Energy Materials

Supplementary Material

Functionalized polypropylene separator coated with polyether/polyester blend for high-performance lithium metal batteries

Weixin Ye[#], Zixin Fan[#], Xingping Zhou*, Zhigang Xue*

Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China.
[#]Authors contributed equally.

***Correspondence to:** Prof. Zhigang Xue, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Luoyu Road 1037, Wuhan 430074, Hubei, China. E-mail: zgxue@mail.hust.edu.cn; Prof. Xingping Zhou, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Luoyu Road 1037, Wuhan 430074, Hubei, China. E-mail: xpzhou@mail.hust.edu.cn

EXPERIMENTAL

Materials

Poly(ethylene oxide) (PEO, Adamas, average $M_V \sim 600, 000$), poly(ε-caprolactone) (PCL, Adamas, $M_w \sim 50, 000$), lithium bis (trifluoromethanesulfony) imide (LiTFSI, Adamas, 99%), polyacrylic acid (PAA, Aladdin, average $M_w \sim 450, 000$), and lithium hydroxide monohydrate ($LiOH \cdot H_2O$, Sinopharm) were used as received. Polyvinylidene fluoride (PVDF, HSV900), $LiFePO_4$ (LFP), $LiNi_{0.8}Mn0.1Co_{0.1}O_2$ (NCM811), and carbon black powder were purchased from Saibo electrochemical material Co, Ltd. Microporous polypropylene separator (PP, SQ212F, thickness = 12 μm) was obtained from Shenzhen

Senior Technology Material Co., Ltd. A mixture of 1.0 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (EC/DMC/EMC = 1/1/1 v/v/v) (LB-002) was purchased from DoDoChem and used without further purification.

Preparation of PP separators coated with PEO/PCL blend

PEO and PCL at a constant ratio in acetonitrile (ACN) (PEO/PCL/ACN = 1/2/60 by weight) were mixed for 3 h at 80 °C to obtain the coating solution. A simple blade coating process was used to coat PEO/PCL blend to PP separators. The coated separators were firstly dried for 10 min at room temperature, then further dried in the vacuum for 24 h at 60 °C to completely remove solvent prior. The preparation of PEO-coated PP separators and PCL-coated PP separators are similar with the blended one. To investigate the effect of LiTFSI on the coating of polymers, the preparation of coating solutions was following the same procedure and at the same constituent ratio: (1) PEO/LiTFSI/ACN = 3/2.4/60 by weight (EO:Li = 8:1, molar ratio) for PEO coating solution with LiTFSI and (2) PCL/LiTFSI/ACN = 3/1/60 by weight (CL:Li = 8:1, molar ratio) for PCL coating solution with LiTFSI.

Fabrication of Li||LFP, Li||NCM811 cells

The $LiFePO_4$ (LFP) cathode was prepared by casting a slurry of $LiOH{\cdot}H_2O$, PAA, LFP, and carbon black (CB) in deionized water (LFP:PAALi:CB = 8:1:1, weight ratio) on the Al foil. The obtained cathodes were further dried in the vacuum for 24 h at 60 °C and cut into 16 mm diameter. The NCM811 cathodes were prepared with a similar method by using PVDF as the binder, as well as *N*-methyl-2-pyrrolidone (NMP) as the solvent. Li

plates (diameter of 15 mm and thickness of 1 mm) were used as the anodes. The commercial electrolyte was injected into the separator and assembled coin cells (CR2032). The theoretical specific capacities (1C) of LFP and NCM811 cathodes are 170 and 190 mA h g^{-1}, respectively. Besides, the mass loading of the active material is 2 ~ 3 mg cm^{-2}.

