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Dynamics of the Garnet/Li Interface for Dendrite-Free Solid-State Batteries

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S econdary batteries with high energy densities and enhanced safety are vital in the development of energy storage systems and electric vehicles. The lithium (Li) metal anode is the most promising anode for next-generation batteries due to its high theoretical capacity (3860 mAh g⁻¹), low electrochemical potential (-3.04 V vs SHE), and lightweight (0.53 g cm⁻³).^{1,2} However, although it has been extensively studied for decades, the propagation of Li dendrites and low Coulombic efficiency have hindered the practical application of Li metal batteries with liquid electrolytes.³

Solid-state electrolytes (SSEs) are regarded as the key component of SSBs and are capable of stabilizing and improving the safety of Li metal batteries due to the removal of flammable organic electrolytes. Among the various types of SSEs, garnet-type Li₇La₃Zr₂O₁₂ (LLZO) has proven to be extremely promising.^{4,5} The garnet SSEs exhibit excellent chemical and electrochemical stability toward Li metal as well as competitive ionic conductivity at room temperature.^{6,7} Element doping of Nb and Ta in the LLZO can further increase the ionic conductivity to greater than 10⁻³ S cm⁻¹.^{8,9} LLZO was theoretically predicted to prevent lithium dendrite formation due to its high shear modulus (~55 GPa) and high Li transference number (~1).^{10–12} However, numerous reports have shown that LLZO suffers from even easier Li dendrite penetration compared to liquid-based cells through grain boundaries, 13 interconnected voids, 14 and even single crystals. 15

0.7

Lithiophilic

Dense LLZTO pellet

0.1

Pristine

SI Supporting Information

1.4

3D

Interface

Acid etching

Recently, the investigation of dendrite growth mechanisms has attracted considerable attention.^{16,17} Many analytical models and theories have been proposed to demonstrate the nucleation and growth of Li dendrites. Viswanathan and Ahmad explored the effect of mechanical properties of the SSE/Li interfaces on Li electrodeposition behavior and developed a kinetic model that revealed that not only high shear modulus but also a high molar volume are important in suppressing dendrite growth.¹⁸ Raj and Wolfenstine pioneered the concept of Li electro-chemo-mechanical potential, where the interfacial stress and the electrical potential were combined. The raised Li electro-chemo-mechanical potential due to the high resistance of grain boundaries or current densities at a protuberance can instigate Li dendrite nucleation.¹⁹ Chiang et al. further developed the electrochemo-mechanical potential model and pointed out that the Li-plating in defect sites lead to the onset of Li infiltration.²⁰

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Scheme 1. Schematic of Li Deposition Behavior at (a) a Pristine LLZTO/Li Interface, (b) a Lithiophilic LLZTO/Li Interface, and (c) a 3D-LLZTO/Li Interface



Figure 1.)a) Schematic of the *in situ* acid-etching process. (b) Cross-sectional and (c) top-view SEM images of 3D-LLZTO. (d) XPS results of LLZTO, 3D-LLZTO, and 3D-LLZTO@ZnO. Cross-sectional SEM images of wettability between (e) Li and 3D-LLZTO and (f) Li and 3D-LLZTO@ZnO.

Wang et al. highlighted the high electronic conductivity in LLZO ceramic as the reason behind Li dendrite growth, which was consistent with the scanning electron microscope (SEM) observation of Li precipitation in polycrystalline LLZO under electron injection.^{21,22}

