Ultrathin, flexible, solid polymer composite electrolyte enabled with aligned nanoporous host for lithium batteries

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Supplementary text

Supplementary figures 1a-c show the drastic differences between ultrathin PI matrix and other typical state-of-the-art SSE (commercial glass SSE and homemade PEO/LiTFSI). Supplementary figure 1d shows that the flexible, porous PI film can endure various abuse tests, such as folding and twisting. Notably, the nanoporous PI film shows outstanding flexibility, returning to its original shape after folding and crushing instead of breaking. (supplementary Figure 1) The mechanically strong, highly flexible, ultrathin matrix not only prevents potential short-circuiting issues for LIBs, but also demonstrates the facile fabrication of flexible all-solid-state electrolytes.

Detailed information regarding the thickness, density, and areal density of our SSE, alongside the energy densities of other representative SSEs (of Figure 1d) is summarized in supplementary Table 1. For a fair comparison of the energy densities achievable with different solid electrolytes, the calculation parameters (such as area energy density, cell level energy density etc.) are chosen based on commercial Panasonic 18650 Li-ion batteries.1 For PEO hybrid solid electrolyte, we chose PEO/SiO₂ (with a thickness of 200 µm and a density of 1.5 g/cm³)2 as a representative candidate. For ceramic solid electrolytes, we chose two representative candidates: LLZO and LGPS. The thickness and density of LLZO solid electrolyte is 200 µm and 5.0 g/cm³, respectively,3 while those of LGPS are 240 µm and 2.94 g/cm³.4

The utilization of lightweight solid-state electrolytes is critical to the creation of all solid-state batteries with high energy density. Designing solid-state electrolyte materials with low thickness and density can effectively lead to overall low areal density. The energy density calculation (supplementary Table 1) shows the massive improvement of PI/PEO/LiTFSI (244 Wh/kg) over both typical PEO/SiO₂ hybrid electrolytes (D₃, 58 Wh/kg) and typical ceramic based electrolytes (E₂, E₃, <30 Wh/kg, with minimum thickness of 200 µm). The energy densities of the thinnest ceramic (E₁) and composite type SSEs (D₁, D₂) in literature are around 150 Wh/kg -- still significantly lower than that of PI/PEO/LiTFSI. Supplementary figure 2 is plotted based on the information provided in Supplementary Table 1, where C, D₁-D₃ (polymer ceramic hybrid type SSEs) and E₁-E₃ (ceramic type SSEs) labeled in Figure 1 also correspond to the SSEs listed in Supplementary Table 1. Supplementary figure 2a compares the thickness of our PI/PEO/LiTFSI to other SSEs in the literature, showing that the 8.6 µm thickness is the thinnest among all SSEs. Supplementary figure 2b shows the calculated area densities of all SSEs. To the best of our
knowledge, the lightest SSE (D$_2$) reported in literature still shows an areal density 6 times higher than that of the PI/PEO/LiTFSI. Together with figure 1g and supplementary Table 1, the comparison demonstrates the advantage of the ultrathin PI/PEO/LiTFSI SSEs in achieving high energy density for all-solid-state lithium batteries.

Supplementary figure 3a shows a top view SEM image of the porous PI film with uniformly distributed channels. The areal porosity of the PI film is measured with “ImageJ” software as 11%. The cross-sectional image of supplementary figure 3b shows the vertically aligned channels through the porous PI film.

To obtain the true ionic conductivity of PEO/LiTFSI in the channels, the preparation process of the PI/PEO/LiTFSI for EIS measurement was slightly different from that of the regular PI/PEO/LiTFSI. Instead of first infiltrating the porous PI film with PEO/LiTFSI, gold was sputtered onto both sizes of the porous PI thin film (Supplementary figure 4a). The necessity/advantage of this was threefold: first, it ensured the thickness was fixed at 8.6 μm, and thus that the ionic conductivity we measured was truly from the aligned channels; second, the rigid, flat surface of porous PI compared with PI/PEO/LiTFSI ensured the good adhesion and high continuity of the gold thin film; third, this process prevented the possible disruption of PEO/LiTFSI in the sputtering process and limited the air exposure time of the composite electrolyte.

We used shadow masks for the gold deposition, and controlled the size of the deposited gold thin film to be 0.4cm × 0.4cm (Supplementary figure 4b). The size of the deposited gold thin film was smaller than the porous PI film to avoid shortage between the top and bottom surfaces at the film edge. The thickness of the gold film was controlled to be ~ 50nm (Supplementary figure 4c), and the adhesion between the deposited gold thin film and the PI substrate was strong. We then infiltrated PEO/LiTFSI into the channels, using the same method as the PI/PEO/LiTFSI followed with surface cleaning to avoid residual PEO/LiTFSI on the PI surface. The samples were then transferred into an Ar filled glovebox and heated on a hot plate at 70 °C for more than 48 hours before EIS measurement.