Electrochemical measurements

The temperature-dependance ionic conductivity profiles of PP separator and various coated separators were measured by Autolab PGSTAT302N (Netherlands) from 30 to 80 °C. The linear sweep voltammetry (LSV) method with a scan rate of 1 mV s^{-1}, frequency range of 10^{-1} ~ 10^{6} Hz, and the voltage range from 0 to 7 V was used to test the electrochemical stability window (versus Li^+/Li) of coin cells assembled with the stainless steel (SS) and lithium metal at 60 °C. The lithium deposition performance of symmetrical Li||Li cell was charged-discharged with a current density of 0.5 mA cm^{-2}. The cell cycling and charge-discharge rate performance of Li||LFP cells (CR2032) was tested by LAND CT2001A (Wuhan Land Electronics Co. Ltd., China) at room temperature from 2.5 to 4.2 V. The lithium-ion transference number (t_{Li^+}) of Li symmetric cells of various coated separators were measured by potentiostatic polarization method with the voltage of 10 mV, and the value of t_{Li^+} was calculated by the following equation:

$$t_{Li^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

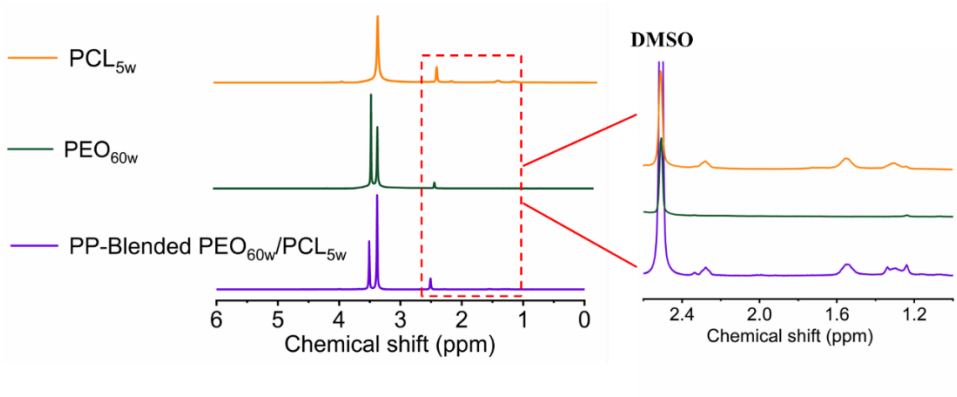
where I_0 and I_S are the initial currents and the steady-state currents, respectively, and ΔV is the polarization voltage. R_0 and R_S are the bulk resistance and the interfacial resistance measured by EIS before and after the potentiostatic polarization.

Material characterization

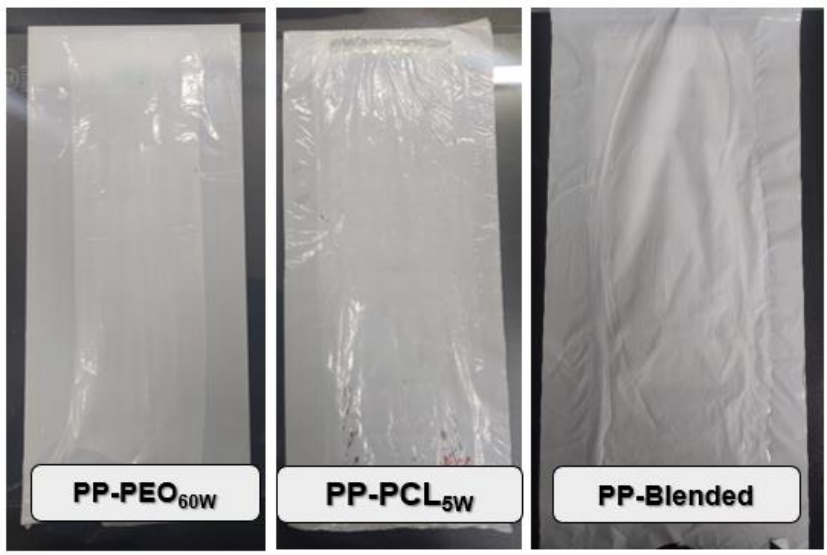
The coated separators were tested by Fourier transform infrared spectroscopy (FTIR) spectra with ATR mode of the FT interferometer (Equinox 55, Bruker, Germany) over the range of 4000 to 500 cm^{-1}. The PEO_{60W}, PCL_{5W} and PP-blended PEO_{60W}/PCL_{5W} separator were tested by Nuclear Magnetic Resonance (NMR, Bruker AV400, DMSO-d_6 as the solvent). N_2 adsorption/desorption measurements were conducted using ASAP2460-4MP automatic surface area and pore analyzer at a degassing temperature of 60 °C. An electronic universal testing machine (UTM2103) was used to test the mechanical properties of separators. The thermal stability of coated separators was also carried out by a thermogravimetric analyzer (TGA, 4000 PerkinElmer, USA) from 30 to 800 °C (10 °C min^{-1}). The surface morphology of separators and LFP cells were visualized by scanning electron microscopy (SEM, Nova NanoSEM 450, 5.0 kV). Contact angles of separators were tested by Optical contact angle measuring instrument (OCA20, Datapphysics). In order to test separator shrinkage at high temperature, the separators are heated at 120 °C for an hour. The thermal shrinkage ratio was calculated by the following equation:

$$\text{Thermal shrinkage ratio (\%)} = \frac{A_i - A_f}{A_i} \times 100\%$$

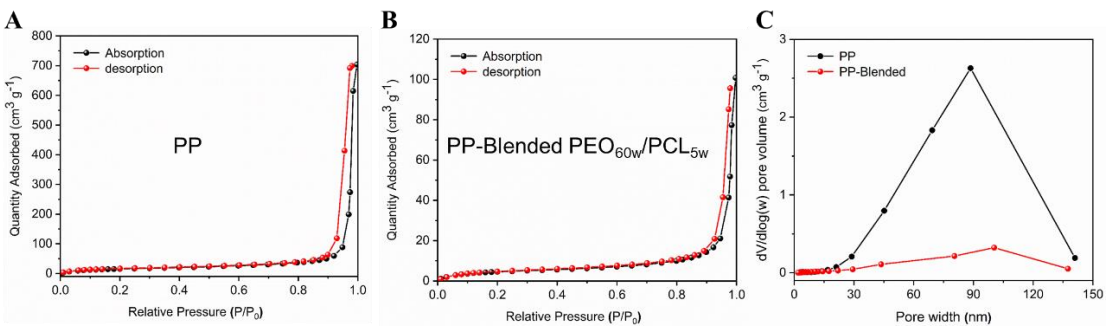
The variables A_i and A_f indicate the separator areas before and after high temperature storage, respectively.



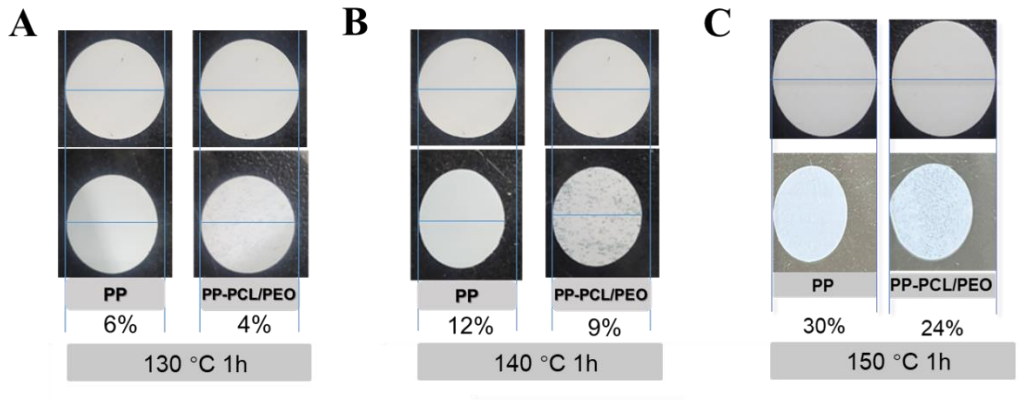
Supplementary Figure 1. ^{1}H NMR spectra (400 MHz, DMSO-d_6) of PCL_{5w}, PEO_{60w} and PP-Blended PEO_{60w} /PCL_{5w} separator.