Although the mechanisms for dendrite growth still remain elusive, it is generally acknowledged that interface properties play a critical role in altering the local kinetics of Li electrodeposition. Due to the effects of lithiophobicity, LLZO shows poor wettability with Li metal, thus causing Li dendrite nucleation. Various methods have targeted interface modification to enhance the wettability between LLZO and Li metal, such as the introduction of intermediate layers,^{23–25} higher operating temperature or pressure,^{26,27} and removing surface Li₂CO₃ passivation layers.^{28,29} These strategies indeed

enhance the interfacial contact and thus improve dendrite suppression to some extent. However, when extending the cycling time (e.g., >500 h) or increasing the current density (e.g., >1.0 mA cm⁻²), Li penetration still occurs.³⁰ The aforementioned issues suggest that the interfacial transport kinetics as well as stability during cycling are major factors in dendrite growth.³¹ However, due to the subsurface nature of interfaces and the absence of operando techniques, few studies reported the relationship between the interface evolution during cycling and dendrite growth. Therefore, it is worthwhile to investigate the LLZO/Li interface dynamics for better design of dendrite-free SSBs.

Herein, three different interfaces were constructed between Ta-doped LLZO (LLZTO) ceramic and Li metal, including a pristine interface, a lithiophilic interface and a three-dimensional (3D) interface (Scheme 1). The changes at the interface and Li penetration behavior were studied by electrochemical impedance spectroscopy (EIS) and charge/discharge voltage hysteresis (ΔV) during critical current density (CCD) testing. Considering the high overpotential and high charge/discharge ΔV as the driving force for Li dendrite growth, the Li symmetric cell with pristine LLZO/Li interfaces rapidly experiences short circuits even at 0.1 mA cm^{-2,32} A Li symmetric cell with lithiophilic interfaces shows an improved CCD from 0.1 to 0.7 mA cm⁻². However, the interface stability is much more susceptible to the Li volume change during cycling, especially with a thin Li anode. According to EIS, the current density that induced Li dendrite nucleation is much lower than the ultimate CCD. In contrast, the Li symmetric cell with 3D interfaces exhibits high interface stability due to the decreased local current density and alleviated Li volume change. The stable interface and low charge/discharge ΔV leads to a high CCD of 1.4 mA cm⁻² and over 600 h of longterm stable cycling at 0.5 mA cm⁻². Full cells with a LiFePO₄ (LFP) cathode and different LLZTO/Li interfaces were also assembled for comparison. The "all-in-one" cell with 3D interfaces of both Li anode and LFP cathode exhibits excellent rate and cycle performance.

The fabrication of high-density LLZTO ceramic pellets was introduced in our previous work.³³ As shown in Figure 1a, LLZTO with a 3D framework (3D-LLZTO) was fabricated by a novel acid etching process. Previously, the template method with a scalable tape casting procedure was proposed to fabricate the 3D garnet electrolytes, which provides abundant experience for the construction of SSBs with Li metal and highenergy-density cathodes.³⁴⁻³⁶ In particular, Hu et al. reported a thick 3D framework (50 μ m) and a thin dense layer (10 μ m) by low-cost tape casting, which not only can decrease the areaspecific resistances but also suppress the Li dendrite growth.³⁶ The porosity and thickness of the 3D structure can be adjusted by changing the content of porogens, which is beneficial for the large-scale production. However, the removal of organic porogens and densification of the green body during subsequent co-sintering may be a challenge. The acid etching approach can demonstrate a simplified process and improved contact between dense and porous layers. When the asobtained LLZTO ceramic was immersed into the 1 M HCl solution, HCl first reacted with the Li2CO3 surface contaminant, releasing CO2 gas.^{28,37} Then, the acid corroded the LLZTO ceramic bulk preferentially along the grain boundary, leading to a 3D-LLZTO framework on the ceramic surface. Due to the acid etching pathway, it not only can remove the surface contaminants but also cleans the impurities at grain boundaries.³⁸ In addition, the *in situ* etched pores are formed uniformly, which is beneficial for the Li metal infiltration and continuous Li⁺ migration within the 3D matrix. As shown in Figure S1a and b, after acid etching for 1 h, the whole thickness of the 3D-LLZTO plate is decreased from 1.007 to 0.959 mm. The side-view SEM image shows a 30 μ m porous LLZTO framework on either side of 3D-LLZTO, which is strongly bound to the dense substrate layer with no gaps in between (Figure 1b). The top-view SEM image in Figure 1c shows that the porous layer consists of interconnected garnet grains. The open-pore size is 1-10 μ m. The thicknesses of the 3D framework can be adjusted by the concentration of HCl solution and the etching time (Figure S2). And the sizes of pores can be controlled by some surface-active agents in the HCl solution.

