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Flexible Garnet Solid-State Electrolyte Membranes Enabled by Tile-and-Grout Design

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Supporting Information

ABSTRACT: Inorganic solid-state electrolytes for lithium metal batteries have attracted significant interest, but their brittle nature creates a severe hurdle to widespread application in flexible electronics. Herein, we propose the rational design of a flexible electrolyte membrane with a tile-and-grout pattern in which garnettype electrolyte tile-like chips are joined together without gaps by styrene-butadiene copolymer using additive manufacturing. The dimensions of the garnet chips are optimized through fracture mechanics analysis, which effectively suppresses the strain energy below the fracture toughness of the garnet solid-state electrolyte, eliminating random cracking. The garnet chips function as fast lithium-ion transport channels, while the styrene-butadiene copolymer grid serves as a deformable buffer to further reduce the stress transferred to the garnet chips. The tile-and-grout design



electrolyte membrane presents good flexibility and can be readily bent without breaking. Our facile and pragmatic strategy presents a new design principle for solid-state electrolytes to address the brittleness issues.

The booming growth in consumer electronics, electric vehicles, and large-scale energy storage drives the surging need for energy storage devices with high energy density, long cycling stability, and high safety.¹⁻⁸ Lithium metal has recently been revisited as a promising anode candidate to replace conventional ion intercalation anode materials due to its low reduction potential (\sim -3.040 V versus a standard hydrogen electrode) and high specific energy (3860 mAh/g theoretically).⁹⁻¹⁴ Lithium continues to be problematic as an anode material, however, where issues with cycling stability and dendritic-growth-induced safety concerns prevent the widespread use of Li-metal batteries.^{10,15,16} The development of inorganic solid-state electrolytes (SSEs) is a promising strategy for addressing these issues,¹⁷⁻²⁰ with cubic-phase garnet-based electrolyte (Li7La3Zr2O12, usually doped with tantalum or niobium) $^{21-25}$ being heavily investigated for its high ionic conductivity, excellent chemical and electrochemical stability, and high modulus. However, the brittleness of inorganic SSEs leads to poor flexibility, greatly limiting their scalability and potential for use in flexible electronic devices. To mitigate this brittleness issue,²⁶⁻³¹ researchers have developed hybrids between inorganic and polymer electrolytes. Styrene-butadiene copolymer (SBC) is widely used as an elastomeric component for various industrial products. In energy storage fields, it is usually employed as a binder additive

for negative electrodes in lithium-ion batteries^{32–35} and as the structural framework for some polymer electrolytes.³⁶

In this work, we designed an SBC/garnet composite SSE with an architecture of garnet-type electrolyte chip "tiles" glued by SBC "grout" to achieve an attractive coexistence between flexibility and excellent electrochemical properties. Figure 1a illustrates the tile-and-grout structure design of this flexible electrolyte membrane. The top and bottom of each square electrolyte chip is left exposed without SBC to promote fast lithium-ion transport in the direction perpendicular to the membrane. By modulating the dimensions of the $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZO) garnet chips, we have successfully suppressed the strain energy below the fracture toughness of the garnet SSE, thus eliminating further random electrolyte cracking. Figure 1b schematically demonstrates the major fabrication steps to produce the flexible LLZO SSE membrane. A piece of cubic-phase garnet (c-LLZO) membrane was fabricated as the starting material. The membrane was then cleaved into uniform square chips with appropriate side lengths calculated through both mechanical analysis and experimental approaches. We then pneumatically

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Figure 1. Schematic demonstrating the methodology for the fabrication of a flexible *c*-LLZO SSE membrane. (a) SBC was employed to join the square *c*-LLZO chips together. (b) General procedure for the fabrication of the flexible composite electrolyte. A piece of *c*-LLZO membrane was cut into square chips with optimized diameters. Then, the SBC ink was extruded from a 3D printer nozzle to firmly bind the neighboring *c*-LLZO chips together. The resulting tile-and-grout structure membrane maintains the existing advantages of SSEs while also demonstrating good flexibility.

