

# **Superionic composite electrolytes with continuously perpendicular-aligned pathways for pressure-less all-solid-state lithium batteries**

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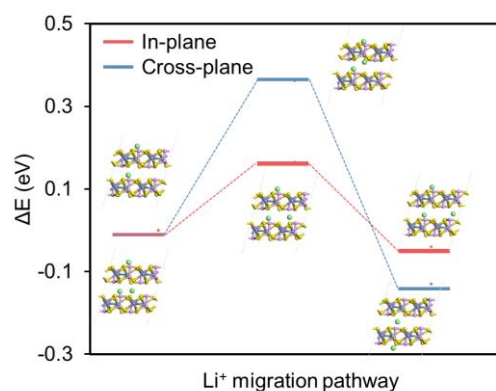
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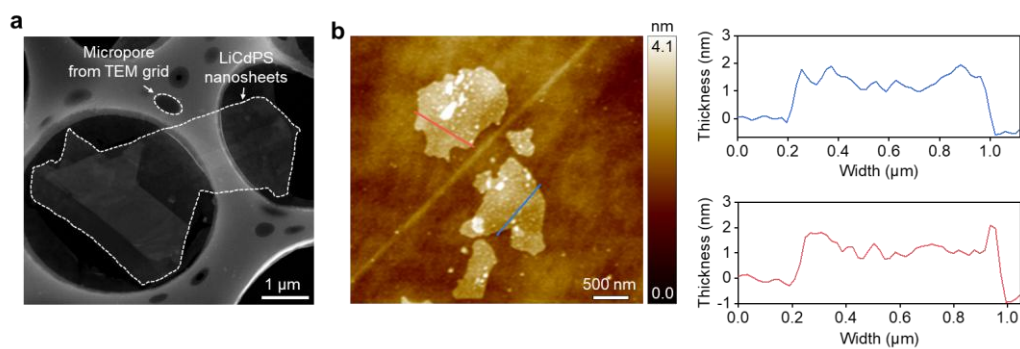
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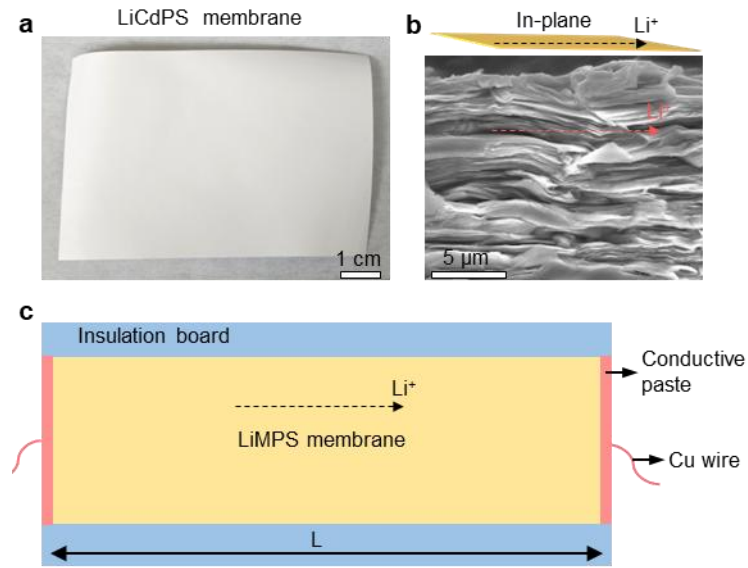
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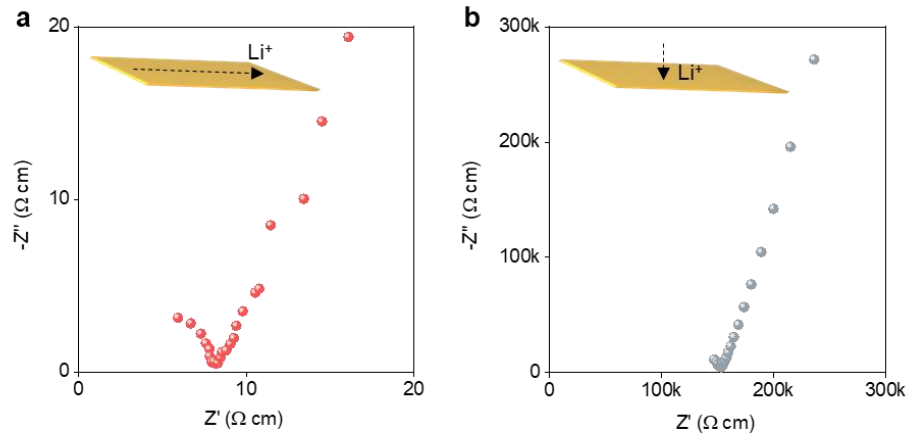
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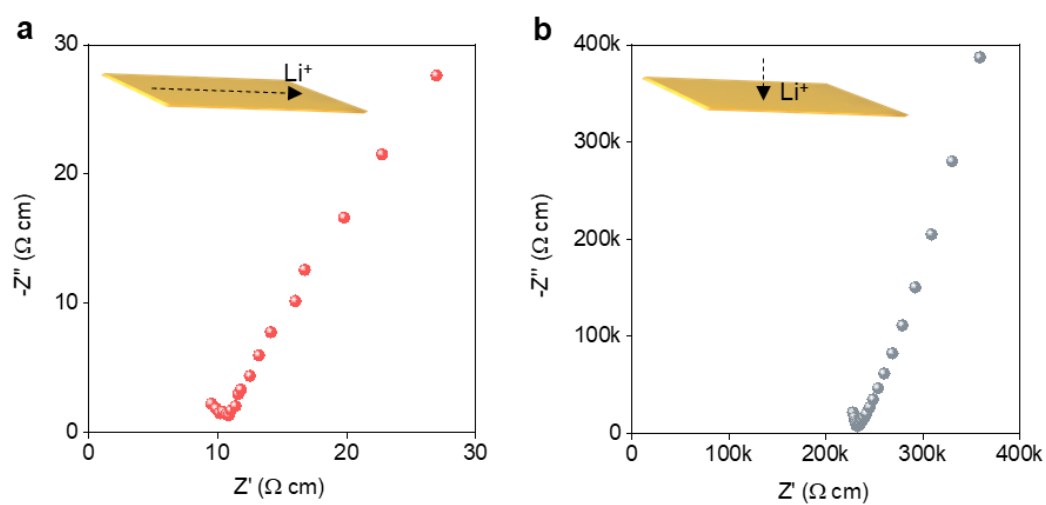
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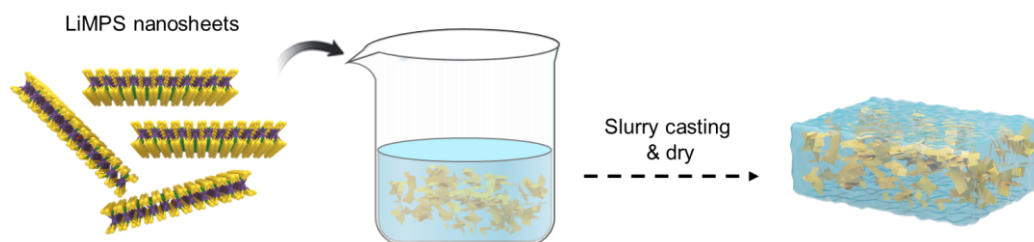
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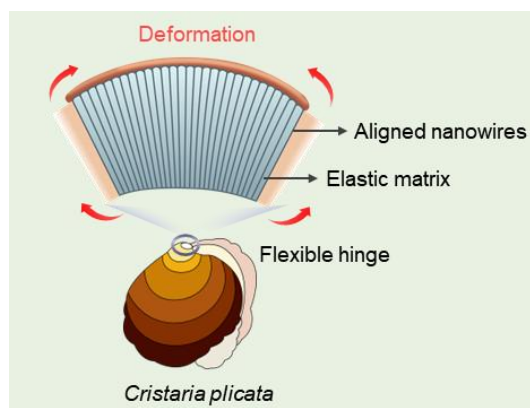