Phase purity and bulk properties of the LLZTO electrolytes were tested before and after acid etching. As the X-ray diffraction (XRD) pattern in Figure S3 shows, the peaks of pristine LLZTO match perfectly with the standard pattern of cubic LLZO electrolytes (JCPDS: 80-0457). After acid etching, the cubic phase of 3D-LLZTO remains intact without impurity phases. The pristine LLZTO shows a high conductivity of 8.2×10^{-4} S cm⁻¹ at 25 °C due to the relative density over 99% by hot pressing, while the conductivity of 3D-LLZTO decreases to 1.3×10^{-4} S cm⁻¹ after acid etching (Figure S4). This could be attributed to the incomplete coverage of the Au electron-conductive layer on the 3D-LLZTO layer, which was obtained by magnetron sputtering for the EIS test. The 3D-LLZTO pellets etching for 1 and 2 h show a similar ionic conductivity due to the similar thickness of the porous structure. This result indicates that the decreased ionic conductivity of 3D-LLZTO results from the porous LLZTO framework on top of the LLZTO pellets, instead of the proton exchange. When the two sides of the porous layers are sanded, the ionic conductivity can recover to 8.1×10^{-4} S cm^{-1} (Figure S1c). X-ray photoelectron spectroscopy (XPS) data further confirms the cleaning effect of acid etching. The C 1s spectrum of pristine LLZTO exhibits two peaks at ~285.0 and ~290.0 eV, which corresponds to hydrocarbon and carbonate species (Figure 1d).^{38,39} The ratio of Li_2CO_3 to the C peak is 48.5%. Almost no peak at 290.0 eV exists in the 3D-LLZTO, indicating the removal of the Li₂CO₃ contaminant. the surface Li₂CO₃ contaminant is also proved by the O 1s peak at 531.8 eV. The intensity of the Li₂CO₃ peak is dramatically reduced with the appearance of O 1s peak at 529.8 eV in 3D-LLZTO. This indicates that the photoelectrons are from O ions in cubic garnet due to Li₂CO₃ removal on the surface. In addition, Figure S5 shows the Raman spectra of the LLZTO and 3D-LLZTO. Typical peaks at 158 and 1090 cm⁻¹ are obtained in LLZTO, which corresponds to the surface Li_2CO_3 contaminant by the vibration of CO_3^{2-} , while the peaks of Li₂CO₃ disappear in 3D-LLZTO.

The, 3D garnet/Li interface was constructed by infiltration of molten Li into the porous garnet framework at 250 °C. For better Li infiltration, an ultrathin ZnO layer was coated by atomic layer deposition (ALD) to increase the wettability between LLZTO and Li (Figure S6).⁴⁰ SEM images and the corresponding energy dispersive spectrum (EDS) elemental mappings clearly show the uniformly coated ZnO layer on the 3D-LLZTO surface (Figure S7). XPS data also confirms the chemistry of the ZnO layer. Both O 1s peak at 530.7 and Zn 2p_{3/2} peak at 1022.1 eV correspond to the ZnO coating in 3D-LLZTO@ZnO (Figure 1d). It should be noted that our previous study demonstrated that a Li2CO3-free LLZTO surface was intrinsically lithiophilic, which showed excellent wettability against Li.^{28,29} However, as shown in Figure 1e, it is difficult for molten Li to infiltrate the 3D-LLZTO framework without the ZnO coating, which renders a bulk Li layer on the top surface of 3D-LLZTO pellet without infiltration. This could be attributed to the fact that the capillary resistance between the 3D pores hinders the Li infiltration. In contrast, molten Li can infiltrate through the whole 3D-LLZTO@ZnO porous layer with continuous contact between the interconnected garnet grains (Figure 1f). This intimate contact can be realized due to the conversion reaction between ZnO and Li, which provides the driving force for molten Li flowing into the garnet framework (Figure S6).⁴⁰



