**Supplementary Information**



Figure S1 a) Synthesis route of PP12FSI. b) Optical photographs of PP12FSI at room temperature. c)DSC curves of Li0.5(PP12)0.5FSI with different lower limit temperature.



Figure S2 a) Chemical structure and corresponding hydrogen atom of PP12FSI. b) 1H NMR full spectra of Lix(PP12)1-xFSI (0%≤x≤90%，in molar ratio), c)DMSO-d6 peak and d)N-CH3 peak in Lix(PP12)1-xFSI.



Figure S3 Raman spectra of Lix(PP12)1-xFSI (0%≤x≤100%，in molar ratio) a) full spectra, b)in the range of 800~ 650 cm-1 and c) in the range of 1500~1400 cm-1.



Figure S4 a) temperature dependance of ionic conductivity of Lix(PP12)1-xFSI (25%≤x≤40%) and (b) amperometric i-t curves of Li/Li0.4(PP12)0.6FSI/Li cells (Insert: the impedance responses of the cell under initial/steady-state conditions)

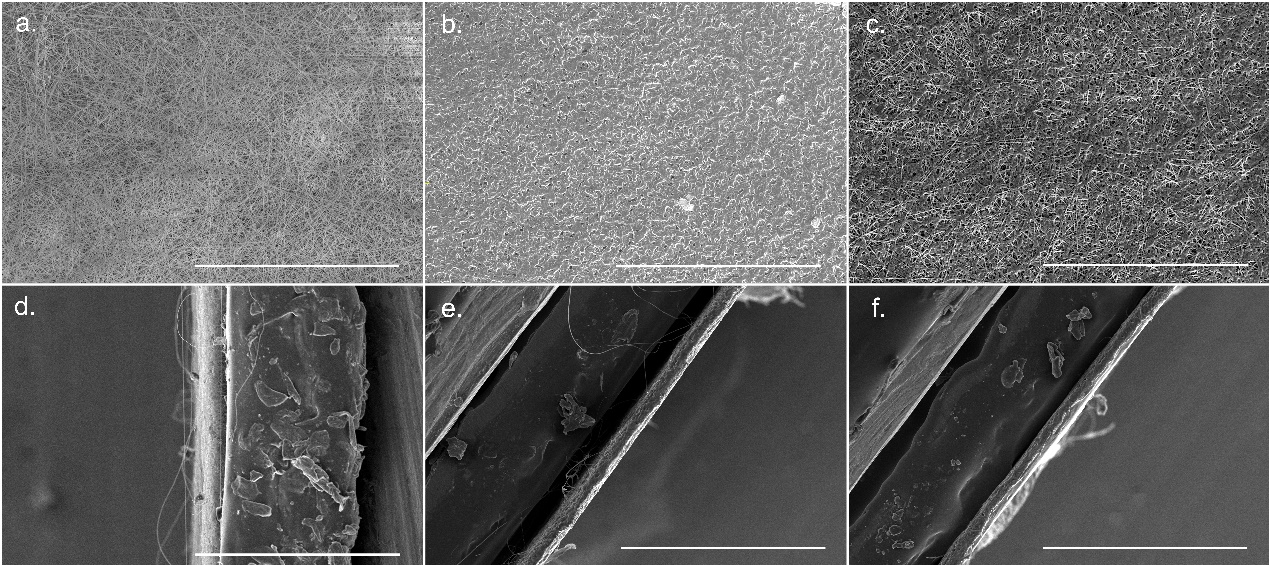


Figure S5 Top-view SEM images of a) PI; b) PI-SN and c) PI-PP12FSI. Side-view SEM images of d) PI; e) PI-SN and f) PI-PP12FSI. (scale bar: 200 μm)