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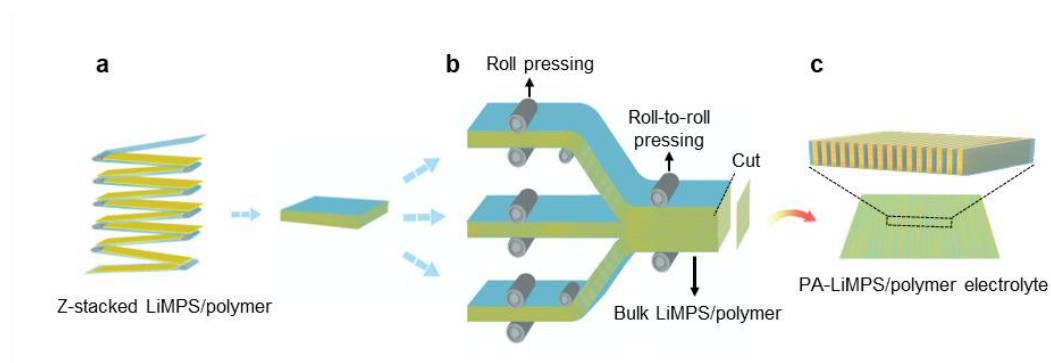
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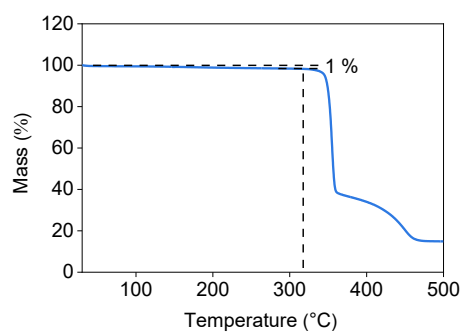
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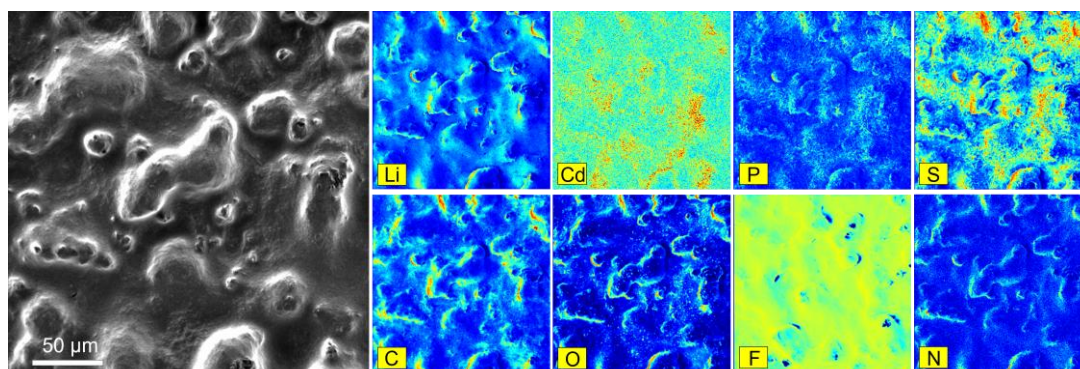
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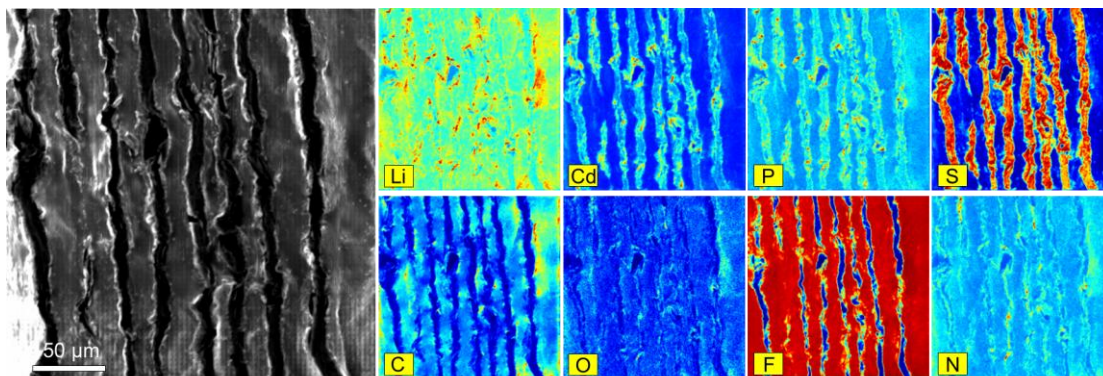
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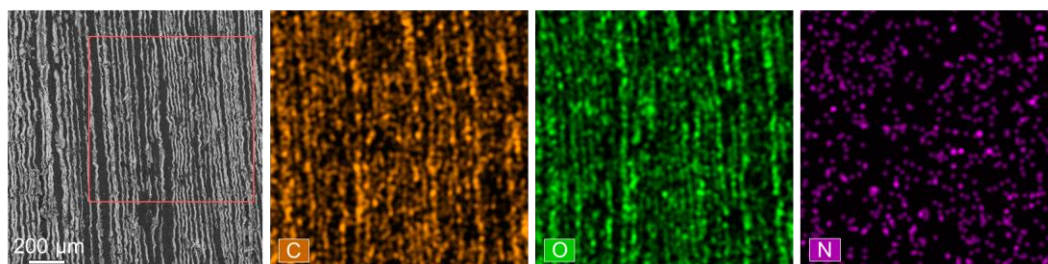
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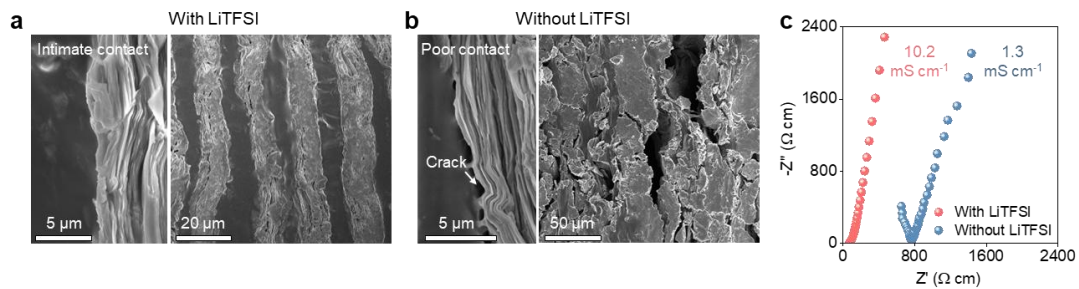
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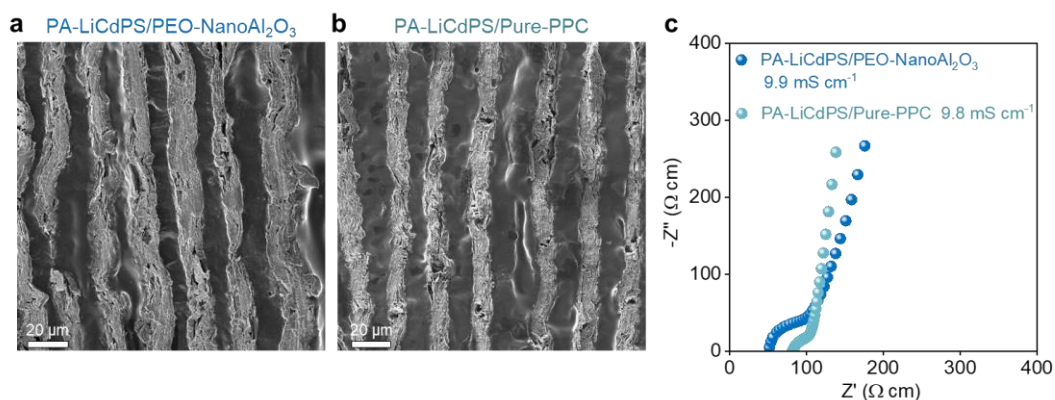
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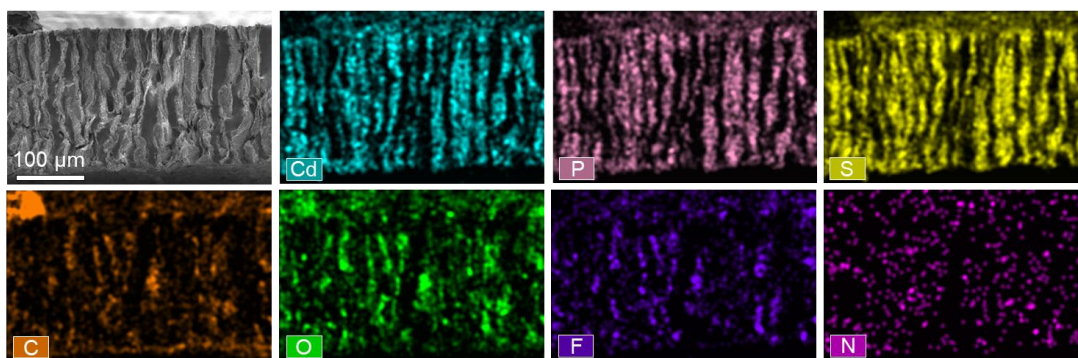
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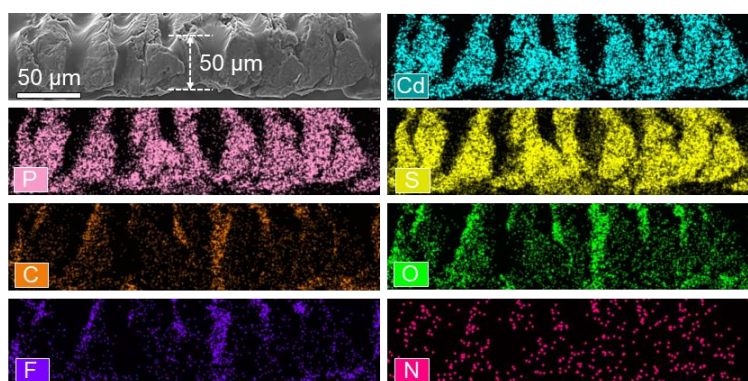