Figure 2. (a) Critical current density, (b) resistance values, and (c) charge/discharge voltage hysteresis of the Li/LLZTO/Li cell. (d) Critical current density, (e) resistance values, and (f) charge/discharge voltage hysteresis of the Li/LLZTO@ZnO/Li cell. (g) Critical current density, (h) resistance values, and (i) charge/discharge voltage hysteresis of the Li/3D-LLZTO@ZnO/Li cell.

Li symmetric cells were assembled with different interfacial conditions for CCD testing, including an LLZTO/Li interface, an LLZTO@ZnO/Li interface, and a 3D-LLZTO@ZnO/Li interface. CCD is defined as the current density where the cell reaches a short circuit. The current density was increased from 0.1 to 1.6 mA cm⁻² at a rate of 0.1 mA cm⁻² h⁻¹ at 25 °C. Ideally, the overpotential during each galvanostatic cycling remains constant according to Ohm's law. However, the Li⁺ migration across the dynamic electrolyte interfaces under different depths of charge/discharge or current densities causes a response in electrochemical overpotential. The voltage difference between the initial and maximum overpotential is defined as the voltage hysteresis (ΔV).⁴¹ After each cycling step, EIS was used and the charge/discharge ΔV was recorded to investigate the changing interface kinetics and correlated electrochemical response to Li penetration behavior. Note that a strict separation of the charge and discharge processes was not conducted because no reference electrode was used. Due to the poor interfacial wettability, the Li/LLZTO/Li cell shows an initial total resistance of 2945.6 Ω cm² with a calculated interfacial resistance as high as 1393.8 Ω cm² before cycling (Figures 2b and S8a). The sluggish Li⁺ migration across the interface leads to the huge charge/discharge ΔV (0.791/0.355) V) even at a low current density of 0.1 mA cm^{-2} , which drives the Li dendrite growth through LLZTO pellets (Figure 2c).²² Thus, the CCD of Li/LLZTO/Li cell is only 0.1 mA cm⁻² (Figure 2a). Note that the initial discharge overpotential (0.035 V) at 0.1 mA cm⁻² is far smaller than the estimated open-circuit voltage (0.295 V), indicating the short circuit of cells at an earlier stage. However, the overpotential increases after 5 min and further recovers to 0.390 V at the end of the

discharge process, rendering a dissolved Li dendrite. This effect is likely due to the ability of the Li dendrite to reversibly grow under an opposite galvanostatic current, thus recovering the overpotential. This "dynamic short circuiting" mechanism is consistent with our previous study based on polymer electrolytes.⁴² The EIS spectra further prove this effect. The total resistance decreases from 2945.6 to 1885.3 Ω cm² due to the soft short circuit after cycling at 0.1 mA cm⁻², while the subsequent resistance drops to 20.1 Ω cm² which suggests a hard short circuit after cycling at 0.2 mA cm⁻².

Due to the enhanced wettability of the lithiophilic ZnO layer, the total resistances of Li/LLZTO@ZnO/Li and Li/3D-LLZTO@ZnO/Li cells are dramatically decreased to 259.8 and 288.2 Ω cm², respectively (Figures 2e,h and S8b,c). However, the CCD of Li/LLZTO@ZnO/Li cell is 0.7 mA cm⁻², while the CCD of Li/3D-LLZTO@ZnO/Li cell is as high as 1.4 mA cm⁻² (Figure 2d and g). The EIS spectra and recorded charge/discharge ΔV reveal their quite different interface kinetics and dendrite penetration behavior during CCD cycling. Figure 2f shows the gradually increased ΔV of Li/LLZTO@ZnO/Li with increasing current density. The charge/discharge ΔV is 4.4/4.1 mV for 0.1 mA cm⁻², while charge/discharge ΔV increases to 88.7/20.8 mV for 0.7 mA cm^{-2} . The differences in ΔV are reflective of an interface where the Li stripping kinetics surpass that of the plating process. Thus, electrochemical cycling leads to the formation of voids at the interface which accumulate during further cycling. The reappearing point contacts at the interface lead to the short circuit of SSBs.^{31,43} Interestingly, it is found that the charge ΔV values are always larger than the discharge ΔV values. It is because the freshly deposited Li exhibits improved migration

