

## Supplemental Information

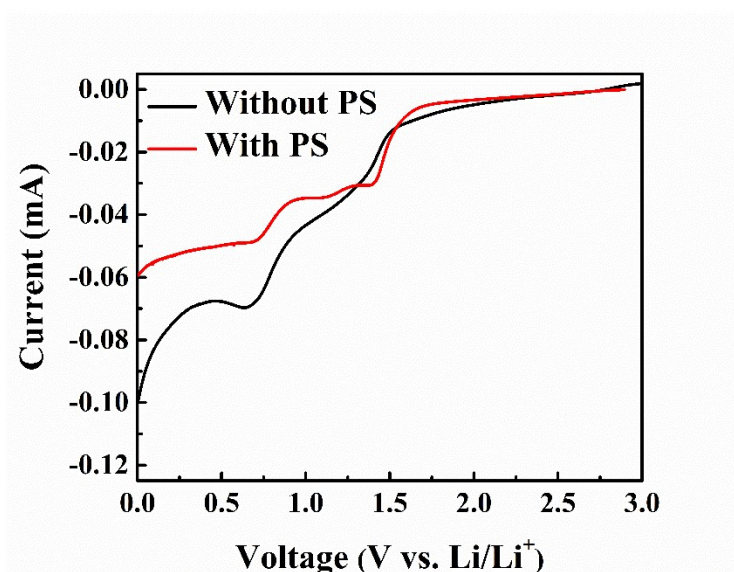
### **A Functional Electrolyte Additive Enabling Robust Interphases in High-Voltage Li||LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> Batteries at Elevated Temperature**

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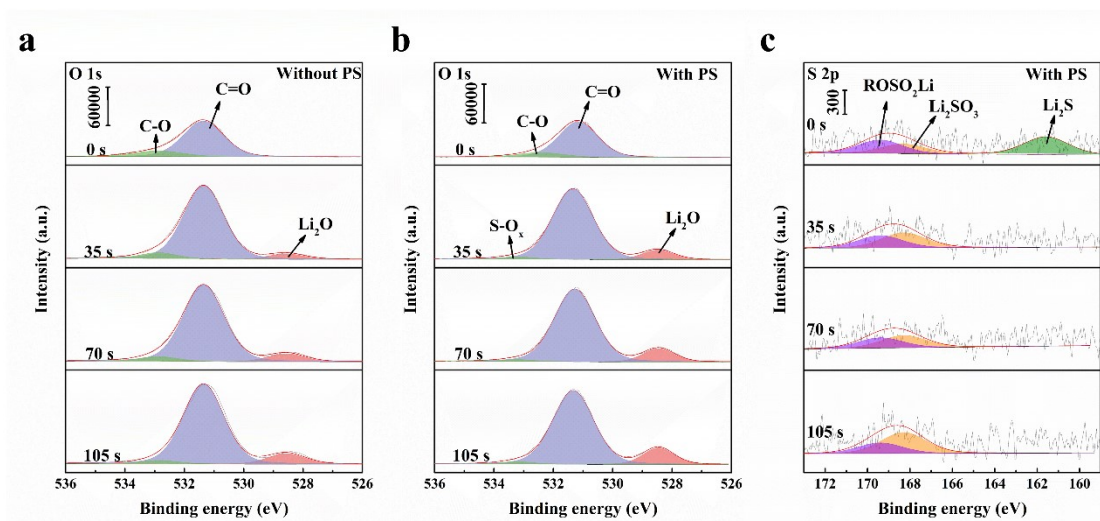
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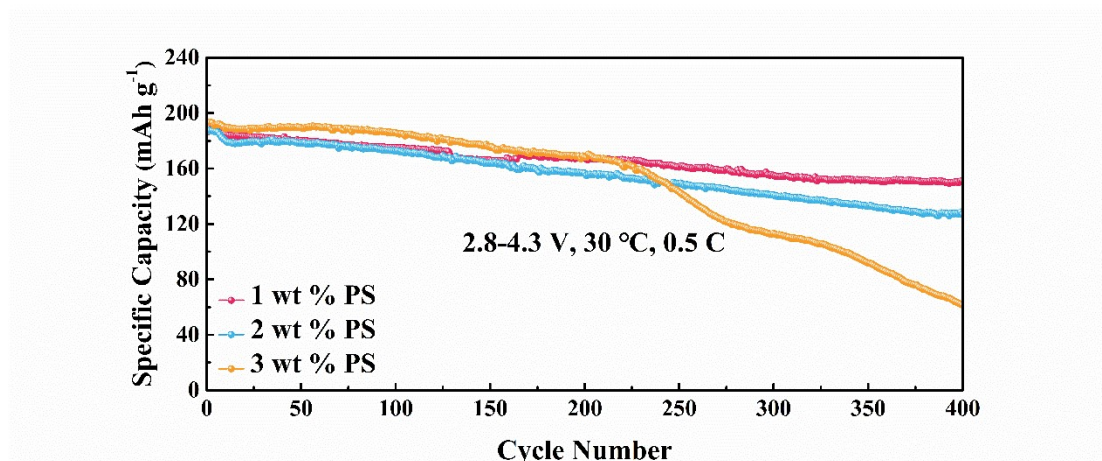
**Figure S1** Reduction stability of both electrolytes in three-electrode cell system tested by linear sweep voltammetry (LSV) and the scan rate was 1 mV s<sup>-1</sup>.