extruded an SBC ink from the nozzle of an additive manufacturing printer at a controlled raster rate to ensure even and complete adhesion of neighboring LLZO chips, which resulted in the formation of a continuous electrolyte membrane without gaps. Meanwhile, the SBC functions as a strain releaser, helping to buffer the stress introduced during manufacturing, packaging, and transport, as well as during application. Superb flexibility can be achieved with an ultimate tensile strength 3-5 times higher than the poly(ethylene oxide)-based polymer electrolyte, as well as significant extensibility of up to 220%. In addition, the as-synthesized garnet SSE membrane maintains good electrochemical performance and features attractive compatibility with modern microelectronic manufacturing technologies. Our facile and pragmatic tile-and-grout design strategy provides a promising methodology for addressing the brittleness of inorganic SSEs

and enables the potential for a roll-to-roll process of flexible LLZO electrolyte membrane fabrication.

To achieve optimal chip dimensions, we conducted a parametric finite element analysis (FEA) based on fracture mechanics to investigate the crack formation process. In the inorganic electrolyte, rupture is an energetic competition between the deformation strain energy, which serves as the driving agency of crack growth, and the surface energy, which resists fracture progression. In the analysis model, c-LLZO chips with strain energy above their fracture surface energy would generate cracks and stress release along with the formation of smaller segmented parts, giving rise to the decrease of chip dimensions. When the strain energy that decreased along with the volume reduction of the chip was inadequate to overcome its fracture surface energy to initiate new cracks or to drive the growth of existing cracks, dimensions of the chip side length were eventually stabilized into a certain value range in which new cracks stopped forming. Note that the stable chip length was significantly influenced by the bending curvature. In this analysis, c-LLZO chips with thickness from 50 to 250 μ m were evaluated under different bending states, in which the c-LLZO chips were approximated as elastic materials because the strain generated during the simulated bending process is sufficiently small. Parameters employed in the analysis about the intrinsic properties of c-LLZO SSE are based on experimental results in the literature: the Young's Modulus of c-LLZO is 150 GPa, the Poisson ratio is 0.26, and the fracture toughness $K_{\rm IC}$ is 39.528 MPa·mm^{1/2}.^{37,38}

Figure 2a presents a simulation model of a *c*-LLZO chip square with a side length of 1.4 mm and a thickness of 200 μ m under different bending states. As the chip is bent, the top surface of the chip is under tensile stress, while the bottom surface is under compression. A small notch with a depth of 1.8 μ m and a width of 0.20 μ m (small enough that would not influence the overall analysis) was designed on the top surface to function as a crevice generator for the stress concentration and trigger the fracture event in the analysis process. The stress evolution around the notch on the top surface in Figure 2a clearly indicates that the stress concentration near the notch edge becomes more severe as the bending radius R_b increases from flat to 6.25 mm. On the other hand, under the same bending state (e.g., $R_b = 10$ mm), the concentrated stresses near the notch edge are significantly decreased when the length



Figure 2. (a) Analysis of a 200 μ m thick *c*-LLZO chip (side length = 1.2 mm) while being bent. A close-up view of the stress evolution around the notch is highlighted by red dashed rectangles (1.8 μ m in depth and 0.20 μ m in width). (b) Stress analysis of 200 μ m thick *c*-LLZO chips with different side lengths under the same bending radius (10 mm).

of the *c*-LLZO chip decreases from 1.8 to 0.6 mm (Figure 2b). At the critical state, the decreased fracture energy provided by the stress in the short *c*-LLZO chip can no longer enable crack propagation.

