

Supplementary materials for

**A self-healing plastic ceramic electrolyte by an aprotic dynamic polymer network for lithium metal batteries**

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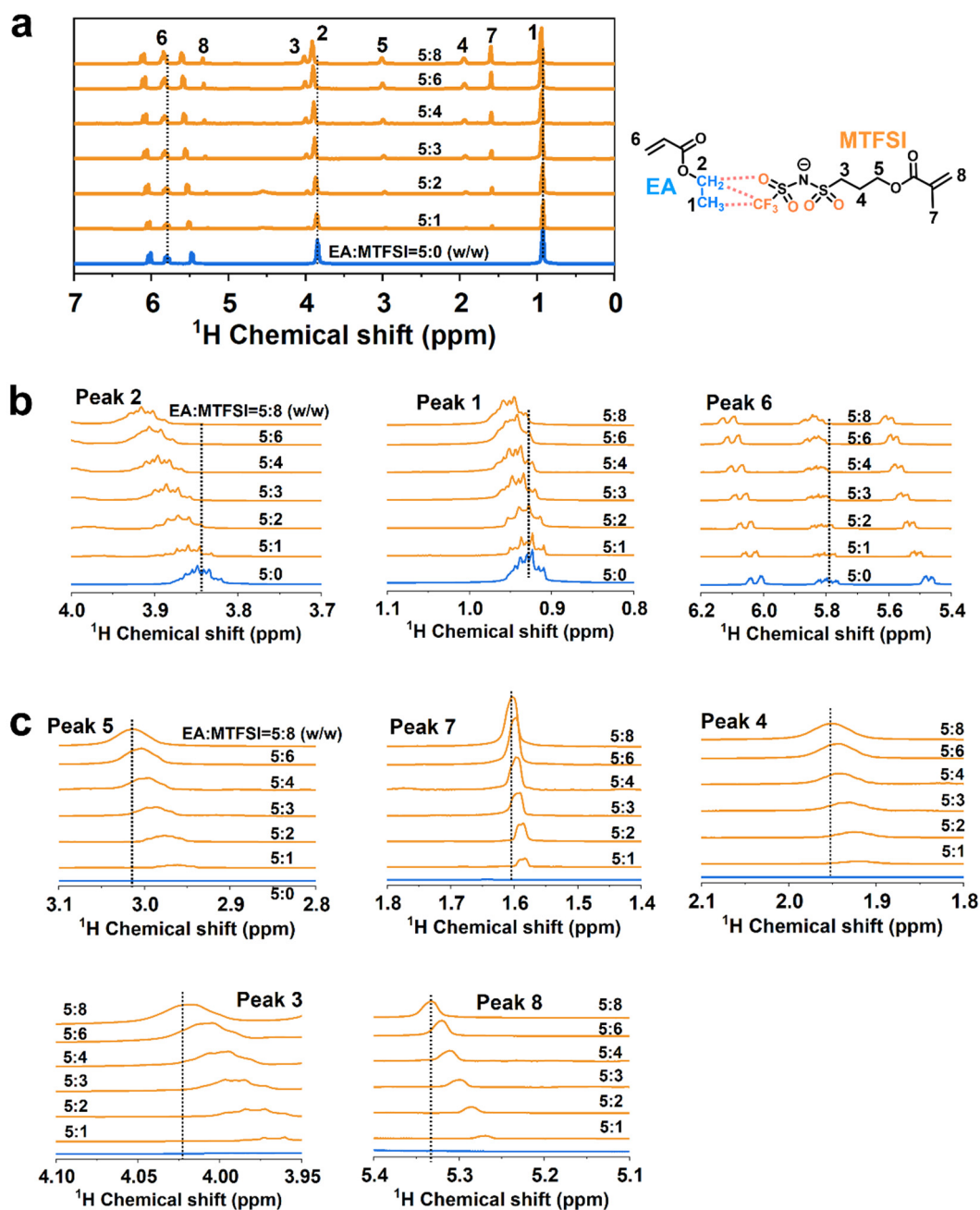
||These authors contributed equally to this work.

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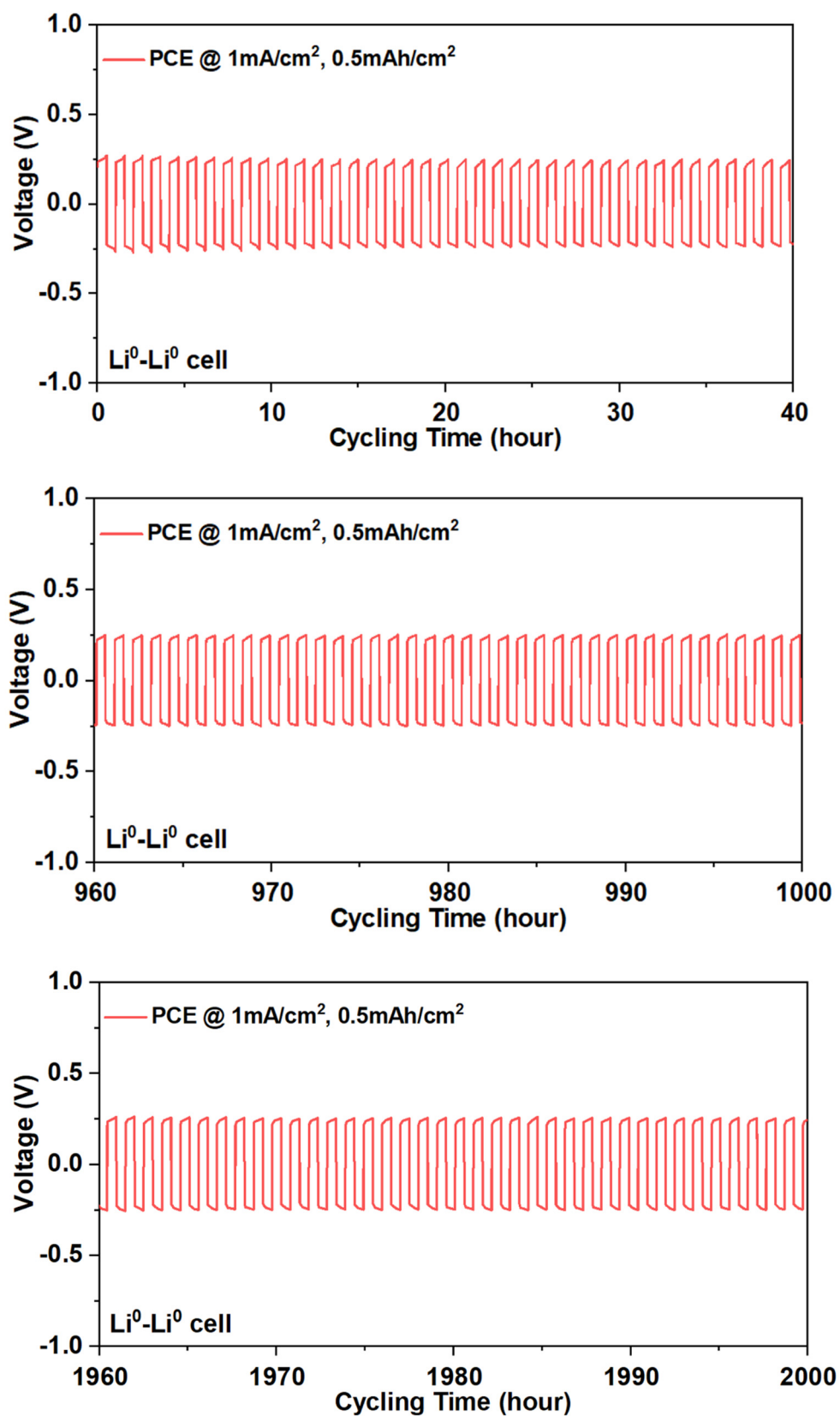
Supplementary Figure S1-S38

Supplementary Table S1-S3

Supplementary References



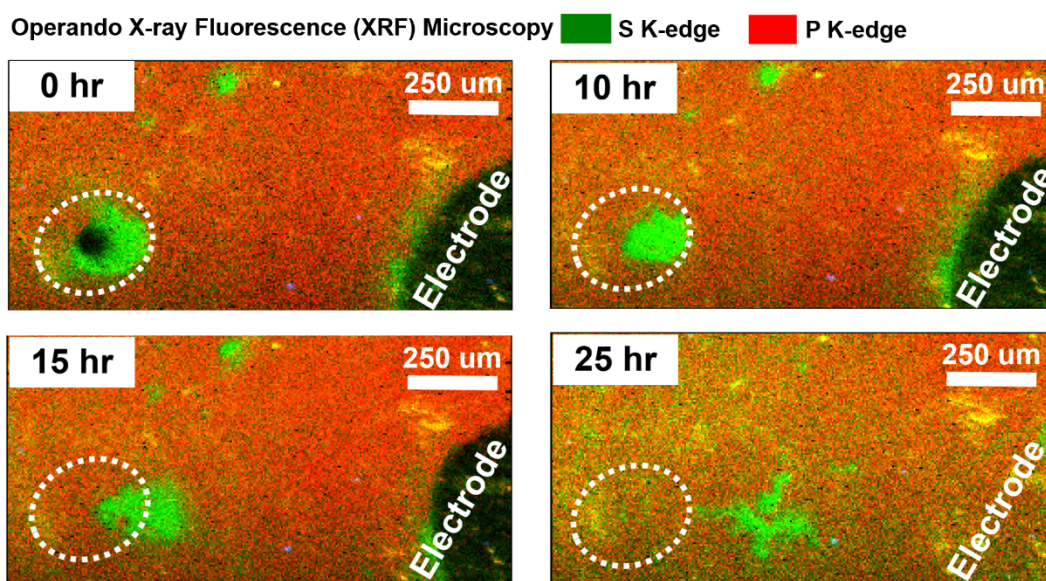
**Figure S1.** **a.** Full range Magic Angle Spinning Solid-State NMR (MAS-ssNMR) spectra of EA/MTFSI mixture at different mass ratio. The spectra were referenced against trimethylsilane (TMS, 0 ppm). The spinning rate of sample is 2000 Hz. **b.** Enlarged MAS-ssNMR spectra showing the downfield shifting of EA signals with increasing MTFTSI content. **c.** Enlarged MAS-ssNMR spectra showing the upfield shifting of MTFSI signals with increasing EA content.



**Figure S2.** Enlarged voltage-time profiles as a supplement to  $\text{Li}^0|\text{PCE}|\text{Li}^0$  cell performance shown in Figure 1e. The cell was cycled at  $1\text{mA}/\text{cm}^2$ ,  $0.5\text{mAh}/\text{cm}^2$ , and r.t. The cell was rested for 60s after charging and discharging for 0.5hr.

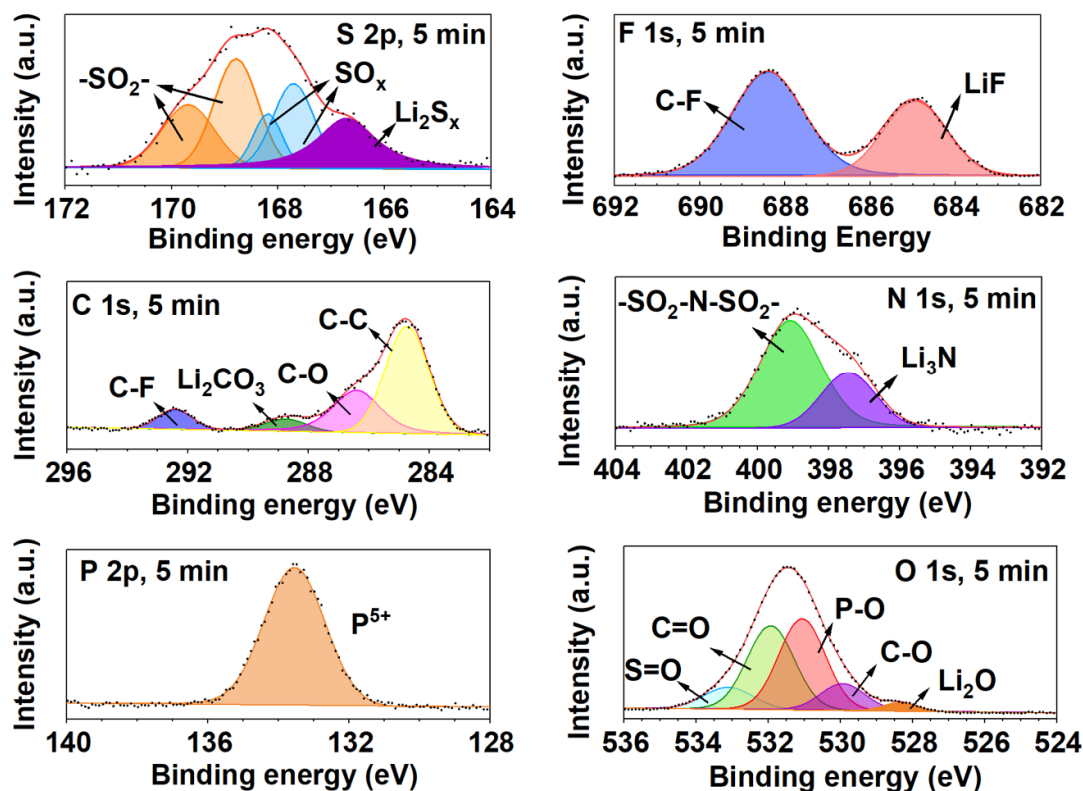


**Figure S3.** Photographs showing the thickness of PCE film is 350  $\mu\text{m}$ .

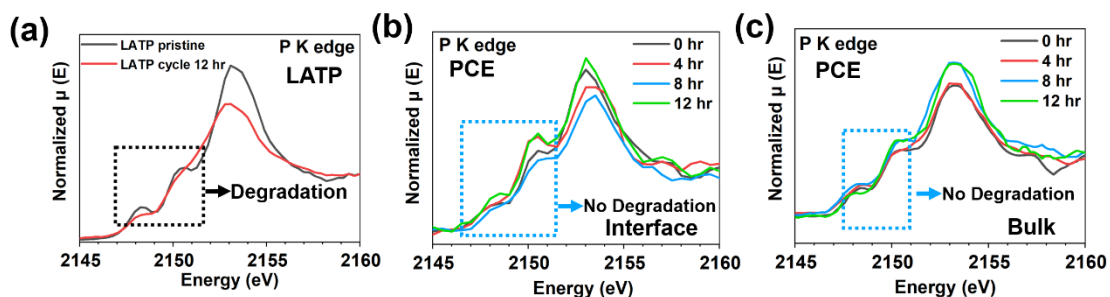


**Figure S4.** High-resolution XRF images at the PCE-electrode interface showing the excellent wettability and interface compatibility of PCE towards the electrode. As illustrated by the tube geometry of the *in-situ* cell (Figure 2b), the SS electrode's diameter is slightly smaller than the inner diameter of the Kapton® tube, allowing for its insertion into the tube. This creates a small gap between the SS electrode and the Kapton® tube. Over cycling time, PCE infiltrates this gap in a manner similar to its infiltration into voids during the self-healing process. Consequently, the electrode becomes obscured by the infiltrated PCE. This observation suggests good wettability and interface compatibility of the PCE with the electrode.