kinetics when it deposits back.⁴⁴ The total resistance starts to decrease after 0.5 mA cm⁻² implies the Li dendrite nucleation, which causes a decrease of bulk resistance. The total resistance dramatically decreases to 68.0 Ω cm² at 0.8 mA cm⁻² due to a hard short circuit, which is consistent with the CCD of 0.7 mA cm⁻².

In comparison with Li/LLZTO@ZnO/Li cell, the Li/3D-LLZTO@ZnO/Li cell exhibits a smaller charge/discharge ΔV_{i} indicating faster Li⁺ migration kinetics at the 3D interface (Figure 2i). Even at a high current density of 1.2 mA cm⁻², the Li/3D-LLZTO@ZnO/Li cell shows a smaller charge/ discharge ΔV (46.2/58.5 mV) than that of the Li/LLZTO@ ZnO/Li cell (88.7/20.8 mV) at 0.7 mA cm⁻² (Figure 2f and i). Hu et al. also reported a porous-dense-porous trilayer with a high CCD of 10 mA cm⁻².³⁶ This is because the 3D-LLZTO structure with a large interface area can lower the local current density at the interface. It is beneficial for the balance between Li stripping and plating to avoid voids and to retain good contact at the interface, thus suppressing Li dendrite nucleation. In addition, the 3D-LLZTO matrix can restrict the volume change of the Li metal during the repeated platting/striping process, further decreasing the risk of interface deterioration.³⁶ Similar ΔV values are obtained for the charge process compared with the discharge process (Figure 2i). It may be attributed to the enhanced uniformity for Li plating/stripping across a 3D interface, where most of the Li is deposited back to its original areas. Different from the increased resistance of the Li/LLZTO@ZnO/Li cell during the initial cycling, the Li/3D-LLZTO@ZnO/Li cells show a slightly decreased resistance from 288.2 to 276.0 Ω cm² after cycling at 0.1 mA cm⁻² due to more complete wetting of Li in the 3D host. The current density that nucleates the Li dendrite increases from 0.5 to 1 mA cm^{-2} as the total resistance starts to decrease after 1 mA cm⁻². In order to increase the Li utilization, thin Li anodes are required for the practical application of SSBs. When decreasing the thickness of Li metal from ~200 to ~30 μ m, the CCD of the Li/LLZTO@ZnO/Li cell decreases from 0.7 to 0.3 mA cm^{-2} , while the CCD of the Li/LLZTO@ZnO/Li cell is still over 1 mA cm⁻² (Figure S9). It indicates that the 2D LLZTO/Li interface shows a susceptible interface kinetics by Li volume change, especially with thin Li metal. In contrast, the 3D interface is much more stable with a high-current-density tolerance.

The long-term interfacial stability was evaluated by galvanostatic Li plating/stripping experiments at 25 °C. As shown in Figure 3a, the Li/LLZTO/Li cell exhibits an overpotential over 0.12 V for the first charge/discharge cycle at 0.1 mA cm⁻² (0.05 mAh cm⁻²), indicating inhomogeneous Li deposition. A short circuit occurs within five cycles (Figure 3b). However, due to the enhanced interface wettability by the ZnO layer, both Li/LLZTO/Li and Li/3D-LLZTO@ZnO/Li cells can continuously operate over 600 h with a steady overpotential of 27.1 and 30.0 mV at 0.1 mA cm⁻², respectively (Figure 3a and 3c). When increasing the current density to 0.5 mA cm⁻² (0.25 mAh cm⁻²), the poor LLZTO/Li contact and sluggish Li⁺ transfer of Li/LLZTO/Li cell can hardly afford cycling even for 2 h (Figure 3d and e). The high LLZTO/Li interfacial resistance induces uneven distribution of local current density, thus leading to the dendrite growth.⁸ After disassembling the short-circuited cell and sanding the surface Li metal, the dark spots clearly show the areas where the Li dendrites have grown into the garnet pellets (Figure S10a). This is confirmed by SEM imaging (Figure S10b). The cross-