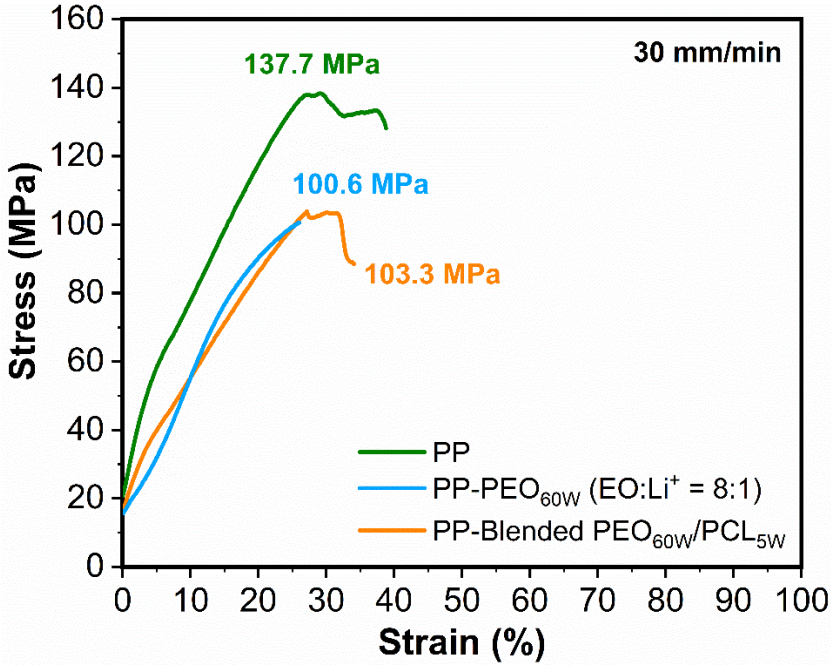
Supplementary Figure 2. Coating states of PEO_{60w}, PCL_{5w}, blended PEO_{60w} /PCL_{5w}.



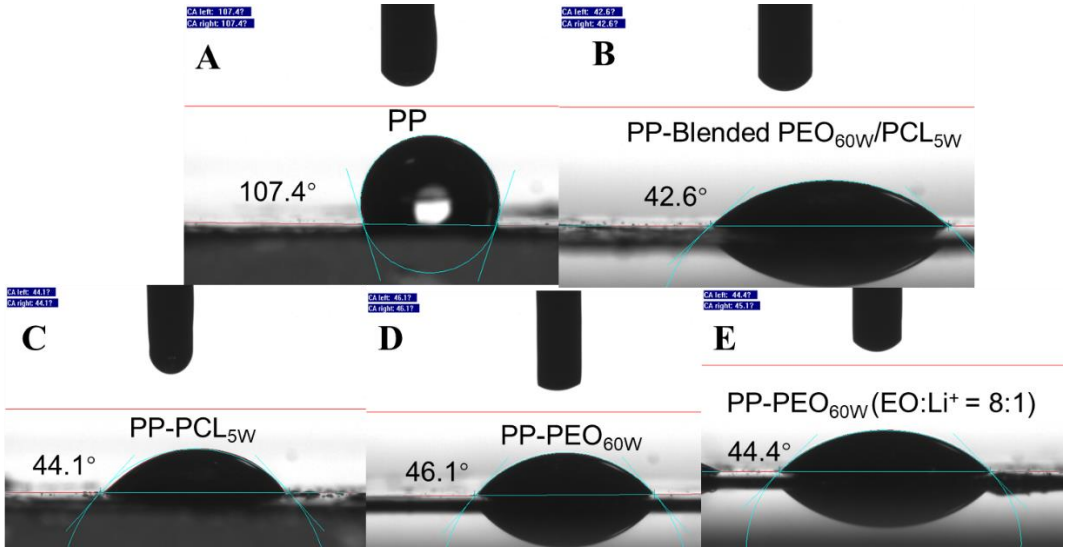
Supplementary Figure 3. N_2 adsorption/desorption isotherms of PP (A) separator and PP-Blended PEO_{60w}/PCL_{5w} separator (B); (C) Pore size distributions of the PP and PP-Blended PEO_{60w}/PCL_{5w} separators.



