

# In-situ Polymerized Siloxane Cages for an Interface-Stable Gel Polymer Electrolyte in Lithium-Metal Batteries

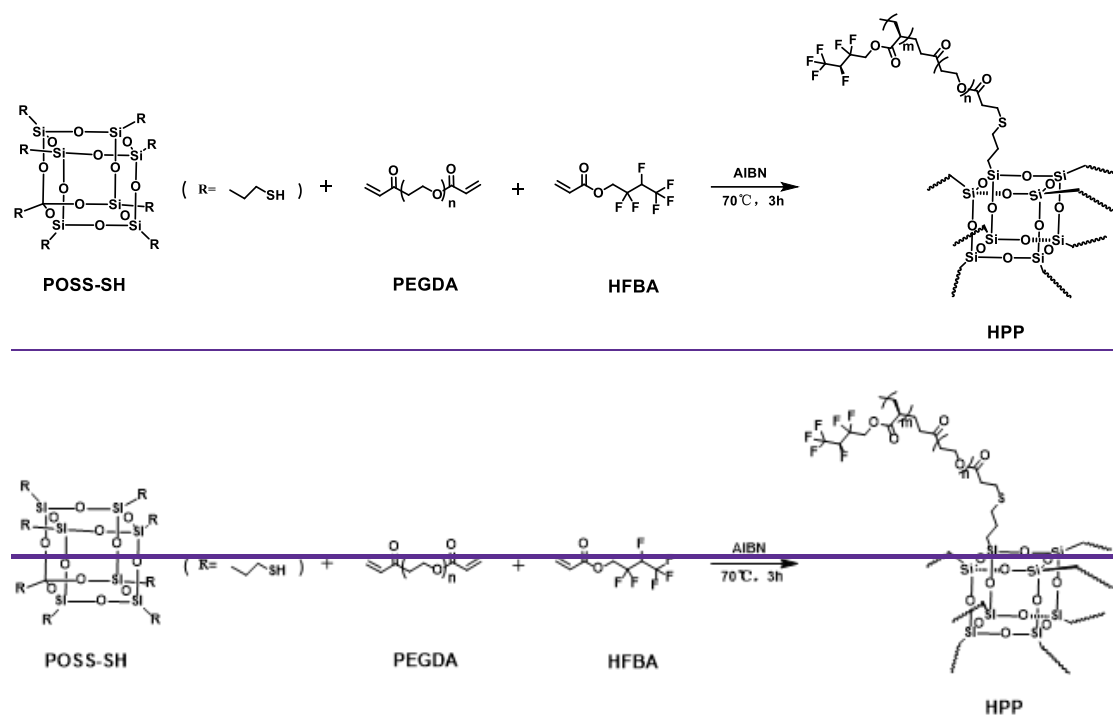
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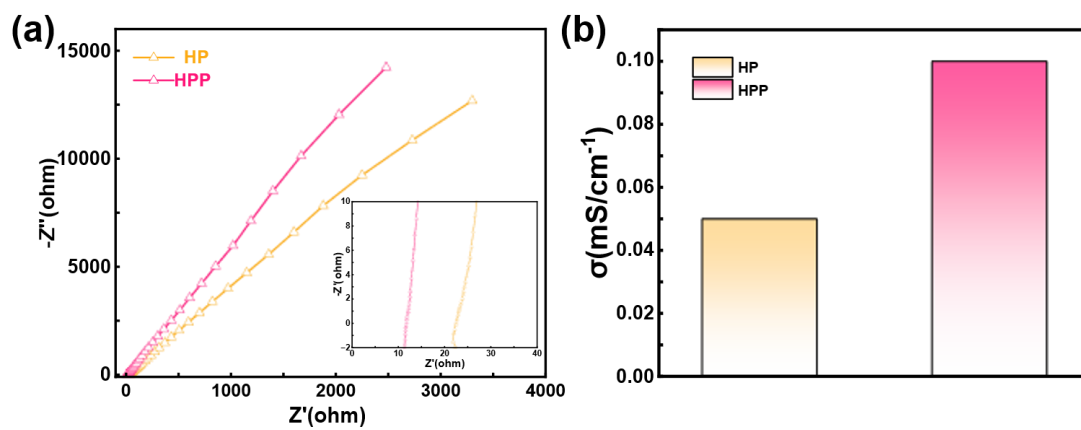
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**Figure S1** Schematic diagram of the molecular synthesis strategy for the HPP polymer.