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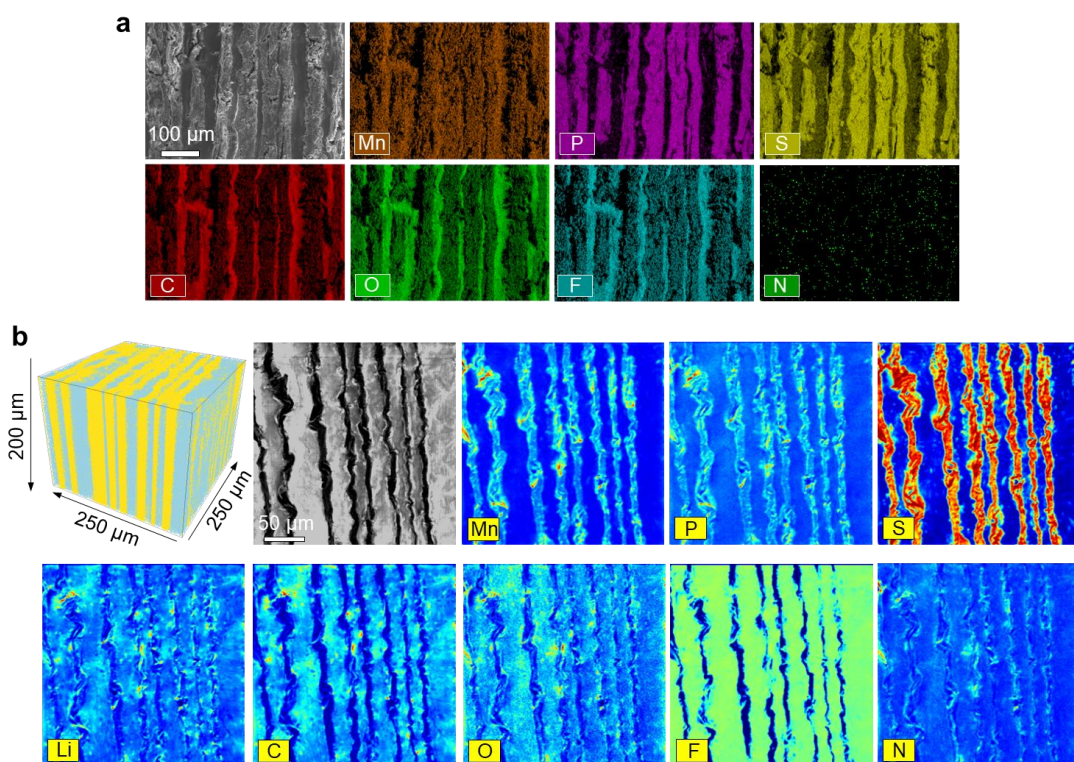
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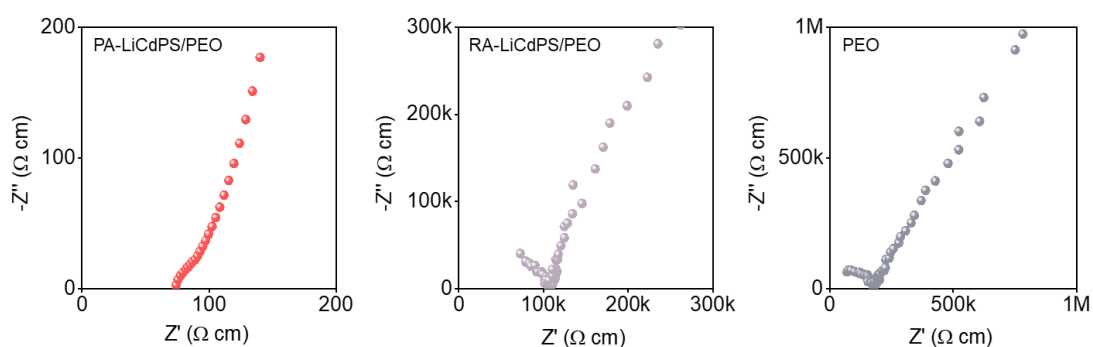
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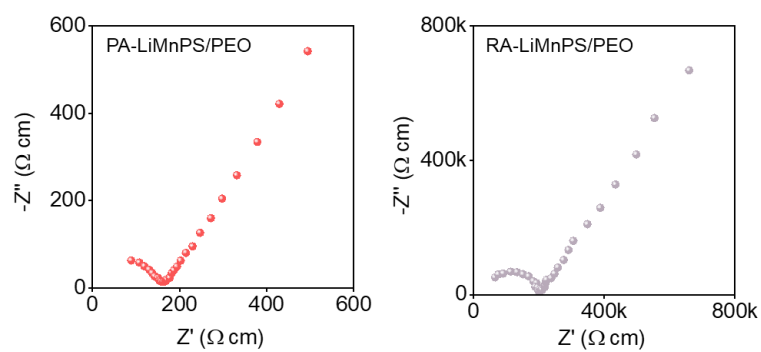
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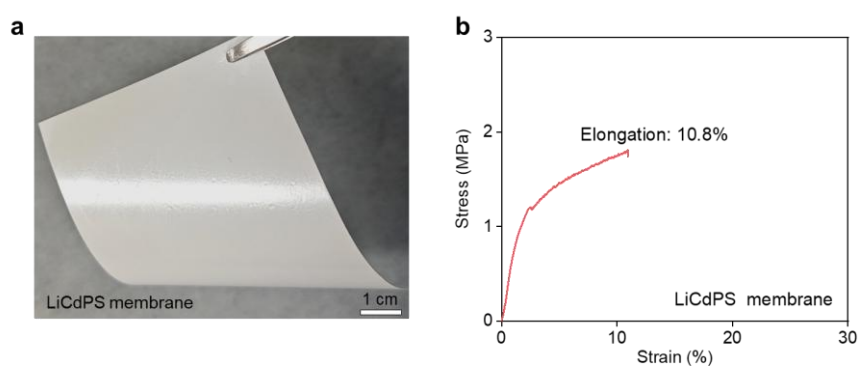
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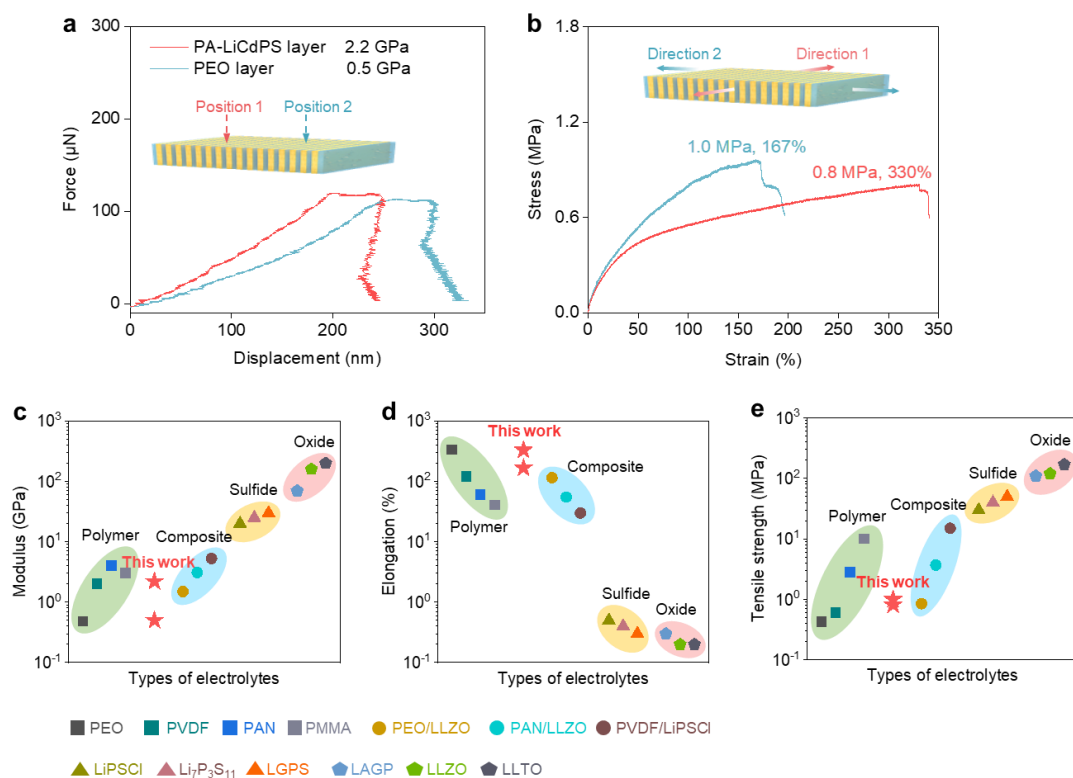
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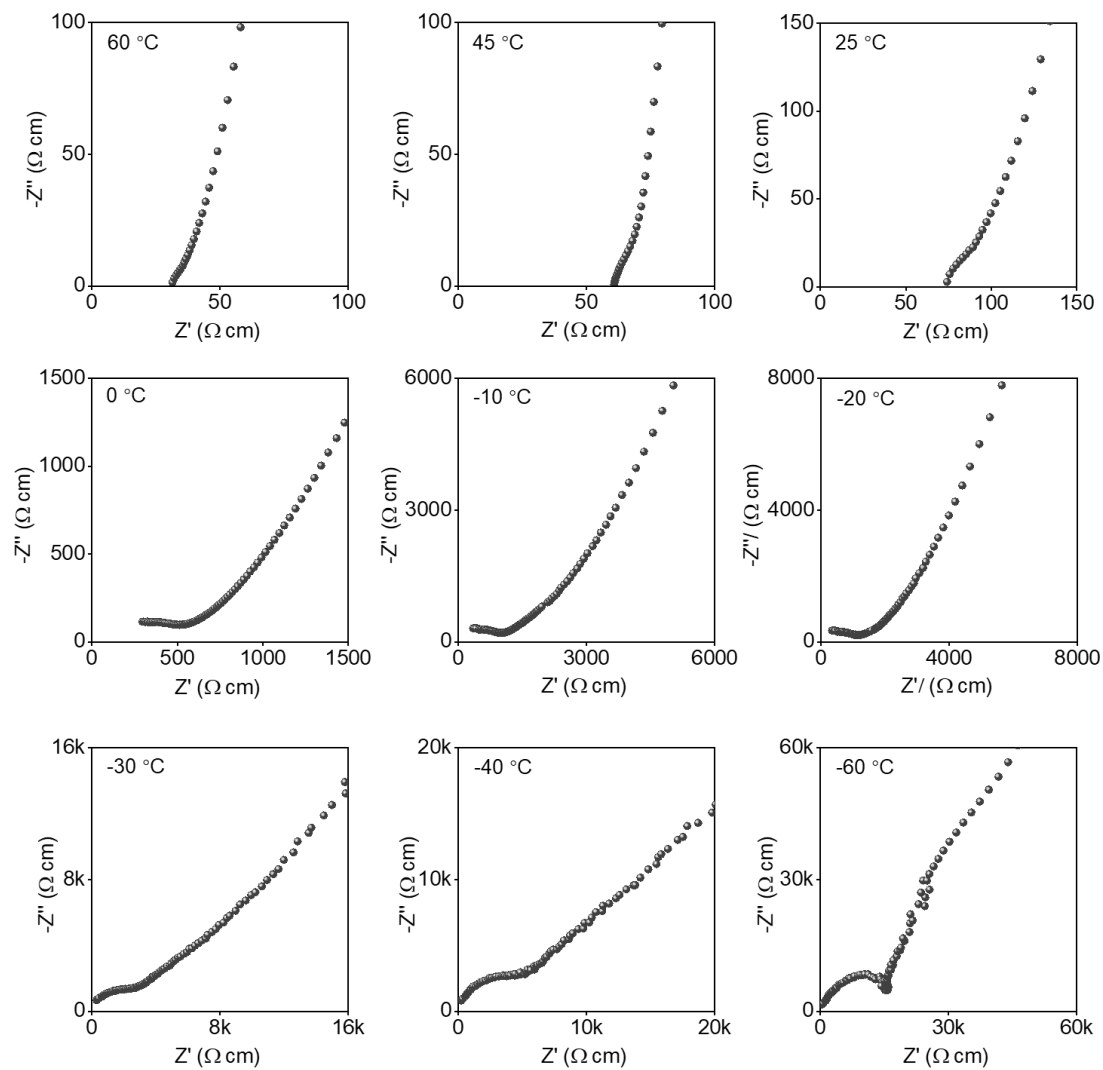
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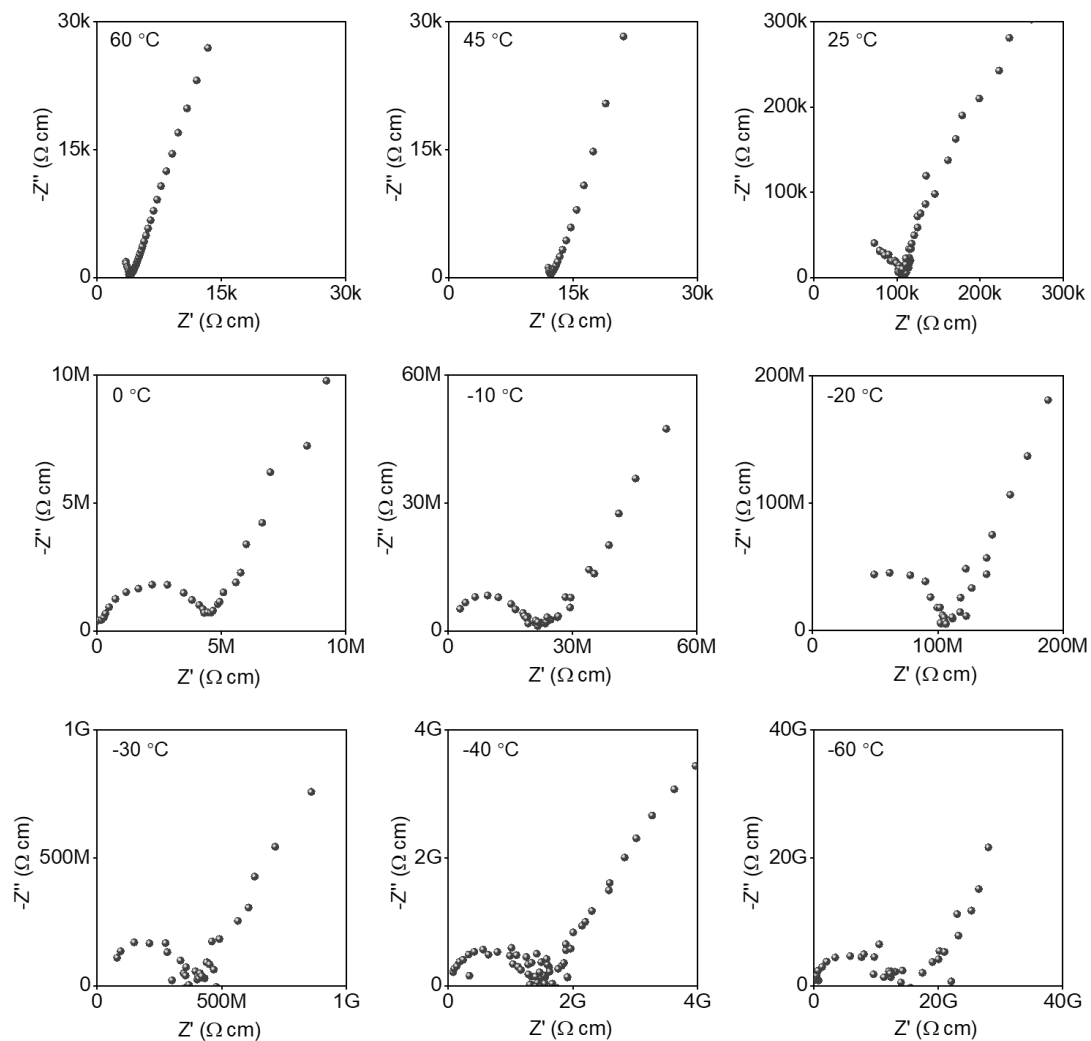
**Supplementary Fig. 20** Optical image (a) and tensile stress-strain curve (b) of the LiCdPS membrane, without polymer and LiTFSI salt.