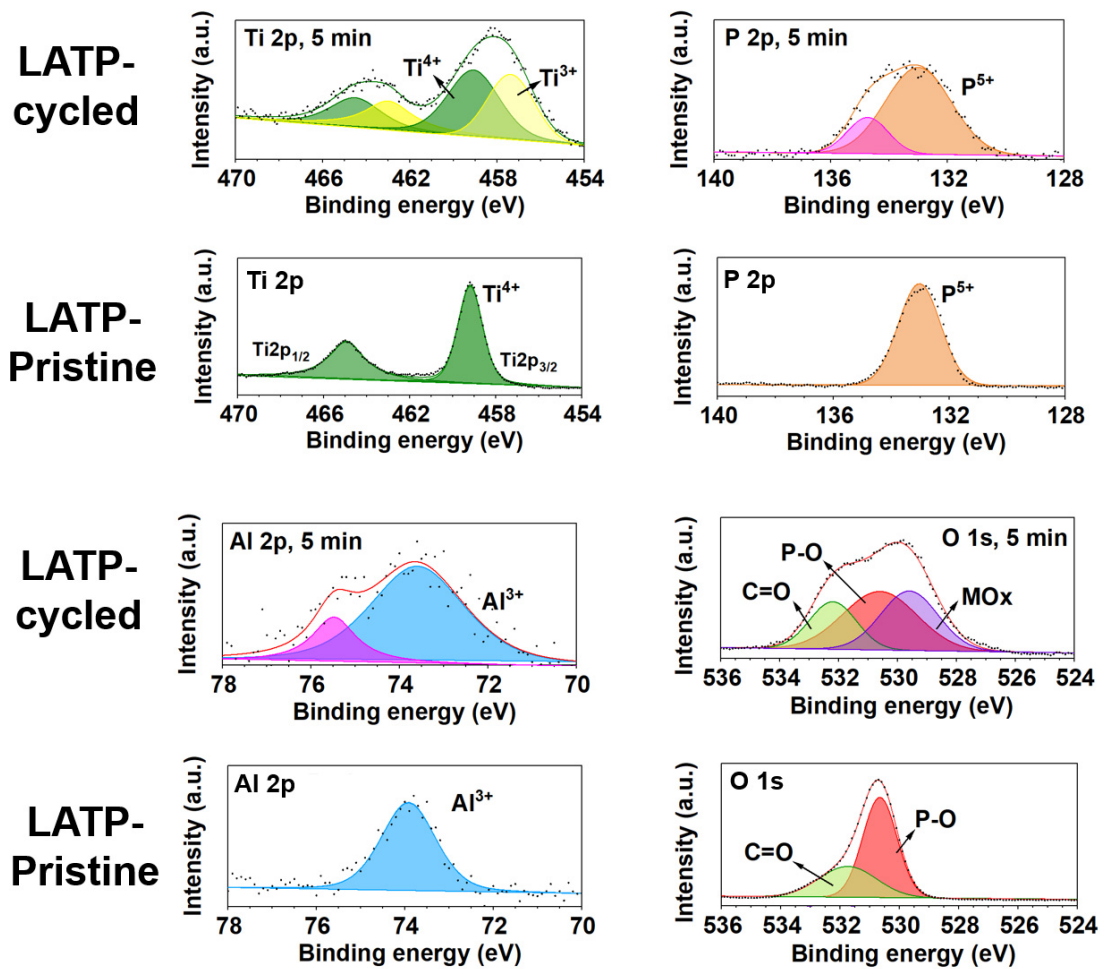
## PCE after Cycling



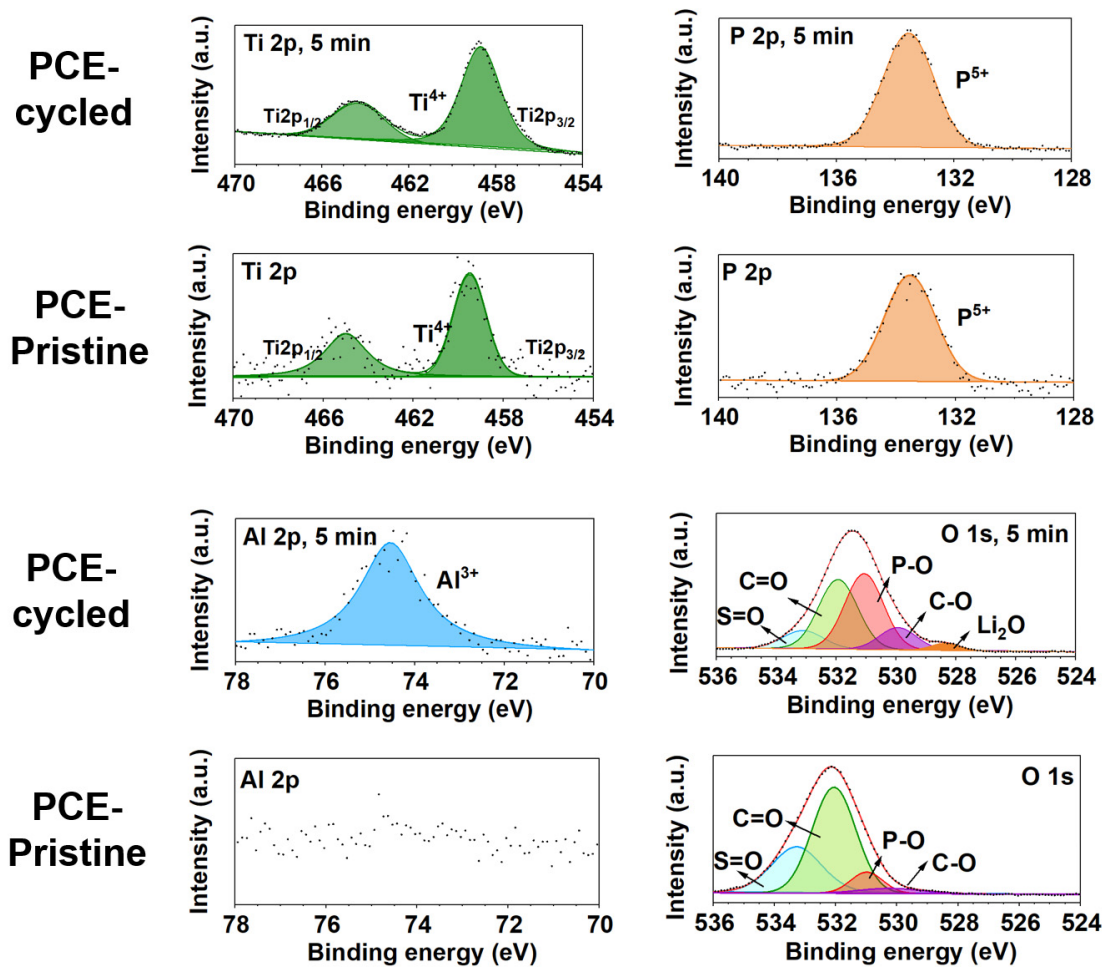
**Figure S5.** S 2p, F 1s, C 1s, N 1s, P 2p, and O 1s XPS profiles of the PCE derived SEI after Ar sputtering for 5 minutes.  $\text{SO}_x$ ,  $\text{Li}_2\text{S}_x$ , LiF,  $\text{Li}_2\text{O}$ ,  $\text{Li}_3\text{N}$ , and  $\text{Li}_2\text{CO}_3$  in SEI were mainly originated from the electrochemical reduction of SH-SPE, while P 2p and O 1s profiles suggest the successful protection of LATP from degradation.



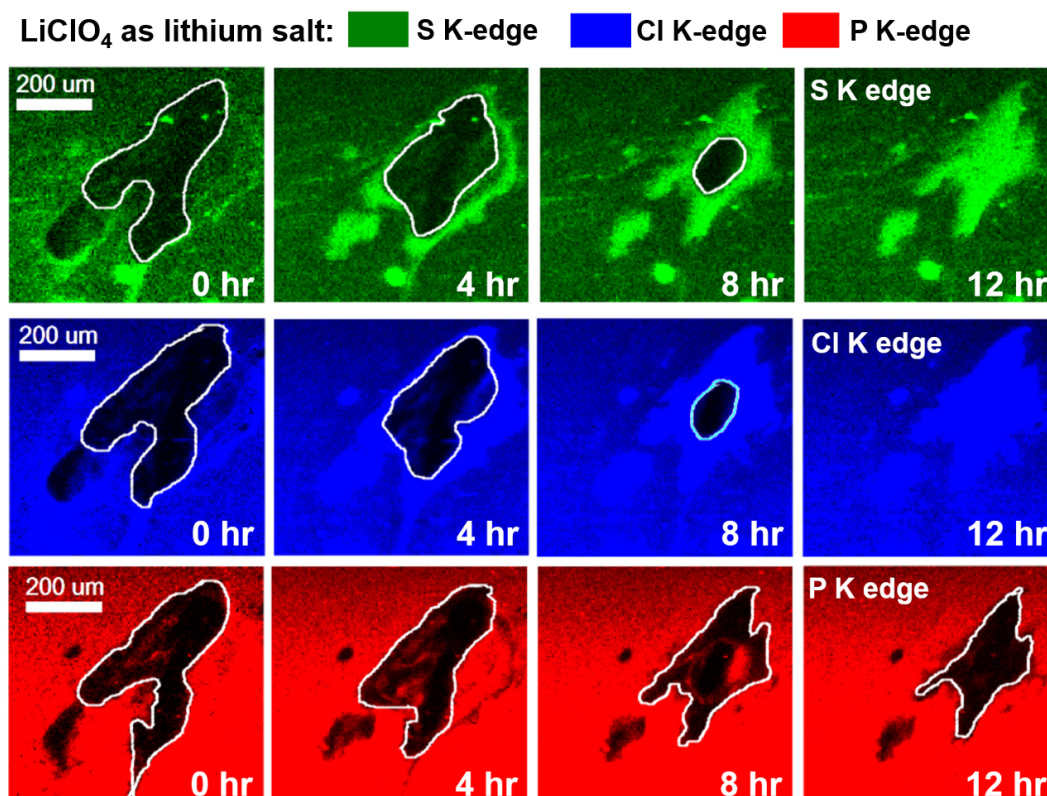
**Figure S6.** (a) Ex-situ P K-edge XAS of LATP before and after cycling in a  $\text{Li}^0\text{-Li}^0$  symmetric cell; (b, c) Operando P K-edge XAS obtained at PCE-electrode interface (b) and bulk PCE area (c).



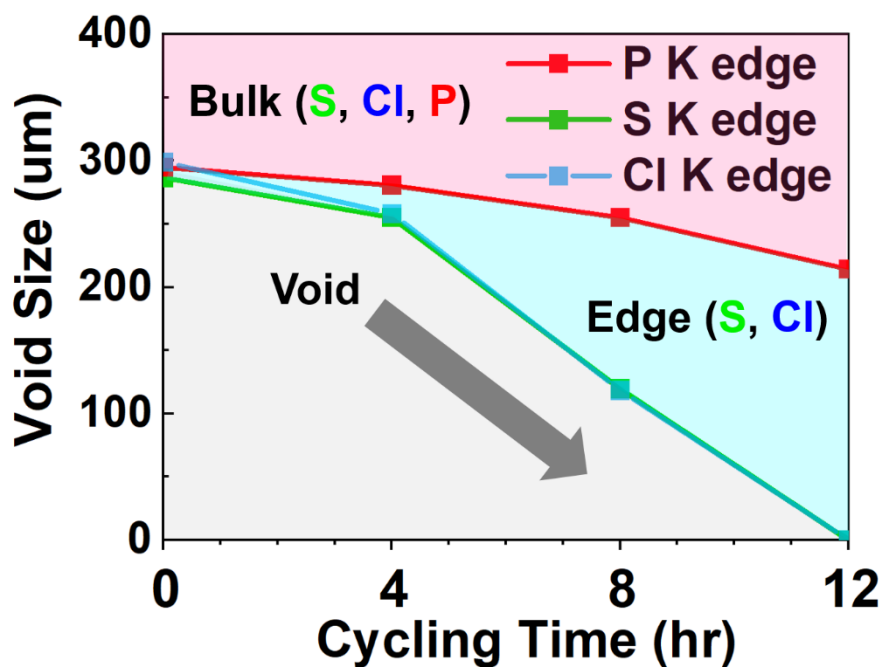
**Figure S7.** Ti 2p, P 2p, Al 2p, and O 1s XPS profiles of pristine LATP, and LATP-derived-SEI after cycling in a  $Li^0$ - $Li^0$  symmetric cell. The emergence of reduced P signal and MO<sub>x</sub> signal suggest the degradation of LATP.



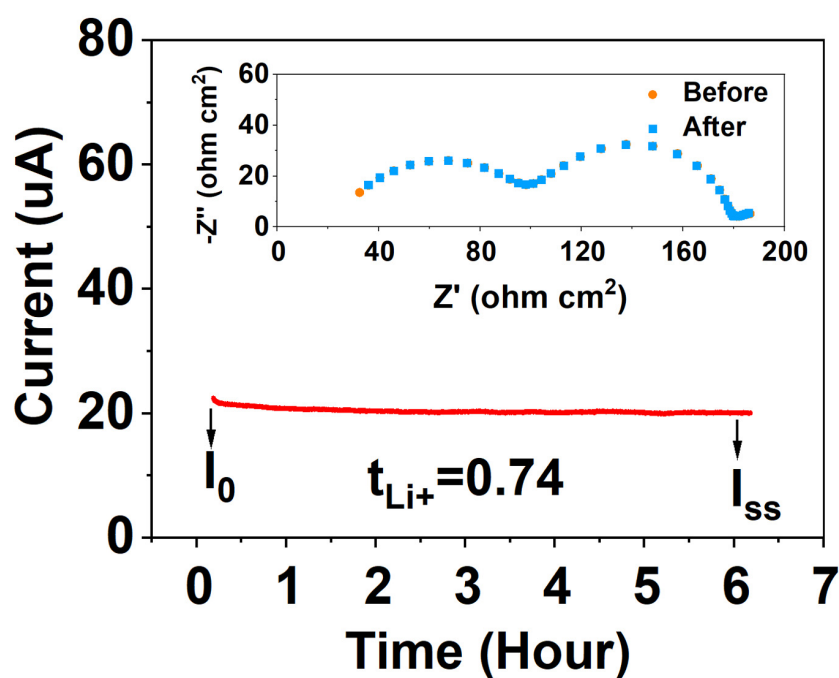
**Figure S8.** Ti 2p, P 2p, Al 2p, and O 1s XPS profiles of pristine PCE, and PCE-derived-SEI after cycling in a  $Li^0$ - $Li^0$  symmetric cell. Ti, P, and Al signals remain unchanged because the SH-SPE-derived SEI prevent the degradation of LATP.



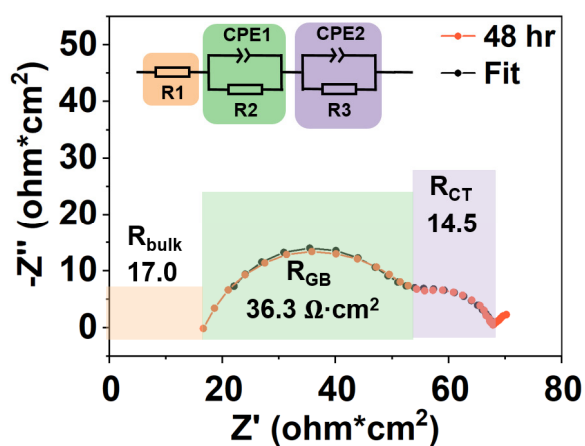
**Figure S9.** Individual S, Cl, and P K-edge XRF mapping showing the migration of polymer mainchain (S), lithium salt (Cl), and LATP (P).



**Figure S10.** Calculated void size evolution based on the P, S, and Cl mapping.

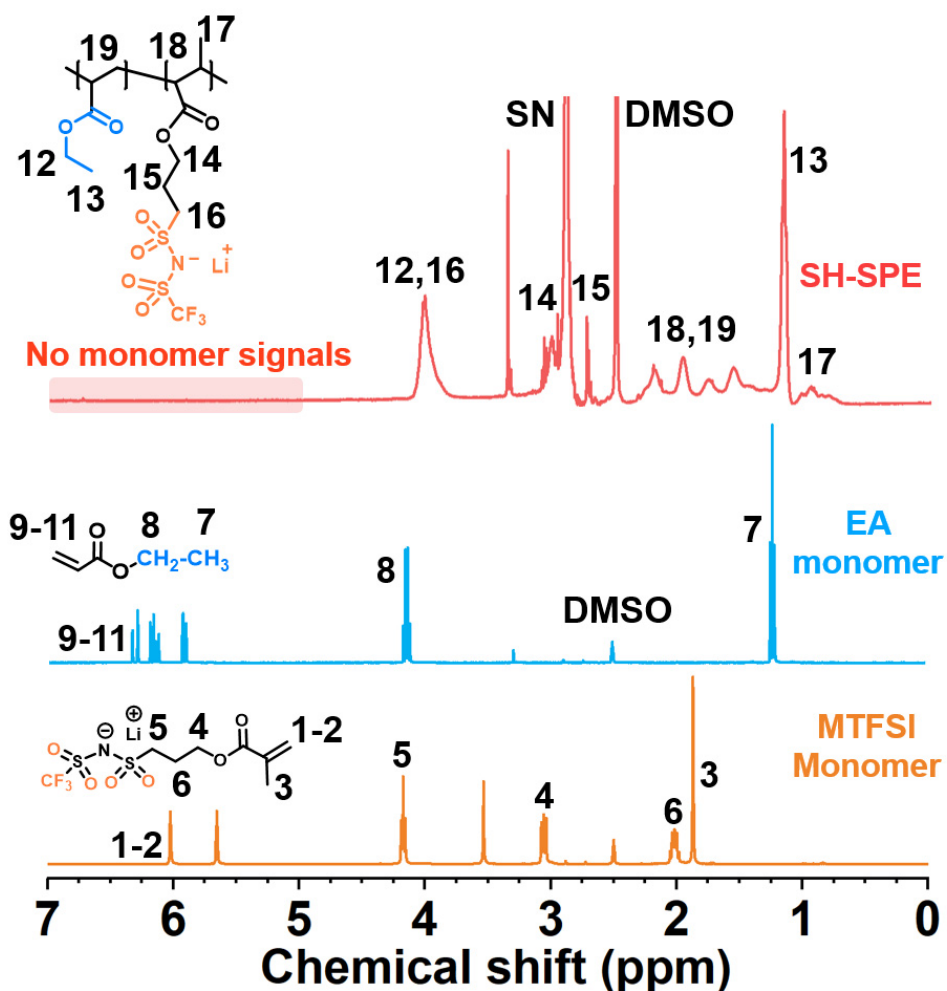


**Figure S11.**  $\text{Li}^+$  transference number ( $t_{\text{Li}^+}$ ) of PCE measured under a  $\text{Li}^0\text{-Li}^0$  symmetric cell configuration and r.t.