**Figure S2** (a) Impedance spectra measured with blocking electrodes on both sides at room temperature and their magnified views.

(b) Ionic conductivities of HP and HPP polymers calculated from the impedance data.



**Figure S3** Flame retardancy performance diagrams of HPP and HP.

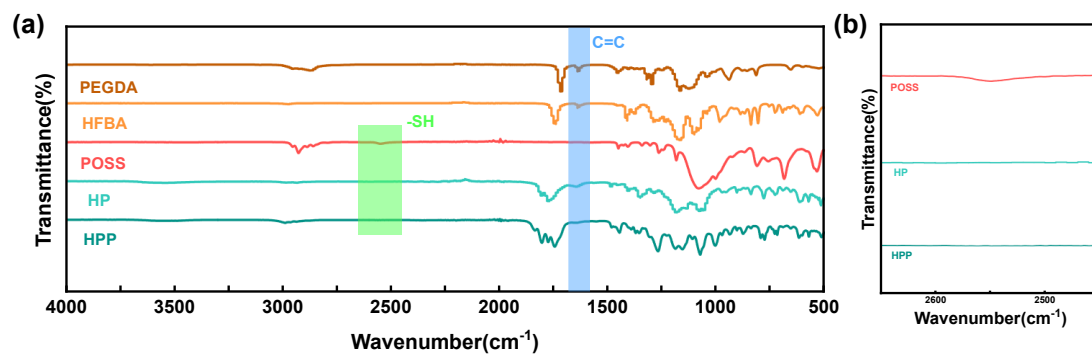


Figure S4 (a) FTIR spectra of polymer precursors and the polymers. (b) Magnified view of the thiol peak.