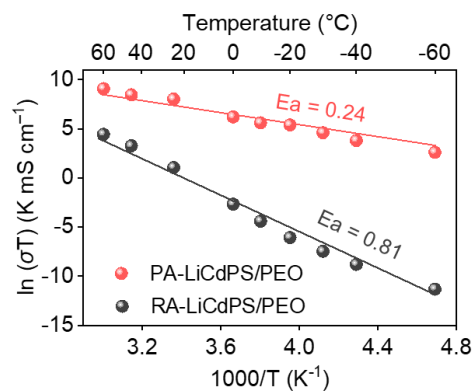
**Supplementary Fig. 21** (a) Load-displacement curves in a nanoindentation test and (b) tensile stress-strain curves for the PA-LiCdPS/PEO electrolyte with LiTFSI salt. (c-e) Comparison of the modulus (c), elongation (d), and tensile strength (e) of PA-LiCdPS/PEO (with LiTFSI salt) with representative organic polymer electrolytes<sup>1-5</sup>, composite electrolytes<sup>6-10</sup>, inorganic sulfide<sup>11-15</sup> and oxide<sup>16-18</sup> electrolytes.



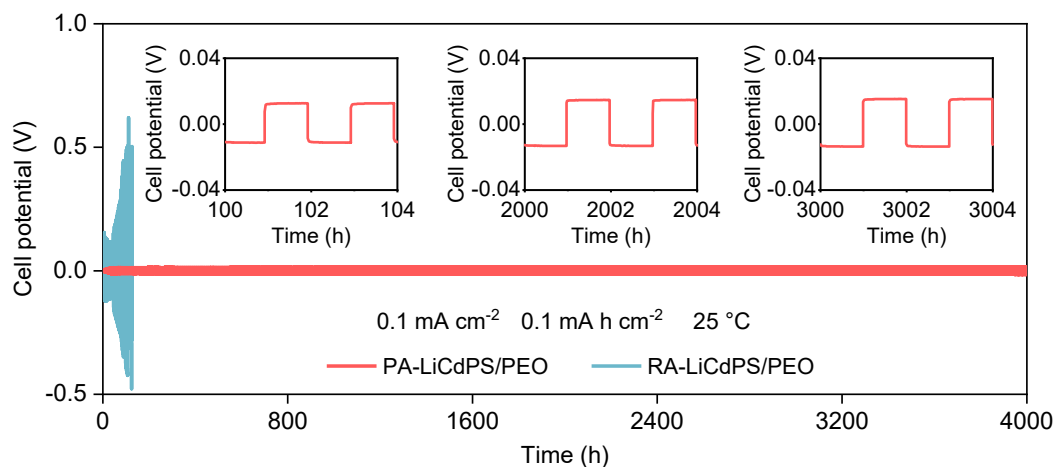
**Supplementary Fig. 22** Nyquist plots of the PA-LiCdPS/PEO electrolyte with LiTFSI salt at temperatures ranging from -60 °C to 60 °C.



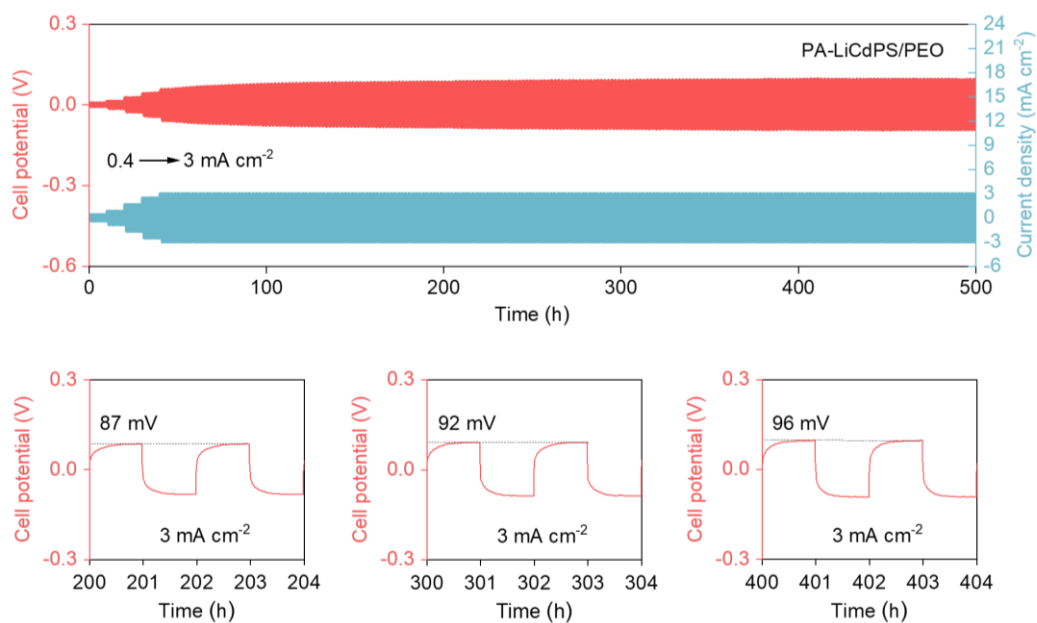
**Supplementary Fig. 23** Nyquist plots of the RA-LiCdPS/PEO electrolyte with LiTFSI salt at temperatures ranging from -60 °C to 60 °C.



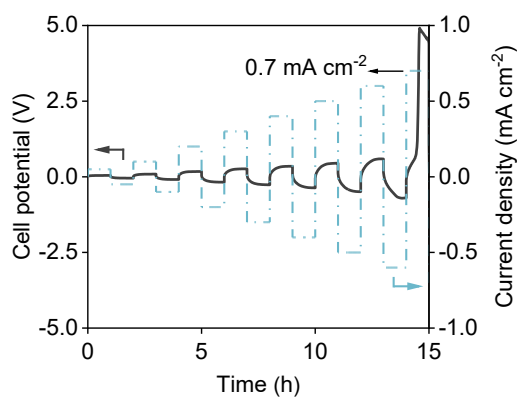
**Supplementary Fig. 24** Arrhenius plots for the ionic conductivities of PA-LiCdPS/PEO and RA-LiCdPS/PEO electrolytes with LiTFSI salt.



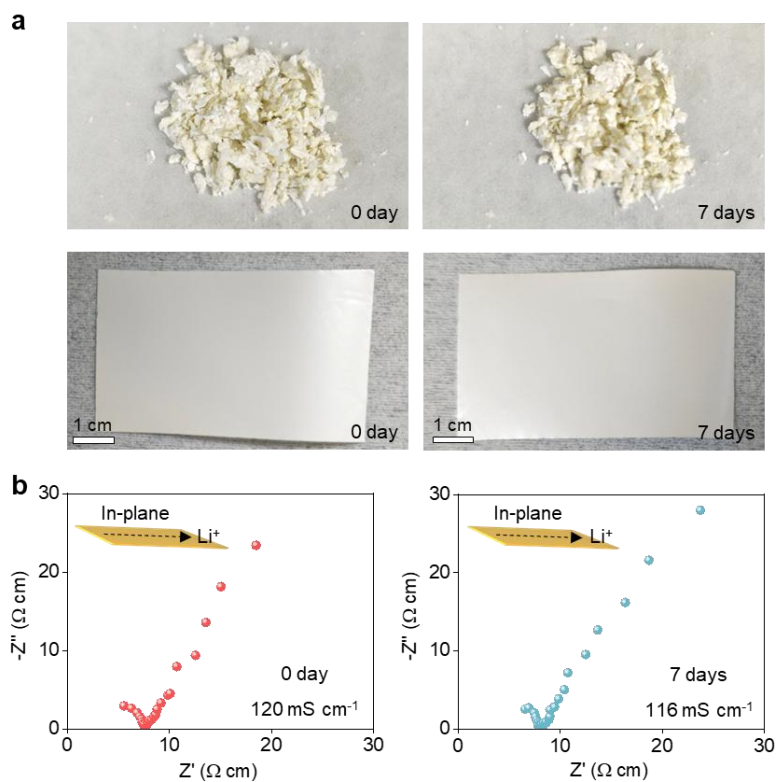
**Supplementary Fig. 25** Long cycling performance of symmetric Li||Li coin cells at  $0.1 \text{ mA cm}^{-2}$ ,  $0.1 \text{ mA h cm}^{-2}$ , and  $25^\circ\text{C}$ , with PA-LiCdPS/PEO and RA-LiCdPS/PEO electrolytes with LiTFSI salt.



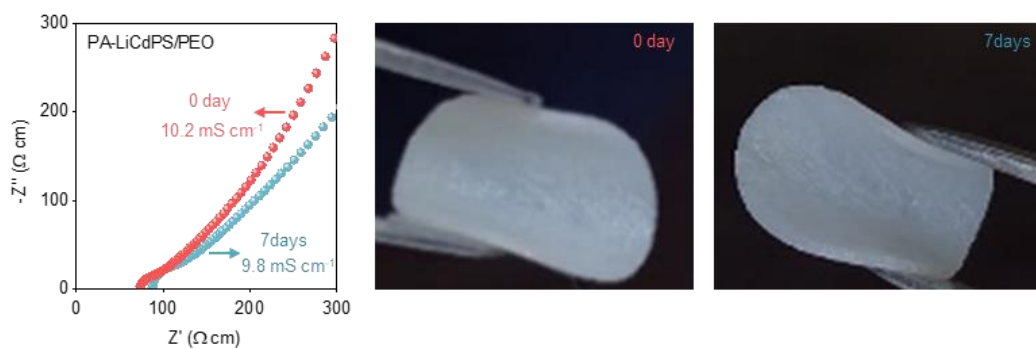
**Supplementary Fig. 26** Cycling performance of Li||Li coin cells with the PA-LiCdPS/PEO electrolyte with LiTFSI salt at 25 °C, with the current density gradually increased from 0.4 mA cm<sup>-2</sup> to 3 mA cm<sup>-2</sup>, followed by cycling stability tests at 3 mA cm<sup>-2</sup>.