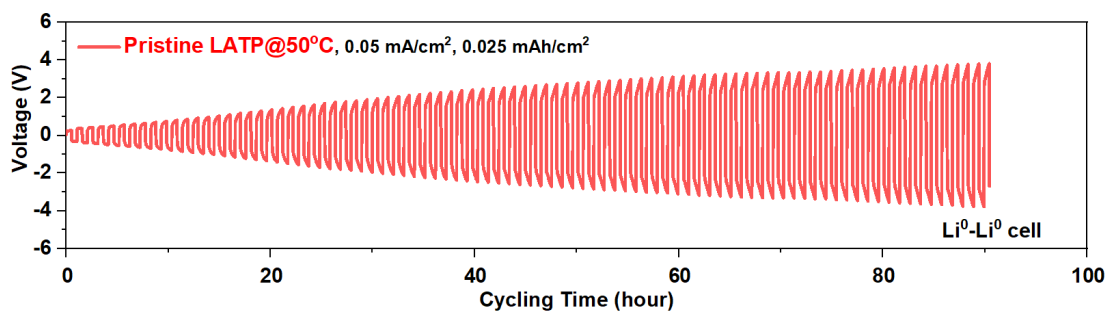


|                                 | $R_b$ | $R_{gb}$ | $R_{CT}$ |
|---------------------------------|-------|----------|----------|
| Value<br>(ohm*cm <sup>2</sup> ) | 17.0  | 36.3     | 14.5     |
| Error<br>(%)                    | 2.1   | 4.6      | 9.2      |

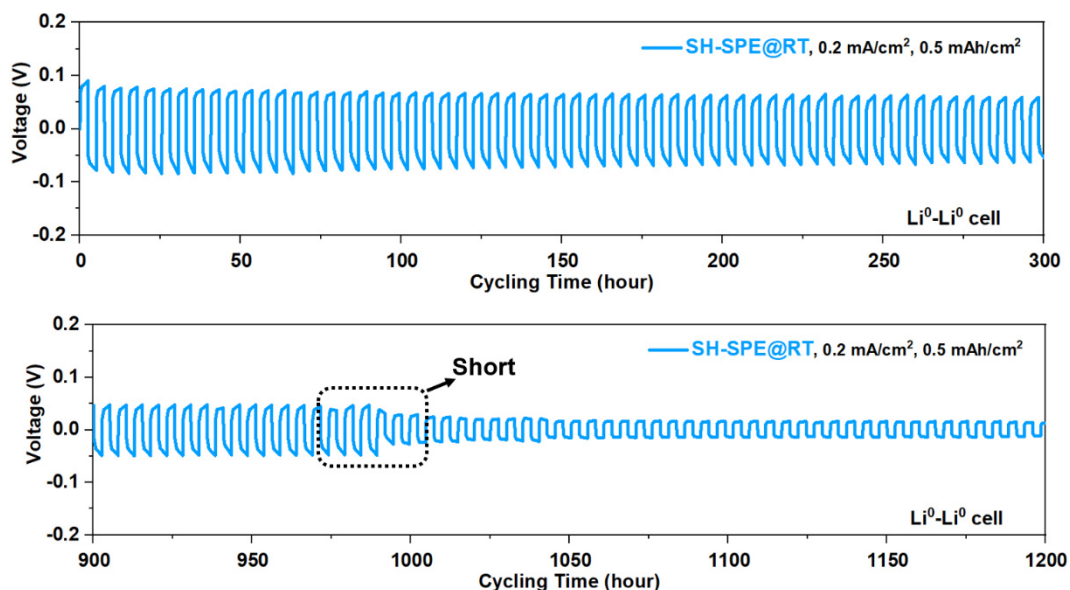
**Figure S12.** Equivalent circuit fitting for EIS plot of  $\text{Li}^0|\text{PCE}|\text{Li}^0$  cells after cycling at  $0.2 \text{ mA/cm}^2$  for 48 hours.  $R_b$ ,  $R_{gb}$ , and  $R_{CT}$  are bulk resistance, grain boundary resistance, and charge transfer resistance, respectively.



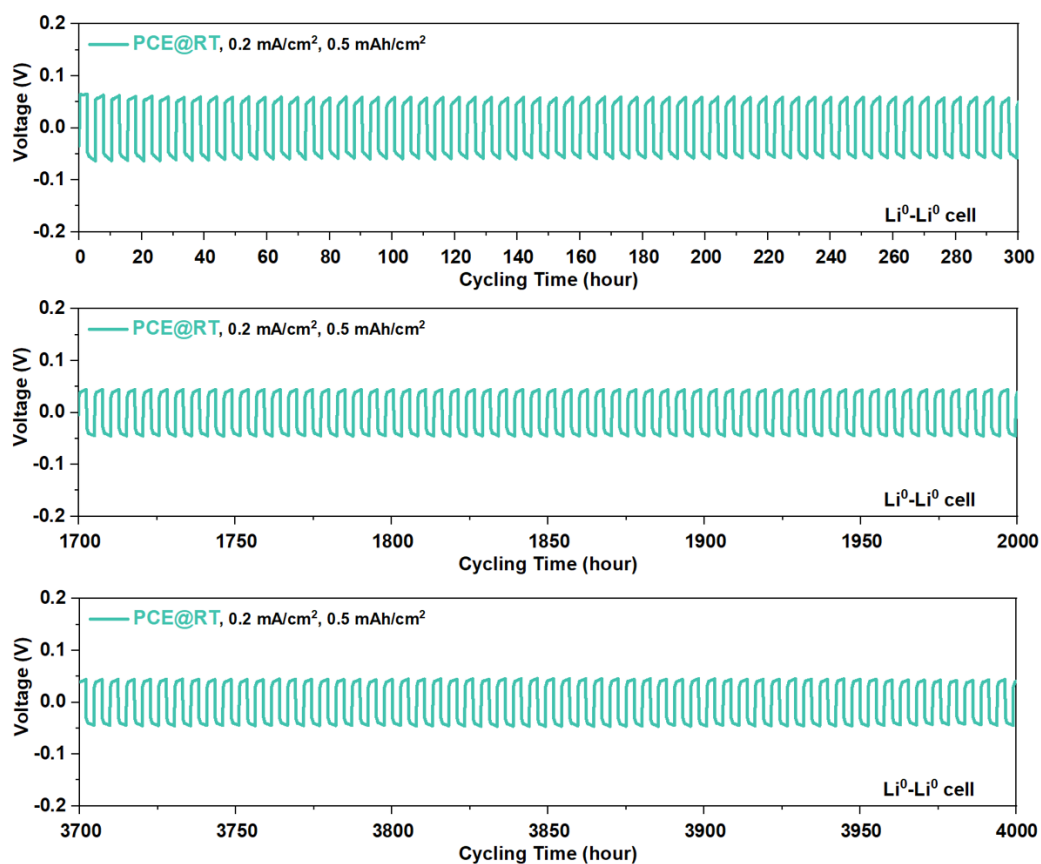
**Figure S13.**  $^1\text{H}$  NMR spectra of EA, MTFSI, and SH-SPE showing the monomer conversion yield and polymer structure of SH-SPE.



**Figure S14.** Voltage-time profiles at 0-100 hours of solid-state  $\text{Li}^0\text{-Li}^0$  cells employing **pristine LATP** as electrolyte. The  $\text{Li}^0|\text{LATP}|\text{Li}^0$  before 100 hour due to rapid overpotential build-up caused by uncontrolled side reactions.

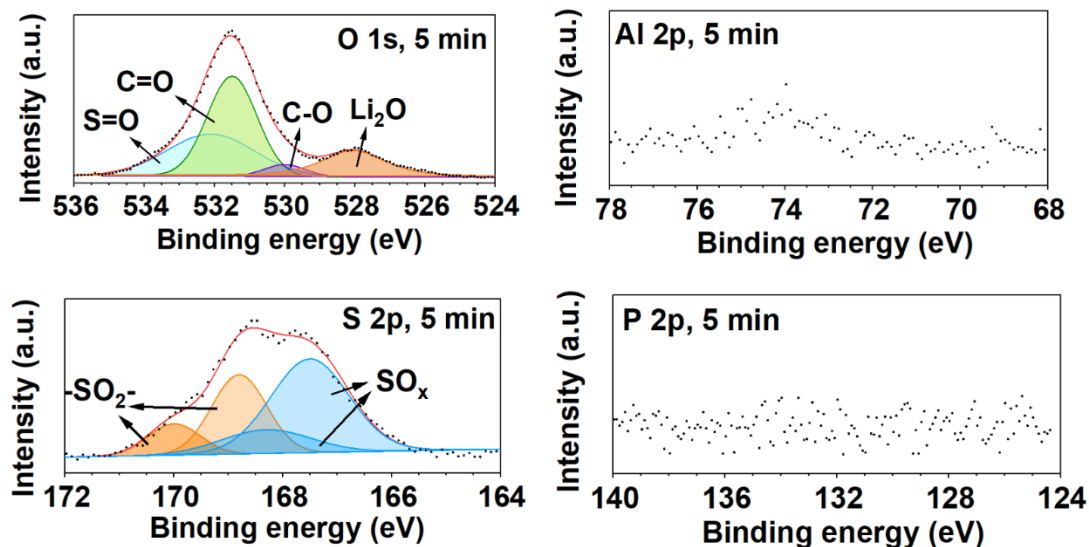


**Figure S15.** Enlarged voltage-time profiles as a supplement to  $\text{Li}^0|\text{SH-SPE}|\text{Li}^0$  cell performance shown in Figure 5a. The cell was cycled at  $0.2\text{mA}/\text{cm}^2$ ,  $0.5\text{mAh}/\text{cm}^2$ , and r.t. The cell was rested for 5mins after charging and discharging for 2.5hr.

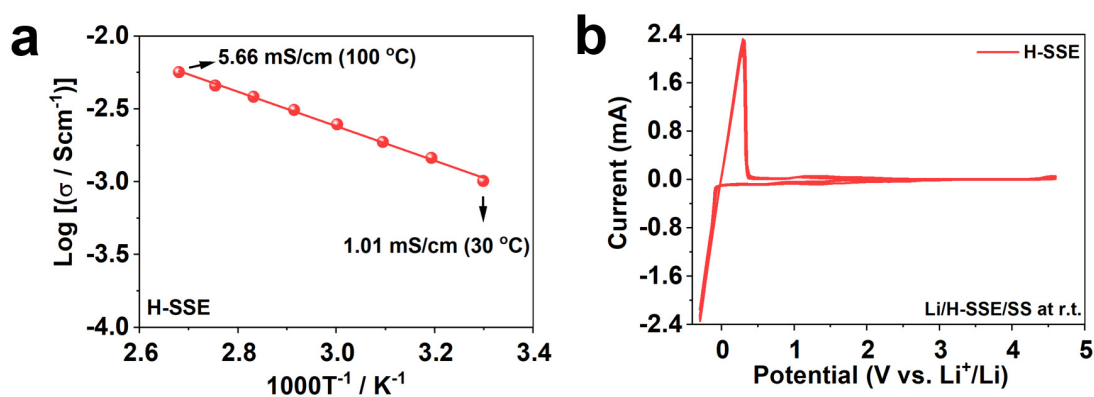


**Figure S16.** Enlarged voltage-time profiles as a supplement to  $\text{Li}^0|\text{PCE}|\text{Li}^0$  cell performance shown in Figure 5a. The cell was cycled at  $0.2\text{mA}/\text{cm}^2$ ,  $0.5\text{mAh}/\text{cm}^2$ , and r.t. The cell was rested for 5mins after charging and discharging for 2.5hr.

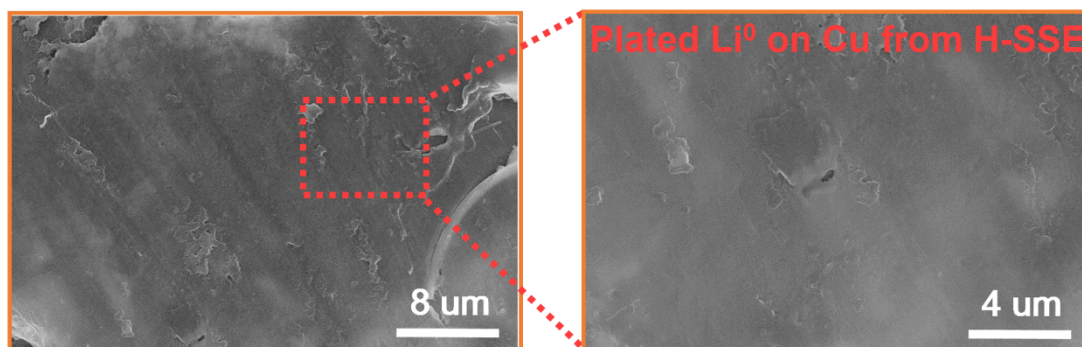
## H-SSE-derived SEI



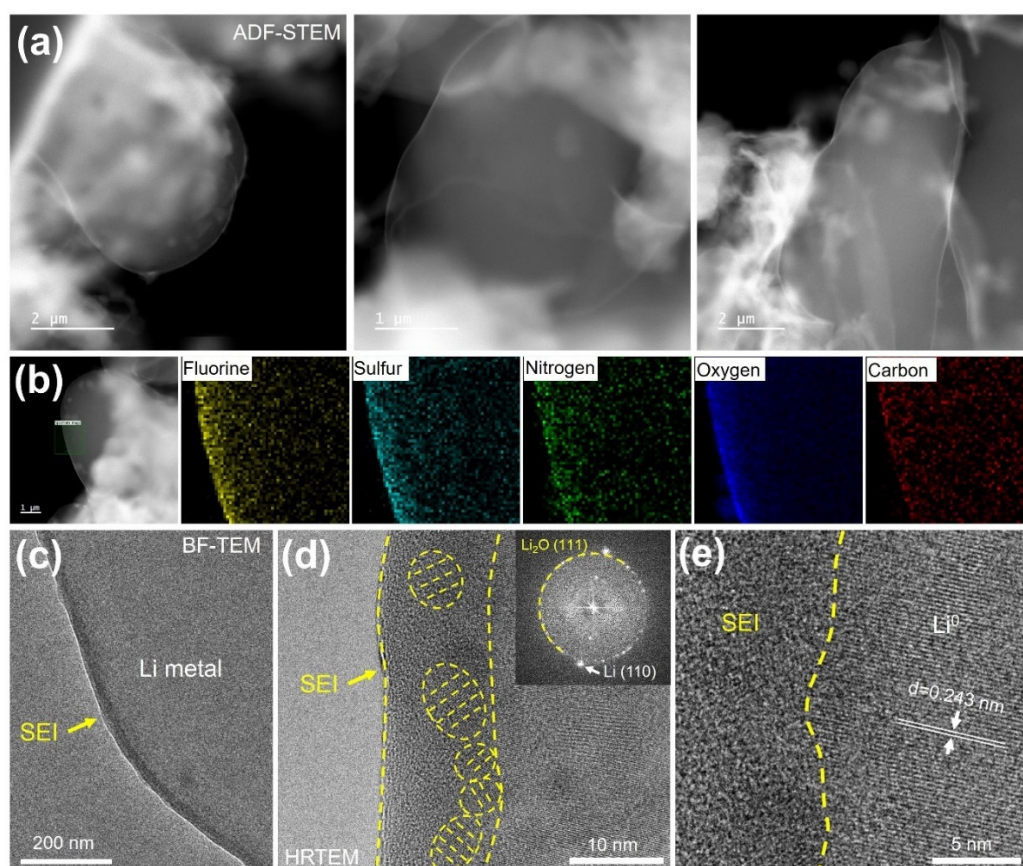
**Figure S17.** O 1s, S 2p, P 2p, and Al 2p XPS profiles of the H-SSE-derived-SEI after Ar sputtering for 5 minutes. The absence of Ti, P, and Al elements in the SEI suggests complete isolation of LATP from Li<sup>0</sup> anode by the PA-SPE buffer layer.



**Figure S18.** (a) Temperature-dependent conductivity of H-SSE and the Arrhenius fitting in the form of  $\sigma = Ae^{-\frac{E_a}{kT}}$ . (b) Cyclic voltammetry (CV) of the Li|H-SSE|SS cell at r.t. and 1mV/s showing the electrochemical stability window of H-SSE.

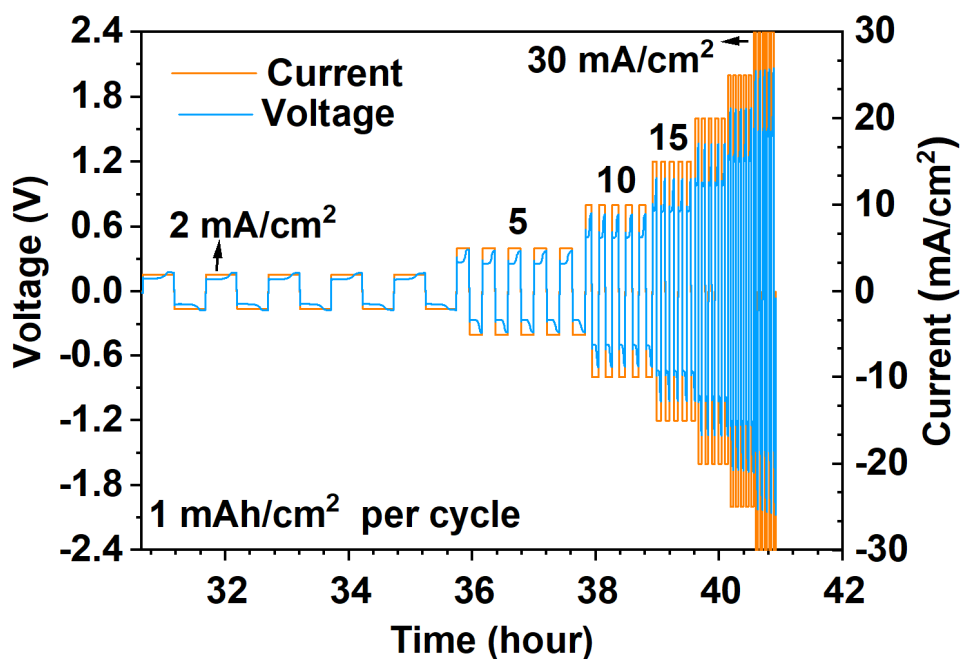


**Figure S19.** SEM images showing the surface morphology of  $\text{Li}^0$  deposits after discharging a  $\text{Li}^0|\text{H-SSE}|\text{Cu}$  cell at  $0.2 \text{ mA/cm}^2$  for 10 hours at r.t.