Comparing the stress intensity factor evolution with the *c*-LLZO fracture toughness³⁷ (red dashed line in Figure 3a), the



Figure 3. (a) Relationship between the stress intensity factor and the bending curvature for 200 μ m thick *c*-LLZO chips with different lengths ranging from 0.2 to 3.6 mm. (b) Relationship between the stress intensity factor and chip length under different bending curvatures (from 0.0 to 0.20 mm⁻¹) for 200 μ m *c*-LLZO chips. (c) Specific surface containing all of the critical points derived from the analysis. Depending on the bending curvature (bending radius) and the thickness of the *c*-LLZO chips, a suggested safe region where the chips can resist cracking is presented beneath the surface.

critical bending state was determined for c-LLZO chips with different side lengths. The stress intensities associated for various chip lengths at different bending curvatures in Figure 3a show that c-LLZO chips with shorter side lengths can sustain a higher bending curvature. Figure 3b shows that the critical side length of the c-LLZO chips is also influenced by the bending curvature as c-LLZO chips under higher degrees of bending possess shorter critical side lengths. For c-LLZO chips with various thickness values ranging from 50 to 250 μ m, detailed FEA analysis results are shown in Figures S1 and S2, which illustrate a very similar trend for the influence of various chip side lengths and bending curvature. From the fracture mechanics analysis, we developed the three-dimensional diagram in Figure 3c to show the relationship among chip side dimension, thickness, and bending curvature. The calculated critical points indicate the largest chip dimensions that can still suppress the formation of cracks. Each color represents a different selected thickness value. The specific surface containing all of these critical points divides the space into two different spatial regions. The region beneath the specific surface is the safe region, which indicates that chips with dimensions falling in the region are strong enough to resist the generation of cracks. These results provide a guide for designing a stable c-LLZO electrolyte membrane with reasonably sized c-LLZO chips. To avoid cracking or crevice

propagation, the dimensions of the *c*-LLZO electrolyte chips should be designed to be in the safe region. For example, an electrolyte chip with a thickness of 200 μ m that can readily be bent under a curvature radius of 6 mm should possess a maximum side length of 1 mm.

To verify the calculation result in Figure 3 and to achieve the appropriate side lengths of the chips for a flexible membrane, round *c*-LLZO pellets 200 μ m thick and 10 mm in diameter were employed to conduct experiments at different bending curvatures (Figure 4a). Polyethylene tape was used to bond



Figure 4. (a) Experimental results of the chip side length distribution for 200 μ m thick *c*-LLZO pellets (the chip edges are marked with red dashed lines). The chip side lengths for the various rod diameters demonstrate typical Gaussian distributions, with lengths ranging from several hundred micrometers to several millimeters. (b) Experimentally achieved dimension values derived from *c*-LLZO chip side lengths (blue points) fall within the predicted safe region (blue background) and are below the critical side lengths of the FEA analysis.

each pellet on one side during testing while the other side was attached to steel rods with diameters of 10, 18, and 26 mm. The different diameters of the rods were connected with the achievable maximum bending curvature for electrolyte pellet samples. Namely, the maximum bending radii of curvature for the three pellet groups were 5, 9, and 13 mm, respectively. Pressure was exerted on the pellets to generate cracking with the steel rods until new cracks stopped forming. The same operation was repeated on the same pellet at a 90° rotation. When no more cracks were generated, the average side length of the chips reached a stable value in which the strain energy fell below the fracture surface energy.

We scrutinized the side lengths of the as-formed chips on these three different steel rods, which are statistically shown in Figure 4a (the cracks are marked with red dash lines) and compared the side length distribution with the mechanical analysis results above. The average side lengths of the chips for pellets at the same bending state are strongly correlated with the critical length value that resists fracture. Our experimental results show that the chip side lengths for the various rod diameters feature typical Gaussian distributions, with lengths ranging from several hundred micrometers to several millimeters. The average chip side lengths are 0.7, 1.2, and 1.5 mm for bending curvature radii of 5, 9, and 13 mm, respectively. We note that the average side lengths of the chips become larger as the rod diameter increases. Figure 4b compares the experimentally determined chip side lengths at different bending curvatures with the analysis extracted from the three-dimensional diagram in Figure 3c. The safe region predicted by FEA analysis in which the chips maintain their shape and effectively resist the formation and propagation of cracks is shaded blue to compare with the crack-forming region (in red). The experimental critical values derived from the side lengths fall far in the blue region, demonstrating excellent consistency between the experimental results and theoretical predictions, which suggests optimal chip dimensions for various thicknesses.