Figure 3. (a) Galvanostatic cycling performance of Li/LLZTO/Li, Li/LLZTO@ZnO/Li, and Li/3D-LLZTO@ZnO/Li cells at 0.1 mA cm⁻² (0.05 mAh cm⁻²) at 25 °C. The voltage curves in an enlarged view of (b) 0–10 h and (c) 400–410 h. (d) Galvanostatic cycling performance of Li/LLZTO/Li, Li/LLZTO@ZnO/Li, and Li/3D-LLZTO@ZnO/Li cells at 0.5 mA cm⁻² (0.25 mAh cm⁻²) at 25 °C. The voltage curves in an enlarged view of (e) 0–10 h and (f) 150–160 h.

sectional SEM image clearly shows the proliferation of Li dendrites along the LLZTO grain boundaries (Figure S10c), which causes a short circuit of the cell. Different from the longterm stability at 0.1 mA cm⁻², the Li/LLZTO@ZnO/Li cell stably cycles for the first 100 h at 0.5 mA cm^{-2} , and shows a gradual increase in overpotential from 0.12 to 1 V during the following cycles with a short circuit after 152 h cycling (Figure 3d and f). The dark spots and Li dendrites along the grain boundary are also observed based on the Li/LLZTO@ZnO/Li cell (Figure S10d-f). In contrast, the Li/3D-LLZTO@ZnO/ Li cell continuously operates for over 600 h with an overpotential of 0.13 V at 0.5 mA cm^{-2} (Figure 3d). The surface of the 3D-LLZTO remains white, and no dark spots are present after sanding (Figure S10g). SEM images further confirm a dendrite-free Li deposition during cycling (Figure S10h and i). These again indicate the excellent stability at the 3D-LLZTO@ZnO/Li interface.

The optical and cross-sectional SEM images were obtained before and after cycling at 0.5 mA cm⁻² (0.25 mAh cm⁻²) to further investigate the interface evolution during galvanostatic cycling. Figure 4a shows a lithiophobic nature of the pristine LLZTO pellet with molten Li. The molten Li forms a sphere on the LLZTO surface, indicating poor wetting behavior. Micro gaps at the interface is consistent with the high interfacial resistance of 1393.8 Ω cm² shown in Figure 2b. The continuous poor interface contacts cause the high overpotential and short circuit in the end (Figure 4d). Both LLZTO@ZnO and 3D-LLZTO@ZnO show the enhanced



Figure 4. SEM images of the (a) LLZTO/Li interface, (b) LLZTO@ZnO/Li interface, and (c) 3D-LLZTO@ZnO/Li interface. Insets are the corresponding digital images showing the wetting behaviors of molten Li on bare LLZTO, LLZTO-ZnO, and 3D-LLZTO-ZnO. Cross-sectional SEM images of the (d) LLZTO/Li interface and (e) LLZTO@ZnO/Li interface after a short circuit. Cross-sectional SEM image of the (f) 3D-LLZTO@ZnO/Li interface after 600 h cycling at 0.5 mA cm⁻² (0.25 mAh cm⁻²).