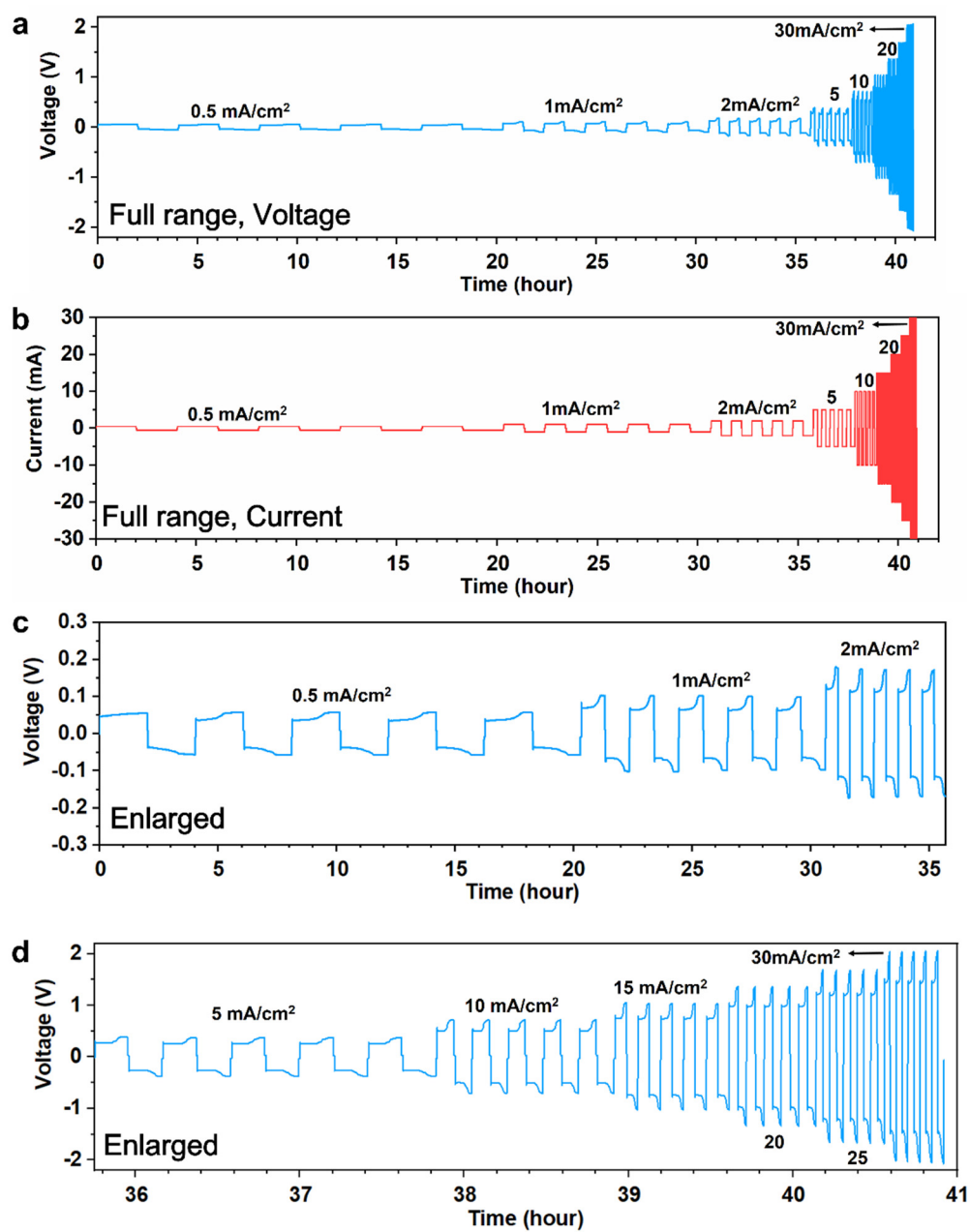


**Figure S20.** Cryo-TEM images showing the morphology of  $\text{Li}^0$  deposited under H-SSE. (a) Representative cryogenic transmission electron microscopy (Cryo-TEM) images showing the smooth chunk morphology of the deposited  $\text{Li}^0$  with H-SSE. The image was obtained in high-angle annular dark-field (HAADF) mode; (b) High-angle annular dark-field STEM (HAADF-STEM) image, and energy-dispersive spectroscopic (EDS) maps of the deposited  $\text{Li}^0$  with the H-SSE electrolyte. The result shows that a thin and uniform layer of solid electrolyte interface (SEI) enriched in C, N, O, F, and S forms on the  $\text{Li}^0$  surface; (c) High-magnification bright-field TEM (BF-TEM) image showing the uniform SEI formed on the  $\text{Li}^0$  surface; (d) Atomic-resolution Cryo-STEM image showing the structure of the  $\text{Li}^0$  deposit and SEI. The SEI comprises nano-sized domains (e.g.,  $\text{Li}_2\text{O}$  indicated by

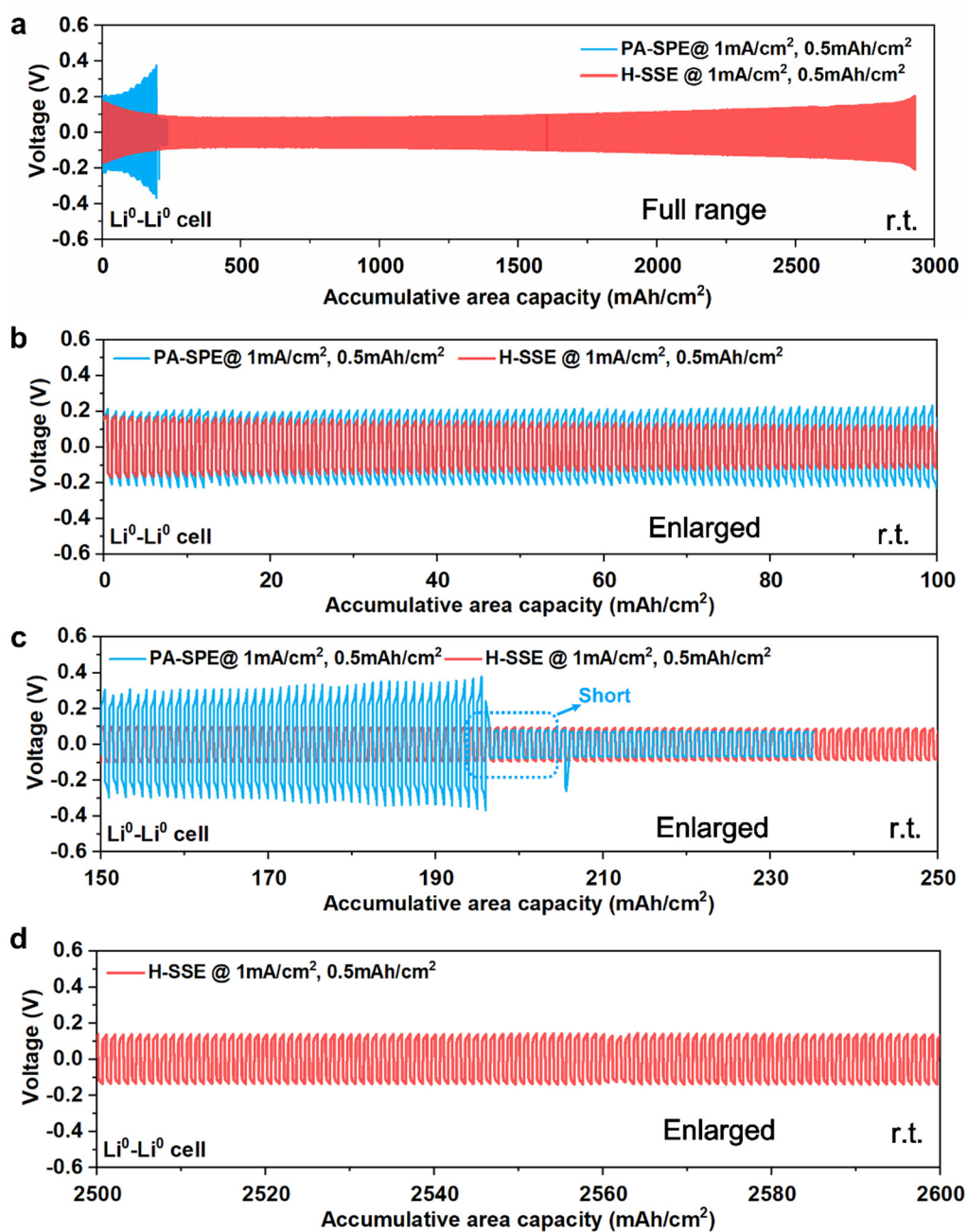
dash circles) with varied crystallographic orientations. The Bragg spots and polycrystalline ring in the fast Fourier transform (FFT) correspond to the  $\text{Li}^0$  (110) and  $\text{Li}_2\text{O}$  (111) crystallographic planes, respectively; (e) Enlarged image showing the interface between the SEI and the  $\text{Li}^0$  deposit. The (110) plane corresponding to  $\text{Li}^0$  is identified in the image.



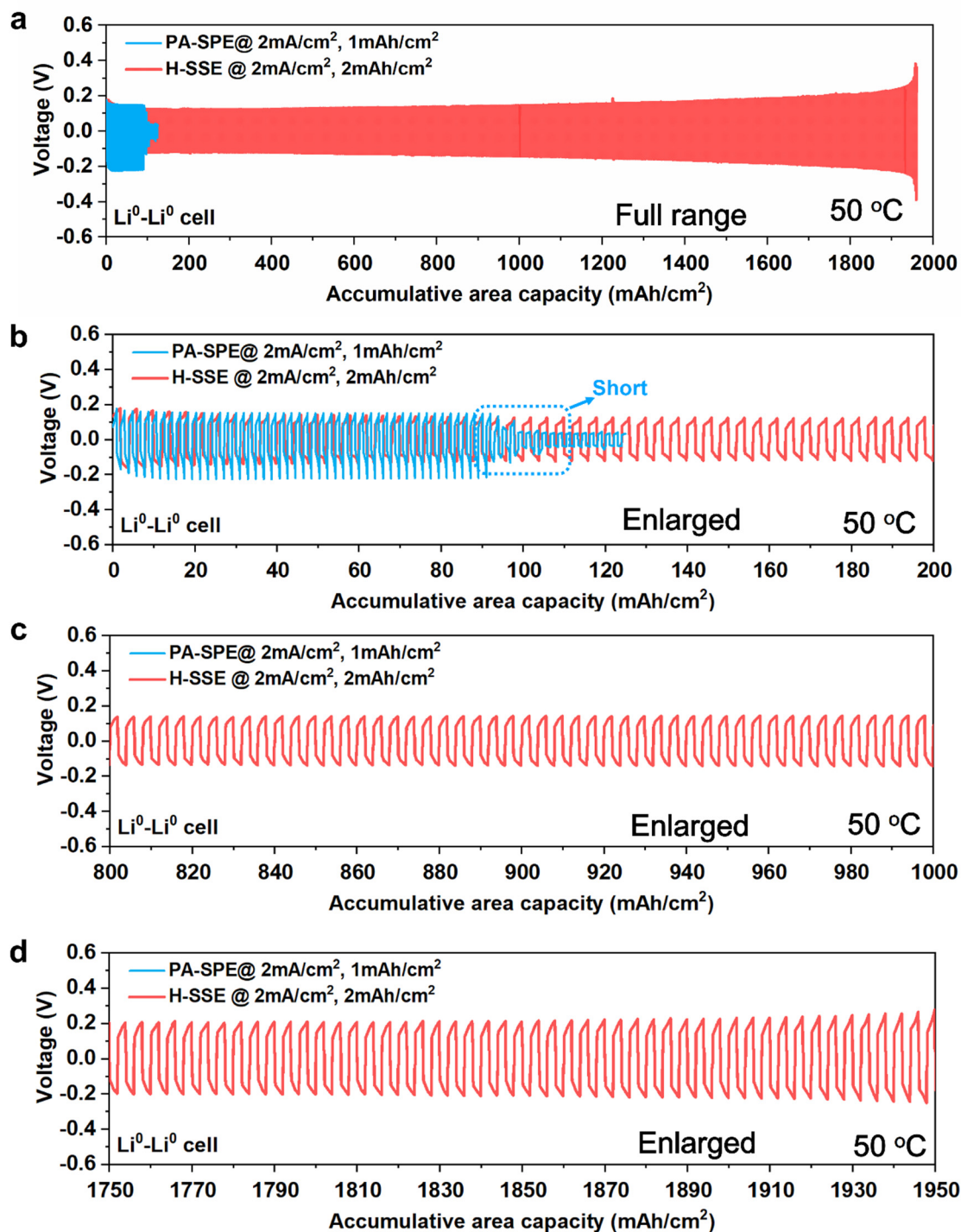
**Figure S21.** The critical current density of  $\text{Li}^0|\text{H-SSE}|\text{Li}^0$  cell measured at step-up current densities and areal capacities of  $1 \text{ mAh/cm}^2$ . The Voltage-time curve at lower current densities ( $0.2\text{-}1 \text{ mA/cm}^2$ ) was shown in Figure S22. The testing temperature is  $50^\circ\text{C}$ .



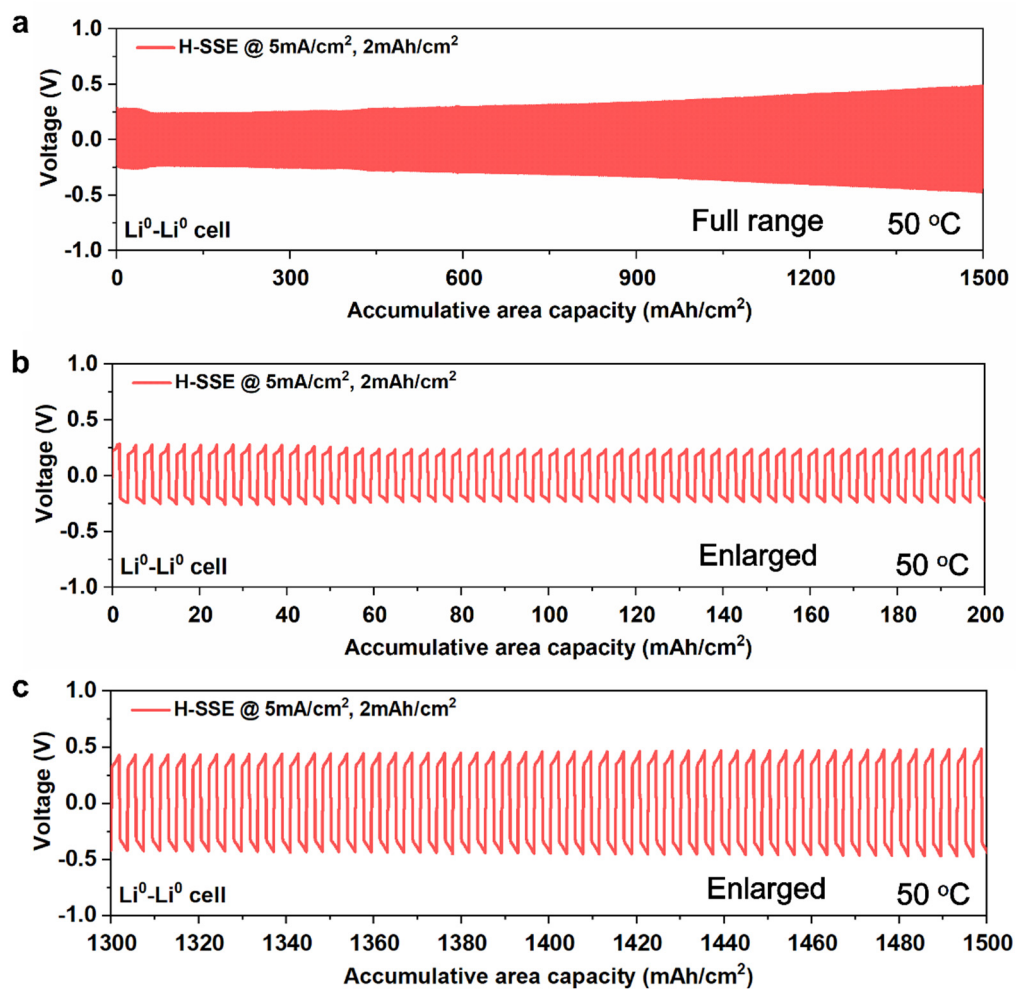
**Figure S22.** Supplementary enlarged voltage-time profiles showing the critical current density of  $\text{Li}^0|\text{H-SSE}|\text{Li}^0$  cell.



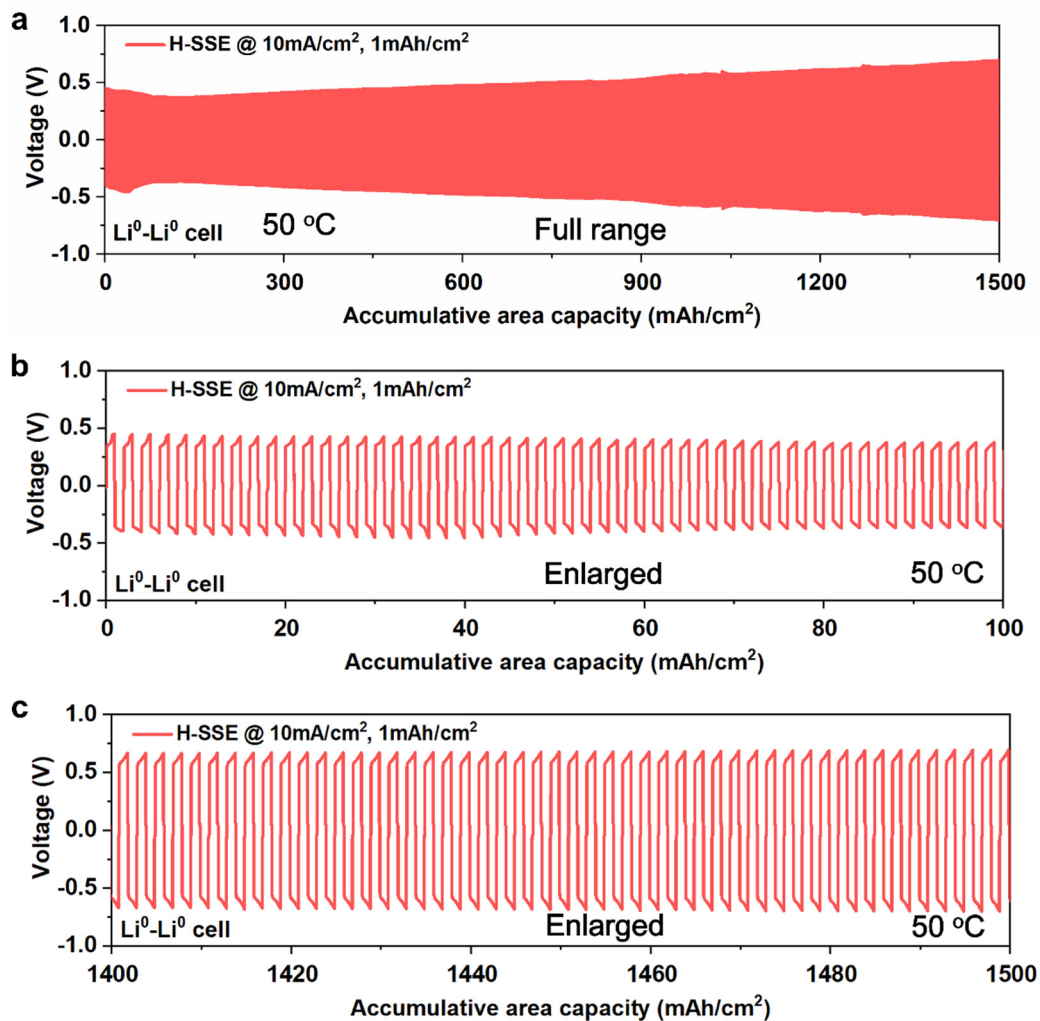
**Figure S23.** a, Durability comparison of  $\text{Li}^0\text{-Li}^0$  cells based on H-SSE and PA-SPE at  $1\text{mA}/\text{cm}^2$ ,  $0.5\text{mAh}/\text{cm}^2$ . b, c, d, Supplementary enlarged profiles. The cell was rested for 3mins after charging and discharging for 0.5hr.