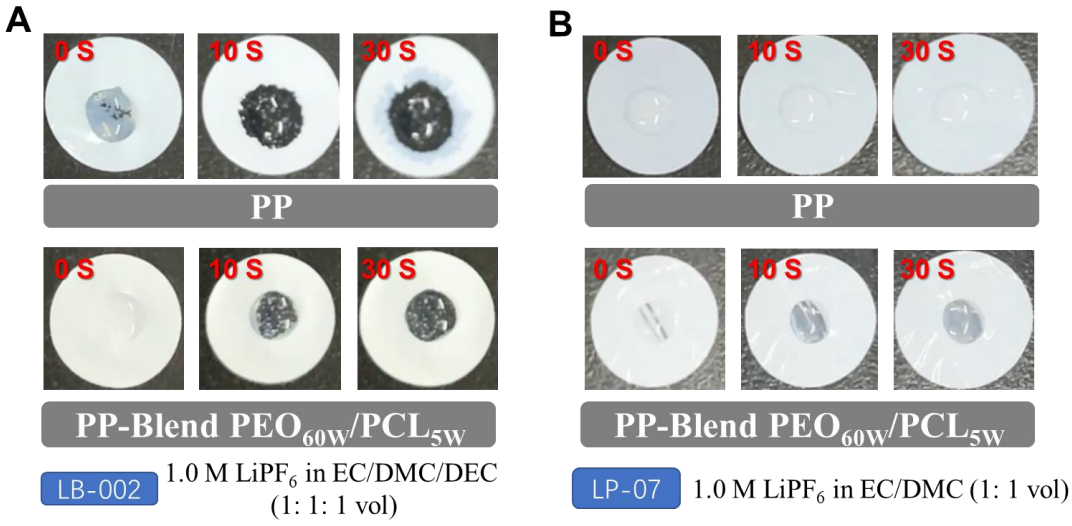
Supplementary Figure 4. Thermal shrinkage of PP and PP-Blended PEO_{60w}/PCL_{5w} separators exposed at 130 °C (A), 140 °C (B), 150 °C (C) for an hour.



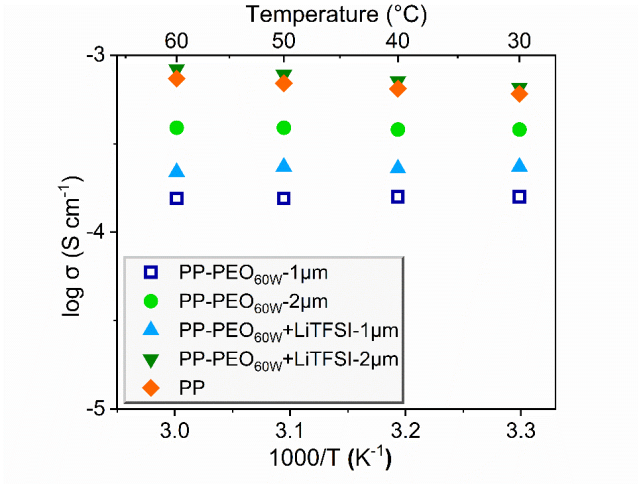
Supplementary Figure 5. Stress–strain behavior of PP, PP-PEO_{60w} (EO:Li^+ = 8:1) and PP-blended PEO_{60w}/PCL_{5w} separators at 30 mm min^{-1}.



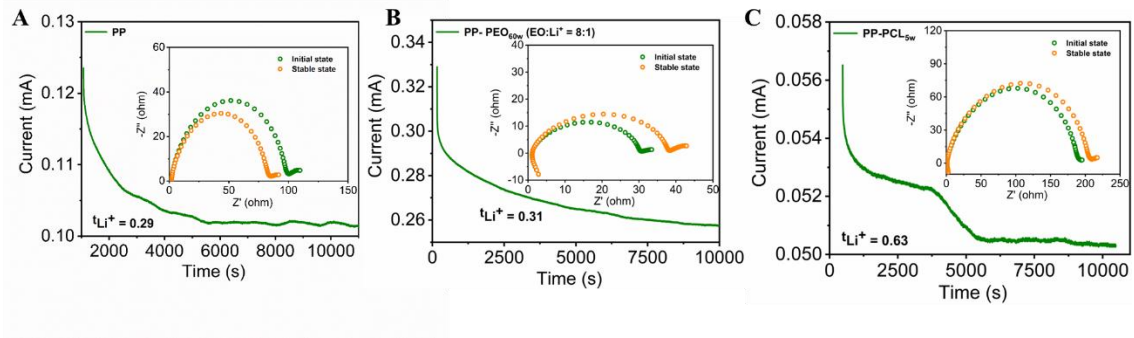
Supplementary Figure 6. The contact angles between the H_2O and PP separator (A), PP-Blended PEO_{60W}/PCL_{5W} separator (B); The contact angles between the electrolyte and PP-PCL_{5W} separator (C), PP-PEO_{60W} separator (D) and PP-PEO_{60W} ($EO:Li^+$ = 8:1) separator (E).