Following the fracture mechanics analysis that determined the stable chip lengths, we employed wafer dicing to precleave the *c*-LLZO SSE into an array of 1.2 mm × 1.2 mm square chips with stiffness strong enough to resist fracture according to the analysis prediction. Gaps between neighboring square chips were controlled to around 200 μ m, which is wide enough to ensure no extra interference between neighboring chips. Figure 5a shows a photo of the 3D printing process to bind together the *c*-LLZO chip array. The binder setup (SBC ink stored in a syringe) was vertically mounted to the 3D printer's



Figure 5. (a) Photograph of the binding process using SBC extruded from a 3D printer nozzle to attach the separate c-LLZO chips into a unified membrane. (b) Photograph of the final c-LLZO SSE membrane. (c) Magnified photograph of the square chips bound by SBC (scale bar: 1 mm). (d,e) SEM images showing the surface morphology of the connecting areas of the c-LLZO and SBC. (f) Cross-sectional SEM image of the membrane. (g) EDS mapping showing the C, Zr, and La elemental distribution.

stage, and precleaved c-LLZO chips were attached on the silicon wafer with preprogrammed coordinates. A nozzle with an inner diameter of 150 μ m was used to extrude the SBC ink to traverse the gaps between the chips. The printing speed was set to 5 mm/s, controlled by a benchtop robot with a preprogrammed patterning procedure, and the ink output was carefully tuned by air flow to uniformly fill the gaps and seamlessly bind the neighboring c-LLZO chips. Figure 5b shows a sample of the as-synthesized c-LLZO electrolyte membrane after the as-printed SBC had completely cured at room temperature for 24 h. A magnified photograph further illustrates the local composite structure, in which the precleaved c-LLZO chips appear as white squares (Figure 5c) surrounded by an enclosing framework of SBC to support the chip array. The polymer also provides buffering features to improve the flexibility of the membrane, further protecting the c-LLZO chips from abnormal cracking. The SBC polymer was confined to the side faces of the chips without deposition on the top or bottom surfaces of the c-LLZO chips.

Figure 5d,e shows scanning electron microscopy (SEM) images of the surface morphology of the membrane, and Figure 5f presents the cross-sectional image of a 100 μ m thick membrane, in which the yellow dashed lines mark the edges of c-LLZO chips. An interface with good bond connection was observed between each c-LLZO chip and the SBC, which are essential for desirable mechanical properties. Figure 5g shows the energy-dispersive X-ray (EDS) mapping results of the membrane, in which the Zr and La elements belong to the c-LLZO electrolyte and the carbon is derived from the SBC, which clearly indicates a notable distinction between the SSE and the SBC framework. The composite structure guarantees outstanding functionality of the c-LLZO chips as fast Li-ionconducting channels, together with the SBC as both a binder to bridge the chips and also as a separator to set apart the anode and cathode active materials in battery systems.

Figure 6a shows the X-ray diffraction (XRD) patterns of the composite SSE membrane, in which the diffraction peaks are consistent with cubic-phase garnet Li₇La₃Zr₂O₁₂ ((JCPDS No.: 01-080-4947, Joint Committee on Powder Diffraction Standards). No extra peaks were observed besides the c-LLZO phase, indicating good stability of the electrolyte during the fabrication, which guarantees their high ionic conducting capabilities. Figures 6b and S3 show the typical Fourier transform infrared (FTIR) transmittance spectra of the interfacial region of the composite electrolytes, together with the data for both pure SBC and individual *c*-LLZO membrane as controls. We attribute the absorption bands located at 3000 and 3080 cm⁻¹ to aromatic hydrogen or unsaturated carbon, while the signals at 2915 and 2844 cm⁻¹ are related to the peaks of methylene groups,^{39,40} which are derived from the vibration of the functional groups in the SBC. FTIR spectra of the electrolyte membrane present no significant change in the interfacial region compared with pure SBC, indicating good compatibility of the SBC with c-LLZO electrolyte, which is consistent with the XRD result above. Note that, compared with pure SBC, the composite SSE membrane presents a significant absorption band at 864 cm⁻¹ due to the strong characteristic vibration of Zr-O-Zr groups in the c-LLZO phase.^{38,41}