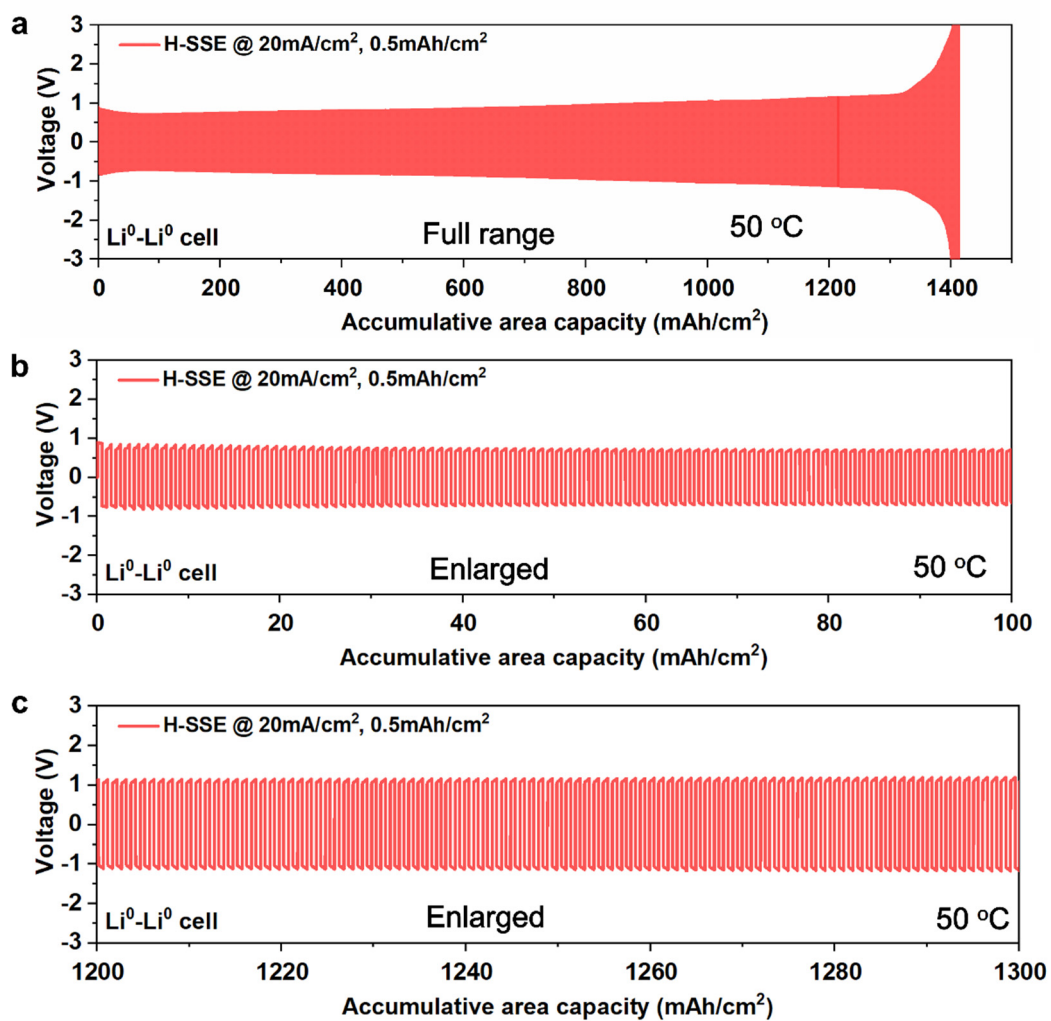
**Figure S24.** **a**, Durability comparison of  $\text{Li}^0\text{-Li}^0$  cells based on H-SSE and PA-SPE at  $2\text{mA}/\text{cm}^2$ . **b**, **c**, **d**, Supplementary enlarged profiles. The cell was rested for 5mins after charging and discharging for 1hr.



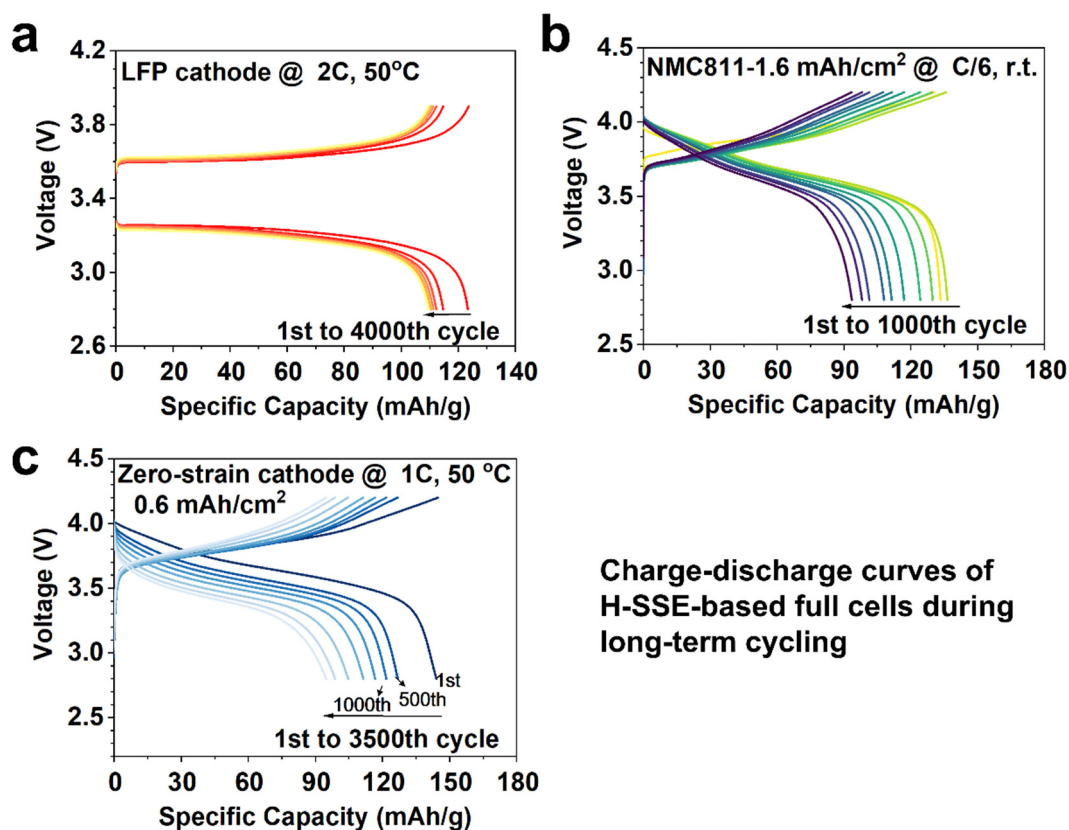
**Figure S25.** a, Durability of  $\text{Li}^0|\text{H-SSE}|\text{Li}^0$  cells at  $5\text{mA}/\text{cm}^2$ ,  $2\text{mAh}/\text{cm}^2$ . b, c, Supplementary enlarged profiles. The cell was rested for 2mins after charging and discharging for 0.4hr.



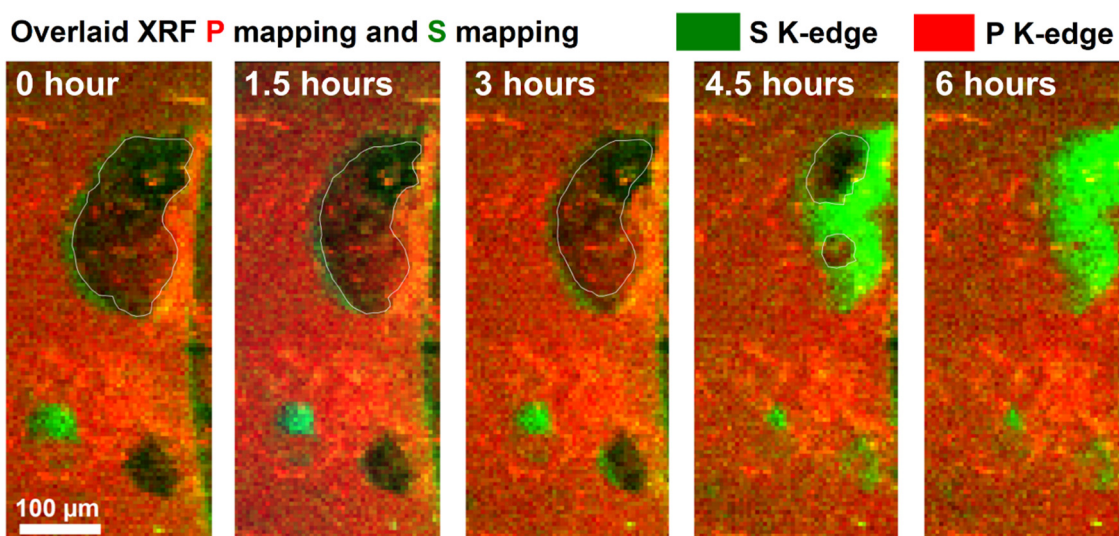
**Figure S26.** a, Durability of Li<sup>0</sup>|H-SSE|Li<sup>0</sup> cells at 10 mA/cm<sup>2</sup>, 1 mAh/cm<sup>2</sup>. b, c, Supplementary enlarged profiles. The cell was rested for 30s after charging and discharging for 0.1 hr.



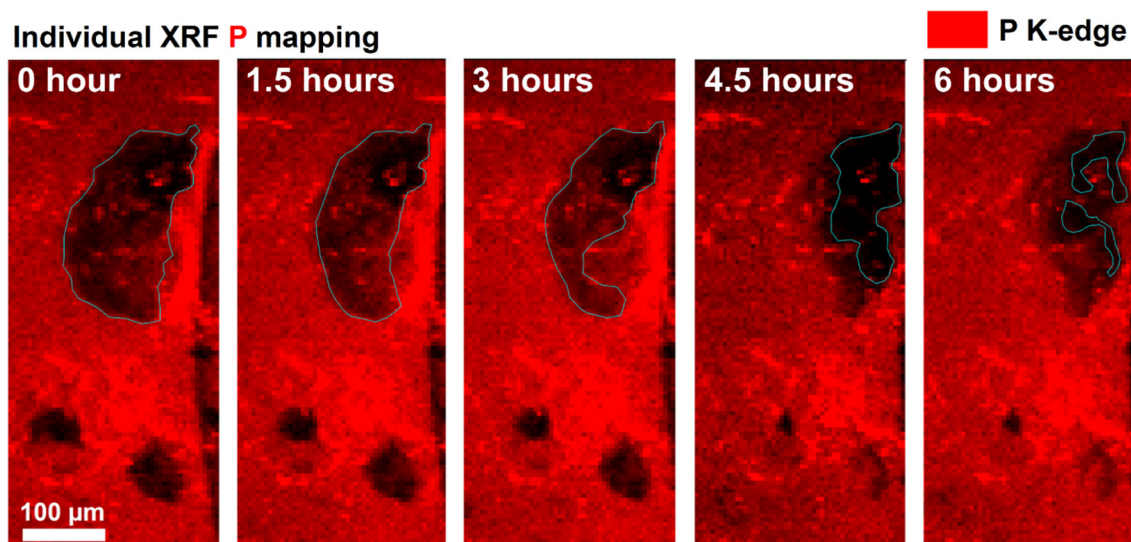
**Figure S27.** a, Durability of  $\text{Li}^0|\text{H-SSE}|\text{Li}^0$  cells at  $20\text{mA}/\text{cm}^2$ ,  $0.5\text{mAh}/\text{cm}^2$ . b, c, Supplementary enlarged profiles. The cell was rested for 0.1s after charging and discharging for 1.5 min.



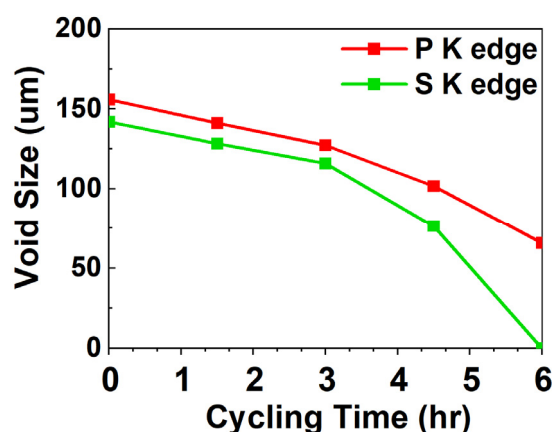
**Figure S28.** Charge-discharge curves of H-SSE based full cells when employing LFP (a), NMC811 (b), and a high-Ni, zero-Co, zero-strain cathode (c).



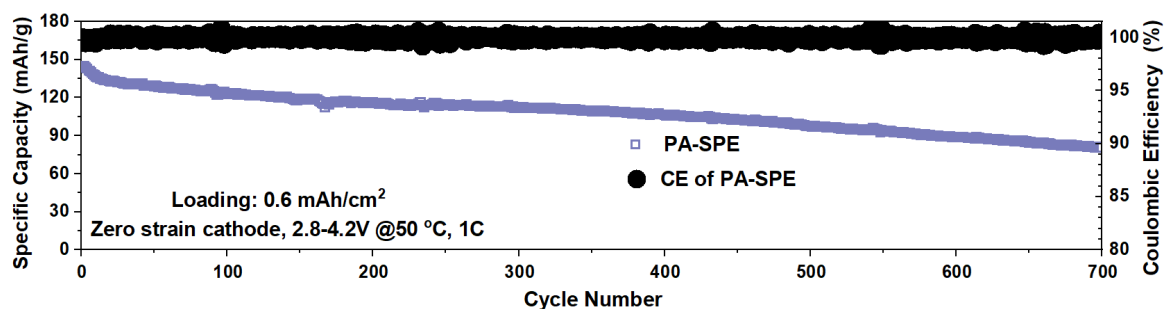
**Figure S29.** Overlaid S K-edge and P K-edge XRF mappings of the PCE-based *in-situ* cell when cycling at 0.05 mA/cm<sup>2</sup> for 6 hours.



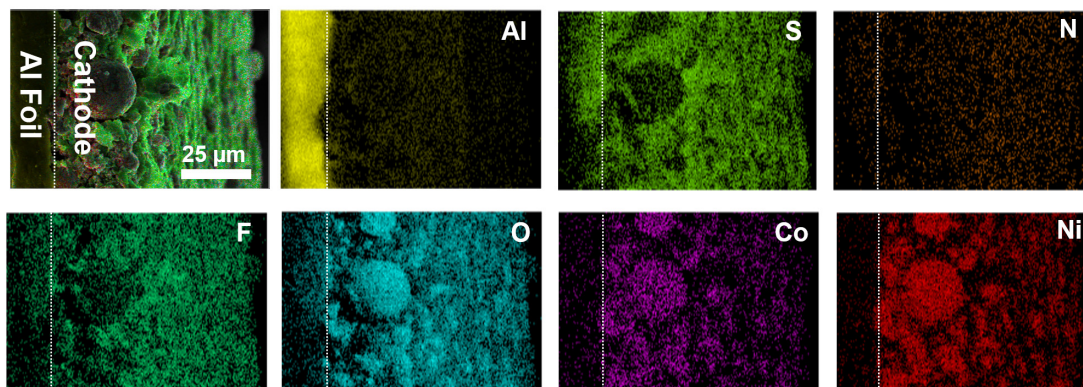
**Figure S30.** Individual P K-edge XRF mappings of the PCE-based *in-situ* cell when cycling at 0.05 mA/cm<sup>2</sup> for 6 hours.



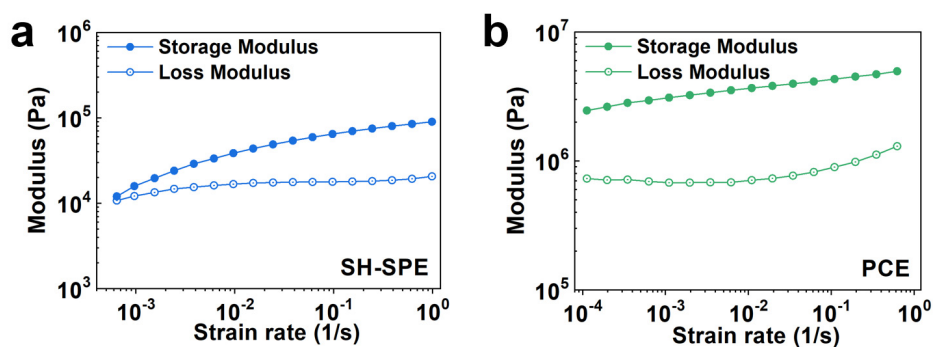
**Figure S31.** Size evolution of the 150- $\mu\text{m}$ -sized void when cycling the *in-situ* cell at 0.05 mA/cm<sup>2</sup>.