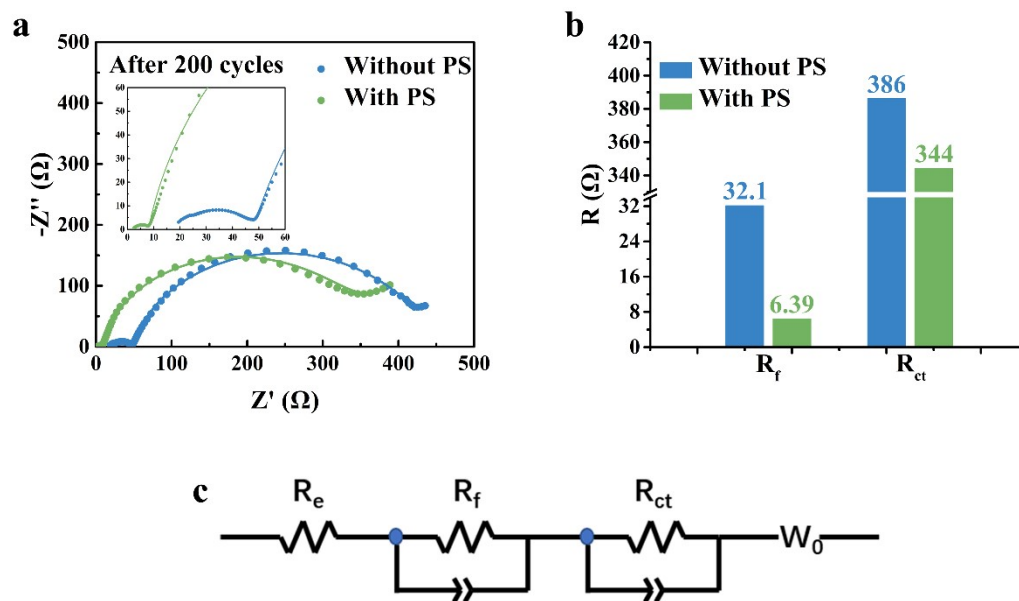
**Figure S2** The blank electrolytes (two bottles on the left) and PS-electrolytes (two bottles on the right) stored at elevated temperature of 45°C for different times.