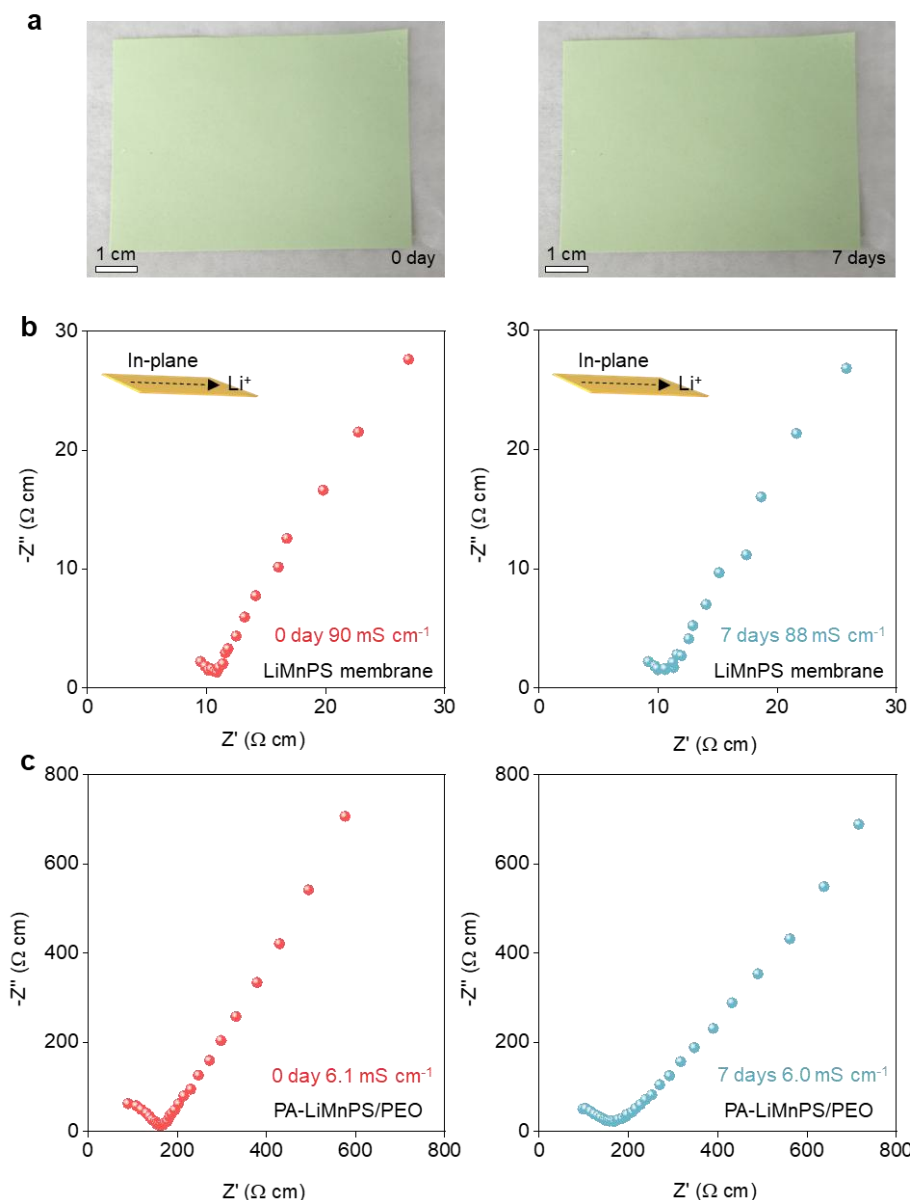
**Supplementary Fig. 27** Critical current density test of RA-LiCdPS/PEO electrolyte with LiTFSI salt in symmetric Li||Li coin cells at 25 °C.



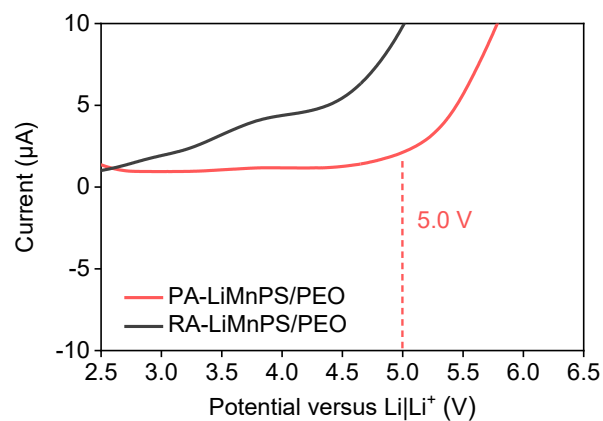
**Supplementary Fig. 28** (a) Photographic picture of LiCdPS powders and membranes before and after exposure to air with a relative humidity of 30-40%. (b) Nyquist plots measured for the in-plane ionic conductivity of LiCdPS, using the LiCdPS powders before and after exposure to air with a relative humidity of 30-40%. These measurements were conducted at 25 °C.



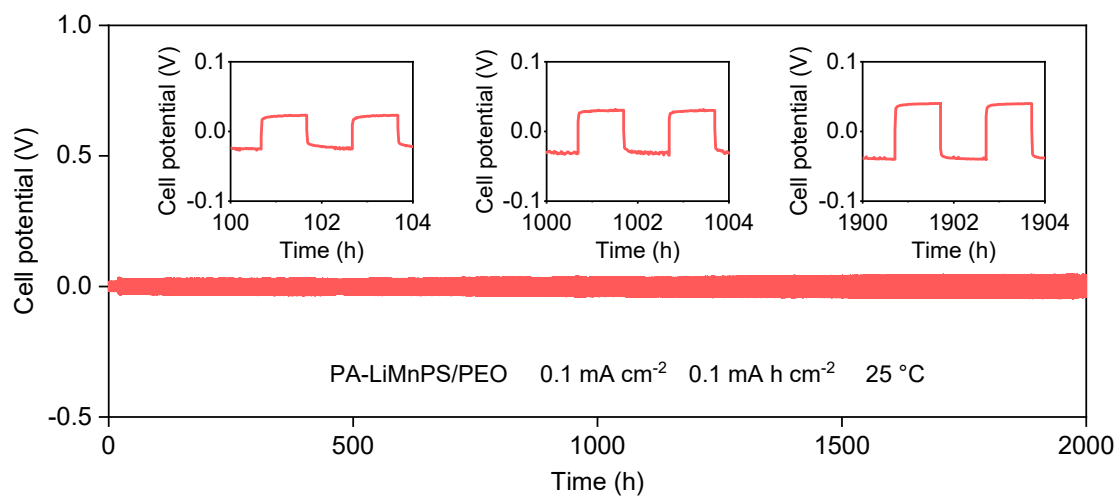
**Supplementary Fig. 29** Nyquist plots (with the calculated ionic conductivities) and optical images of the PA-LiCdPS/PEO electrolyte membranes with LiTFSI salt before and after exposure to air with a relative humidity of 30-40%. These measurements were conducted at 25 °C.



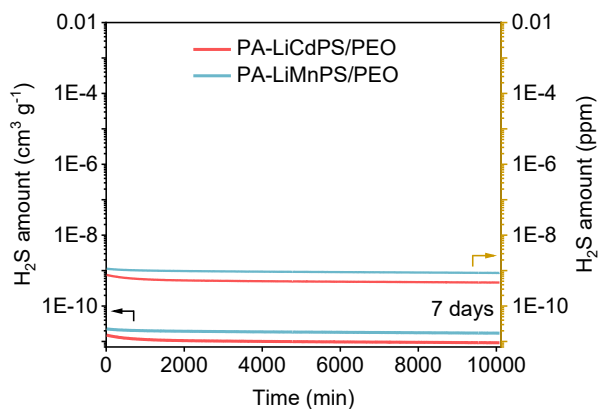
**Supplementary Fig. 30** (a) Photo images of LiMnPS membranes before and after exposure to air with a relative humidity of 30-40%. (b) Nyquist plots with the calculated in-plane ionic conductivity values of LiMnPS membranes before and after exposure to air with a relative humidity of 30-40%. (c) Nyquist plots with calculated the ionic conductivity values of PA-LiMnPS/PEO electrolytes with LiTFSI salt before and after exposure to air with a relative humidity of 30-40%. These measurements were conducted at 25 °C.



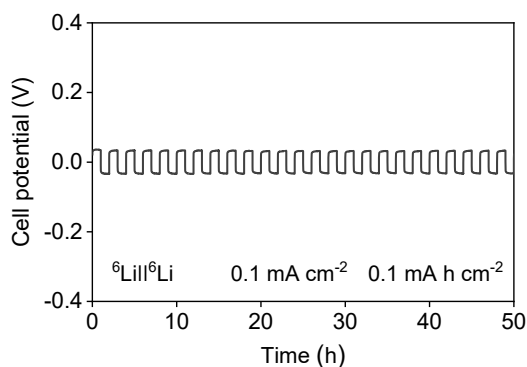
**Supplementary Fig. 31** Linear sweep voltammetry curves of PA-LiMnPS/PEO and RA-LiMnPS/PEO electrolytes with LiTFSI salt.



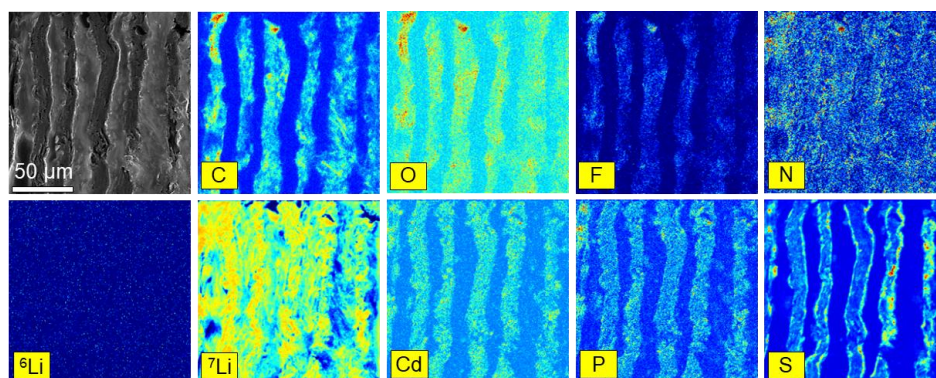
**Supplementary Fig. 32** Cycling performance of symmetric  $\text{Li}||\text{Li}$  coin cells with the PA-LiMnPS/PEO electrolyte with LiTFSI salt.



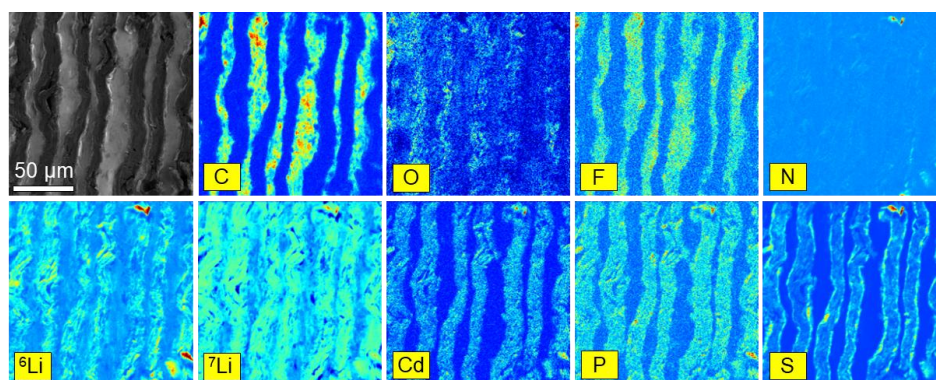
**Supplementary Fig. 33** H<sub>2</sub>S amount released of PA-LiCdPS/PEO and PA-LiMnPS/PEO electrolytes with LiTFSI salt when exposed to flowing air with a relative humidity of 30-40%, tested at 25 °C. A comparison of the air endurance times for different electrolytes can be found in Supplementary Note 2 and Supplementary Table 1.