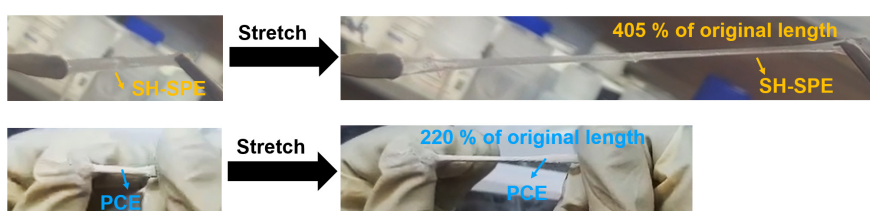
**Figure S32.** Performance of PA-SPE-based full cells when employing the high-Ni, zero-Co, zero-strain cathode. The left y-axis displays the discharge capacity, while the right y-axis represents the Coulombic efficiency of the cell.



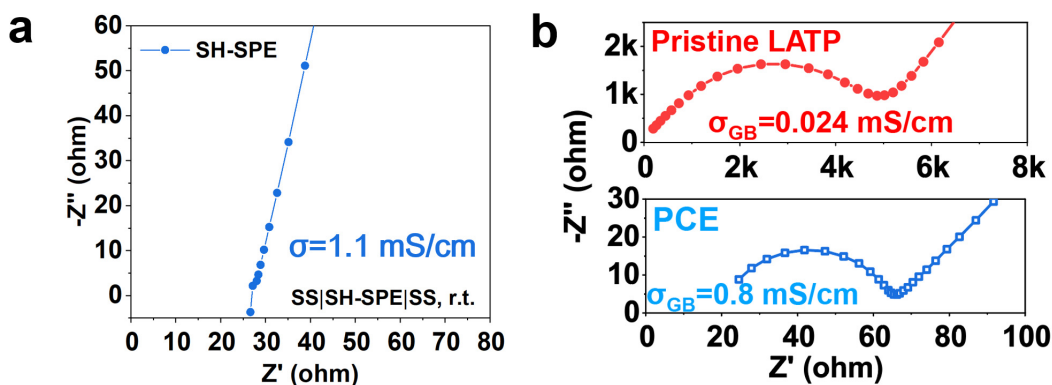
**Figure S33.** SEM-EDS mapping of the cross-section of the NMC811 cathode after cycling with H-SSE. The homogeneous distribution of N and S elements within the cathode indicates successful infiltration of lithium salt (LiTFSI) and succinonitrile solid crystal plasticizer into the cathode pores, thereby creating an ion conduction pathway.



**Figure S34.** Viscoelasticity of SH-SPE (a) and PCE (b) showing the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) with increasing strain rate.

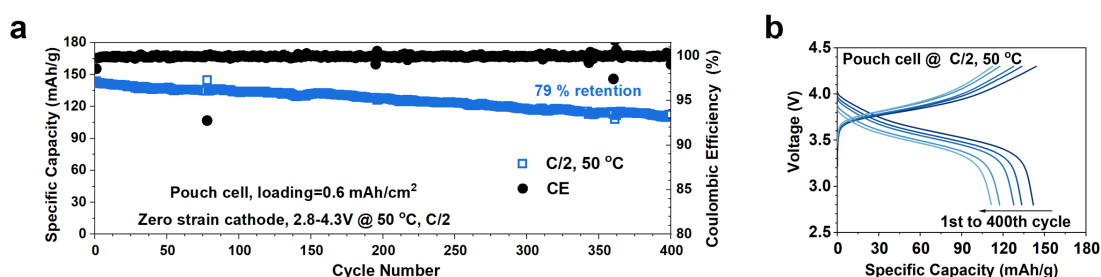


**Figure S35.** Photographs showing the stretchability of SH-SPE and PCE.

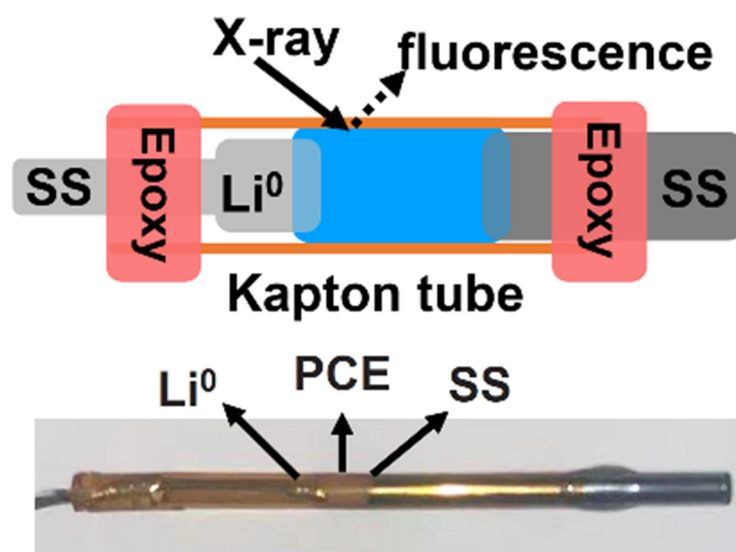


**Figure S36. a**, EIS plot of SS|SH-SPE|SS showing ionic conductivity of SH-SPE. SS refers to stainless steel blocking electrodes. **b**, EIS plots of SS|LATP|SS and SS|PCE|SS cells showing the grain boundary resistance and ionic conductivity.

Note: The differences in ionic conductivity between phases could cause  $\text{Li}^+$  to preferentially transport through the more conductive phase, resulting in higher local current density and leading to non-uniform lithium deposition. In this study, the pristine SH-SPE exhibits a room temperature conductivity of 1.1 mS/cm, while the pristine LATP has a lower room temperature conductivity of 0.024 mS/cm due to its high grain boundary resistance. However, the infiltration of SH-SPE into the grain boundaries of LATP (Figure 1d) significantly enhances  $\text{Li}^+$  conduction between LATP particles, reducing the grain boundary resistance to 55  $\text{ohm} \cdot \text{cm}^2$ , corresponding to a grain boundary conductivity of 0.8 mS/cm. Thus, in the PCE, both the polymer phase and ceramic phase show comparable conductivities of 1.1 mS/cm and 0.8 mS/cm, respectively.



**Figure S37. a**, Performance of H-SSE when paired with a zero-strain cathode in pouch cells. The effective area of the zero-strain cathode is 7.8  $\text{cm}^2$ , with a mass loading of 3.06  $\text{mg}/\text{cm}^2$ . The cell was cycled at C/2 and 50  $^{\circ}\text{C}$ , with cut-off voltage of 2.8-4.3 V. **b**, Charge-discharge profiles of pouch cell when cycling at C/2 and 50  $^{\circ}\text{C}$ .



**Figure S38.** A schematic illustration of the tube battery and experimental set-up for XRF and XAS characterization.

**Table S1.** Comparison of the Li<sup>0</sup>-Li<sup>0</sup> symmetric cell durability and full cell performance with previous Li<sup>0</sup>-anode batteries on PEO-based solid polymer electrolytes.

a) Critical current density; b) 3V-class cathode: LiFePO<sub>4</sub>; 4V-class cathode: NMC, LiCoO<sub>2</sub>, etc.

| References                              | CCD <sup>a)</sup><br>(mA/cm <sup>2</sup> ) | Li <sup>0</sup> -Li <sup>0</sup> cell<br>Current/life/temp. | Current×<br>cycle life<br>(mAh/cm <sup>2</sup> ) | Cathode <sup>b)</sup> | Current<br>Density | capacity/cycle<br>life/retention | Loading<br>(mg/cm <sup>2</sup> ) | Loading<br>(mAh/cm <sup>2</sup> )<br>×cycle number |
|-----------------------------------------|--------------------------------------------|-------------------------------------------------------------|--------------------------------------------------|-----------------------|--------------------|----------------------------------|----------------------------------|----------------------------------------------------|
| This work                               | 30                                         | 1/2900hr/r.t.                                               | <b>2900</b>                                      | 3 V                   | C/2                | 127/2400/84%                     | 4.5                              | <b>1836</b>                                        |
|                                         |                                            | 2/1000hr/50°C                                               | <b>2000</b>                                      | 3 V                   | 2C                 | 123/4000/88%                     | 2.3                              | <b>1564</b>                                        |
|                                         |                                            | 5/300hr/50°C                                                | <b>1500</b>                                      | 4 V                   | 1C                 | 144/2860/80%                     | 3                                | <b>1844</b>                                        |
|                                         |                                            | 10/150hr/50°C                                               | <b>1500</b>                                      | 4V                    | C/6                | 130/1000/71%                     | 7.4                              | <b>1600</b>                                        |
| 2024 Nat. Energy <sup>1</sup>           | 3.7                                        | 0.5/1000hr/                                                 | <b>500</b>                                       | 4V                    | C/2                | 210/400/80%                      | 5.3                              | <b>460</b>                                         |
| 2024 Nat. Nanotechnol. <sup>2</sup>     | NA                                         | 0.1/1000hr/60°C                                             | <b>100</b>                                       | 3 V                   | 0.5C               | 138/200/90%                      | 1.5                              | <b>51</b>                                          |
|                                         |                                            |                                                             |                                                  | 3 V                   | 0.07C              | 130/35/95%                       | 6.8                              | <b>41</b>                                          |
| 2024 Nat. Commun. <sup>3</sup>          | 0.5                                        | 0.1/2250hr/90°C                                             | <b>225</b>                                       | 3 V                   | 0.5C               | 160/1000/78%                     | 1.6                              | <b>270</b>                                         |
| 2024 Nat. Mater. <sup>4</sup>           | NA                                         | 0.05/1500hr/30°C                                            | <b>75</b>                                        | 3 V                   | 0.05C              | 147/40/92%                       | 8.8                              | <b>53</b>                                          |
| 2024 Angew. Chem. <sup>5</sup>          | 1.1                                        | 0.4/1500hr/60°C                                             | <b>600</b>                                       | 3V                    | 2C                 | 123/1500/80%                     | 2                                | <b>510</b>                                         |
| 2024 Energy Environ. Sci. <sup>6</sup>  | NA                                         | 0.1/100hr/25°C                                              | <b>10</b>                                        | 3 V                   | 0.1C               | 147/100/88%                      | 1.2                              | <b>21</b>                                          |
|                                         |                                            |                                                             |                                                  | 4 V                   | 0.1C               | 152/100/66%                      | 1.2                              | <b>26</b>                                          |
| 2024 Nano Energy <sup>7</sup>           | 0.5                                        | 0.1/1600hr/NA                                               | <b>160</b>                                       | 4 V                   | 0.1C               | 166/250/92%                      | 3                                | <b>161</b>                                         |
|                                         |                                            | 0.2/400hr/NA                                                | <b>80</b>                                        | 4 V                   | NA                 | 178/100/82%                      | 10                               | <b>215</b>                                         |
| 2024 ACS Energy Lett. <sup>8</sup>      | NA                                         | 0.4/500hr/70°C                                              | <b>200</b>                                       | 3 V                   | 2C                 | 130/1000/76%                     | 2.5                              | <b>425</b>                                         |
| 2023 J. Am. Chem. Soc. <sup>9</sup>     | NA                                         | 0.1/400hr/25°C                                              | <b>40</b>                                        | 3 V                   | 0.5C               | 130/250/96%                      | 2.5                              | <b>106</b>                                         |
|                                         |                                            |                                                             |                                                  | 4 V                   | 0.1C               | 134/100/84%                      | 2.5                              | <b>42.5</b>                                        |
| 2023 Angew. Chem. <sup>10</sup>         | 0.3                                        | 0.1/1000hr/60°C                                             | <b>100</b>                                       | 3 V                   | 0.2C               | 149/600/75%                      | 1.2                              | <b>122</b>                                         |
| 2023 PNAS <sup>11</sup>                 | 2                                          | 0.5/700hr/25°C                                              | <b>350</b>                                       | 3 V                   | 0.5C               | 135/300/92%                      | 2.5                              | <b>117</b>                                         |
|                                         |                                            |                                                             |                                                  | 3 V                   | 0.2C               | 160/100/80%                      | 8                                | <b>136</b>                                         |
| 2023 Nano Energy <sup>12</sup>          | NA                                         | 0.1/2000hr/60°C                                             | <b>200</b>                                       | 3 V                   | 1C                 | 127/300/99%                      | 1                                | <b>51</b>                                          |
| 2023 Nano Energy <sup>13</sup>          | NA                                         | 0.5/600hr/NA                                                | <b>300</b>                                       | 4 V                   | 0.5C               | 145/100/92%                      | 2.2                              | <b>28</b>                                          |
| 2023 Nano Energy <sup>14</sup>          | 0.7                                        | 0.1/900hr/25°C                                              | <b>90</b>                                        | 3 V                   | 0.2C               | 155/330/95%                      | 1.7                              | <b>95</b>                                          |
|                                         |                                            |                                                             |                                                  | 4 V                   | 0.1C               | 152/100/83%                      | 1.1                              | <b>24</b>                                          |
| 2023 Nano Energy <sup>15</sup>          | 0.2                                        | 0.1/320hr/60°C                                              | <b>32</b>                                        | 3 V                   | 0.1C               | 148/100/93%                      | NA                               | <b>NA</b>                                          |
| 2023 Adv. Energy Mater. <sup>16</sup>   | NA                                         | 0.3/500hr/60°C                                              | <b>150</b>                                       | 3 V                   | 1C                 | 147/300/99.7%                    | 2                                | <b>102</b>                                         |
| 2022 Joule <sup>17</sup>                | NA                                         | 0.75/1300hr/r.t.                                            | <b>974</b>                                       | 3 V                   | 0.25C              | 160/100/97%                      | 4                                | <b>68</b>                                          |
| 2022 ACS Energy Lett. <sup>18</sup>     | NA                                         | 0.1/445hr/70°C                                              | <b>45</b>                                        | 4 V                   | C/20               | 160/80/80%                       | 4.7                              | <b>80</b>                                          |
| 2022 Nano Energy <sup>19</sup>          | NA                                         | 0.2/2400hr/60°C                                             | <b>480</b>                                       | 3 V                   | 0.5C               | 133/1350/83%                     | 3.9                              | <b>895</b>                                         |
| 2022 Adv. Energy Mater. <sup>20</sup>   | 0.9                                        | 0.5/300hr/60°C                                              | <b>150</b>                                       | 3 V                   | 0.5C               | 160/500/70%                      | 3                                | <b>255</b>                                         |
| 2022 Energy Environ. Sci. <sup>21</sup> | NA                                         | 0.2/2200hr/NA                                               | <b>440</b>                                       | 4 V                   | 0.5C               | 188/1000/80%                     | 2.5                              | <b>537</b>                                         |
| 2022 Nat. Commun. <sup>22</sup>         | NA                                         | 0.1/3800hr/90°C                                             | <b>380</b>                                       | 3 V                   | 0.5C               | 158/400/98%                      | 1.5                              | <b>102</b>                                         |
|                                         |                                            |                                                             |                                                  | 4 V                   | 0.5C               | 145/100/87%                      | 1.5                              | <b>25.2</b>                                        |

|                                         |     |                 |             |     |       |              |     |             |
|-----------------------------------------|-----|-----------------|-------------|-----|-------|--------------|-----|-------------|
| 2022 Nat. Commun. <sup>23</sup>         | 1.2 | 0.1/1200hr/NA   | <b>120</b>  | 3 V | 0.25C | 167/1200/87% | 2   | <b>480</b>  |
|                                         |     | 1.2/120hr/NA    | <b>144</b>  |     |       |              |     |             |
| 2022 J. Am. Chem. Soc. <sup>24</sup>    | NA  | 0.1/500hr/70°C  | <b>50</b>   | 3 V | C/3   | 151/200/86%  | 4   | <b>136</b>  |
| 2021 J. Am. Chem. Soc. <sup>25</sup>    | 2   | 0.4/400hr/NA    | <b>160</b>  | 3 V | 0.15C | 160/120/78%  | 5   | <b>102</b>  |
|                                         |     | 1.2/100hr/NA    | <b>120</b>  | 4 V | 0.24C | 140/120/86%  | 3   | <b>77.4</b> |
| 2021 Adv. Mater. <sup>26</sup>          | NA  | 0.1/1200hr/NA   | <b>120</b>  | 4 V | 0.1C  | 177/100/78%  | 21  | <b>450</b>  |
|                                         |     | 1/1100hr/NA     | <b>1100</b> | 4 V | 0.1C  | 163/100/89%  | 23  | <b>450</b>  |
| 2021 Nano Lett. <sup>27</sup>           | NA  | 0.1/300hr/60°C  | <b>30</b>   | 3 V | 1C    | 146/1000/84% | 1   | <b>170</b>  |
| 2020 Adv. Mater. <sup>28</sup>          | 0.5 | 0.1/1300hr/NA   | <b>130</b>  | 3 V | 0.5C  | 144/500/86%  | 2.4 | <b>204</b>  |
| 2020 Energy Environ. Sci. <sup>29</sup> | NA  | 0.2/2500hr/NA   | <b>500</b>  | 3 V | C/3   | 160/210/97%  | 3.3 | <b>118</b>  |
|                                         |     |                 |             | 4 V | 0.1C  | 135/110/90%  | 3.5 | <b>82</b>   |
| 2020 Nano Lett. <sup>30</sup>           | NA  | 0.1/300hr/60°C  | <b>30</b>   | 3 V | 0.2C  | 140/300/95%  | 1.5 | <b>76.5</b> |
| 2020 Nano Lett. <sup>31</sup>           | NA  | 0.05/600hr/25°C | <b>30</b>   | 3 V | 0.1C  | 166/250/77%  | 5   | <b>212</b>  |
| 2020 Nano Lett. <sup>32</sup>           | NA  | 1/560hr/90°C    | <b>560</b>  | 3 V | 1C    | 140/200/86%  | 2.5 | <b>85</b>   |
|                                         |     | 2/260hr/90°C    | <b>520</b>  | 4 V | C/20  | 160/50/80%   | 2.5 | <b>27</b>   |