Nyquist plots of a typical cell at 20 °C, 25 °C and 30 °C are shown in Supplementary figure 5. For example, at 25 °C, the resistance is 344.9 Ohm. The ionic conductivity can be calculated from equation (1):
\[ \sigma = \frac{d}{R \cdot A} \]  

(1)

where “d” is the distance between the two surfaces, “A” is the overlapping area of the conductor and “R” the resistance.

In our case, the distance is 8.6 μm, the area is 0.16 cm², and the resistance at 25 °C, is 344.9 Ohm. From equation (1), the ionic conductivity of the calculated area is \( 1.56 \times 10^{-5} \) S/cm. Since the PEO/LiTFSI takes up about 11% of the area, the effective ionic conduction area is only 11% of the 0.16 cm². As a result, the true ionic conductivity of PEO/LiTFSI in vertically aligned PI channels is \( 1.4 \times 10^{-4} \) S/cm at 25 °C. This matches the values of figure 2e and 2f in the manuscript.

Nyquist plots of a typical cell with an electrode area of 0.49 cm² (0.7cm × 0.7cm) at 20°C, 25°C and 30°C are also shown in supplementary figure 6. These new ionic conductivity values (from PEO/LiTFSI in nanochannels) are comparable to those measured with smaller area (0.16 cm²) cells (\( 1.2 \times 10^{-4} \) S/cm at 25 °C). These result from a larger area test evidenced that the nanochannels of PI indeed enhances the ionic conductivity of PEO/LiTFSI.

Supplementary figure 7a and 7b shows the schematic of 2D-XRD with PEO/LiTFSI in vertical aligned channels in reflection mode. We used an EO:Li ratio of 16:1 to ensure the existence of crystalline regions that could be identified with 2D-XRD. Schematic 2D-XRD patterns shown in supplementary figure 7c and 7d (real patterns in figure 7g and figure 7h) are displayed by supplementary figure 7b to rotate clockwise along x-axis at 90 degrees. The isotropic ring pattern in supplementary figure 7c indicate the isotropic nature of PEO/LiTFSI film. However, the polarized 2D-XRD pattern in supplementary figure 7d indicates the anisotropic nature of the PEO/LiTFSI confined in vertical aligned channels. In this case, the inner circle of the 2D-XRD ring concentrated along the y-axis reveals the crystallites are textured along the channels of the sample. The XRD analysis data of figures 7g and 7h was obtained by integrating their pattern intensities, which is shown in supplementary figure 7e and 7f. The PEO/LiTFSI film (supplementary figure 7e) shows two sets of peaks, labelled with the black dots and the red triangles. Red triangles at 11.3° and 14.6° indicate the existence of PEOₓLiTFSI complex crystallites, and the black dots at 19.1° and 23.3° suggest the formation of PEO crystallites. However, the PEO/LiTFSI in vertical aligned channels (supplementary figure 7f) only shows the existence of PEO crystallites (black dots), which may also result from the nanoconfinement effect.
The relative intensities of the 19.1° and 23.3° peaks in these two cases are different, also indicating the different crystallite textures in the two samples.

Li/SPE/Li symmetric cells cycled at 0.1 mA/cm², 40 °C are shown in supplementary figure 9. Li/PI/PEO/LiTFSI/Li is stable for much longer than the Li/PEO/LiTFSI/Li cells, as expected from the superior mechanical properties of PI/PEO/LiTFSI.

In addition, we tested the performance of Li/PI/PEO/LiTFSI/Li at different current densities and areal capacities in an environmental chamber at 60 °C (with high current densities and higher areal capacities). Note that in these tests we coated the Li foil with a very thin layer of PEO/LiTFSI/Al₂O₃ nanoparticles (~2µm, PEO:LiTISI:Al₂O₃=3:2:2 by weight) to improve the contact between Li and PI/PEO/LiTFSI (as shown in Supplementary figure 10a). Some residual PEO/LiTFSI may remain on the PI/PEO/LiTFSI solid electrolyte surface (due to the fabrication process) upon cell assembly. Cells were first activated by running five cycles at a low current density (0.05mA/cm², 0.025mAh/cm²). As shown in Supplementary figure 10b, Li/PI/PEO/LiTFSI/Li shows a very stable performance at various current densities and capacities (0.1mA/cm², 0.3mAh, marked in pink; 0.2mA/cm², 0.5mAh, marked in orange; 0.3mA/cm², 0.75mAh, marked in green; 0.4mA/cm², 1mAh, marked in blue) for 400 hours, and the zoomed-in images can be found in Supplementary figures 10c-10f. A control cell with only PEO/LiTFSI/Al₂O₃ coated Li metal (without PI/PEO/LiTFSI, Supplementary figure 10g) was also made. This symmetrical cell ran at exactly the same current density and capacity steps with the Li/PI/PEO/LiTFSI/Li cell until 200h. The control cell shorted easily in around 5 hours at a low current density (0.05 mA/cm², 0.025 mAh, Supplementary figure 10h and 10i), which proves that the PEO/LiTFSI/Al₂O₃ coating will not prevent the two Li metals from short circuiting upon cycling, and the stable performance of the Li/PI/PEO/LiTFSI/Li cell came from the protection of PI/PEO/LiTFSI.