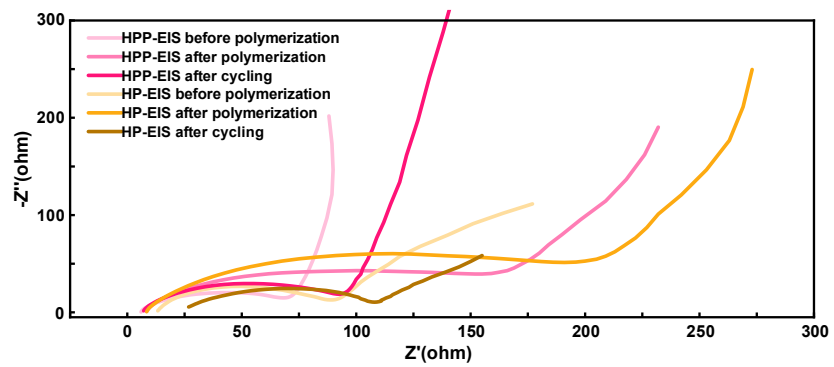
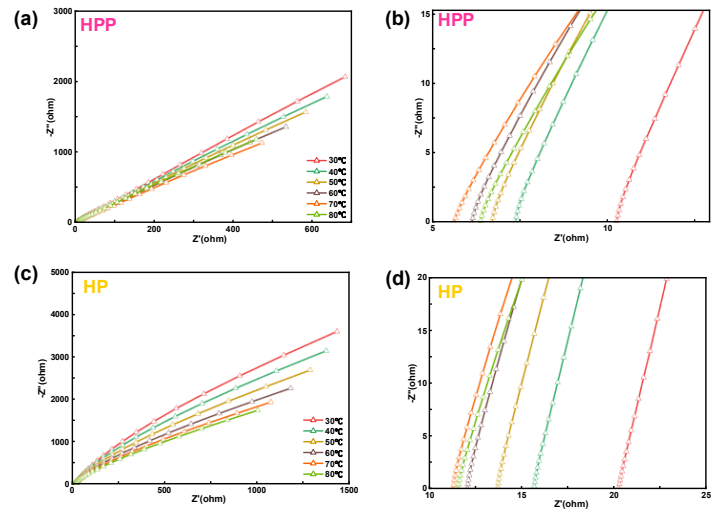
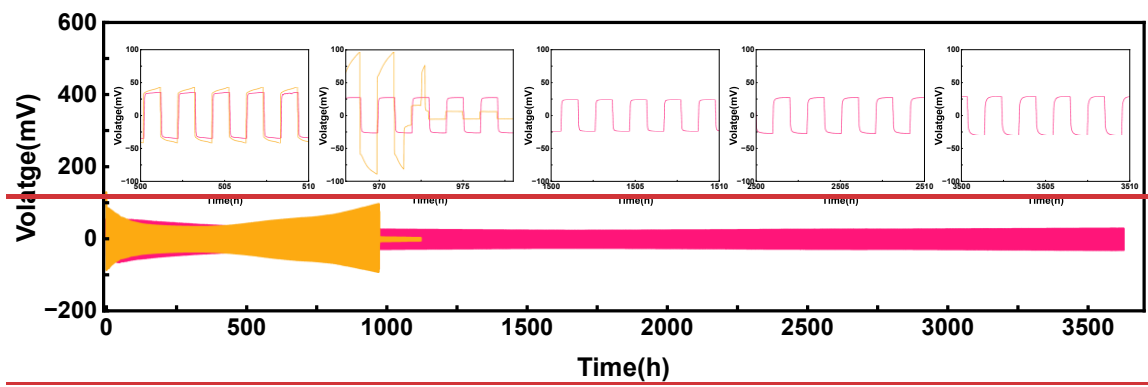
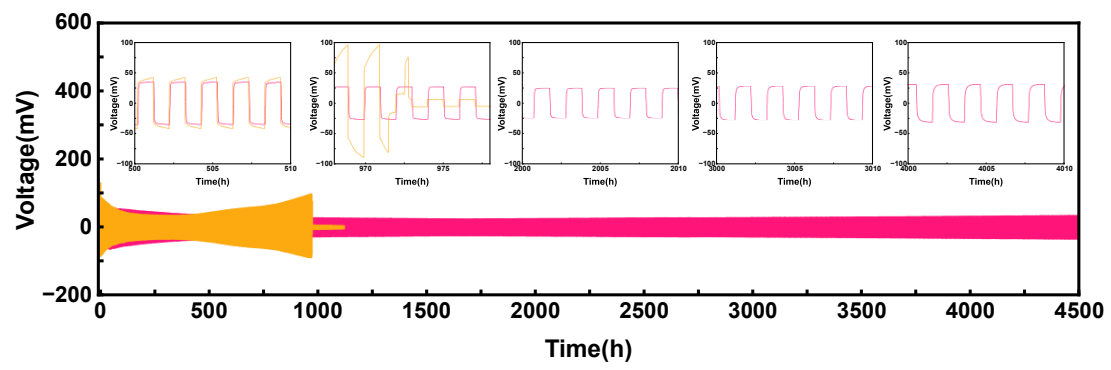


Figure S5 Impedance changes before polymerization, after polymerization, and after 200 cyclescycling.