**Table S2.** Comparison of the Li<sup>0</sup>-Li<sup>0</sup> symmetric cell durability and full cell performance with previous Li<sup>0</sup>-anode batteries on beyond-PEO solid polymer electrolytes.

a) Critical current density; b) 3V-class cathode: LiFePO<sub>4</sub>; 4V-class cathode: NMC, LiCoO<sub>2</sub>, etc.

| References                          | CCD <sup>a)</sup><br>(mA/cm <sup>2</sup> ) | Li <sup>0</sup> -Li <sup>0</sup> cell<br>Current/life/temp. | Current×<br>cycle life<br>(mAh/cm <sup>2</sup> ) | Cathode <sup>b)</sup> | Current<br>Density | capacity/cycle<br>life/retention | Loading<br>(mg/cm <sup>2</sup> ) | Loading<br>(mAh/cm <sup>2</sup> )<br>×cycle number |
|-------------------------------------|--------------------------------------------|-------------------------------------------------------------|--------------------------------------------------|-----------------------|--------------------|----------------------------------|----------------------------------|----------------------------------------------------|
| This work                           | 30                                         | 1/2900hr/r.t.                                               | <b>2900</b>                                      | 3 V                   | C/2                | 127/2400/84%                     | 4.5                              | <b>1836</b>                                        |
|                                     |                                            | 2/1000hr/50°C                                               | <b>2000</b>                                      | 3 V                   | 2C                 | 123/4000/88%                     | 2.3                              | <b>1564</b>                                        |
|                                     |                                            | 5/300hr/50°C                                                | <b>1500</b>                                      | 4 V                   | 1C                 | 144/2860/80%                     | 3                                | <b>1844</b>                                        |
|                                     |                                            | 10/150hr/50°C                                               | <b>1500</b>                                      | 4 V                   | C/6                | 130/1000/71%                     | 7.4                              | <b>1600</b>                                        |
| 2024 Nano Lett. <sup>33</sup>       | 0.5                                        | 0.1/1500hr/60°C                                             | <b>150</b>                                       | 3 V                   | 0.2C               | 160/300/99%                      | 1.9                              | <b>97</b>                                          |
|                                     |                                            | 0.5/400hr/60°C                                              | <b>200</b>                                       | 4 V                   | 0.2C               | 150/1/NA                         | 1.9                              | <b>0.4</b>                                         |
| 2024 Angew. Chem. <sup>34</sup>     | 1                                          | 0.1/200hr/NA                                                | <b>20</b>                                        | 3 V                   | 0.5C               | 140/500/70%                      | 1.5                              | <b>128</b>                                         |
|                                     |                                            |                                                             |                                                  | 4 V                   | 0.2C               | 271/15/99%                       | 11                               | <b>45</b>                                          |
| 2023 Nat. Commun. <sup>35</sup>     | NA                                         | 0.1/2500hr/NA                                               | <b>250</b>                                       | 4 V                   | 0.5C               | 164/200/89%                      | 0.8                              | <b>34.4</b>                                        |
| 2023 Angew. Chem. <sup>36</sup>     | NA                                         | 0.1/500hr/60°C                                              | <b>50</b>                                        | 3 V                   | 0.1C               | 150/440/99%                      | 2.5                              | <b>187</b>                                         |
| 2023 Angew. Chem. <sup>37</sup>     | NA                                         | 0.1/1000hr/60°C                                             | <b>100</b>                                       | 4 V                   | 0.1C               | 175/200/70%                      | 3                                | <b>129</b>                                         |
| 2023 Angew. Chem. <sup>38</sup>     | NA                                         | 0.1/1400hr/60°C                                             | <b>140</b>                                       | 3 V                   | 1C                 | 137/350/97%                      | 2                                | <b>119</b>                                         |
|                                     |                                            | 0.2/800hr/60°C                                              | <b>160</b>                                       | 3 V                   | 2C                 | 114/700/80%                      | 2                                | <b>238</b>                                         |
| 2023 Adv. Mater. <sup>39</sup>      | NA                                         | 0.5/700hr/NA                                                | <b>350</b>                                       | 4 V                   | 0.5C               | 170/700/84%                      | 1.8                              | <b>270</b>                                         |
| 2023 Adv. Mater. <sup>40</sup>      | NA                                         | 1/1000hr/NA                                                 | <b>1000</b>                                      | 3 V                   | 2C                 | 128/600/92%                      | 1.2                              | <b>122</b>                                         |
| 2023 ACS Energy Lett. <sup>41</sup> | 0.5                                        | 0.05/2000hr/40°C                                            | <b>100</b>                                       | 4 V                   | 2C                 | 140/300/84%                      | 2.3                              | <b>148</b>                                         |
|                                     |                                            |                                                             |                                                  | 4 V                   | 0.2C               | 160/100/86%                      | 10.6                             | <b>228</b>                                         |

|                                         |     |                 |       |     |       |              |     |      |
|-----------------------------------------|-----|-----------------|-------|-----|-------|--------------|-----|------|
| 2022 Nature <sup>42</sup>               | NA  | 10/1500hr/r.t.  | 15000 | 3 V | 1C    | 93/1000/95%  | 1.5 | 260  |
|                                         |     |                 |       | 4 V | 0.3C  | 110/100/88%  | 10  | 213  |
| 2022 Angew. Chem. <sup>43</sup>         | NA  | 0.5/300hr/45°C  | 150   | 3 V | 0.15C | 159/350/82%  | 3.2 | 190  |
| 2022 Adv. Mater. <sup>44</sup>          | 2.4 | 0.1/4000hr/NA   | 400   | 3 V | 0.4C  | 160/300/96%  | 1.5 | 76.5 |
| 2022 Energy Environ. Sci. <sup>45</sup> | NA  | 0.5/2200hr/NA   | 1100  | 3 V | 0.5C  | 122/1200/99% | 1   | 204  |
|                                         |     | 1/800hr/NA      | 800   | 4 V | 2C    | 160/200/82%  | 4   | 172  |
| 2022 Nano Energy <sup>46</sup>          | NA  | 0.5/800hr/NA    | 400   | 4 V | 1C    | 150/100/89%  | 2   | 32   |
| 2022 Nano Energy <sup>47</sup>          | 2   | 0.1/2200hr/NA   | 220   | 4 V | 2C    | 133/1500/74% | 2   | 645  |
| 2022 Nano Energy <sup>48</sup>          | 2.4 | 0.2/3000hr/NA   | 600   | 3 V | 2C    | 140/200/67%  | 2   | 68   |
|                                         |     |                 |       | 4 V | 0.2C  | 120/150/75%  | 4   | 129  |
| 2022 Nano Energy <sup>49</sup>          | BA  | 0.5/1200hr/NA   | 600   | 4 V | 1C    | 128/300/99%  | 4.6 | 297  |
| 2022 Adv. Energy Mater. <sup>50</sup>   | 0.5 | 0.3/550hr/NA    | 165   | 4 V | 2C    | 130/300/90%  | 2.3 | 148  |
| 2021 Nat. Mater. <sup>51</sup>          | 1   | 0.2/2000hr/r.t. | 400   | NA  | NA    | NA           | NA  | NA   |
| 2020 Adv. Energy Mater. <sup>52</sup>   | NA  | 0.1/800hr/NA    | 80    | 4 V | 0.5C  | 191/200/85%  | 1.5 | 64   |

**Table S3.** Comparison of the Li<sup>0</sup>-Li<sup>0</sup> symmetric cell durability and full cell performance with previous Li<sup>0</sup>-anode batteries on self-healing solid polymer electrolytes.

a) Critical current density; b) 3V-class cathode: LiFePO<sub>4</sub>; 4V-class cathode: NMC, LiCoO<sub>2</sub>, etc.

| References                                  | CCD <sup>a)</sup><br>(mA/cm <sup>2</sup> ) | Li <sup>0</sup> -Li <sup>0</sup> cell<br>Current/life/temp. | Current×<br>cycle life<br>(mAh/cm <sup>2</sup> ) | Cathode <sup>b)</sup> | Current<br>Density | capacity/cycle<br>life/retention | Loading<br>(mg/cm <sup>2</sup> ) | Loading<br>(mAh/cm <sup>2</sup> )<br>×cycle number |
|---------------------------------------------|--------------------------------------------|-------------------------------------------------------------|--------------------------------------------------|-----------------------|--------------------|----------------------------------|----------------------------------|----------------------------------------------------|
| This work                                   | 30                                         | 1/2900hr/r.t.                                               | 2900                                             | 3 V                   | C/2                | 127/2400/84%                     | 4.5                              | 1836                                               |
|                                             |                                            | 2/1000hr/50°C                                               | 2000                                             | 3 V                   | 2C                 | 123/4000/88%                     | 2.3                              | 1564                                               |
|                                             |                                            | 5/300hr/50°C                                                | 1500                                             | 4 V                   | 1C                 | 144/2860/80%                     | 3                                | 1844                                               |
|                                             |                                            | 10/150hr/50°C                                               | 1500                                             | 4V                    | C/6                | 130/1000/71%                     | 7.4                              | 1600                                               |
| 2024 Nat. Commun. <sup>53</sup>             | NA                                         | 0.2/6000hr/60°C                                             | 300                                              | 3 V<br>(SPAN)         | 0.3C               | 602/400/99.7%                    | 2.1                              | 506                                                |
| 2024 Adv. Funct. Mater. <sup>54</sup>       | 0.5                                        | 0.2/2100hr/NA                                               | 105                                              | 3 V                   | 0.3C               | 157/480/80%                      | 6                                | 490                                                |
|                                             |                                            |                                                             |                                                  | 4 V                   | 0.3C               | 167/330/85%                      | 1.5                              | 106                                                |
| 2023 Angew. Chem. <sup>10</sup>             | 0.3                                        | 0.1/1000hr/60°C                                             | 100                                              | 3 V                   | 0.2C               | 149/600/75%                      | 1.2                              | 122                                                |
| 2023 Mater. Horiz. <sup>55</sup>            | NA                                         | 0.05/1600hr/r.t.                                            | 80                                               | 3 V                   | 0.5C               | 134/400/68%                      | 2.8                              | 190                                                |
| 2023 ACS Appl. Energy Mater. <sup>56</sup>  | 1                                          | 1/20hr/25°C                                                 | 20                                               | NA                    | NA                 | NA                               | NA                               | NA                                                 |
| 2023 Materials Today Energy <sup>57</sup>   | NA                                         | 0.05/1400hr/r.t.                                            | 70                                               | 3 V                   | 0.2C               | 150/300/94%                      | 1.4                              | 71                                                 |
| 2023 Adv. Funct. Mater. <sup>58</sup>       | NA                                         | 0.15/1300hr/NA                                              | 195                                              | 3 V                   | 0.5C               | 151/230/98%                      | 3                                | 117                                                |
|                                             |                                            |                                                             |                                                  | 4 V                   | 0.3C               | 186/120/80%                      | 3                                | 77                                                 |
| 2022 Energy Storage Materials <sup>59</sup> | 0.1                                        | 0.05/500hr/60°C                                             | 25                                               | 3 V                   | 0.1C               | 160/100/92%                      | NA                               | NA                                                 |
| 2022 Nano Energy <sup>49</sup>              | NA                                         | 0.5/1200hr/NA                                               | 600                                              | 4 V                   | 1C                 | 128/300/99%                      | 4.6                              | 297                                                |
| 2020 Angew. Chem. <sup>60</sup>             | NA                                         | 0.2/600hr/NA                                                | 120                                              | 4 V                   | 0.1C               | 115/200/86%                      | 1.5                              | 64                                                 |

|                                      |     |                   |              |     |      |             |     |           |
|--------------------------------------|-----|-------------------|--------------|-----|------|-------------|-----|-----------|
| 2020 ACS Energy Lett. <sup>61</sup>  | NA  | 0.1/700hr/NA      | <b>70</b>    | 4 V | 0.1C | 112/120/80% | 1.2 | <b>31</b> |
| 2020 ACS Macro Lett. <sup>62</sup>   | 0.1 | 0.05/200hr/60°C   | <b>10</b>    | 3 V | 0.1C | 145/70/79%  | NA  | <b>NA</b> |
| 2019 J. Am. Chem. Soc. <sup>63</sup> | NA  | 0.015/0.44hr/60°C | <b>0.006</b> | NA  | NA   | NA          | NA  | <b>NA</b> |

## Supplementary References

1. Zhang, W., Koverga, V., Liu, S., Zhou, J., Wang, J., Bai, P., Tan, S., Dandu, N.K., Wang, Z., Chen, F., et al. (2024). Single-phase local-high-concentration solid polymer electrolytes for lithium-metal batteries. *Nature Energy* 9, 386-400. 10.1038/s41560-023-01443-0.
2. Wan, J., Xie, J., Kong, X., Liu, Z., Liu, K., Shi, F., Pei, A., Chen, H., Chen, W., Chen, J., et al. (2019). Ultrathin, flexible, solid polymer composite electrolyte enabled with aligned nanoporous host for lithium batteries. *Nat Nanotechnol* 14, 705-711. 10.1038/s41565-019-0465-3.
3. Zhu, G.R., Zhang, Q., Liu, Q.S., Bai, Q.Y., Quan, Y.Z., Gao, Y., Wu, G., and Wang, Y.Z. (2023). Non-flammable solvent-free liquid polymer electrolyte for lithium metal batteries. *Nat Commun* 14, 4617. 10.1038/s41467-023-40394-8.
4. Han, S., Wen, P., Wang, H., Zhou, Y., Gu, Y., Zhang, L., Shao-Horn, Y., Lin, X., and Chen, M. (2023). Sequencing polymers to enable solid-state lithium batteries. *Nat Mater* 22, 1515-1522. 10.1038/s41563-023-01693-z.
5. Cheng, Y., Cai, Z., Xu, J., Sun, Z., Wu, X., Han, J., Wang, Y.H., and Wang, M.S. (2024). Zwitterionic Cellulose-Based Polymer Electrolyte Enabled by Aqueous Solution Casting for High-Performance Solid-State Batteries. *Angew Chem Int Ed Engl* 63, e202400477. 10.1002/anie.202400477.
6. Li, R., Hua, H., Yang, X., Tian, J., Chen, Q., Huang, R., Li, X., Zhang, P., and Zhao, J. (2024). The deconstruction of a polymeric solvation cage: a critical promotion strategy for PEO-based all-solid polymer electrolytes. *Energy & Environmental Science* 17, 5601-5612. 10.1039/d4ee01188k.
7. Gong, Y., Wang, C., Xin, M., Chen, S., Xu, P., Li, D., Liu, J., Wang, Y., Xie, H., Sun, X., and Liu, Y. (2024). Ultra-thin and high-voltage-stable Bi-phasic solid polymer electrolytes for high-energy-density Li metal batteries. *Nano Energy* 119. 10.1016/j.nanoen.2023.109054.
8. Guo, K., Li, S., Wang, J., Shi, Z., Wang, Y., and Xue, Z. (2024). In Situ Orthogonal Polymerization for Constructing Fast-Charging and Long-Lifespan Li Metal Batteries with Topological Copolymer Electrolytes. *ACS Energy Letters* 9, 843-852. 10.1021/acsenergylett.3c02422.
9. Ding, P., Wu, L., Lin, Z., Lou, C., Tang, M., Guo, X., Guo, H., Wang, Y., and Yu, H. (2023). Molecular Self-Assembled Ether-Based Polyrotaxane Solid Electrolyte for Lithium Metal Batteries. *J Am Chem Soc* 145, 1548-1556. 10.1021/jacs.2c06512.
10. Chen, J., Deng, X., Gao, Y., Zhao, Y., Kong, X., Rong, Q., Xiong, J., Yu, D., and Ding, S. (2023). Multiple Dynamic Bonds-Driven Integrated Cathode/Polymer Electrolyte for Stable All-Solid-State Lithium Metal Batteries. *Angew Chem Int Ed Engl* 62, e202307255. 10.1002/anie.202307255.
11. Li, C., Hu, A., Zhang, X., Ni, H., Fan, J., Yuan, R., Zheng, M., and Dong, Q. (2023). An intrinsic polymer electrolyte via in situ cross-linked for solid lithium-based batteries with high performance. *PNAS Nexus* 2, pgad263. 10.1093/pnasnexus/pgad263.
12. Han, L., Liu, Y., Liao, C., Zhao, Y., Cao, Y., Kan, Y., Zhu, J., and Hu, Y. (2023). Noncombustible 7  $\mu\text{m}$ -thick solid polymer electrolyte for highly energy density solid state lithium batteries. *Nano Energy* 112. 10.1016/j.nanoen.2023.108448.
13. Saleem, A., Iqbal, R., Majeed, M.K., Hussain, A., Akbar, A.R., Hussain, Z., Jabar, B., Rauf, S., and Shaw, L.L. (2024). Boosting lithium-ion conductivity of polymer electrolyte by selective introduction of covalent organic frameworks for safe lithium metal batteries. *Nano Energy* 128. 10.1016/j.nanoen.2024.109848.
14. Zheng, J., Liu, S., Huang, H., Zhou, H., Li, H., Li, L., Jiang, G., Zhang, H., Geng, X., An, B., and Sun, C. (2023). Heterocyclic polymer supported cathode/Li interface layers to lower the operational temperature of PEO-based Li-batteries. *Nano Energy* 118. 10.1016/j.nanoen.2023.108975.
15. Chen, Z., Jia, H., Yan, S., and Gohy, J.-F. (2023). Polymer-coated silica dual functional fillers to improve the performance of poly(ethylene oxide)-based solid electrolytes. *Nano Energy* 114. 10.1016/j.nanoen.2023.108637.
16. Kim, E., Jamal, H., Jeon, I., Khan, F., Chun, S.E., and Kim, J.H. (2023). Functionality of 1-Butyl-2,3-Dimethylimidazolium Bromide (BMI-Br) as a Solid Plasticizer in PEO-Based Polymer Electrolyte for Highly Reliable Lithium Metal Batteries. *Advanced Energy Materials* 13. 10.1002/aenm.202301674.
17. Cheng, Q., Jin, T., Miao, Y., Liu, Z., Borovilas, J., Zhang, H., Liu, S., Kim, S.-Y., Zhang, R., Wang, H., et al. (2022). Stabilizing lithium plating in polymer electrolytes by concentration-polarization-induced phase transformation. *Joule* 6, 2372-2389. 10.1016/j.joule.2022.08.001.
18. Arrese-Igor, M., Martínez-Ibañez, M., Pavlenko, E., Forsyth, M., Zhu, H., Armand, M., Aguesse, F., and López-Aranguren, P. (2022). Toward High-Voltage Solid-State Li-Metal Batteries with Double-Layer Polymer Electrolytes. *ACS Energy Letters* 7, 1473-1480. 10.1021/acsenergylett.2c00488.
19. Yang, L., Nie, Y., Liu, Y., Zheng, Y., Luo, D., Yang, N., Ma, Q., Xu, M., Ma, X., Yu, A., et al. (2022). The plasticizer-free composite block copolymer electrolytes for ultralong lifespan all-solid-state lithium-metal batteries. *Nano Energy* 100. 10.1016/j.nanoen.2022.107499.
20. Ma, Y., Wan, J., Yang, Y., Ye, Y., Xiao, X., Boyle, D.T., Burke, W., Huang, Z., Chen, H., Cui, Y., et al. (2022). Scalable, Ultrathin, and High-Temperature-Resistant Solid Polymer Electrolytes for Energy-Dense Lithium Metal Batteries. *Advanced Energy Materials* 12. 10.1002/aenm.202103720.
21. Wang, H., Song, J., Zhang, K., Fang, Q., Zuo, Y., Yang, T., Yang, Y., Gao, C., Wang, X., Pang, Q., and Xia, D. (2022).