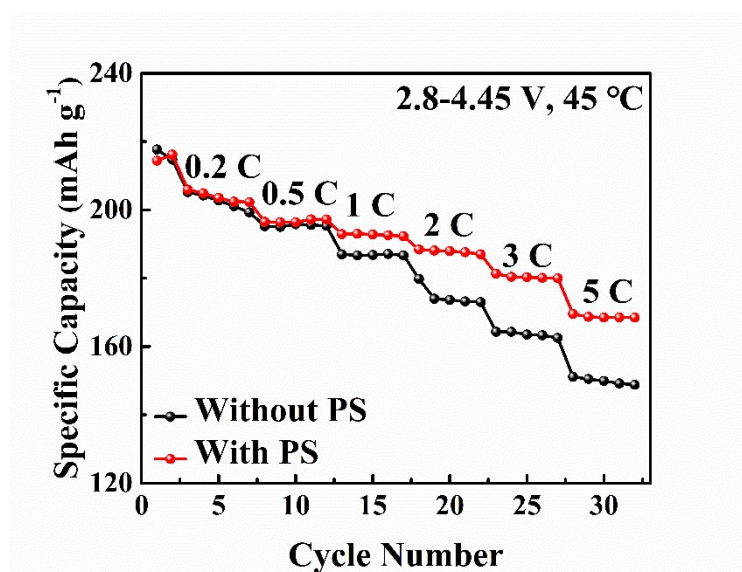
**Figure S3** O 1s (a, b) and S 2p (c) spectra of SEI formed on Li metal surface after 10 cycles by using different electrolytes.



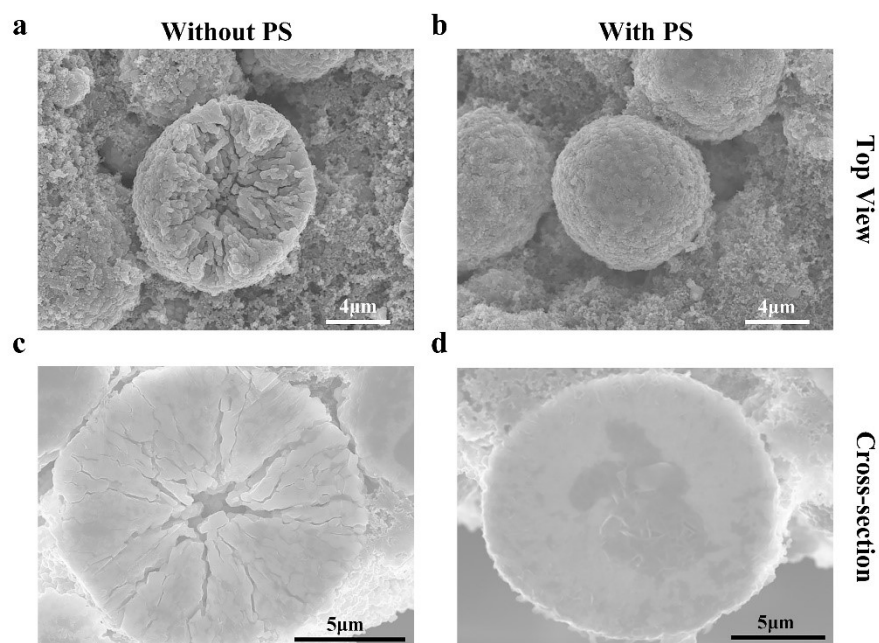
**Figure S4** Cycling performance of Li||NCM811 half-cells using different PS content in electrolytes between 2.8 to 4.3 V at 0.5 C.



**Figure S5** (a) Nyquist plots for Li||NCM811 cells after 200 cycles during 2.8-4.45 V, at 45 °C using different electrolytes. (b) fitted  $R_f$  and  $R_{ct}$  value according to (c) the equivalent circuit.