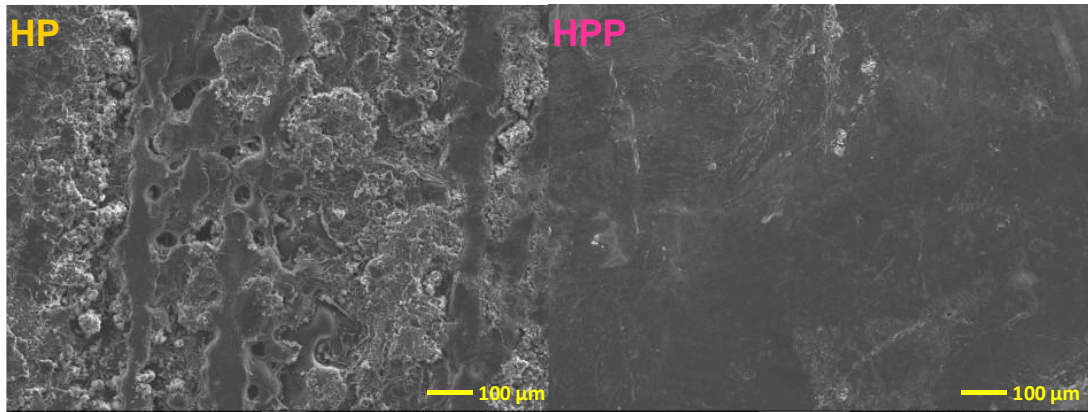


**Figure S6** Temperature-dependent impedance plots of HPP (a) and HP (c). Magnified views of HPP (b) and HP (d) impedance

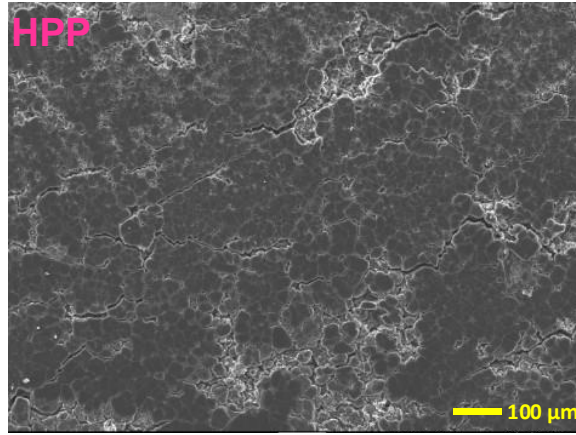
plot.



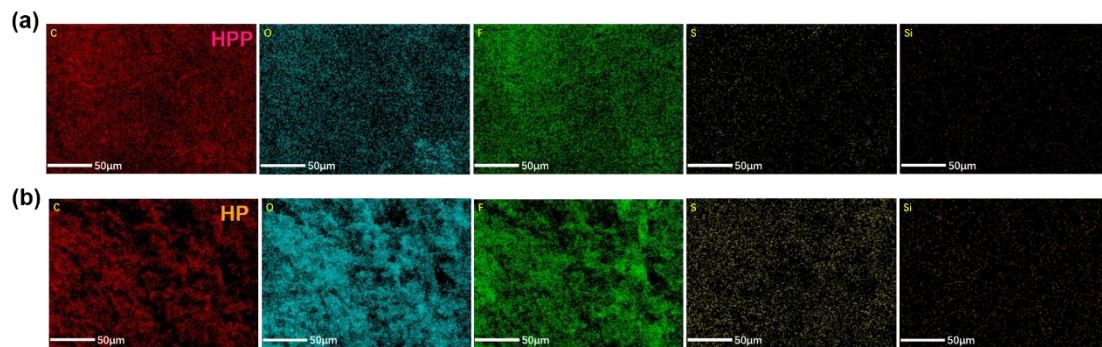
**Figure S7** Long-term cycling performance of Li||Li symmetric cells using HPP and HP. Pink curves represent HPP, and yellow curves represent HP.