We further cycled the cell at 0.5 mA/cm², 1.5 mAh for another 500h (supplementary figure 11a), which continuously demonstrated its stable cycling performance. Supplementary figure 11b and supplementary figure 11c also provide the zoomed in view of one Li plating/stripping cycle at around the 500th and 800th hour.

To determine the thickness of the PEO/LiTFSI/Al₂O₃ nanoparticle film on Li metal, we applied a focused-ion-beam (FIB) characterization to the Li/PEO/LiTFSI/Al₂O₃ sample. The preparation of the Li/PEO/LiTFSI/Al₂O₃ sample was the same as for the Li/PI/PEO/LiTFSI/Li cell,
except the PEO/LiTFSI/Al$_2$O$_3$ was supported by a PTFE thin film so that it was easier to peel off for FIB characterization (Li foil was first scratched to remove surface contamination so that pure Li could be exposed in the glovebox before applying the coating film). The Li/PEO/LiTFSI/Al$_2$O$_3$ sample was loaded on an SEM stage and sealed tightly with Aluminum pouch bags in the Ar filled glovebox before loading into the FIB. The FIB used was a FEI Helios NanoLab 600i DualBeam FIB/SEM. The Li/PEO/LiTFSI/Al$_2$O$_3$ was exposed to air for less than 3 seconds before being transferred into the FIB chamber.

As shown in supplementary figure 12a, a 50µm×50µm×30µm opening was cut by FIB into the sample (Li/PEO/LiTFSI/Al$_2$O$_3$ surface, top view). The zoomed-in image (tilted view) in supplementary figure 12b shows the edge of Li/PEO/LiTFSI/Al$_2$O$_3$. A further zoom in (from the yellow box in Supplementary figure 12b) shows the cross-sectional image (tilted view) of the Li/PEO/LiTFSI/Al$_2$O$_3$ sample near the surface (Supplementary figure 12c). The 3D structure of Supplementary figure 12c’s colored region is illustrated in Supplementary figure 12d to identify the thickness of the PEO/LiTFSI/Al$_2$O$_3$ layer. In Supplementary figure 12c and Supplementary figure 12d, the light green color stands for the top surface of the PEO/LiTFSI/Al$_2$O$_3$ layer, the dark green color stands for the cross-sectional image of the PEO/LiTFSI/Al$_2$O$_3$ layer (where the Al$_2$O$_3$ particles with diameters of 50nm can be easily identified), and the grey color stands for the cross section of bulk Lithium. The thickness of the PEO/LiTFSI/Al$_2$O$_3$ layer is identified to be around 2 µm (corrected length with tilted angle).

To supplement the electrochemical test results, we disassembled the Li/PI/PEO/LiTFSI/Li symmetrical cell after cycling. For the purpose of further characterization, the PI/PEO/LiTFSI film was peeled off of the cell and cleaned with acetonitrile to wash away the residual polymer electrolyte on PI. The SEM images of pristine PI (supplementary figure 13a) are taken from Figure 2a (main text) and supplementary figure 3a (supplementary information) for direct comparison with the cycled PI film (supplementary figure 13c and 13d). From the SEM images, no obvious difference can be found between the pristine film and the cycled film at different magnifications. No noticeable cleavage or rupture of channels is found. This phenomenon indicates that in a stable cell, the Li deposition does not damage the channels in the PI film. A number of SEM images (at different magnifications) with intact surface structure of the PI film after cycling are also displayed in supplementary figure 14.
To understand why the deposition of Li does not penetrate through the “soft” channel region of this high modulus matrix/high ionic conductivity (soft) filler structure, we did theoretical calculations in two steps. We first carried out theoretical simulations to understand the distribution of current density and lithium ions in the battery. The parameters of the model are set to be identical to the real coin cells; details of the model can be found in the method part at the end of the supplementary information. Supplementary figure 15a shows the schematic image and dimensions of the model system. The gray channels in between two PEO/Al₂O₃ buffer layers are the Li ion conducting channels in the porous PI film, where the Li ion concentration is 3 mol/L. A 0.4 mA/cm² current density is then applied through the sandwich structure. At steady state (time = 100s), the Li ion concentration changed, but the variation is very limited (0.02 mol/L difference from top to bottom). This means the high ionic conductivity of PEO in the channels is sufficient to support the current density of 0.4 mA/cm², such that no Li ion depletion or severe concentration gradient would occur at these conditions.