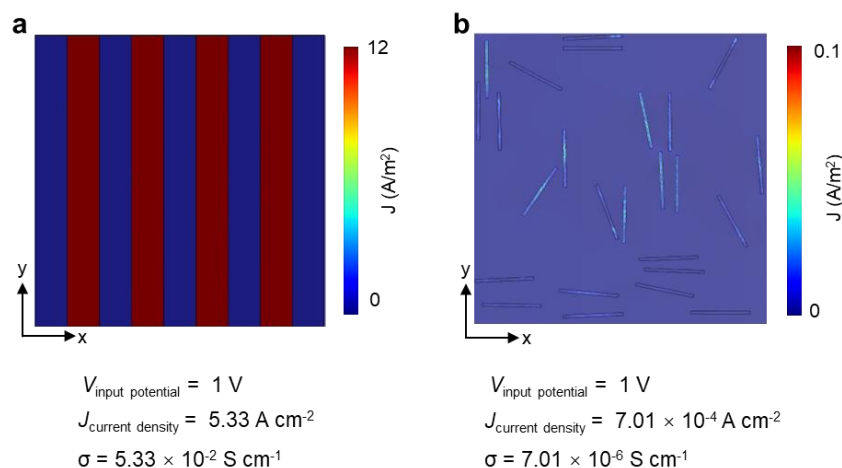
**Supplementary Fig. 34** Cycling performance of symmetric <sup>6</sup>Li||<sup>6</sup>Li coin cells with PA-LiCdPS/PEO electrolyte with LiTFSI salt, tested at 25 °C.



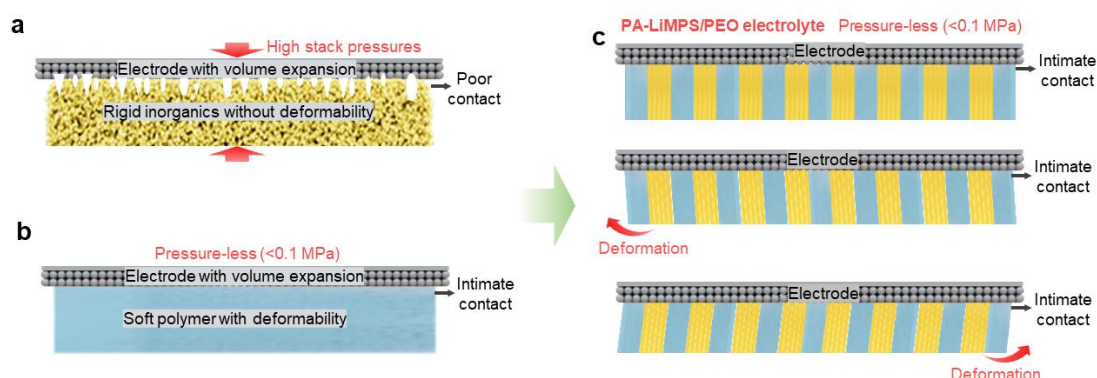
**Supplementary Fig. 35** FIB image and TOF-SIMS element maps obtained from the pristine (before cell assembly) PA-LiCdPS/PEO electrolyte with LiTFSI salt.



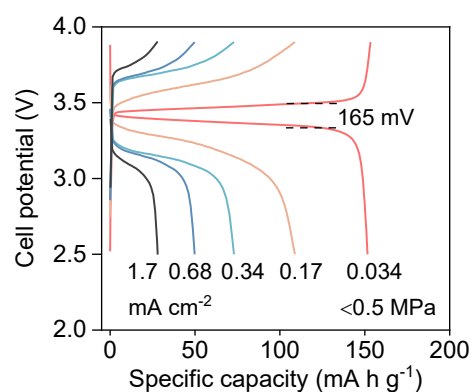
**Supplementary Fig. 36** FIB image and TOF-SIMS element maps of the cycled PA- LiCdPS/PEO electrolyte (with LiTFSI salt) in symmetric  ${}^6\text{Li}||{}^6\text{Li}$  cells after 50 h of cycling at  $0.1 \text{ mA cm}^{-2}$  and  $25^\circ\text{C}$ .



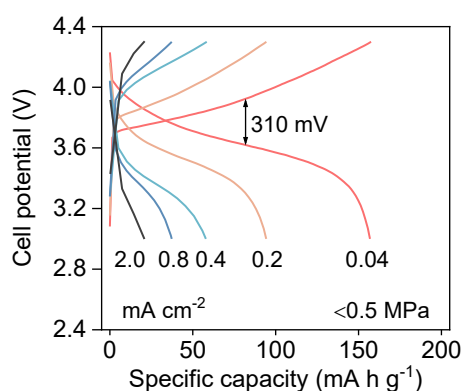
**Supplementary Fig. 37** COMSOL simulation analysis of the PA-LiCdPS/PEO (a) and RA-LiCdPS/PEO (b) electrolytes with LiTFSI salt, showing their current densities and ionic conductivities. The temperature in this simulation was set to 25 °C.



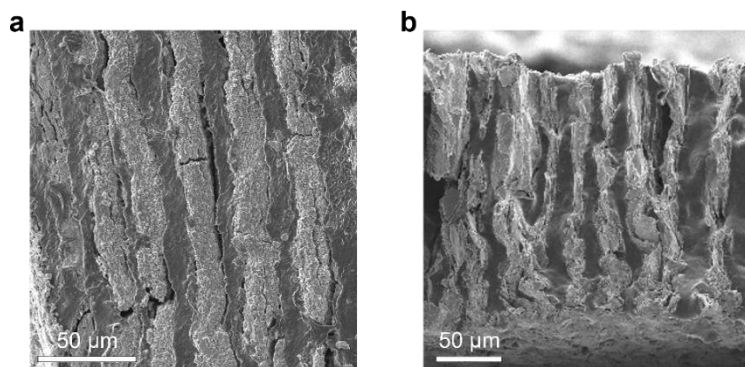
**Supplementary Fig. 38** (a, b) Electrode|electrolyte interfaces in all-solid-state batteries using inorganic (a) and polymer (b) electrolytes. (c) Electrode|electrolyte interface in solid-state batteries using PA-LiMPS/PEO electrolyte (containing LiTFSI salt) with deformability. The yellow region in (a) denotes the inorganic electrolyte. The blue region in (b) denotes the polymer electrolyte. The blue and yellow regions in (c) denote the PEO layer and PA-LiMPS layer. The gray rectangle at the top of the electrolytes indicates the electrode.



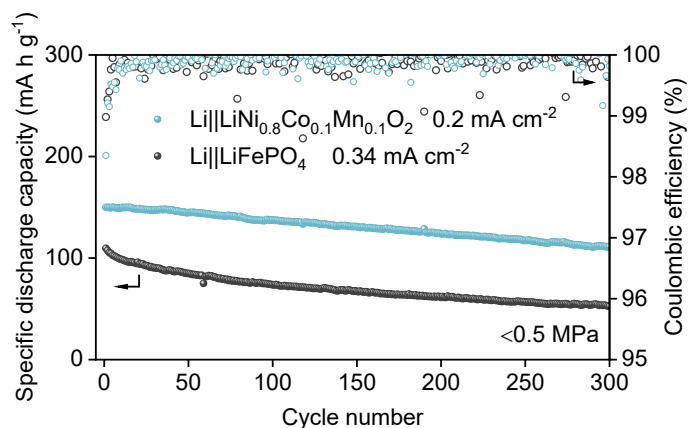
**Supplementary Fig. 39** Charge and discharge profiles of Li||LiFePO<sub>4</sub> coin cells with the RA-LiCdPS/PEO electrolyte with LiTFSI salt at 25 °C, tested at 0.034, 0.17, 0.34, 0.68, and 1.7 mA cm<sup>-2</sup>.



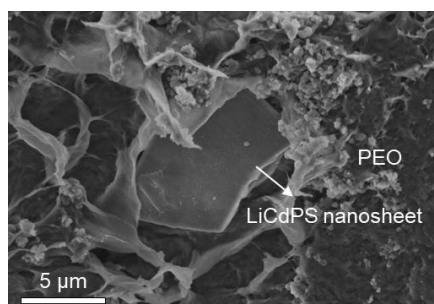
**Supplementary Fig. 40** Charge and discharge profiles of Li||LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> coin cells with the RA-LiCdPS/PEO electrolyte with LiTFSI salt at 25 °C, tested at 0.04, 0.2, 0.4, 0.8, and 2.0 mA cm<sup>-2</sup>.



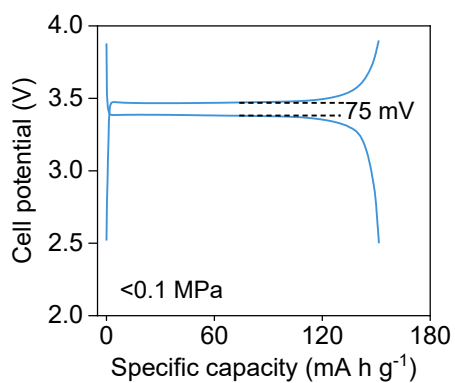
**Supplementary Fig. 41** Surface (a) and cross-sectional (b) SEM images of the PA-LiCdPS/PEO electrolyte with LiTFSI salt after 600 cycles in Li||LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> coin cells at 0.2 mA cm<sup>-2</sup>.



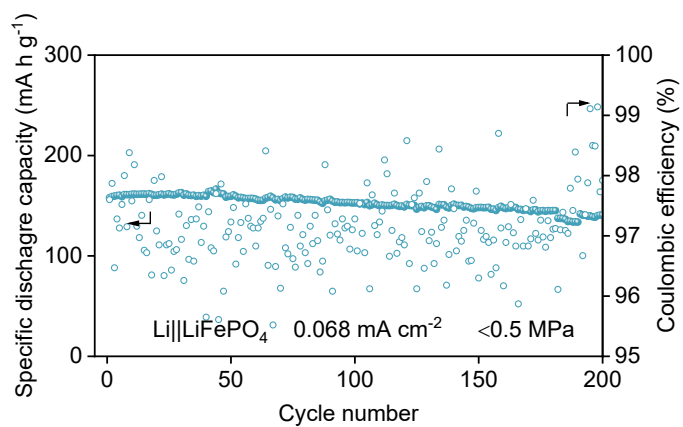
**Supplementary Fig. 42** Long-term cycling performance of Li||LiFePO<sub>4</sub> and Li||LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> coin cells with the RA-LiCdPS/PEO electrolyte with LiTFSI salt, tested at 25 °C.



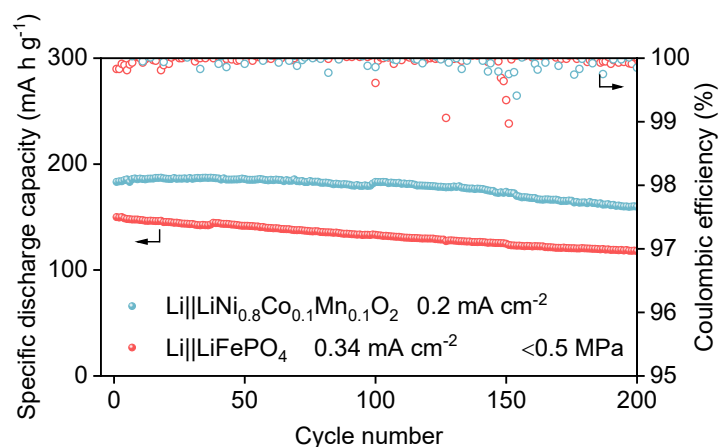
**Supplementary Fig. 43** Surface SEM image of the RA-LiCdPS/PEO electrolyte with LiTFSI salt after 600 cycles in Li||LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> coin cells at 0.2 mA cm<sup>-2</sup>.