- A strongly complexed solid polymer electrolyte enables a stable solid state high-voltage lithium metal battery. *Energy & Environmental Science* *15*, 5149-5158. 10.1039/d2ee02904a.
22. Su, Y., Rong, X., Gao, A., Liu, Y., Li, J., Mao, M., Qi, X., Chai, G., Zhang, Q., Suo, L., et al. (2022). Rational design of a topological polymeric solid electrolyte for high-performance all-solid-state alkali metal batteries. *Nat Commun* *13*, 4181. 10.1038/s41467-022-31792-5.
  23. Hu, J., Lai, C., Chen, K., Wu, Q., Gu, Y., Wu, C., and Li, C. (2022). Dual fluorination of polymer electrolyte and conversion-type cathode for high-capacity all-solid-state lithium metal batteries. *Nat Commun* *13*, 7914. 10.1038/s41467-022-35636-0.
  24. Qiao, L., Rodriguez Pena, S., Martinez-Ibanez, M., Santiago, A., Aldalur, I., Lobato, E., Sanchez-Diez, E., Zhang, Y., Manzano, H., Zhu, H., et al. (2022). Anion pi-pi Stacking for Improved Lithium Transport in Polymer Electrolytes. *J Am Chem Soc* *144*, 9806-9816. 10.1021/jacs.2c02260.
  25. Xu, B., Li, X., Yang, C., Li, Y., Grundish, N.S., Chien, P.H., Dong, K., Manke, I., Fang, R., Wu, N., et al. (2021). Interfacial Chemistry Enables Stable Cycling of All-Solid-State Li Metal Batteries at High Current Densities. *J Am Chem Soc* *143*, 6542-6550. 10.1021/jacs.1c00752.
  26. He, F., Tang, W., Zhang, X., Deng, L., and Luo, J. (2021). High Energy Density Solid State Lithium Metal Batteries Enabled by Sub-5 microm Solid Polymer Electrolytes. *Adv Mater* *33*, e2105329. 10.1002/adma.202105329.
  27. Han, L., Liao, C., Mu, X., Wu, N., Xu, Z., Wang, J., Song, L., Kan, Y., and Hu, Y. (2021). Flame-Retardant ADP/PEO Solid Polymer Electrolyte for Dendrite-Free and Long-Life Lithium Battery by Generating Al, P-rich SEI Layer. *Nano Lett* *21*, 4447-4453. 10.1021/acs.nanolett.1c01137.
  28. Wang, H., Wang, Q., Cao, X., He, Y., Wu, K., Yang, J., Zhou, H., Liu, W., and Sun, X. (2020). Thiol-Branched Solid Polymer Electrolyte Featuring High Strength, Toughness, and Lithium Ionic Conductivity for Lithium-Metal Batteries. *Adv Mater* *32*, e2001259. 10.1002/adma.202001259.
  29. Yang, X., Jiang, M., Gao, X., Bao, D., Sun, Q., Holmes, N., Duan, H., Mukherjee, S., Adair, K., Zhao, C., et al. (2020). Determining the limiting factor of the electrochemical stability window for PEO-based solid polymer electrolytes: main chain or terminal -OH group? *Energy & Environmental Science* *13*, 1318-1325. 10.1039/d0ee00342e.
  30. Cui, Y., Wan, J., Ye, Y., Liu, K., Chou, L.Y., and Cui, Y. (2020). A Fireproof, Lightweight, Polymer-Polymer Solid-State Electrolyte for Safe Lithium Batteries. *Nano Lett* *20*, 1686-1692. 10.1021/acs.nanolett.9b04815.
  31. He, Y., Chen, S., Nie, L., Sun, Z., Wu, X., and Liu, W. (2020). Stereolithography Three-Dimensional Printing Solid Polymer Electrolytes for All-Solid-State Lithium Metal Batteries. *Nano Lett* *20*, 7136-7143. 10.1021/acs.nanolett.0c02457.
  32. Li, X., Zheng, Y., Duan, Y., Shang, M., Niu, J., and Li, C.Y. (2020). Designing Comb-Chain Crosslinker-Based Solid Polymer Electrolytes for Additive-Free All-Solid-State Lithium Metal Batteries. *Nano Lett* *20*, 6914-6921. 10.1021/acs.nanolett.0c03033.
  33. Ye, F., Wang, Z., Li, M., Zhang, J., Wang, D., Liu, M., Liu, A., Lin, H., Kim, H.T., and Wang, J. (2024). High-Entropy Polymer Electrolytes Derived from Multivalent Polymeric Ligands for Solid-State Lithium Metal Batteries with Accelerated Li(+) Transport. *Nano Lett* *24*, 6850-6857. 10.1021/acs.nanolett.4c00154.
  34. Zhao, Y., Li, L., Zhou, D., Ma, Y., Zhang, Y., Yang, H., Fan, S., Tong, H., Li, S., and Qu, W. (2024). Opening and Constructing Stable Lithium-ion Channels within Polymer Electrolytes. *Angew Chem Int Ed Engl* *63*, e202404728. 10.1002/anie.202404728.
  35. Tang, L., Chen, B., Zhang, Z., Ma, C., Chen, J., Huang, Y., Zhang, F., Dong, Q., Xue, G., Chen, D., et al. (2023). Polyfluorinated crosslinker-based solid polymer electrolytes for long-cycling 4.5 V lithium metal batteries. *Nat Commun* *14*, 2301. 10.1038/s41467-023-37997-6.
  36. Zhou, H.Y., Ou, Y., Yan, S.S., Xie, J., Zhou, P., Wan, L., Xu, Z.A., Liu, F.X., Zhang, W.L., Xia, Y.C., and Liu, K. (2023). Supramolecular Polymer Ion Conductor with Weakened Li Ion Solvation Enables Room Temperature All-Solid-State Lithium Metal Batteries. *Angew Chem Int Ed Engl* *62*, e202306948. 10.1002/anie.202306948.
  37. Xie, X., Wang, Z., He, S., Chen, K., Huang, Q., Zhang, P., Hao, S.M., Wang, J., and Zhou, W. (2023). Influencing Factors on Li-ion Conductivity and Interfacial Stability of Solid Polymer Electrolytes, Exemplified by Polycarbonates, Polyoxalates and Polymalonates. *Angew Chem Int Ed Engl* *62*, e202218229. 10.1002/anie.202218229.
  38. Zhao, Z., Zhou, X., Zhang, B., Huang, F., Wang, Y., Ma, Z., and Liu, J. (2023). Regulating Steric Hindrance of Porous Organic Polymers in Composite Solid-State Electrolytes to Induce the Formation of LiF-Rich SEI in Li-Ion Batteries. *Angew Chem Int Ed Engl* *62*, e202308738. 10.1002/anie.202308738.
  39. Qi, S., Li, M., Gao, Y., Zhang, W., Liu, S., Zhao, J., and Du, L. (2023). Enabling Scalable Polymer Electrolyte with Dual-Reinforced Stable Interface for 4.5 V Lithium-Metal Batteries. *Adv Mater* *35*, e2304951. 10.1002/adma.202304951.
  40. Mu, K., Wang, D., Dong, W., Liu, Q., Song, Z., Xu, W., Yao, P., Chen, Y., Yang, B., Li, C., et al. (2023). Hybrid Crosslinked Solid Polymer Electrolyte via In-Situ Solidification Enables High-Performance Solid-State Lithium Metal Batteries. *Adv Mater* *35*, e2304686. 10.1002/adma.202304686.
  41. Dong, X., Mayer, A., Liu, X., Passerini, S., and Bresser, D. (2023). Single-Ion Conducting Multi-block Copolymer Electrolyte for Lithium-Metal Batteries with High Mass Loading NCM811 Cathodes. *ACS Energy Letters* *8*, 1114-1121. 10.1021/acsenergylett.2c02806.

42. Lee, M.J., Han, J., Lee, K., Lee, Y.J., Kim, B.G., Jung, K.N., Kim, B.J., and Lee, S.W. (2022). Elastomeric electrolytes for high-energy solid-state lithium batteries. *Nature* *601*, 217-222. 10.1038/s41586-021-04209-4.
43. Li, W., Gao, J., Tian, H., Li, X., He, S., Li, J., Wang, W., Li, L., Li, H., Qiu, J., and Zhou, W. (2022). SnF(2) -Catalyzed Formation of Polymerized Dioxolane as Solid Electrolyte and its Thermal Decomposition Behavior. *Angew Chem Int Ed Engl* *61*, e202114805. 10.1002/anie.202114805.
44. Su, Y., Rong, X., Li, H., Huang, X., Chen, L., Liu, B., and Hu, Y.S. (2023). High-Entropy Microdomain Interlocking Polymer Electrolytes for Advanced All-Solid-State Battery Chemistries. *Adv Mater* *35*, e2209402. 10.1002/adma.202209402.
45. Xiang, J., Zhang, Y., Zhang, B., Yuan, L., Liu, X., Cheng, Z., Yang, Y., Zhang, X., Li, Z., Shen, Y., et al. (2021). A flame-retardant polymer electrolyte for high performance lithium metal batteries with an expanded operation temperature. *Energy & Environmental Science* *14*, 3510-3521. 10.1039/d1ee00049g.
46. Lin, Z., Guo, X., Zhang, R., Tang, M., Ding, P., Zhang, Z., Wu, L., Wang, Y., Zhao, S., Zhang, Q., and Yu, H. (2022). Molecular structure adjustment enhanced anti-oxidation ability of polymer electrolyte for solid-state lithium metal battery. *Nano Energy* *98*. 10.1016/j.nanoen.2022.107330.
47. Chen, L., Gu, T., Ma, J., Yang, K., Shi, P., Biao, J., Mi, J., Liu, M., Lv, W., and He, Y.-B. (2022). In situ construction of Li3N-enriched interface enabling ultra-stable solid-state LiNi0.8Co0.1Mn0.1O2/lithium metal batteries. *Nano Energy* *100*. 10.1016/j.nanoen.2022.107470.
48. Li, J., Zhang, H., Cui, Y., Da, H., Cai, Y., and Zhang, S. (2022). Constructing interfacial gradient layers and enhancing lithium salt dissolution kinetics for high-rate solid-state batteries. *Nano Energy* *102*. 10.1016/j.nanoen.2022.107716.
49. Chang, C., Yao, Y., Li, R., Guo, Z.H., Li, L., Pan, C., Hu, W., and Pu, X. (2022). Self-healing single-ion-conductive artificial polymeric solid electrolyte interphases for stable lithium metal anodes. *Nano Energy* *93*. 10.1016/j.nanoen.2021.106871.
50. Liang, H.P., Zarrabeitia, M., Chen, Z., Jovanovic, S., Merz, S., Granwehr, J., Passerini, S., and Bresser, D. (2022). Polysiloxane-Based Single-Ion Conducting Polymer Blend Electrolyte Comprising Small-Molecule Organic Carbonates for High-Energy and High-Power Lithium-Metal Batteries. *Advanced Energy Materials* *12*. 10.1002/aenm.202200013.
51. Wang, Y., Zanelotti, C.J., Wang, X., Kerr, R., Jin, L., Kan, W.H., Dingemans, T.J., Forsyth, M., and Madsen, L.A. (2021). Solid-state rigid-rod polymer composite electrolytes with nanocrystalline lithium ion pathways. *Nat Mater* *20*, 1255-1263. 10.1038/s41563-021-00995-4.
52. Yu, X., Wang, L., Ma, J., Sun, X., Zhou, X., and Cui, G. (2020). Selectively Wetted Rigid-Flexible Coupling Polymer Electrolyte Enabling Superior Stability and Compatibility of High-Voltage Lithium Metal Batteries. *Advanced Energy Materials* *10*. 10.1002/aenm.201903939.
53. Pei, F., Wu, L., Zhang, Y., Liao, Y., Kang, Q., Han, Y., Zhang, H., Shen, Y., Xu, H., Li, Z., and Huang, Y. (2024). Interfacial self-healing polymer electrolytes for long-cycle solid-state lithium-sulfur batteries. *Nat Commun* *15*, 351. 10.1038/s41467-023-43467-w.
54. Wu, L., Pei, F., Cheng, D., Zhang, Y., Cheng, H., Huang, K., Yuan, L., Li, Z., Xu, H., and Huang, Y. (2023). Flame-Retardant Polyurethane-Based Solid-State Polymer Electrolytes Enabled by Covalent Bonding for Lithium Metal Batteries. *Advanced Functional Materials* *34*. 10.1002/adfm.202310084.
55. Lin, X., Xu, S., Tong, Y., Liu, X., Liu, Z., Li, P., Liu, R., Feng, X., Shi, L., and Ma, Y. (2023). A self-healing polymerized-ionic-liquid-based polymer electrolyte enables a long lifespan and dendrite-free solid-state Li metal batteries at room temperature. *Mater Horiz* *10*, 859-868. 10.1039/d2mh01289h.
56. Daniels, E.L., Runge, J.R., Oshinowo, M., Leese, H.S., and Burchard, A. (2023). Cross-Linking of Sugar-Derived Polyethers and Boronic Acids for Renewable, Self-Healing, and Single-Ion Conducting Organogel Polymer Electrolytes. *ACS Appl Energy Mater* *6*, 2924-2935. 10.1021/acsaem.2c03937.
57. Ling, C., Naren, T., Liu, X., Yang, J., Xiao, P., Wei, W., Ji, X., Kuang, G.-C., and Chen, L. (2023). In-situ polymerization induced phase separation to develop high-performance self-healable polymeric electrolytes for lithium metal battery. *Materials Today Energy* *36*. 10.1016/j.mtener.2023.101372.
58. Zhao, L., Du, Y., Zhao, E., Li, C., Sun, Z., Li, Y., and Li, H. (2023). Dynamic Supramolecular Polymer Electrolyte to Boost Ion Transport Kinetics and Interfacial Stability for Solid-State Batteries. *Advanced Functional Materials* *33*. 10.1002/adfm.202214881.
59. Huang, Y., Shi, Z., Wang, H., Wang, J., and Xue, Z. (2022). Shape-memory and self-healing polyurethane-based solid polymer electrolytes constructed from polycaprolactone segment and disulfide metathesis. *Energy Storage Materials* *51*, 1-10. 10.1016/j.ensm.2022.06.021.
60. Jaumaux, P., Liu, Q., Zhou, D., Xu, X., Wang, T., Wang, Y., Kang, F., Li, B., and Wang, G. (2020). Deep-Eutectic-Solvent-Based Self-Healing Polymer Electrolyte for Safe and Long-Life Lithium-Metal Batteries. *Angew Chem Int Ed Engl* *59*, 9134-9142. 10.1002/anie.202001793.
61. Liu, Q., Zhou, D., Shanmukaraj, D., Li, P., Kang, F., Li, B., Armand, M., and Wang, G. (2020). Self-Healing Janus Interfaces for High-Performance LAGP-Based Lithium Metal Batteries. *ACS Energy Letters* *5*, 1456-1464. 10.1021/acsenrgylett.0c00542.
62. Zhou, B., Yang, M., Zuo, C., Chen, G., He, D., Zhou, X., Liu, C., Xie, X., and Xue, Z. (2020). Flexible, Self-Healing, and Fire-Resistant Polymer Electrolytes Fabricated via Photopolymerization for All-Solid-State Lithium Metal Batteries.

- ACS Macro Lett *9*, 525-532. 10.1021/acsmacrolett.9b01024.
63. Jing, B.B., and Evans, C.M. (2019). Catalyst-Free Dynamic Networks for Recyclable, Self-Healing Solid Polymer Electrolytes. *J Am Chem Soc* *141*, 18932-18937. 10.1021/jacs.9b09811.