The current density distribution is also calculated through the above model. As shown in supplementary figure 16a, current density soon became uniform at 0.4 mA/cm² after passing the channels. The current density taken at 1 µm deep shows a very flat line at 0.4 mA/cm² (Figure supplementary figure 16b). Even when the PEO/Al₂O₃ layer decreases to 0.3 µm as more Li is deposited (supplementary figure 16c), very limited current fluctuations occur at the electrode surface. (supplementary figure 16d) Thus, at this stage, the non-depleted, uniform current density will tend towards a uniform Li deposition at the electrode surface, instead of forming dendritic Li at initial lithium plating stages.⁶,⁷ Nevertheless, when the deposition front is very close (e.g. <300nm) to the nanochannel, current non-uniformity increases.

To understand the possibly non-uniform lithium deposition behavior when the Li deposition front is very close (< 300 nm) to the nanochannel, we applied a phase-field simulation of the lithium deposition process. (The parameters of the modeling are set to be identical to the real coin cells and details of the modeling can be found in the method part at the end of the supplementary information.) The phase-field simulation computationally reproduced the processes of multiphase morphology evolution (supplementary figure 17a-f), Li ion concentration redistribution (supplementary figure 17g-l) and electrostatic overpotential variation (supplementary figure 17m-r) during Li plating, starting from a pristine Li metal anode surface in the solid electrolyte half-cell. At the initial stages (supplementary figure 17a-c), the flat Li metal surface protrudes towards the Li-ion conductive PEO channel due to the locally elevated Li ion
flux. After contact with solid electrolyte (supplementary figure 17c-f), the Li metal protrusion growth (in Y direction) is slowed down and gradually dominated by the lateral growth (in X direction) along the deformed electrolyte surface (supplementary figure 17f). Supplementary video of the Li deposition process with phase-field simulation can also be found in the supplementary files.

From the simulated morphologies demonstrated above, the PEO-filled nanochannels cannot be penetrated by Li deposits. This is further validated by an analysis of the driving force contribution at the channel region over plating time (supplementary figure 18). The morphological evolution process involves competition between surface/interface, mechanical and electrochemical energies; only the electrochemical part contributes positively to the growth of Li metal phase. In this nanoscale system of study, the surface/interface energy contribution maintains a notably high percentage (~ 40% in average) of the total throughout the entire process. When elastic deformation occurs after around 200 s (supplementary figure 17c), the negative contribution from the surface/interface and mechanical driving forces begins to increase prominently. At around 270 s, the contribution of electrochemical driving force decreases below 50%, and thus can no longer overcome the interfacial and elastic energy barrier to nucleate Li nano-dendrites into the channel. Therefore, the deposited Li metal tends to push forward the electrolyte phase as a whole rather than penetrating through the nanochannel.

To validate our hypothesis, we fabricated Li/PI/PEO/LiTFSI/Cu (2 µm PEO/Al₂O₃ on both Li and Cu surface) coin cells with 0.4 mA/cm², 1 mAh/cm² Li deposition (same Li plating condition of liquid electrolyte in figure 3c). We chose Cu instead of Li because Cu has a very flat surface, making it convenient to observe and determine the deposited Li morphology. After Li deposition, we disassembled the coin cells and took out the Li deposited Cu foil for further characterization. As shown in supplementary figure 19a, the surface under PI/PEO/LiTFSI obtains many cone-like protrusions. Statistics on the size of these cone-like protrusions (supplementary figure 19b) shows that most of them are in the range of 2-3 µm, with a few even larger than 4 µm. It is also noticeable that none of them have sizes that are smaller than 1 µm. This indicates that the deposition of Li follows the phase field modeling prediction, in which deposited Li metal tends to form large cone-like protrusions and push forward the electrolyte phase as a whole rather than penetrating through the channel.
FIB was then applied to open the cone-like protrusions and validate that these are deposited Li instead of polymer electrolyte protrusions left behind by an incomplete removal process. A pristine protrusion is shown in supplementary figure 20a. After the FIB (supplementary figure 20b) was applied, its cross section shows a distinct contrast between the inner material and surface material. This can also be observed in other protrusions as shown in Figure supplementary figure 20c and supplementary figure 20e-f. SEM images in backscattered electron (BSE) mode are displayed in supplementary figure 20d (normal secondary electron counterpart image shown in Figure supplementary figure 20c), which also shows the core-shell structure. The darker colored core can be identified as deposited Li and the lighter color shell as the solid (Lithium)-solid (solid electrolyte) interface and residual PEO/Al2O3.

From the above discussions, we conclude that at normal battery operation conditions, the deposited Li will not tend to grow into the soft channel region, validating the effectiveness of the soft-vertical-nanochannel/hard-matrix SPE structures. According to our phase field simulation, such phenomenon can be understood as the electrochemical driving force being unable to overcome the interfacial and elastic energy barrier required to nucleate Li nano-dendrites into the channel. Our results agree with previous reports that use ceramic separators with straight, vertical nanochannels in liquid or gel type electrolytes to demonstrate safe Li deposition behavior under normal battery operation conditions.

Supplementary figure 21 displays the stable cycling performance of Li/PI/PEO/LiTFSI/LFP at C/5. Voltage profile of Li/PI/PEO/LiTFSI/LFP at C/5, 40 °C is shown in supplementary figure 22 (LFP loading of 1.5 mg/cm², areal capacity of ~0.2 mAh/cm²).

