaces is ~150 Ω cm2 (Fig. 6b). This resistance value is dominated by the contribution of LLZT-cathode interface in view of the small resistance (5 Ω cm2) of Li-LM@LLZT interface. This cathode interface resistance (143 Ω cm2) is not high and comparable to those for Al and graphite29,51, and its possible reaction products are still stable Li5GaO4 and LiGaO2 phases (no reaction between Li5GaO4 and garnet). Therefore the Li-Ga-O interphases would not passivate the interface with Li2CO3.

In contrast, for the lithiated LM@LLZT sample, the Li2CO3 peak is weakened and the La signals are not expected result because the upper Li2CO3 coverage is attenuated after etching process. This is an expected result because the upper Li2CO3 coverage is attenuated after etching process. This is an expected result because the upper Li2CO3 coverage is attenuated after etching process. This is an expected result because the upper Li2CO3 coverage is attenuated after etching process. This is an expected result because the upper Li2CO3 coverage is attenuated after etching process.

Discussion

The advantage of LM painting decoration lies in the high affinity between LM-oxide skin and Li2CO3, which enables the disconnection of Li2CO3 network into Li2CO3 fragments separated by LM-oxide nanodomains. Therefore Li-ions can bypass the insulating Li2CO3 moieties and instead transfer along the lithium LM and oxide domains at the interlayer zone. This dissipation effect of Li2CO3 is expected to become more pronounced after lithiation as indicated by the peak evolution of Li2CO3 XPS spectra (Supplementary Figs. 25 and 26). For the pristine LM@LLZT surface, the Li2CO3 peak is weakened and the La peaks become pronounced after etching process. This is an expected result because the upper Li2CO3 coverage is attenuated and meantime more LLZT surfaces are exposed during etching. In contrast, for the lithiated LM@LLZT sample, the Li2CO3 peak in turn becomes stronger after etching. Since the lithiation treatment thickens the LM interlayer, the La signals are not

![Image](https://doi.org/10.1038/s41467-020-17493-x)
The poor crystallinity of oxide skin endows it with better surface dispersal of Li$_2$CO$_3$ and promote the Li-ion can even be pushed to the top surface of lithiated LM@LLZT. This work provides a scalable way to significantly modulate garnet electrolyte interface by facilely painting LM alloying force. This shuttling process can further delaminate and fragment the Li$_2$CO$_3$ network, agreeing with the XPS result afore-mentioned. In brief, both the embrittlement and penetration effects of LM enable a superior manipulation from continuous Li$_2$CO$_3$ layer to its nanoscale fragments.

The electrical Li diffusion coefficient ($D_L$) for Li–Ga alloys has a high value around $10^{-8}$–$10^{-6}$ cm$^2$ s$^{-1}$ at normal temperature (24–30 °C), which is comparable to those of Li–In and Li–Al alloys. The high Li flux in Li–Ga interlayer and improved interface contact are responsible for the driving of high current density. The high Li flux in Li–Ga alloy stems from the high solubility of Li in Ga metal with the existence of multiply intermetallic phases of Li-rich alloys with kinetically favorable conversion. The intimate interface contact can heal the morphological defects and homogenize the lithium growth. Therefore the high Li flux path can be well connected from solid electrolyte to electrode. The high CE values and small voltage hysteresis of Li–Ga modified asymmetric cell can act as evidences for the high utilizability of Li and fast interfacial kinetics (Fig. 5b, c).

In summary, we propose a Li$_2$CO$_3$-affiliative mechanism to modulate garnet electrolyte interface by facilely painting LM coating. This strategy enables a superior wettability of LM with naturally oxidized skin toward both Li metal and LLZT under oxygenated environment. It avoids the requirement on the removal of Li$_2$CO$_3$ passivation layer, which can be delaminated and fragmented by LM penetration. The lithiated NM nanodomains can construct alternative Li-ion transfer route at Li–LLZT interface. Benefiting from this Li$_2$CO$_3$-affiliative mechanism, the interfacial ASR between Li and garnet is as small as 5 ± 2 cm$^2$. The symmetric cell of Li|Li$\text{M}_1\text{M}_2\text{L}$|Li$\text{M}_1\text{L}$|Li$\text{M}_2\text{L}$|Li$\text{M}_1\text{M}_2\text{L}$|Li$\text{M}_1\text{L}$ can cycle for ultralong 9930 h with a small overpotential not more than 12 mV. Even at a high current density of 1 mA cm$^{-2}$, the overpotential is still <30 mV. This work provides a scalable way to significantly improve the interface performance of garnet electrolyte even with exposure to air for several days. The modification direction of designing Li$_2$CO$_3$-affiliative interlayer with dilution and embrittlement of Li$_2$CO$_3$ nanodomains should be emphasized for further development of garnet-based solid-state batteries.

**Methods**

**Synthesis of solid garnet electrolyte.** The Li$_2$CO$_3$, ZrO$_2$, La$_2$O$_3$, and Ta$_2$O$_5$ materials (Shanghai Aladdin Bio-Chem Technology Co., Ltd) with certain molar ratio were used as precursors to prepare garnet $\text{Li}_{x}\text{La}_{1-x}\text{Zr}_{1/2}\text{Ta}_{1/2}\text{O}_2$ (LLZT) by solid-state sintered technology. Fifteen percent excess Li$_2$CO$_3$ was added to offset the volatile loss of lithium in sintering process. Li$_2$CO$_3$ powder was calcined at 900 °C for 12 h to remove crystal water before sintering. These precursor materials were firstly mixed together with absolute ethanol alcohol and then ball-milled for 12 h at 230 r min$^{-1}$. The mixed dry powder was sintered at 900 °C for 12 h to achieve tetragonal LLZT. The tetragonal garnet acquired in the previous step was broken into pieces and ball-milled for 24 h. Then the dry powder was pressed into pellet and sintered at 1250 °C for 1 h and 1150 °C for 6 h to obtain the final cubic garnet electrolyte. All of sintered garnet pellets were exposed in air for 7 days before use. The surface area and thickness of ceramic pellets were fixed at about 0.5 cm$^2$ and 0.8 mm, respectively. The density value of used pellets ranges from 90 to 92%.