Figure 5. (a) Voltage profile of Li plating/stripping in the 3D-LLZTO@ZnO at 0.5 mA cm⁻² (1 mAh cm⁻²). (b) Schematic for the process of Li plating and stripping in the 3D-LLZTO host. (c-e) Cross-sectional SEM images and (f-h) surface SEM images of 3D-LLZTO@ZnO during the process of Li plating and stripping.

wettability against Li metal. Intimate contact between the electrolyte and Li metal is observed without any microgaps being present at the interface (Figure 4b and c). However, the SEM image subsequently shows a broken interface for the Li/

LLZTO@ZnO/Li cell after a short circuit, which agrees with the gradually increased overpotential and short circuit of the Li/LLZTO@ZnO/Li cell (Figure 4e). In contrast, the Li/3D-LLZTO@ZnO/Li can retain a firm interface contact after 600 h cycling, which guarantees the long-term stability of Li deposition (Figure 4f). Moreover, the Li/3D-LLZTO@ZnO/Li cell shows significantly superior performance compared to the Li/LLZTO@ZnO/Li cell when a thinner Li is used at 0.5 mA cm⁻² (Figure S11a). The electrochemical performance indicates that the larger Li volume change by a thin Li can affect the stability of the 2D LLZTO/Li interface, which is also proved by the CCD test in Figure S9. The 3D Li host can effectively alleviate the volume change of the Li metal, thus leading to a stable interface and dendrite-free Li deposition. In addition, the Li/LLZTO@ZnO/Li cell maintains stable cycling over 100 h even at a higher current density of 1 mA cm⁻² (Figure S11b).

To understand the excellent performance by a 3D garnet framework, the Li plating/stripping behavior in a porous LLZTO layer was also investigated; this is shown in Figure 5. As shown in Figure 5a, the Li/3D-LLZTO@ZnO/Li cell was cycled at 0.5 mÅ cm⁻² (1 mAh cm⁻²). The thin Li plate (~30 μ m) was infiltrated into the porous layer at 300 °C with a small amount of Li on the surface. The schematics in Figure 5b show the morphology change during the cycling test.⁴⁵ Initially, the 3D garnet framework is almost filled with Li metal before the stripping (stage 1) (Figure 5c). Because Li metal can conduct the electrons and Li⁺, not only the Li metal in contact with the LLZTO but also the Li at the center of the porous structure can be stripped during the cycling test. With the continuous Li stripping to 1 mAh cm⁻² (stage 2), some voids in the 3D framework are visible (Figure 5d). Benefiting from the decreased local current density by the 3D framework, the LLZTO/Li interface remains an excellent contact. The deposited Li metal can fill the empty space again when the cell is charged with the same capacity of 1 mAh cm⁻² (stage 3) (Figure 5e). During the whole process, the LLZTO framework is coated with Li metal on the top, showing a flat surface (Figure 5f-h). It not only can effectively conduct the electrons, but also can constrain the Li volume change to guide dendritefree Li deposition.

Full SSBs with an LFP cathode and a Li metal anode were constructed using 3D-LLZTO@ZnO in comparison with pristine LLZTO and LLZTO@ZnO. Figure S12a shows a schematic configuration of the "all-in-one" SSBs, where Li anode and LFP cathode are fully infiltrated into the porous LLZTO frameworks. The cross-sectional SEM image and corresponding EDS element mapping show that the LFP particles are uniformly distributed in the LLZTO framework (Figure S12b and c). The excellent contact between LFP cathode materials and a continuous LLZTO framework not only can enhance the Li migration between cathode and SSE but also can alleviate the cathode volume change during charge/discharge processes, thus improving the electrochemical performance of full SSBs. Galvanostatic charge/ discharge tests were performed at 60 °C. As shown in Figure S13, the LFP/3D-LLZTO@ZnO/Li cell shows smaller polarizations than the LFP/LLZTO@ZnO/Li and LFP/ LLZTO/Li cells at different current rates. The 3D-LLZTO@ ZnO cell is shown to possess an initial discharge capacity of 143.2 mAh g⁻¹. The discharge capacities are 129.1, 111.4, and 82.2 mAh g^{-1} at 0.2, 0.5, and 1 C, respectively (Figure S12d). After high-rate cycling, the cell recovers a discharge capacity of 140.0 mAh g⁻¹ at 0.1 C. The excellent rate performance results from the special "all-in-one" structure, where the porous LLZTO matrix provides a rapid Li⁺ migration pathway and remains an excellent interface contact for both cathode and Li