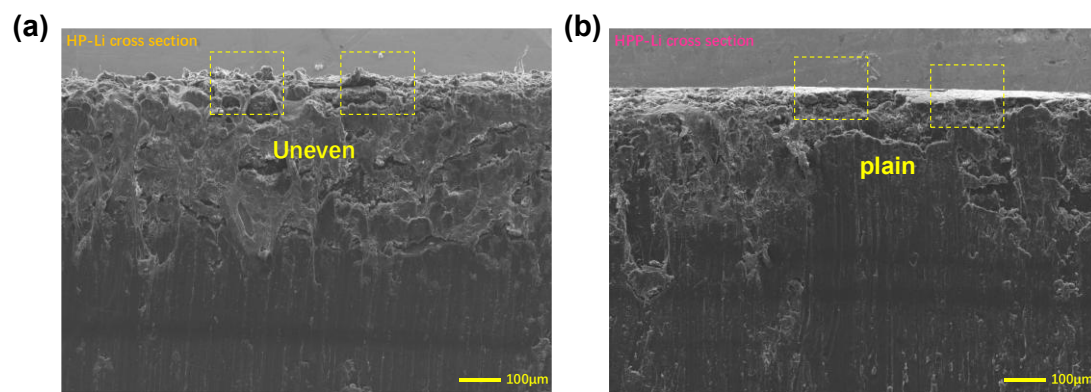
**Figure S8** SEM morphologies of the lithium metal surfaces of HP and HPP at a  $100\ \mu\text{m}$  scale.



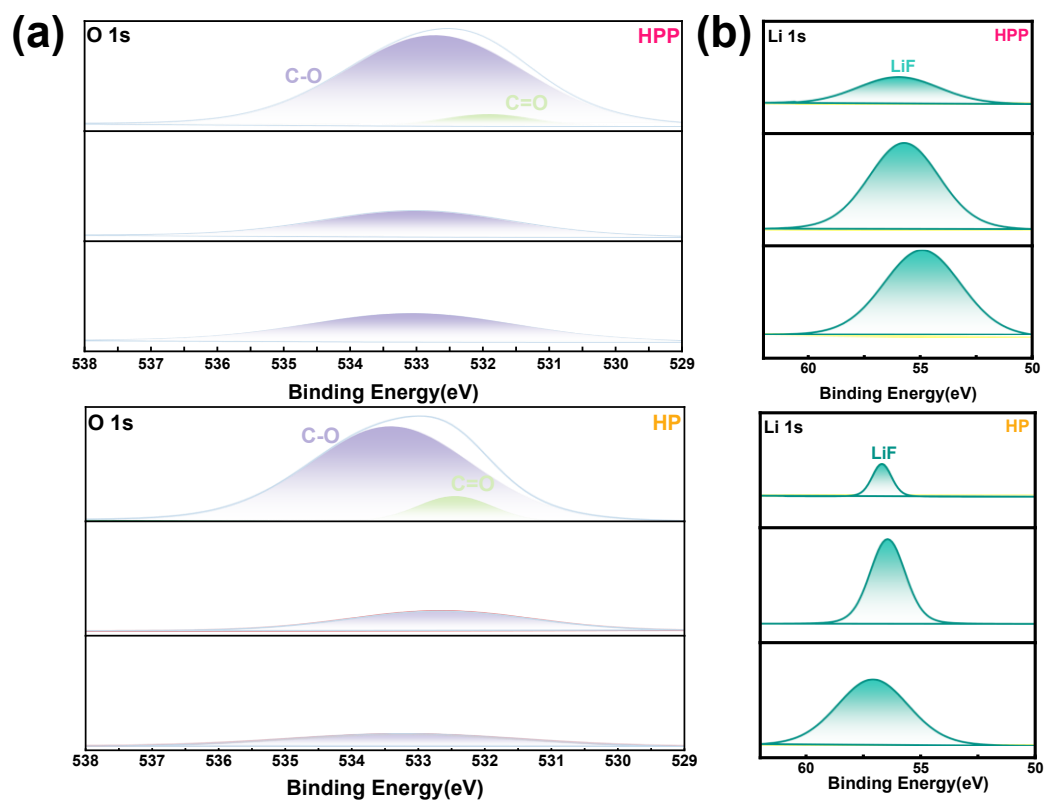
**Figure S9** SEM morphology of the most severely dendritic region on the surface of the HPP lithium metal at a 100  $\mu\text{m}$  scale.