Supplementary figure 23 displays the cycling performance of Li/PI/PEO/LiTFSI/LFP at C/10 (LFP loading of 1.5 mg/cm², areal capacity of ~0.2 mAh/cm²). Voltage profile of Li/PI/PEO/LiTFSI/LFP at C/10, 30°C is shown in supplementary figure 23a. Cycling performance of the Li/PI/PEO/LiTFSI/LFP at C/10 30°C is shown in supplementary figure 23b. The slight increase of specific capacity with cycle may result from the “activation” of battery materials. The fact that Li/PI/PEO/LiTFSI/LFP can be stable cycled at low temperatures such as 40 °C and 30 °C indicates PI/PEO/LiTFSI as a promising polymer-polymer composite SSE.

To further demonstrate the compatibility of our solid electrolyte under high cathode loading conditions, we tested batteries with PI/PEO10/LiTFSI electrolytes with different cathode loading at 40 °C. As shown in supplementary figure 24a, the areal capacity of
LFP/PI/PEO/LiTFSI\textsubscript{10}/Li cells can achieve stable cycling performance of 0.91 mAh/cm\textsuperscript{2} and 0.47 mAh/cm\textsuperscript{2} with LFP loadings of 6.9 mg/cm\textsuperscript{2} and 3.9 mg/cm\textsuperscript{2}, respectively. Voltage profiles of these batteries are shown in supplementary figure 24b and supplementary figure 24c. These demonstrate that the PI/PEO/LiTFSI composite electrolyte system is compatible with high cathode loading near ambient conditions.
Supplementary Methods

Current redistribution modeling Models were created using COMSOL Multiphysics with a 2D model and the physical module “Tertiary Current Distribution, Nernst-Planck”. The current density supplied by the Li counter electrode was set to 0.4 mA/cm$^2$. The diffusion coefficient of Li was set to $3.48 \times 10^{-7}$ cm$^2$/s for PEO/LiTFSI in the pores and $8.93 \times 10^{-8}$ cm$^2$/s for PEO/LiTFSI/Al$_2$O$_3$. The pore diameter was set to 200 nm, corresponding to the size of the track-etched pores. The spacing between the pores was set as 375 nm, corresponding to a PI membrane porosity of 11%, assuming a hexagonally close-packed pore array. Initial concentration of Li in the solid electrolyte was set to 3 M, corresponding to a EO:Li ratio of 10:1. A 2 µm thick layer of PEO/LiTFSI/Al$_2$O$_3$ was placed on the counter Li electrode.

The steady state current distribution was found by applying the current density for 100 s. The results were confirmed to be steady state by making sure the current and concentration profiles did not change over 10s of seconds.

Li deposition Phase Field modeling A multiphase-field model incorporating elasticity and nonlinear Butler-Volmer kinetics was developed for Li electrodeposition in a polymer composite solid electrolyte half-cell system. Two phase-field order parameters, $\xi$ and $\phi$, were introduced to describe the relative mass density of different phases: \{\(\xi = 1; \phi = 0\) for Li metal, \(\xi = 0; \phi = 1\) for solid electrolyte and \(\xi = 0; \phi = 0\) for the PEO interlayer in between the anode and electrolyte. The phase-fields vary continuously between 1 and 0 with a finite thickness of diffuse interfaces at phase boundaries. Due to the interfacial affinity, the PI-PEO composite electrolyte is treated as one phase-field mathematically, but defined with different moduli and Li ion conductivities. Given the 4–5 order of magnitude difference in elastic modulus between PEO and PI/Li metal, the PEO interlayer resistance to Li deposit growth is assumed small enough. The total free energy of the system, including chemical, interfacial, electrostatic and mechanical contributions, is written as

\[
G = \int \left[ f_{\text{chem}}(\tilde{c}) + f_{\text{intf}}(\tilde{c}) + f_{\text{elec}}(\tilde{c}, \varphi) + f_{\text{mech}}(\tilde{c}) \right] dV
\]