anode. In contrast, the bare LLZTO cell delivers a discharge capacity of 98.1 mAh g^{-1} with a high overpotential at 0.1 C. The discharge capacity decreases to 71.4 and 32.2 mAh g^{-1} at 0.2 and 0.5 C, respectively. The poor performance can be ascribed to a less favorable Li interface and a sluggish Li⁺ transport in LFP cathode. The LFP/LLZTO@ZnO/Li shows the performance between LFP/3D-LLZTO@ZnO/Li and LFP/LLZTO/Li cells. A lithiophlic LLZTO@ZnO/Li interface enables an increased discharge capacity compared with LFP/LLZTO/Li cell, while the unstable 2D interfaces lead to the poorer performance than "all-in-one" LFP/3D-LLZTO@ ZnO/Li cell. To further obtain insights into the advantages of 3D LFP cathode, full SSBs with a 3D Li metal but 2D LFP cathode were assembled. The LFP cathode slurry with similar loading was casted on the 3D-LLZTO@ZnO pellet via doctorblade, where one side of the porous framework was sanded. Galvanostatic intermittent titration technique (GITT) was used to measure the polarization of the electrodes and evaluate the Li⁺ transportation in cathodes. As shown in Figure S14, SSB with a 3D LFP cathode exhibits a much lower polarization than SSB with a 2D LFP cathode, indicating faster Li⁺ migration in the 3D LFP cathode. Moreover, the "all-in-one" SSB maintains 77.7% capacity after 300 cycles at 0.2 C at 60 °C (Figure S12e).

In this work, the Li penetration behavior based on three different interfaces is systematically investigated by EIS, including an LLZTO/Li interface, LLZTO@ZnO interface, and 3D-LLZTO@ZnO/Li interface. The broken interfaces with large interfacial resistances and large charge/discharge voltage hysteresis are considered as the driving force to push the Li dendrite proliferation in the LLZO bulk. The Li/ LLZTO/Li cell shows a rapid short circuit even at 0.1 mA cm^{-2} due to the initially large interfacial resistance from lithiophobicity. The Li/LLZTO@ZnO/Li cell shows an enhanced ability of dendrite suppression due to the ZnO intermediate layer. However, such improvement is limited by the Li volume change at an elevated current density, which causes the point contact again to guide Li dendrite nucleation. The 3D-LLZTO@ZnO/Li interface created by a novel acidetching method is highly stable, which can efficiently lower the local current density and alleviate the Li volume change to remain an intact interfacial contact. The Li/3D-LLZTO@ ZnO/Li cell exhibits a CCD as high as 1.4 mA cm⁻² and over 600 h constant cycling at 0.5 mA cm^{-2} . In addition, the "all-inone" LFP/3D-LLZTO@ZnO/Li cell shows rapid Li⁺ transport in the 3D cathode and Li anode matrix, leading to an excellent rate and cycling performance. This work sheds light on understanding the effect of interface dynamics on Li dendrite growth and can serve as a guideline toward the design of dendrite-free SSBs with high energy density and high safety.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c00789.

Experimental details; XRD, SEM images, and Raman spectra of 3D-LLZTO by the acid etching process; additional EIS and electrochemical performance of the symmetric Li cells and "all-in-one" LFP/3D-LLZTO@ ZnO/Li cells (PDF)

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Author Contributions

H.H. conceived and designed the experimental work and prepared the manuscript; J.L., X. Li, and X. Lin helped with SEM characterization; N.Z. fabricated the garnet ceramic pellets. Y.Z. and K.A. helped with ALD coating. X.G. and X.S. supervised the overall project. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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