**Figure S10** EDS spectra of C, O, F, S, and Si elements in HPP (a) and HP (b).



**Figure S11** Cross-sectional SEM images of HP (a) and HPP (b).



**Figure S12** XPS spectra of O 1s (a) and Li 1s (b) from HPP and HP symmetric cells.

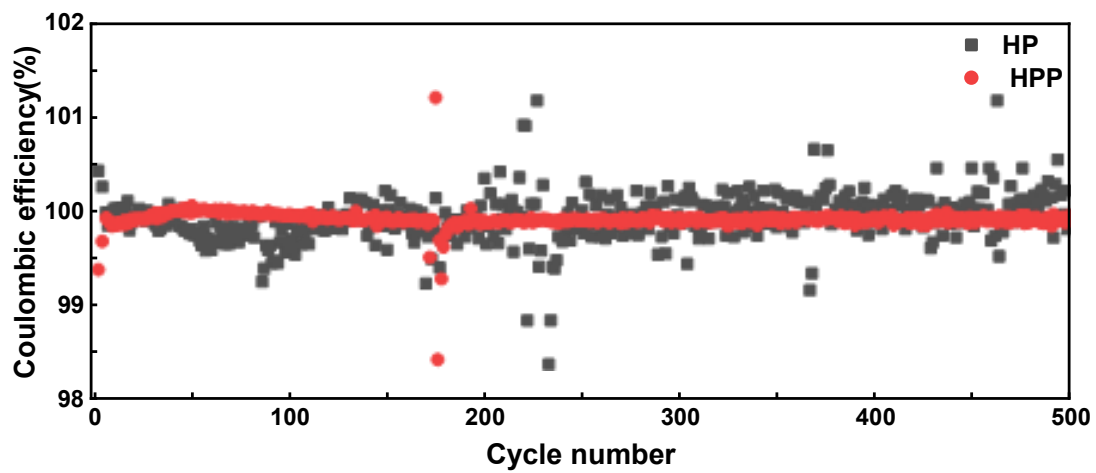


Figure S13 Coulombic efficiency of NCM811 full cells using HP and HPP electrolytes during long-term cycling at a 0.5 C rate.

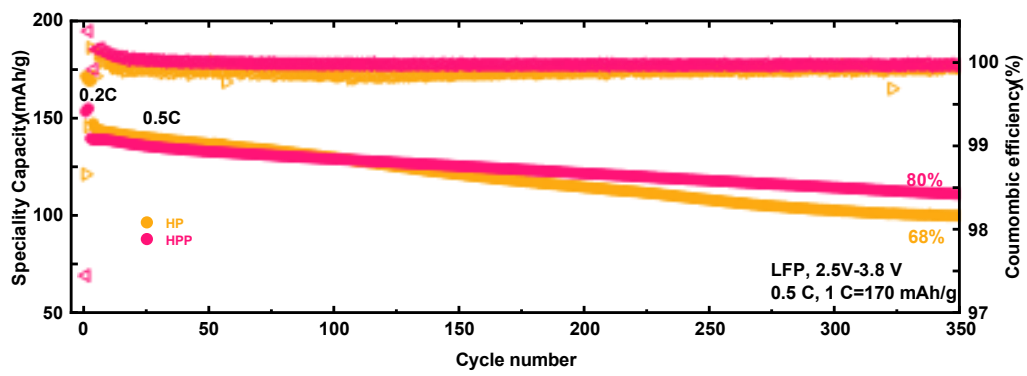
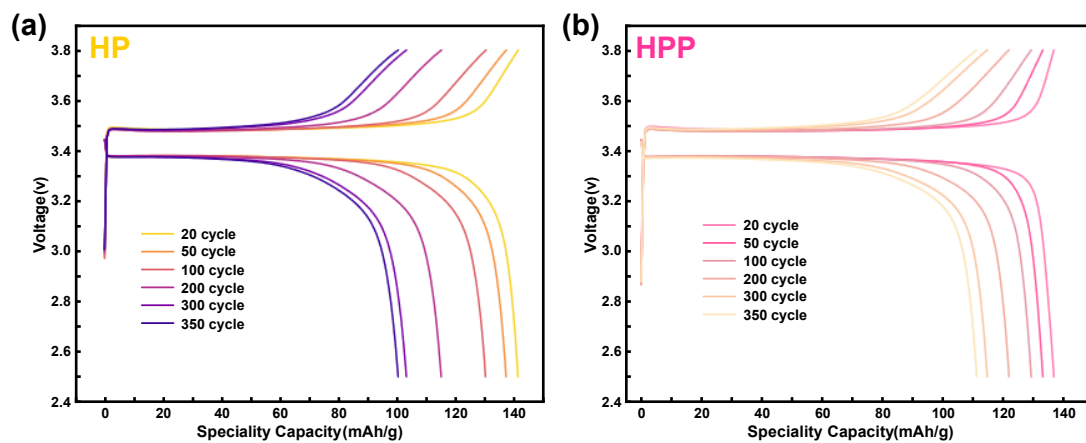
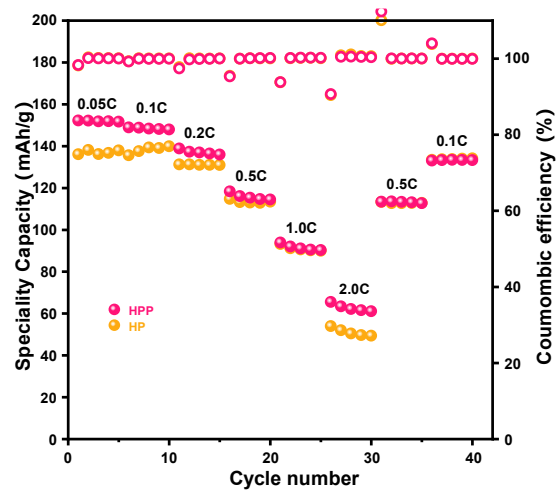