$\tilde{c}$ is a set of dimensionless densities/concentrations, $\tilde{c} = \{\rho_{\text{Li}}/\rho_0^{\text{Li}}, \rho_{\text{SE}}/\rho_0^{\text{PI-PEO}}, \phi, c_{\text{Li}}/c_0 = \tilde{c}_+\}$, where $\rho_0^{\text{Li}}, \rho_0^{\text{PI-PEO}}$ and $c_0$ are the mass density of Li metal, PI-PEO composite, and the Li ion bulk concentration of solid electrolyte, respectively. $f_{\text{chem}} = f_0(\xi, \phi) + c_0 RT \sum_i \tilde{c}_i \ln \tilde{c}_i + $
\[ \sum c_i \mu_i^\theta \] is the bulk energy density in the standard reference state \((\theta)\), where the local free energy density \(f_0(\xi, \phi) = A\phi^2(1-\phi)^2 + B\xi^2(1-\xi)^2 + \frac{C}{2} \phi^2 \xi^2 \) consists of two double-well functions and a cross term. The phenomenological parameters are set to be \(A = B = \frac{1}{4}C = 1\), such that \(f_0\) has degenerate minima representing each phase with equal depth located at equilibrium states. The interfacial energy density takes the form of \(f_{\text{int}f} = \frac{1}{2} \kappa_\xi (\nabla \xi)^2 + \frac{1}{2} \kappa_\phi (\nabla \phi)^2\), where \(\kappa_\xi\) and \(\kappa_\phi\) are gradient energy coefficients associated with the surface/interface energies of Li metal and solid electrolyte. The Li dendrite growth anisotropy is described by the gradient energy coefficient \(\kappa_\xi\), in the form of \(\kappa_\xi(\theta) = \kappa_{Li}[1 + \delta \cos(\omega \theta)]\), where \(\kappa_{Li}\) is related to the Li metal surface energy, \(\delta\) and \(\omega\) are the strength and mode of the anisotropy, and \(\theta\) is the angle between the normal vector of the local interface and the reference axis. The electrolyte is assumed isotropic and thus \(\kappa_\phi\) is constant. \(f_{\text{elec}}(\overline{c}, \varphi) = F \sum z_i c_i \varphi\) is the electrostatic energy density, where \(F\) is Faraday constant, \(\varphi\) is electrostatic potential, and \(z_i\) is the valence of charged species. The elastic energy density is written as \(f_{\text{mech}} = \frac{1}{2} C_{ijkl} \epsilon_{kl} \epsilon_{ij}\), where the stiffness \(C_{ijkl} = [h(\xi)E_{ijkl}^\xi + \sum h(\phi_i)E_{ijkl}^\phi]\) is expressed in term of interpolating function \(h(\xi) = \xi^3(10 - 15\xi + 6\xi^2)\) and the elasticity tensors of Li metal \((E_{ijkl}^\xi)\) and electrolyte \((E_{ijkl}^\phi)\). Considering the random orientation of Li metal/electrolyte interfaces, we incorporated the isotropic case of elasticity. Therefore, the phase morphology evolution equation for the Li metal phase is governed by the Butler-Volmer kinetics coupled Allen-Cahn equation,

\[
\frac{\partial \xi}{\partial t} = -L_\sigma^\xi \left\{ \frac{\partial f_0}{\partial \xi} - \kappa_\xi \nabla^2 \xi + \frac{\partial f_{\text{mech}}}{\partial \xi} \right\} - L_\eta^\xi h'(\xi) \left[ -\bar{c}_+ \exp \frac{-\alpha F \eta}{RT} + \exp \frac{(1 - \alpha) F \eta}{RT} \right]
\]

where \(L_\sigma^\xi\) and \(L_\eta^\xi\) are interface mobility and reaction constant, respectively. \(\alpha\) is the Butler-Volmer symmetric factor and \(\eta\) is the overpotential. Likewise, the evolution equation for electrolyte phase is

\[
\frac{\partial \phi}{\partial t} = -M_\phi \left\{ \frac{\partial f_0}{\partial \phi} - \kappa_\phi \nabla^2 \phi + \frac{\partial f_{\text{mech}}}{\partial \phi} \right\}
\]