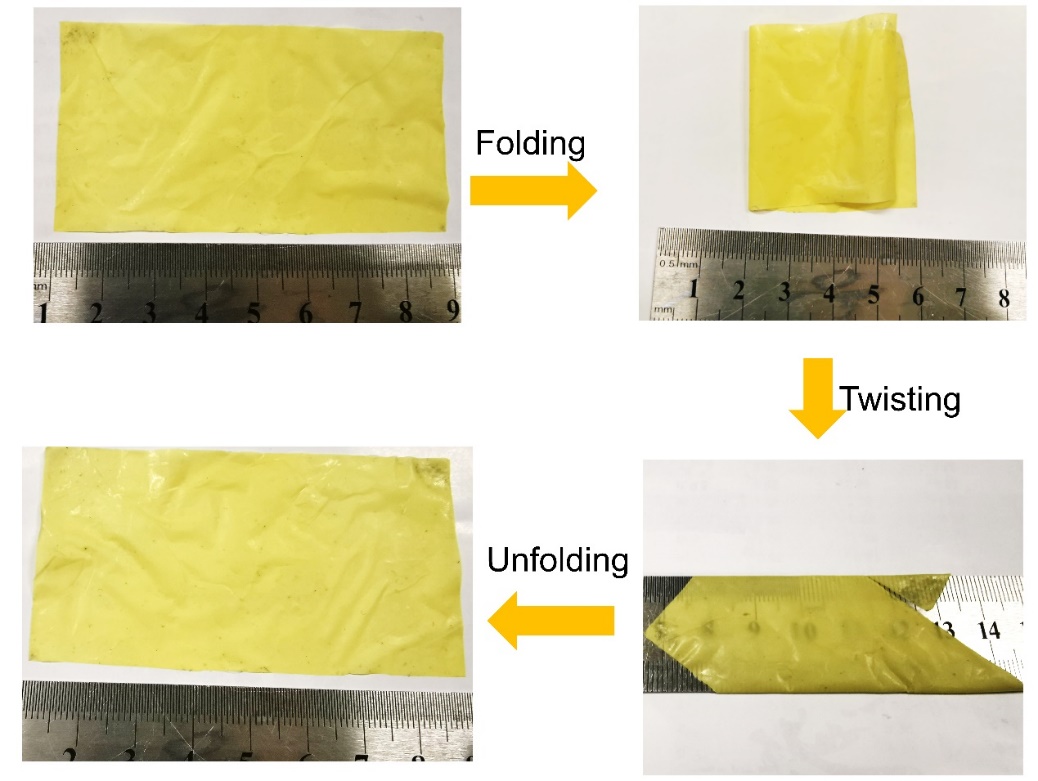


Figure S6 Photo images of 84 cm2 PI-PP12FSI free-standing electrolytes being abused test via folding, twisting and unfolding.



Figure S7 Nyquist plot of a) SS/PI-SN/Cu and b) SS/PI-PP12FSI/Cu at different temperatures. Electrochemical impedance spectra of c) Li/PI-SN/Li and d) Li/PI-PP12FSI/Li cells under initial/steady-state conditions



Figure S8 a) Symmetrical Li cells with PPCEs at virous current densities and the magnified part of Figure a under b)0.2 mA cm-2, c)0.5 mA cm-2 and d) 2.0 mA cm-2. Optical photograph of the compatibility of lithium metal with e) SN, f) and g) PP12FSI.

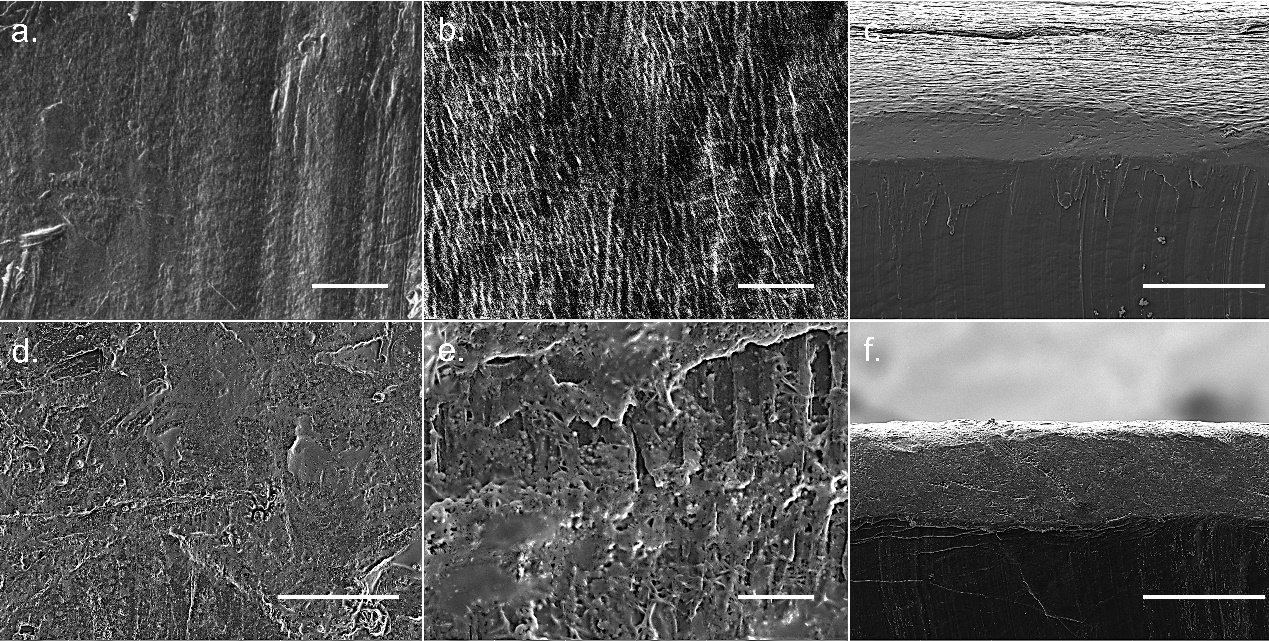


Figure S9 a), b) Top-view and c) cross-section of pristine lithium foil. d), e) Top-view and f) cross-section of pristine lithium foil in symmetric cells with PI-PP12FSI under 1.0 mA cm-2 after 1000h (Figure 4c). Scale bars for a), b), d), e) are 100 μm and for c), f) is 5 μm.