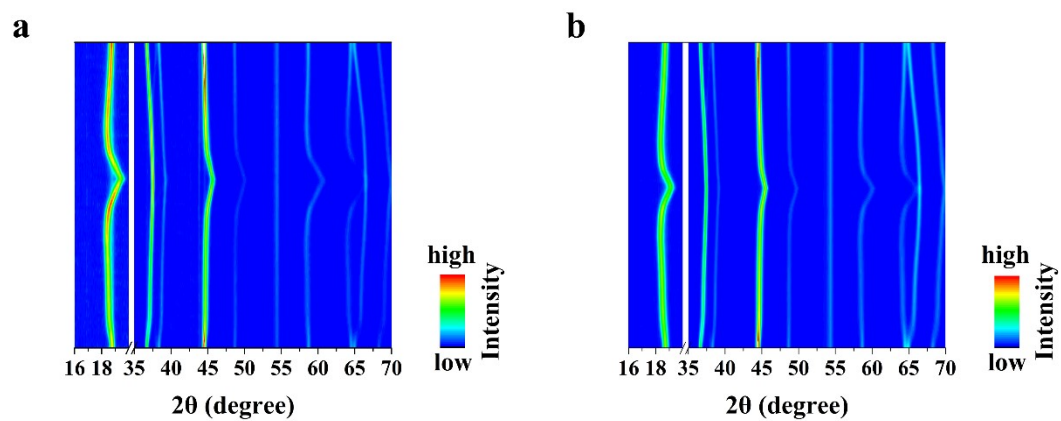


**Figure S6** Rate performance of Li||NCM811 half-cells using the blank electrolyte and PS-electrolyte after two formation cycles at 0.1 C, then cycled at 0.2, 0.5, 1.0, 2.0, 3.0 and 5.0 C subsequently within the voltage of 2.8-4.45 V at elevated temperature.

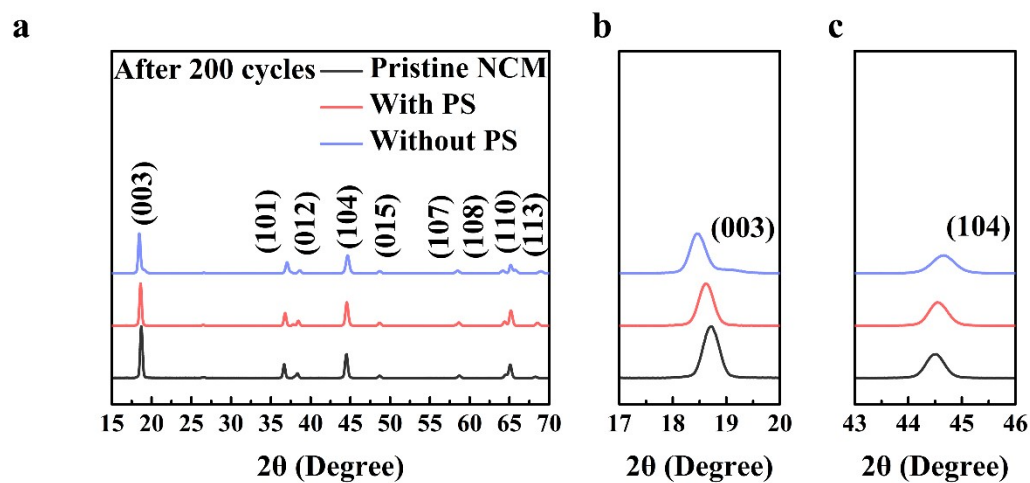


**Figure S7** (a, b) The top-view and (c, d) cross-sectional SEM images of cathodes in Li||NCM811 half-cells using the (a, c) blank electrolyte and (b, d) PS-electrolyte after 100 cycles to 4.45 V and at 45 °C.