To evaluate the mechanical properties of the membrane, we conducted tensile testing to investigate the bond strength between the *c*-LLZO chips and SBC. Figure 6c shows the stress-stain curves for the composite membrane, which we



Figure 6. (a) XRD patterns of the membrane. (b) FTIR of the fingerprint region from 1100 to 640 cm⁻¹. The absorption peaks at around 864 cm⁻¹ in the membrane are due to Zr-O-Zr group vibration in the *c*-LLZO electrolyte. (c) Stress-strain curve for the as-synthesized membrane and its comparison with commonly used PEO-based polymer⁴² and hybrid electrolyte with NASICON-type electrolyte filler.⁴³ (d) Photo demonstrating the good flexibility of the membrane. (e) EIS profile of the membrane at room temperature. (f) Voltage profile of the lithium plating/stripping process for the symmetric cell, cycled at a current density of 0.1 mA/cm² at room temperature.

compared with reports of other flexible electrolytes in the literature.^{42,43} Our composite membrane demonstrates a high ultimate tensile strength of 5.12 MPa, which indicates strong bonding between *c*-LLZO and SBC, which is consistent with the earlier discussed SEM results. Furthermore, our membrane possesses high extensibility and good stretchability, allowing it to be stretched 220% before rupture, further ensuring its excellent flexibility (Figure 6d). The strength and flexibility of the membrane are attributed to the cross-linking network of the molecules in the SBC. The polystyrene blocks function as the strength improver and the polybutadiene blocks as the rubbery matrix, ensuring exceptional elasticity and high durability in practical applications. As a result, our membrane presents good stretchability (Figure S5).

To evaluate the cycling capability of the composite SSE membrane, a symmetric LilelectrolytelLi cell was employed to carry out the charge and discharge processes. Figure 6e presents the typical Nyquist plot of the LilelectrolytelLi cell achieved from electrochemical impedance spectroscopy (EIS). The inset figure illustrates the equivalent circuit to fit the plot. The two semicircles are attributed to the impedance of the garnet SSE (high frequency R1) and the interface resistance (low frequency R2), respectively. Two CPEs (constant-phase elements) are used to fit capacitance, which indicates the slightly depressed nature of the semicircle arcs rather than pure capacitors. It is noted that, owing to the deposited Li metal on both sides of the membrane, no ion-diffusion-limited process (Warburg impedance) can be seen in the plot. Figure 6f presents the voltage profiles of the symmetric cell with the electrolyte membrane at a constant current density of 0.1 mA/ cm² at room temperature, and the inset of Figure 6f shows the first 10 cycles. During the charge and discharge processes, lithium ions are plated and stripped through the membrane. It

is worth noting that the cycling process presents smooth and stable curves, which indicates stable impedance and outstanding structural integrity of the flexible composite membrane during electrochemical cycling. The good compatibility of SBC with lithium metal ensures that the composite membrane retains existing advantageous properties of *c*-LLZO electrolyte. The composite electrolyte membrane with superior Li-ion-conducting capability, desirable mechanical strength, and enhanced flexibility presents excellent stability both under static conditions and during electrochemical cycling.