where \(M_\phi\) is the interface mobility of solid electrolyte. The evolution of each phase-field was solved simultaneously with Li ion diffusion, charge conservation and mechanical equilibrium equations. The model details and parameter table are in references.\textsuperscript{12–14}
All phase-field simulations were performed in a $4 \times 4 \mu m$ half-cell system, meshed by a $200 \times 200$ grid, using COMSOL Multiphysics 5.2. Major simulation parameters are set to be consistent with the available experimental data. The diameter of the PEO channel and the thickness of the PEO interlayer are both 200 nm. The Li ion conductivities in channel, interlayer and PI are $10^{-3} \, S/cm$, $3 \times 10^{-4} \, S/cm$ and 0, respectively. The elastic modulus of Li metal, PI and PEO are 4.9 GPa, 850 MPa and 1 MPa, respectively. Excluding the negligible impact of SEI layer,$^{15}$ the surface energies of Li metal and solid electrolyte used in this simulation are 0.48 $J/m^2$ and 0.05 $J/m^2$, respectively.$^{16,17}$ An implicit time integration was used with timestep of 0.2 s. Li plates at a constant overpotential of 0.1 V for 340 s, with an average current density of 0.3 mA/cm$^2$. A Dirichlet boundary condition was applied for electrolyte bulk concentration ($c_0 = 3 \, mol/L$) on the boundary. No noise terms were included in the simulations.
**Supplementary figure 1.** Photo images of a microcaliper measuring (a) porous PI film, (b) commercial glass SSE (on the right cross-sectional SEM image of the same SSE), (c) homemade PEO/LiTFSI, (d) abuse test of porous PI film shows its intrinsic flexibility.
Supplementary figure 2. Comparison of PI/PEO/LiTFSI with state-of-the-art SSEs in literature in terms of (a) thickness (b) area density.
Supplementary figure 3. SEM images of pristine porous PI film (a) top view image (b) cross-sectional image.
Supplementary figure 4 (a) Schematic image of EIS measurement of PI/PEO/LiTFSI with electrochemical (EC) workstation. Top view (b) and side view (c) schematic images to illustrate the size of gold deposition on porous PI thin film.
Supplementary figure 5 Nyquist plot of SS/PI/PEO/LiTFSI/SS (0.16 cm² electrode area) tested at 20 °C, 25 °C and 30 °C.
**Supplementary figure 6** Nyquist plot of SS/PI/PEO/LiTFSI/SS (0.49 cm² electrode area) tested at 20 °C, 25 °C and 30 °C.
Supplementary figure 7 (a) Schematic of 2D-XRD with PEO/LiTFSI in vertical aligned channels. (b) Schematic of X-ray diffraction patterns collected by CCD. Schematic of X-ray diffraction patterns with isotropic materials (c) and highly textured materials along out-of-plane directions (d). XRD analysis of (e) PEO/LiTFSI film and (f) PEO/LiTFSI in vertical aligned channels.
**Supplementary figure 8.** Zoomed in steps of symmetric Li cells from Figure 3a in the manuscript.
Supplementary figure 9. Li/PI/PEO/LiTFSI/Li and Li/PEO/LiTFSI/Li symmetric cell at current density of 0.1 mA/cm² at 40 °C.
Supplementary figure 10 (a). Schematic image of Li/PI/PEO/LiTFSI/Li symmetrical cell, with Li metal coated with PEO/LiTFSI/Al₂O₃ (b). Voltage vs. time plot Li/PI/PEO/LiTFSI/Li symmetrical cell cycled at various current densities and capacities. Zoomed in plot of (b) at different times with (c) 0.1 mA/cm², 0.3 mAh/cm² (d) 0.2 mA/cm², 0.5 mAh/cm²; (e) 0.3 mA/cm², 0.75 mAh/cm²; (f) 0.4 mA/cm², 1 mAh/cm². (g). Schematic image of Li/Li symmetrical cell, where Li metal coated with the same PEO/LiTFSI/Al₂O₃ film as (a). (h) Voltage vs. time plot of Li/PI/PEO/LiTFSI/Li symmetrical cell cycled at various current densities (0.05 mA/cm², 0.025 mAh/cm²; 0.1 mA/cm², 0.3 mAh/cm²; exactly the same program as the Li/PI/PEO/LiTFSI/Li cell before 200 hours) (i). Zoomed in image of (h), clearly shows the short circuiting of Li/Li cells at around 6 hours with 0.05 mA/cm², 0.025 mAh/cm² cycling parameter.
Supplementary figure 11. (a). voltage vs. time plot of Li/PI/PEO/LiTFSI/Li symmetrical cell cycled at a current density of 0.5mA/cm$^2$ and a capacity of 1.5mAh/cm$^2$, started at 500$^{th}$ hour. (b-c). Zoomed in plot of (a) at different times with one lithium plating/striping cycle.
**Supplementary figure 12** SEM and schematic images of Li/PEO/LiTFSI/Al\textsubscript{2}O\textsubscript{3} with FIB. (a) SEM top view of the Li/PEO/LiTFSI/Al\textsubscript{2}O\textsubscript{3}. (b) zoomed-in and tilted view of (a). (c) further zoomed-in figure from yellow box in (b), where the dashed line separates three regions, cross section of bulk Li, cross section of PEO/LiTFSI/Al\textsubscript{2}O\textsubscript{3}, and top surface of PEO/LiTFSI/Al\textsubscript{2}O\textsubscript{3} (from bottom to top), respectively (d) schematic image of a 3D illustration of (c), the grey area represent bulk Li, dark green represent PEO/LiTFSI/Al\textsubscript{2}O\textsubscript{3} (cross section) and light green represent PEO/LiTFSI/Al\textsubscript{2}O\textsubscript{3} (top surface).
Supplementary figure 13. SEM images of pristine PI film (a-b) and PI film after cycling with current density of 0.5mA/cm² and areal capacity of 1.5mAh/cm² in a Li-Li symmetrical cell (c-d).
Supplementary figure 14. A full set of SEM images (with different magnifications) of PI film after cycling with current density of 0.5 mA/cm$^2$ and areal capacity of 1.5 mAh/cm$^2$ in a Li-Li symmetrical cell. (supplementary figure 14d and 14g are the same from supplementary figure 13c and 13d).
Supplementary figure 15. (a) schematic image of the current density redistribution model in the sandwiched structure. (b) Li ion concentration distribution at steady state (time=100s) with current density of 0.4 mA/cm².
Supplementary figure 16. (a) simulation result of current distribution in the two PEO/Al₂O₃ sandwiching PI/PEO/LiTFSI structure, the plot is zoomed in the regions of 2 µm PEO/Al₂O₃ and part of PI/PEO/LiTFSI. (b) current density taken at 1 µm deep, marked in red line in the schematic inset (c) simulation result of current distribution in the two PEO/Al₂O₃ sandwiching PI/PEO/LiTFSI structure, the plot is zoomed in the regions of 0.3 µm PEO/Al₂O₃ and part of PI/PEO/LiTFSI. (d) current density taken at 0.3 µm deep, marked in red line in the schematic inset.
Supplementary figure 17. Evolution snapshots at different time steps from phase-field simulation of Li electrodeposition near the PEO/LiTFSI channel: (a-f) multiphase morphologies, (g-l) Li ion concentration distributions, and (m-r) electrostatic overpotential profiles.
Supplementary figure 18. The phase-field evolution driving forces contribution during Li electrodeposition.
Supplementary figure 19 (a) SEM image of Li deposited on a flat copper substrate. (b) statistics of Li protrusion size from (a).
Supplementary figure 20. Evidence for Li protrusions (a) SEM image of a Li protrusion deposited under PI/PEO/LiTFSI electrolyte (b) SEM image of (a) after FIB cutting; (c) SEM image of another Li protrusion after FIB (d) SEM image of (c) in BSE mode; (e-g) SEM images of multiple Li protrusions after FIB.
Supplementary figure 21 Cycling performance of LFP/PI/PEO/LiTFSI/Li cell at 40 °C.
Supplementary figure 22 Voltage profile of LFP/PI/PEO/LiTFSI/Li cell at 40 °C at C/5.
Supplementary figure 23. (a) Voltage profile and (b) cycling performance of LFP/PI/PEO/LiTFSI/Li at 30°C and a rate of C/10.
Supplementary figure 24 (a). Cycling performance of high cathode loading LFP/PI/PEO/LiTFSI$_{10}$/Li batteries (LFP loading of 6.9 mg/cm$^2$ and 3.9 mg/cm$^2$) running at 40 °C. Voltage profiles of the cathode loading of (b) 6.9 mg/cm$^2$ and (c) 3.9 mg/cm$^2$ batteries.
**Supplementary Table 1.** Energy density calculation of different solid-state electrolyte systems