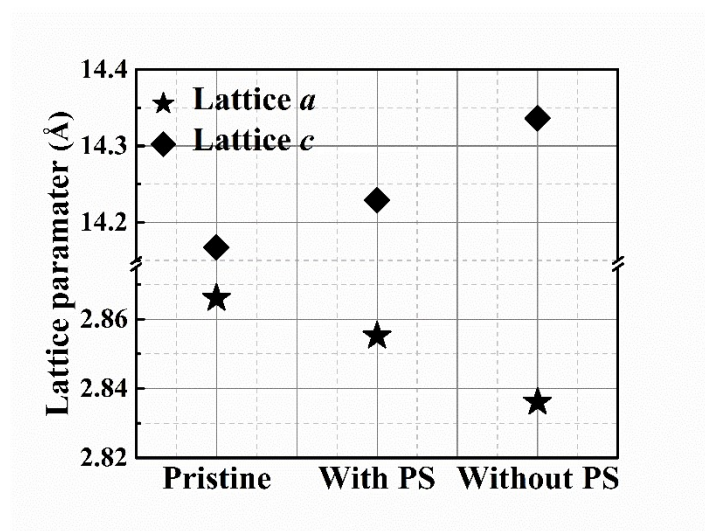




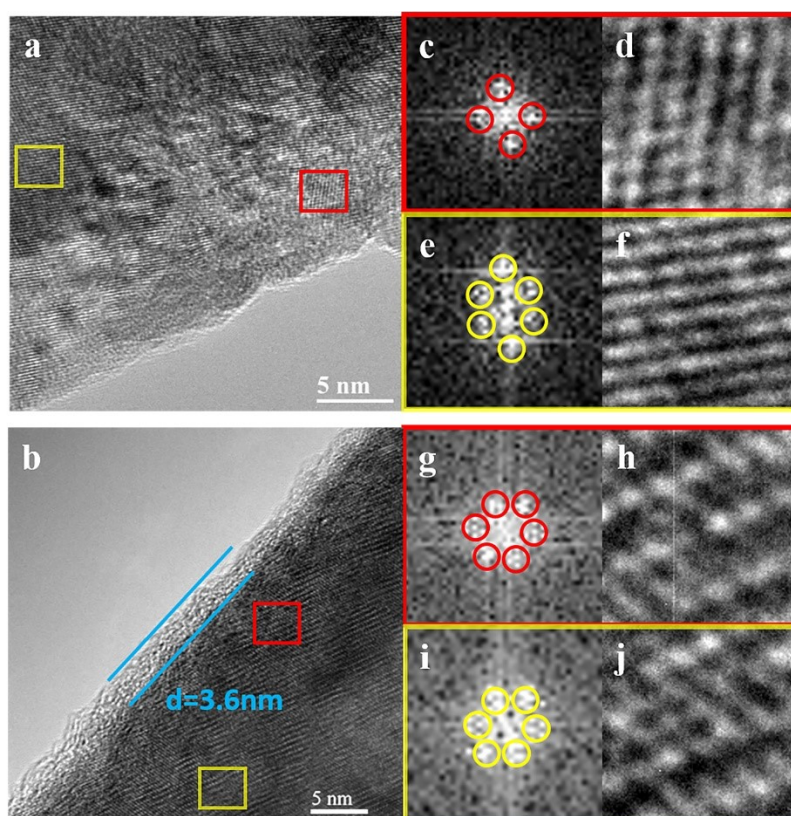
**Figure S8** In-situ XRD contour plots during the first cycle between 2.8-4.45 V using the (a) blank electrolyte and (b) PS-electrolyte.



**Figure S9** Ex-situ XRD patterns for (a) full range, (b) 17-20° and (c) 43-46° for pristine NCM811 and NCM811 after 200 cycles.



**Figure S10** Lattice parameter *a* and *c* values for cycled NCM811 from refinement results.



**Figure S11** HRTEM and Fast Fourier Transform (FFT) and Inverse Fast Fourier Transform (IFFT) images at different regions of cycled NCM811 using the blank electrolyte (upper) and PS-electrolyte (lower).