Figure S14 Comparative long-term cycling performance of LFP full cells using HP and HPP electrolytes at a 0.5 C rate.



**Figure S15** Capacity-voltage profiles of long-term cycling performance for LFP full cells using HP (a) and HPP (b) electrolytes

at a 0.5 C rate.



**Figure S16** Rate capability of HP and HPP electrolytes measured in Li||HP||LFP cells.

**Table S1** Summary of Performance for Li||GPE||NCM Batteries

GPE based LMBs	Conductivity of SPE mS cm <sup>-1</sup>	ESW V	Loading mg/cm <sup>-2</sup>	Initial discharge mAh g <sup>-1</sup>	Cutoff voltage V	Capacity retention %	Ref.
Li  HPP  NCM811	0.1@25°C	5.25	2.5	161.59	4.3	79%@500cycles	<i>This work</i>
Li  PFVS  NCM811	0.63@25°C	5.10	2.5	193.2	4.3	81.5%@100cycles	[1]
Li  PBM-IL-Li  NCM811		4.80		115.3	4.3	80%@~50cycles	[2]
Li  HGPE  NCM811	3.4@25°C	5.00	3	199.7	4.5	83.4%@300cycles	[3]
Li  POSS-DOL  NCM811	0.68@25°C	5.00		180.5	4.3	83.5%@400cycles	[4]
Li  NCM83	0.23@-10°C	4.75	2.0	183.2	4.5	85.7%@150cycles	[5]
Li  HSLE  NCM622-TPP	3.03@25°C	3.6	4.5	150	4.3	93%@100cycles	[6]
Li  ALE  NCM622	4.42@-25°C	4.9	6	200	4.3	80%@100cycles	[7]
Li  PHTGPE  NCM811	3.09@25°C	4.59		172.9	4.3	70%@400cycles	[8]
Li  MB-GPE  NCM622	1.95@25°C	5.12	2.5	157	4.3	80.1%@400cycles	[9]
Li  WSGPE    NCM811	0.4@25°C	5.05	1.6	154.8	4.3	92.5% @300cycles	[10]

## References

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