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<th>#</th>
<th>Solid electrolytes</th>
<th>Thickness (µm)</th>
<th>Density (g/cm³)</th>
<th>Area density of SSE (mg/cm²)</th>
<th>Energy density (Wh/kg)</th>
<th>Reference #</th>
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<tr>
<td>C</td>
<td>PI/PEO/LiTFSI</td>
<td>8.6</td>
<td>1.4</td>
<td>1.2</td>
<td>244.4</td>
<td>Our work</td>
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<tr>
<td>D1</td>
<td>LLZO (25wt%) /PEO/LiTFSI</td>
<td>45</td>
<td>*1.67</td>
<td>7.5</td>
<td>142.7</td>
<td>K. Fu et al. 2016. PNAS, 113, 7094-7099</td>
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<tr>
<td>D2</td>
<td>LLZO (40wt%) /PEO/LiTFSI</td>
<td>35</td>
<td>*1.93</td>
<td>6.8</td>
<td>150.5</td>
<td>C. Zhao et al. 2017. PNAS, 114, 11069-11074</td>
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<td>D3</td>
<td>PEO/LiTFSi SiO₂</td>
<td>200</td>
<td>1.5</td>
<td>30.0</td>
<td>57.7</td>
<td>D. Lin et al. 2016. Nano Lett., 16 (1), 459–465</td>
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<tr>
<td>E1</td>
<td>LLZO (ultrathin)</td>
<td>15</td>
<td>5</td>
<td>7.5</td>
<td>147.9</td>
<td>G. Hitz et al. 2018. Materials today, DOI:10.1016/j.mattod.2018.04.004</td>
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<tr>
<td>E2</td>
<td>LGPS</td>
<td>240</td>
<td>2.94</td>
<td>70.6</td>
<td>28.0</td>
<td>Y. Kato et al. 2016. Nat. Energy, 1, 16030</td>
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<tr>
<td>E3</td>
<td>LLZO</td>
<td>200</td>
<td>5</td>
<td>100.0</td>
<td>20.2</td>
<td>X. Han et al. 2017. Nat. Mater., 16, 572–579</td>
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*Estimated from the data provided in the corresponding references
Supplementary Movie 1. Flame test of PP/PE/PP separator

Supplementary Movie 2. Flame test of PEO/LiTFSI SPE

Supplementary Movie 3. Flame test of PI film

Supplementary Movie 4. Nail penetration test of LFP/PI/PEO/LiTFSI/Li pouch cell

Supplementary Movie 5. Phase evolution of Li deposition with PI/PEO/LiTFSI/PEO/Al₂O₃
References