In summary, we have demonstrated an effective structure design strategy to enable a flexible electrolyte membrane in which the *c*-LLZO square chips are bound together with SBC to form a tile-and-grout structured composite electrolyte. Fracture mechanics analysis was carried out to elucidate the optimal dimensions of the chips with various electrolyte thicknesses under different bending states. Excellent bonding was formed between the c-LLZO chips and SBC framework, which is further confirmed by both SEM analysis and tensile experiment. The membrane demonstrates a high extensibility of up to 220% and an ultimate tensile strength of 5.12 MPa. The tile-and-grout design electrolyte membrane possesses high flexibility and can be readily bent into a small radius without breaking. Our facile and pragmatic strategy present good compatibility with industrially mature manufacturing techniques and demonstrates a new design principle for flexible SSE membranes.

METHODS

Finite Element Parametric Analysis. An c-LLZO chip under bending test was modeled using a FEA approach in ABAQUS 6.13 (see details in the Supporting Information). In the simulation, a displacement load was applied on the two sides of the c-LLZO chip to model the bending process. A notch with a depth of 1.8 μ m and a width of 0.20 μ m was set at the top surface of the c-LLZO chip to calculate the stress intensity. Then, a series of c-LLZO chips with different thicknesses and lengths were modeled to determine the critical side lengths of the c-LLZO chips that can resist the occurrence of fracture.

Materials Synthesis. The Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ garnet powders were synthesized via a solid-state reaction method. Briefly, LiOH·H₂O (99.9%, Sigma-Aldrich), La₂O₃ (\geq 99.9%, Sigma-Aldrich), ZrO₂ (99.9%, Sigma-Aldrich), and Ta₂O₅ (99.9%, Sigma-Aldrich) were used as precursors, with stoichiometric amounts mixed in isopropyl alcohol (IPA) for 12 h. A 10% excess LiOH·H₂O was employed to compensate for the loss of lithium during high-temperature reaction and sintering processes. The stoichiometrically mixed powders were calcined at 920 °C for 12 h in air. Then, the powders were mixed with IPA and ball-milled for 9 h. The resulting powder was pressed into a membrane at 300 MPa and sintered at a temperature of 1150 °C for 9 h in air.

To test the chemical stability between Li metal and SBC ink, a drop of SBC ink was deposited on the Li foil. Figure S4 shows an image of the contact between the two materials. No obvious interface change was observed after the SBC had been completely cured.

Membrane Fabrication. A piece of *c*-LLZO membrane was attached to thermal release tape, and a precision wafer dicing machine was employed to cut the membrane into small square chips with dimensions of $1.2 \text{ mm} \times 1.2 \text{ mm}$ to form the garnet array. A 3D printer was employed to extrude the SBC ink to seal the gap between chips. The 3D printing process was

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carried out with a benchtop robotic printer (Fisnar F4200n) using a preprogrammed patterning procedure. The ink flow was controlled by an air-powered fluid dispenser (DSP501N, Fisnar). After the SBC had completely cured at room temperature for 24 h, the membrane was transferred to a hot plate at a temperature of 80 $^{\circ}$ C to remove the thermal release tape from the garnet array. The two sides of the membrane were polished with fine sandpaper to remove impurities.

Materials Characterization. The morphology of the composite electrolyte was evaluated on a Tescan XEIA Plasma FIB/ SEM. X-ray diffraction (XRD) of the electrolyte was performed on a D8 Bruker Advanced XRD system using a Cu K α radiation source operated at 40 kV and 40 mA. A singlecolumn tabletop model testing system (Instron, USA) was used to perform mechanical tests. A 1000 N load cell was used with a nominal strain rate of 2 mm/min. ImageJ software was used to statistically collect the side length distribution of the chips.