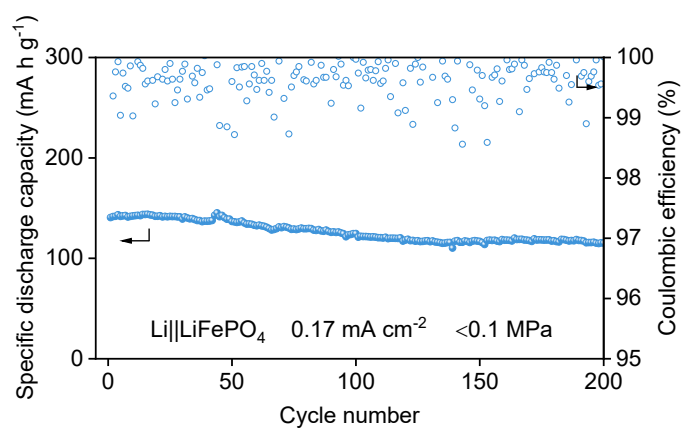
**Supplementary Fig. 44** Charge and discharge profiles of Li||LiFePO<sub>4</sub> pouch cells at 0.034 mA cm<sup>-2</sup> with the PA-LiCdPS/PEO electrolyte with LiTFSI salt, tested at 25 °C.



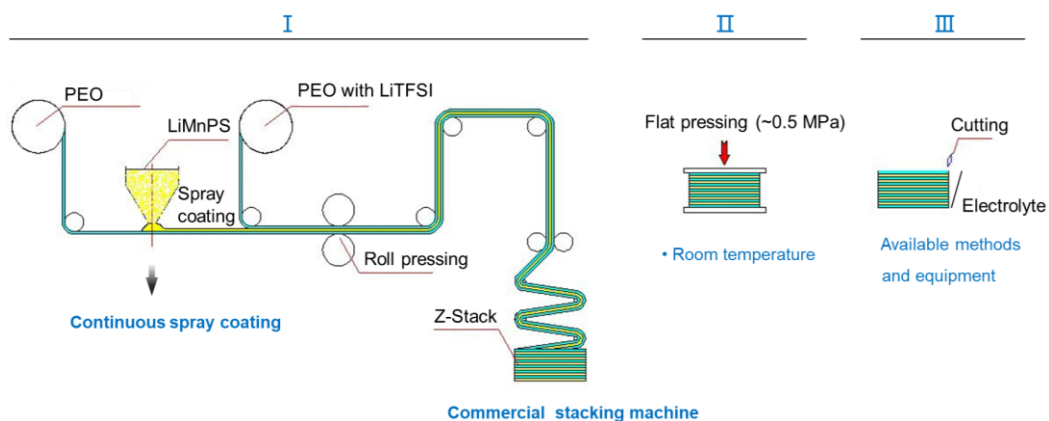
**Supplementary Fig. 45** Cycling performance of Li||LiFePO<sub>4</sub> coin cell at 0.068 mA cm<sup>-2</sup> with the PA-LiMnPS/PEO electrolyte with LiTFSI salt, tested at 25 °C.



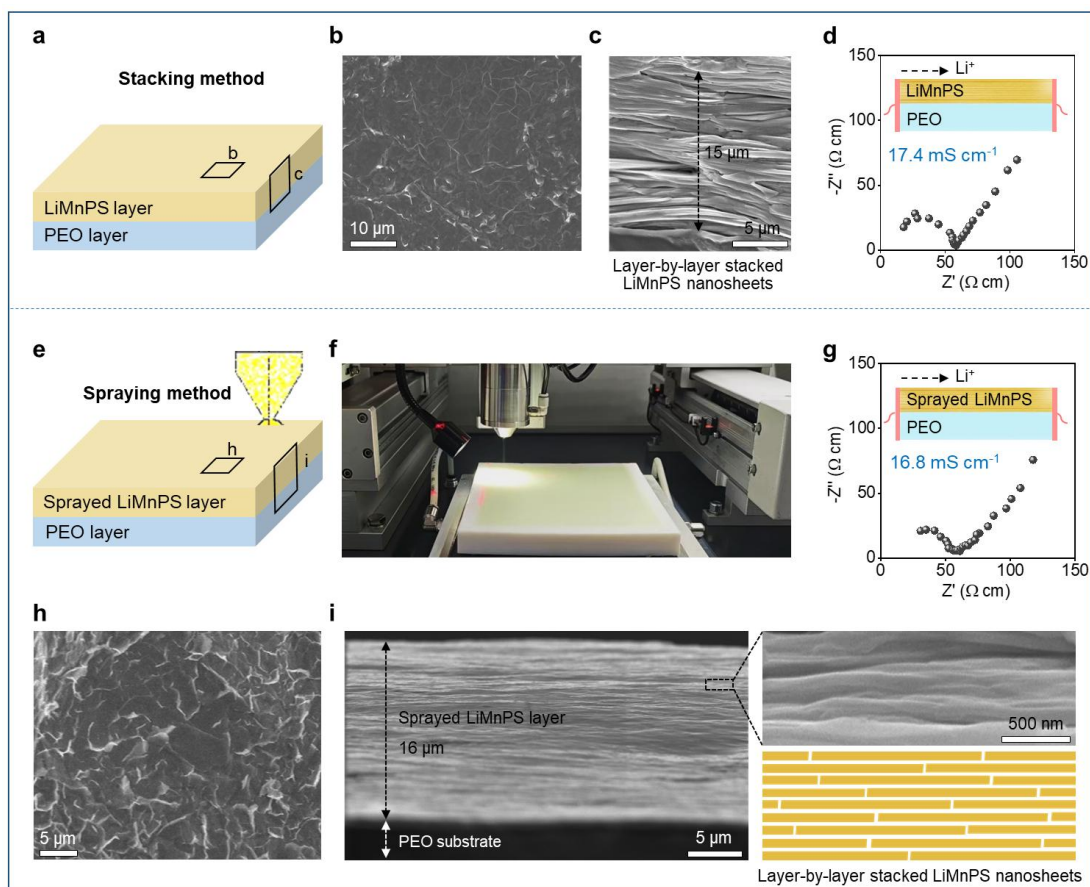
**Supplementary Fig. 46** Cycling performance of Li||LiFePO<sub>4</sub> coin cells at 0.34 mA cm<sup>-2</sup> and Li||LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> coin cells at 0.2 mA cm<sup>-2</sup> with the PA-LiMnPS/PEO electrolyte with LiTFSI salt, tested at 25 °C.



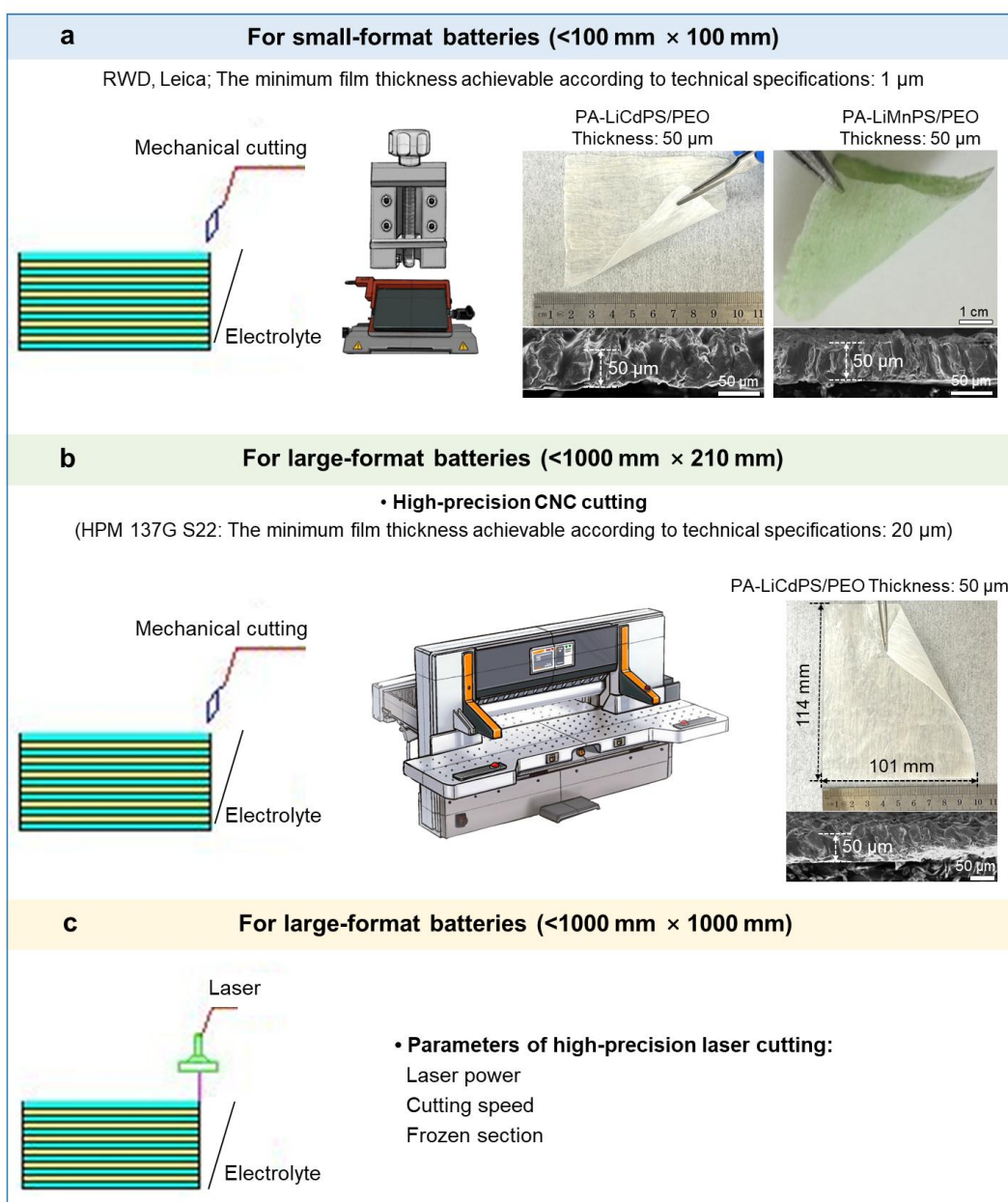
**Supplementary Fig. 47** Cycling performance of Li||LiFePO<sub>4</sub> pouch cell at 0.17 mA cm<sup>-2</sup> with the PA-LiMnPS/PEO electrolyte with LiTFSI salt at 25 °C, with stack pressure <0.1 MPa.



**Supplementary Fig. 48** Schematic representation on a potential scalable production process of PA-LiMnPS/PEO electrolyte with LiTFSI salt. The details about this process can be found in Supplementary Note 4.