**Liquid metal painting and cell fabrication.** LM (Shanghai Aladdin Bio-Chem Technology Co., Ltd) was painted on LLZT surface at 35 °C with a brush until the whole garnet surface is wetted and coated by a gauze with a dark Ga$_2$O$_3$ skin. The excess LM was carefully removed with a brush. This procedure was performed under normal air atmosphere. For interfacial resistance testing, the coin symmetric cell was assembled with LM-painted garnet for 5 min at 230 °C with Ni foam as current collector. During the assembly of asymmetric cell, 10 μL of commercial carbonated electrolyte (1 M LiPF$_6$/EC/DEC, Aladdin) was dropped on the non-Li collector (carbon-coated Al foil, denoted as C@Al, purchased from Hefei Kejing Co., Ltd) for interface wetting. This C@Al electrode was then attached to garnet electrolyte. This procedure was then repeated for Li anode at the other side. For the asymmetric cell based on unpainted garnet, the Li anode side was also wetted by 10 μL of LE, apart from the already wetted C@Al electrode side. To fabricate composite cathode, LiFePO$_4$ powder (100 mg) was mixed with carbon black (60 mg), PEO (Aladdin) (246 mg) and LiTFSI (Sigma-Aldrich) salt (80 mg). The electrode slurry was prepared by mixing this mixture powder with acetonitrile solution based on a molar ratio of [EO]:Li$^+$ of 15:1, which was then stirred for 8 h. Then the solvent was evaporated and the polymer film was dried in vacuum.

**Electrochemical measurement.** To measure the ionic conductivity of sintered LLZT electrolyte, Ag paste which can endure high temperature was coated on ceramics and calcined at 150 °C and then 800 °C for 10 min, respectively, to remove the organic component and ensure a tight contact. Then the EIS of Li$^+$ blocking cell (Ag/LLZT/Ag) was measured by using a Solartron frequency analyzer 1260 (10$^2$–10$^6$ Hz frequency range) with an AC amplitude of 10 mV. The EIS spectra of symmetric cells were also used to estimate the interface ASR with an applied frequency range from 10 MHz to 1 Hz at RT or 60 °C. For the electrochemical performance of symmetric cell, cycling process was performed at a current density of 0.2 or 1 mA cm$^{-2}$ with a fixed plating/stripping interval of 1 or 0.5 h, respectively. The rate performance was performed under the current densities ranging from 0.05 to 1.2 mA cm$^{-2}$ with a fixed plating/stripping interval of 0.5 h. For the CCM measurement, the stepped current density test protocol from 0.1 mA cm$^{-2}$ (1 h per cycle, 0.2 mA cm$^{-2}$ per step) was employed. The asymmetric cell was discharged at a constant current of 0.1 mA cm$^{-2}$ and then was charged to 1.0 V after 5 h deposition of Li. The solid-state full cells were measured at a constant current of 0.15 mA cm$^{-2}$ or at a changed rate ranging from 0.1 mA cm$^{-2}$ to 0.4 mA cm$^{-2}$ in a voltage range of 2.5–3.8 V. All the assembled coin cells were tested on a LAND CT2001A Battery Test System.

**Physical characterization.** SEM (Magellan 400 L, FEI) and EDS mapping were used to analyze the morphology and component distribution of garnet electrolyte. For the morphological observation of electrolyte surface and cross-section, LLZT pellet was smashed to obtain the samples. To prepare the cross-section interface, the Li|$\text{M}_1\text{M}_2\text{L}$|Li symmetric cell was firstly assembled under a pressure of 50 MPa. Under this pressure, the Li|$\text{M}_1\text{L}$|$\text{M}_1\text{L}$|Li|LLZT|Li$\text{M}_2\text{L}$|Li|$\text{M}_1\text{L}$|Li|$\text{M}_1\text{M}_2\text{L}$|Li was washed off from garnet for XRD test. All the samples involved with lithium metal were fabricated in Ar-filled glove-box and sealed in a box when transferred to the testing equipment. The TEM with energy dispersive spectroscopy (Zeiss EM-912, JEO) was operated at 200 kV to characterize the interfacial structure and components of LM mixed Li$_2$CO$_3$ powder. The sample used in TEM was distributed in ethanol under sonication and then was deposited on a Cu wire mesh. Raman spectra for the garnet powder, LM mixed garnet powder and LM mixed Li$_2$CO$_3$ powder were collected by a thermal dispensive spectrometer excited by a laser with the wavelength of 532 nm and the power of 10 mW. To explore the interface components of LM|$\text{M}_1\text{L}$|LLZT before and after lithiation, XPS measurement (Escalab-250) with an Al anode source was also performed. Sample with fresh surface of LM|$\text{M}_1\text{L}$|LLZT was fabricated by simply painting LM on air-exposed garnet surface, while the lithiated LM|$\text{M}_1\text{L}$|LLZT was firstly lithiated by Li metal and then ball-milled for 5 min and then the surface-lithiated garnet was peeled from Li disc.

**Data availability**

The data that support the findings of this study are available from the authors on reasonable request, see author contributions for specific data sets.
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Competing interests
The authors declare no competing interests.

Additional information
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Correspondence and requests for materials should be addressed to C.L.

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