Figure S10 a) Cross-section SEM image of PI-PP12FSI/NCM622 interface and corresponding EDS mapping of (b)Ni, (c)Mn, (d) S, (e)C and (f) O elements (scale bar: 10μm).



Figure S11 a) Charge-discharge curves of Li/PI-SN/NCM622 cells under different rate corresponding to Figure 5b. b) Galvanostatic rate performances of Li/NCM622 cells with different electrolytes from 0.1 C to 2.0 C (2400 stands for Celgard 2400 and LE represents liquid electrolyte). c) Galvanostatic cycle performances of Li/NCM622 cells with different electrolytes under 1.0 C. d) First charge-discharge curves of Li/PI-PP12FSI/NCM622 cells under different cathode loading (the C-rate for 1.7 and 5.4 mg cm-2 loading is 0.1C and for 10.6 mg cm-2 loading is 0.025C).



Figure S12 a) Charge-discharge curves of Li/PI-PP12FSI/LNMO cell under different rate corresponding to Figure 5g. b) Charge-discharge curves of Li/PI-PP12FSI/LNMO cell at different cycles under 1.0C corresponding to Figure 5h.



Figure S13 a) Cell voltage and nail/cell temperature curves during nail penetration test of a) conventional liquid electrolyte and b) PI-PP12FSI.



Figure S14 a) Schematic illustration of the preparation of NCM622 cathode-supported PI-PP12FSI composite and b) corresponding optical photograph of as-prepared sample. c) Nyquist plot of EIS measurements of pouch-type NCM622/PI-PP12FSI/Li cell at 25 oC. d)Corresponding charge-discharge curves of pouch-type NCM622/PI-PP12FSI/Li cell under different rate referred to Figure 6e.

Table S1 Ionic conductivity and lithium transference number of Lix(PP12)1-xFSI

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **XLiFSI (mol%)** | **5** | **10** | **20** | **25** | **30** | **35** | **40** | **50** | **60** |
| Molarity (mol kg-1) | 0.17 | 0.34 | 0.7 | 0.9 | 1.10 | 1.32 | 1.54 | 2.02 | 2.55 |
| (mS cm-1) | 0.12 | 0.35 | 0.56 | 1.20 | 1.18 | 1.45 | 1.11 | 0.49 | 0.46 |
| 𝑡Li+ | 0.15 | 0.17 | 0.24 | 0.53 | 0.48 | 0.56 | 0.55 | 0.39 | 0.47 |

Table S2 Ionic conductivity and VTF(Arrhenius) fitting parameters for PPCEs

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Electrolytes** | **(S cm-1)** | | **S**  **cm-1)** | ***Ea*(eV)** | **(K)** | ***R*2** |
| 25 ℃ | 80 ℃ |
| PI-SN(20-80℃) | 5.87-4 | 1.00-3 | 4.82 | 0.26 | 263.0 | 0.990 |
| PI-PP12FSI (0-40 oC) | 4.07 -4 |  | 0.95 | 2.37 |  | 0.995 |
| PI-PP12FSI (40-80 oC) |  | 8.1810-4 | 5.10 | 0.73 | 242.8 | 0.994 |

Table S3 Corresponding electrochemical impedance spectra of Li/PI-PP12FSI/Li cells after virous current densities

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Current densities (mA cm-2)** | 0 | 0.05 | 0.1 | 0.2 | 0.5 | 1 | 2 |
| **Rb (Ω)** | 12.6 | 11.9 | 10.8 | 10.7 | 10.2 | 11.2 | 9.9 |
| **Ri (Ω)** | 505.3 | 345.5 | 219.2 | 18.32 | 6.2 | 6.1 | 5.8 |

Table S4 Corresponding electrochemical impedance spectra of Li/PI-PP12FSI/NCM622 cells after different cycles

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Cycle number** | 0 | 2 | 20 | 100 | 600 |
| **Rb (Ω)** | 9.38 | 8.82 | 10.3 | 8.72 | 8.5 |
| **Ri (Ω)** | 98.9 | 80.9 | 30.8 | 52.6 | 56.6 |