Electrochemical Measurement. A c-LLZO membrane with thickness of 400 μ m was coated with Li metal on both sides employing atomic layer deposition-assisted wetting treatment, and then, the membrane was cleaved into small chips in a glovebox containing an argon gas environment. SBC ink was employed to fill the gap between the different chips. Electrochemical tests of the Li/garnet/Li symmetric cell were conducted on a BioLogic VMP3 potentiostat at room temperature. EIS was performed with 20 mV AC amplitude in the range of 100 mHz to 1 MHz. After calculation, the asmeasured overall ionic conductivity at room temperature was 1.6×10^{-4} S/cm. Galvanostatic stripping/plating of the Li/ garnet/Li symmetric cell was recorded at room temperature with a current density of 100 μ A/cm². The cell was placed in an argon-filled glovebox to conduct all measurements. A Thermo Nicolet NEXUS 670 FT-IR was used to measure the FTIR spectrum.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.9b01847.

FEA calculation and FTIR (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

Flexible Garnet Solid-State Electrolyte Membranes Enabled by Tile and Grout Design

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Figure S1. The relationship between stress intensity and bending curvature in LLZO chips of different lengths (from 0.2 to 3.6 mm) and thicknesses, including (a) 50 μ m, (b) 100 μ m, (c) 150 μ m, and (d) 250 μ m thick.



Figure S2. The relationship between stress intensity and chip length under different bending curvatures (from 0.0 to 0.25 mm⁻¹) in LLZO chips of different thicknesses, including (a) 50 μm, (b) 100 μm, (c) 150 μm, and (d) 250 μm thick.



Figure S3. FTIR of the SBC and electrolyte membrane from 3250 cm⁻¹ to 640 cm⁻¹.



Figure S4. The stability test of the liquid SBC ink with Li. (a) The Li metal and the SBC ink in contact. (b) The lack of change in the appearance of either material indicates their good co-stability after the SBC had completely cured (48 h).



Figure S5. The strechability of the composite electrolyte membrane

Detailed finite elemental analysis (FEA) method

In the LLZO membrane breaking simulation process, LLZO chips were under bending state due to the constraints. We modeled a single LLZO chip bending process through a standard analysis in ABAQUS 6.13. To determine the critical breaking length of the LLZO chips, four different thicknesses of LLZO chips (50 μ m, 100 μ m, 150 μ m, 200 μ m, 250 μ m) were considered. For each thickness, a series of LLZO chips with different lengths from 0.2 mm to 3.6 mm were

adopted in the modeling. The geometric parameters of the LLZO chips with different lengths and thicknesses are shown in Table S1.

Table S1. Geometric parameters of the LLZO chip used in the FEA modeling															
Models		LLZO chip length (mm)													
		0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	2.0	2.4	2.8	3.2	3.6	
LLZO chip Thickness (µm)	100	1-1	1-2	1-3	1-4	1-5	1-6	1-7	1-8	1-9	1-10	1-11	1-12	1-13	
	150	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8	2-9	2-10	2-11	2-12	2-13	
	200	3-1	3-2	3-3	3-4	3-5	3-6	3-7	3-8	3-9	3-10	3-11	3-12	3-13	
	250	4-1	4-2	4-3	4-4	4-5	4-6	4-7	4-8	4-9	4-10	4-11	4-12	4-13	

These 2D models were analyzed at the plain strain condition. The LLZO chips were simplified as elastic materials. The mechanical parameters are shown in Table S2.

Table S2. Parameters used in the FEA modeling					
Parameters	Values				
$E_{\rm LLZO}$, Young's Modulus of LLZO ^[1]	150 GPa				
v_{LLZO} , Poisson ratio of LLZO ^[2]	0.26				
$K_{\rm IC}$ LLZO Fracture toughness	39. 528 MPa·mm ^{1/2}				

A displacement load was applied on the two sides of the LLZO chip to model the bending process. A notch with a depth of 1.8 µm was introduced in the middle position on the top surface of the LLZO chip for calculating the stress intensity. The bending curvature was calculated based on the displacement load. When the simulated stress intensity exceeded the LLZO fracture

toughness^[3] K_{IC} , the surface notch started to crack. Based on this criterion, the relationship among the critical side lengths of the LLZO chip, the bending curvature (bending radius), and the chip thickness was determined.

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