**Supplementary Fig. 49** (a-c) Schematic of the stacked configuration composed of individual LiMnPS and PEO (with LiTFSI) layers (a), along with SEM images showing the surface morphology (b) and cross-sectional morphology (c) of the LiMnPS layer. (d) Nyquist plot of stacked individual LiMnPS/PEO (with LiTFSI) layers. (e) Schematic diagram of LiMnPS/PEO (with LiTFSI) membrane using spraying method. (f) Optical image of the spraying process. (g) Nyquist plot of sprayed LiMnPS/PEO (with LiTFSI) membrane. (h) Surface SEM image of the sprayed LiMnPS layer. (i) Cross-sectional SEM image of the sprayed LiMnPS layer, a higher-magnification SEM image of a selected region within the sprayed layer, and a schematic illustrating that the sprayed LiMnPS is composed of layer-by-layer stacked LiMnPS nanosheets. The details about spray-coating can be found in Supplementary Note 5.



**Supplementary Fig. 50** Cutting methods for electrolytes with different dimensions ( $L \times W$ , mm). (a) Mechanical precision slicers (e.g., RWD, Leica) and the prepared PA-LiCdPS/PEO and PA-LiMnPS/PEO electrolytes (containing LiTFSI salt) with thicknesses of 50 μm. (b) High-precision mechanical cutter (HPM 137G S22) and the prepared PA-LiCdPS/PEO electrolyte (containing LiTFSI salt) with a thickness of 50 μm. (c) Laser cutting systems and its key parameters. Available techniques and equipment for the cutting process can be found in Supplementary Note 6.

**Supplementary Table 1.** Comparison of the air stabilities of different sulfide-based inorganic solid-state electrolytes. The determination of the air endurance time can be found in Supplementary Note 2.

| Electrolyte                                                                             | Strategy                             | Humidity (%) | Air exposure time | Concentration of released H <sub>2</sub> S                                             | Air endurance time (min) | Reference |
|-----------------------------------------------------------------------------------------|--------------------------------------|--------------|-------------------|----------------------------------------------------------------------------------------|--------------------------|-----------|
| Li <sub>7</sub> P <sub>3</sub> S <sub>11</sub>                                          | -                                    | 40           | 1 min             | 0.2 cm <sup>3</sup> g <sup>-1</sup> (10 ppm)                                           | 1                        | 19        |
| Li <sub>6</sub> PS <sub>5</sub> Cl                                                      |                                      | 50           | 2 min             | 0.2 cm <sup>3</sup> g <sup>-1</sup> (10 ppm)                                           | 2                        | 20        |
| Li <sub>6</sub> PS <sub>5</sub> I                                                       | -                                    | 23-25        | 48 s              | 0.2 cm <sup>3</sup> g <sup>-1</sup> (10 ppm)                                           | 0.8                      | 21        |
| Li <sub>6</sub> PS <sub>5</sub> Br                                                      | -                                    | 30           | 1.5 min           | 0.2 cm <sup>3</sup> g <sup>-1</sup> (10 ppm)                                           | 1.5                      | 22        |
| Li <sub>3</sub> PS <sub>4</sub>                                                         | -                                    | 45-50        | 5 min             | 0.2 cm <sup>3</sup> g <sup>-1</sup> (10 ppm)                                           | 5                        | 23        |
| Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub>                                       | -                                    | 35-40        | 16 min            | 0.2 cm <sup>3</sup> g <sup>-1</sup> (10 ppm)                                           | 16                       | 24        |
| ZIF-8-Li <sub>6</sub> PS <sub>5</sub> Cl                                                | Surface treatment                    | 50           | 10 min            | 0.2 cm <sup>3</sup> g <sup>-1</sup> (10 ppm)                                           | 10                       | 20        |
| Li <sub>6.3</sub> P <sub>0.9</sub> Cu <sub>0.1</sub> S <sub>4.9</sub> Cl <sub>1.1</sub> | Elemental doping                     | 55-60        | 5 min             | 0.2 cm <sup>3</sup> g <sup>-1</sup> (10 ppm)                                           | 5                        | 25        |
| Li <sub>6.6</sub> Ge <sub>0.6</sub> Sb <sub>0.4</sub> S <sub>5</sub> I                  | Elemental doping                     | 35-40        | 65 min            | 0.2 cm <sup>3</sup> g <sup>-1</sup> (10 ppm)                                           | 65                       | 26        |
| <b>This work</b><br><b>PA-LiMPS/PEO</b><br><b>(with LiTFSI salt)</b>                    | Nanoengineered composite electrolyte | 30-40        | 7 days            | <3 × 10 <sup>-11</sup> cm <sup>3</sup> g <sup>-1</sup><br>(1.5 × 10 <sup>-9</sup> ppm) | 10080<br>(7 days)        |           |

### Supplementary Note 1: The fabrication of PA-LiMPS/polymer electrolytes

The fabrication method for PA-LiMPS/polymer electrolytes is similar to the lamination process and the roll-to-roll technique in battery manufacturing. First, large-area, individual LiMPS and polymer membranes were cut to specific sizes and stacked in a zigzag pattern to form a bulk LiMPS/polymer with alternating horizontal arrangements of LiMPS layers and adhesive polymer layers (Supplementary Fig. 8a).

This bulk LiMPS/polymer underwent roll pressing, and multiple pressed bulks are then combined and further roll-pressed (Supplementary Fig. 8b). This process can be repeated to achieve the desired thickness of the bulk LiMPS/polymer. Finally, the bulk LiMPS/polymer was cut perpendicular to the LiMPS plane to obtain the PA-LiMPS/polymer electrolytes (Supplementary Fig. 8c).

### Supplementary Note 2: Evaluation of the air endurance times

In previous studies, there has been a lack of a unified or referenceable standard for relating the release of H<sub>2</sub>S from sulfide electrolytes in moist air to their storage duration. We adopted a threshold of 10 ppm H<sub>2</sub>S concentration as the reference value, based on the occupational exposure limit defined by the National Institute for Occupational Safety and Health (NIOSH). According to (SI Eq.1), the threshold of 10 ppm corresponds to the release of 0.2 cm<sup>3</sup> g<sup>-1</sup> of H<sub>2</sub>S under the condition of 1 g electrolyte in 20 L of air, which is consistent with most reported experiments and practical production lines. Therefore, the air endurance times of different sulfide electrolytes can be compared based on the time when the released H<sub>2</sub>S concentration reaches 10 ppm (0.2 cm<sup>3</sup> g<sup>-1</sup>), as summarized in Supplementary Table 1.

$$V = \frac{C \times L \times 10^{-6}}{m} \quad (\text{SI Eq.1})$$

where  $V$  denotes the total amount of H<sub>2</sub>S generated (cm<sup>3</sup> g<sup>-1</sup>) normalized by the weight  $m$  of the sulfide electrolyte sample (g),  $C$  denotes the H<sub>2</sub>S concentration (ppm), and  $L$  is the volume of the container (cm<sup>3</sup>).

### Supplementary Note 3: The control of stack pressure

Using the PA-LiMPS/PEO electrolyte, the symmetric Li||Li, Li||LiFePO<sub>4</sub>, and Li||LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> coin cells (2025-type) were assembled. The force applied during 2025-type coin cell assembly was set to 0.025 tonne, resulting in a stack pressure of less than 0.5 MPa. For Li||LiFePO<sub>4</sub> pouch cells, the assembly and sealing were carried out through a heat-sealing process with a packaging pressure of less than 0.1 MPa<sup>27</sup>. During electrochemical testing of both coin and pouch cells, no external

pressure was applied.

#### **Supplementary Note 4: A potential scalable production process**

Supplementary Fig. 48 shows a potentially feasible industrial-scale manufacturing process for the PA-LiMnPS/PEO electrolyte with LiTFSI salt, along with the relevant techniques that could be applied at each step. The feasibility of spray-coating has been reported in Supplementary Fig. 49. LiMnPS nanosheets are spray-coated onto a flexible PEO substrate, followed by continuous spraying and roll-to-roll processing to form a long composite LiMnPS/PEO membrane. A “Z”-fold stacking process creates the bulk structure of LiMnPS/PEO. Flat pressing is conducted at 25 °C under low pressure (~0.5 MPa). Finally, the cutting process is adjustable based on the desired solid electrolyte membrane dimensions, with suitable techniques and equipment selected as shown in Supplementary Fig. 50.

#### **Supplementary Note 5: Verification of the spray-coating process**

Spray-coating can directly deposit LiMnPS nanosheets onto large-area PEO (with LiTFSI) membranes, eliminating the need for separate membrane preparation of LiMnPS and PEO (with LiTFSI). As shown in Supplementary Fig. 49, we validated this method using ultrasonic spray deposition to fabricate the LiMnPS/PEO (with LiTFSI) membrane (Supplementary Figs. 49e-i) and conducted comparative studies with previously stacked membranes (Supplementary Figs. 49a-d). The sprayed LiMnPS layer features a surface of interconnected LiMnPS nanosheets (Supplementary Fig. 49h). The cross-sectional structure shows a dense, uniform LiMnPS layer with a thickness of ~16  $\mu\text{m}$  (Supplementary Fig. 49i). A higher-magnification view of a selected region of the sprayed LiMnPS shows that it is composed of layer-by-layer stacked LiMnPS nanosheets without any polymer, as illustrated by the yellow schematic. The PEO (with LiTFSI) substrate ensures a strong interface with the LiMnPS. Therefore, the sprayed LiMnPS layer achieves structural features comparable to those of freestanding LiMnPS membrane. The composite membrane prepared by

directly spray-coating a LiMnPS layer onto PEO (with LiTFSI) shows a  $\sigma_{25\text{ }^{\circ}\text{C}}$  of 16.8 mS cm<sup>-1</sup> (Supplementary Fig. 49g), closely matching that of the stacked configuration composed of separately prepared LiMnPS and PEO (with LiTFSI) layers (17.4 mS cm<sup>-1</sup>, Supplementary Fig. 49d). These results confirm that the sprayed LiMnPS layer preserves the superionic conduction of LiMnPS.

#### **Supplementary Note 6: Available techniques and equipment for the cutting**

High-precision mechanical cutting techniques are suitable for processing PA-LiMnPS/PEO electrolyte (containing LiTFSI salt) with moderate thicknesses (e.g., 200  $\mu\text{m}$ ). For thinner electrolytes, the choice of cutting technique can be tailored to the target dimensions required by different applications. For small-format batteries (length  $\times$  width  $< 100\text{ mm} \times 100\text{ mm}$ ), mechanical precision slicers such as RWD or Leica systems can achieve accurate cuts. For example, we successfully used the RWD *Minux* S700A device to fabricate the PA-LiCdPS/PEO and PA-LiMnPS/PEO electrolytes (containing LiTFSI salt) with thicknesses of 50  $\mu\text{m}$  (Supplementary Fig. 50a). To address the need for large-format batteries, high-precision programmable cutting machines can be employed. Supplementary Fig. 50b shows a PA-LiCdPS/PEO electrolyte (containing LiTFSI salt) with a thickness of 50  $\mu\text{m}$ , precisely cut using a high-precision mechanical cutter (HPM 137G S22) equipped with a precision linear guidance system and a German Dienen blade. This cutter can produce membranes with length and width dimensions up to 1000 mm  $\times$  210 mm. In addition, other cutting solutions can be explored. Current-generation laser cutting systems with micron-level resolution can be adapted for the polymer-inorganic membranes. To ensure high-precision cutting, key parameters such as laser power, cutting speed, and operating temperature must be carefully optimized (Supplementary Fig. 50c). A high-resolution numerical control system is also essential for maintaining cutting accuracy and consistency.

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