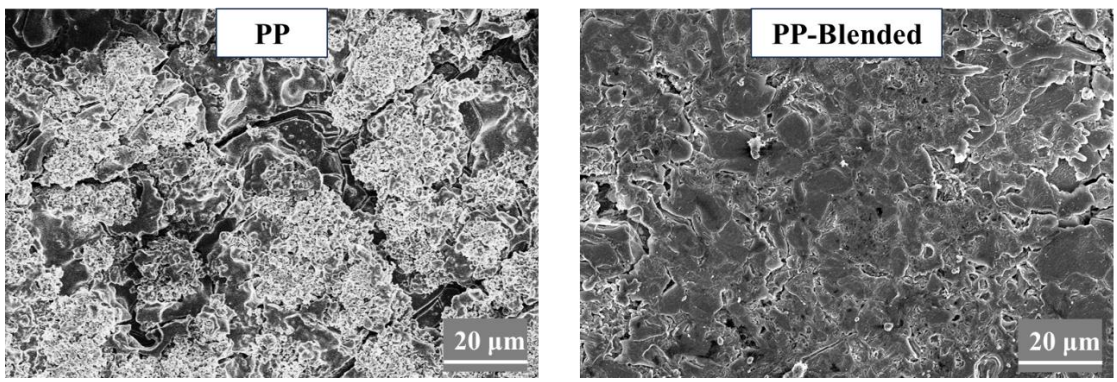
Supplementary Figure 7. The wettability of PP and PP-Blend PEO_{60W}/PCL_{5W} separators with different electrolytes: (A) LB-002; (B) LP-07.



Supplementary Figure 8. Temperature dependence of ionic conductivity of PP, PP-PEO_{60w}-1 μm and 2 μm, PP-PEO_{60w}+LiTFSI-1 μm and 2 μm separators.



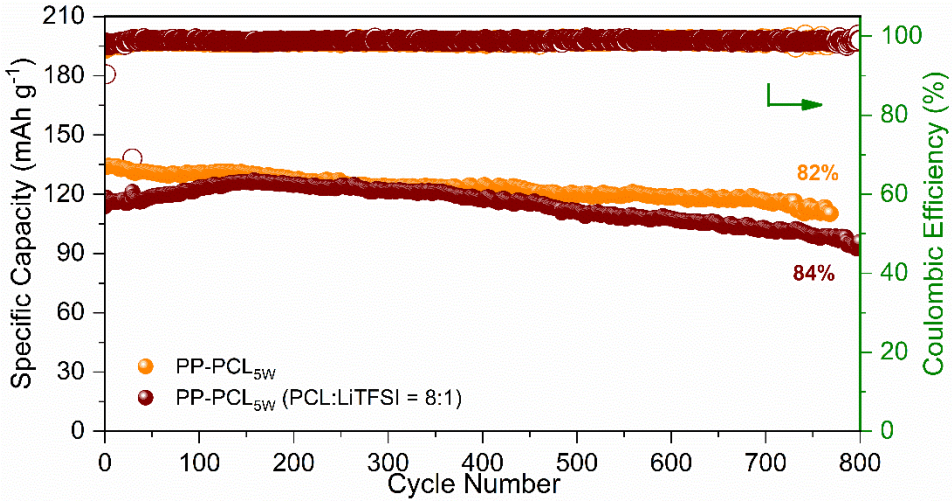
Supplementary Figure 9. Chronoamperometry profile of the Li/Li symmetric cells with PP (A), PP-PEO_{60w} ($EO:Li^+ = 8:1$) (B) and PP-PCL_{5w} separators (C) under a polarization potential of 10 mV and the EIS before and after the polarization (insert).



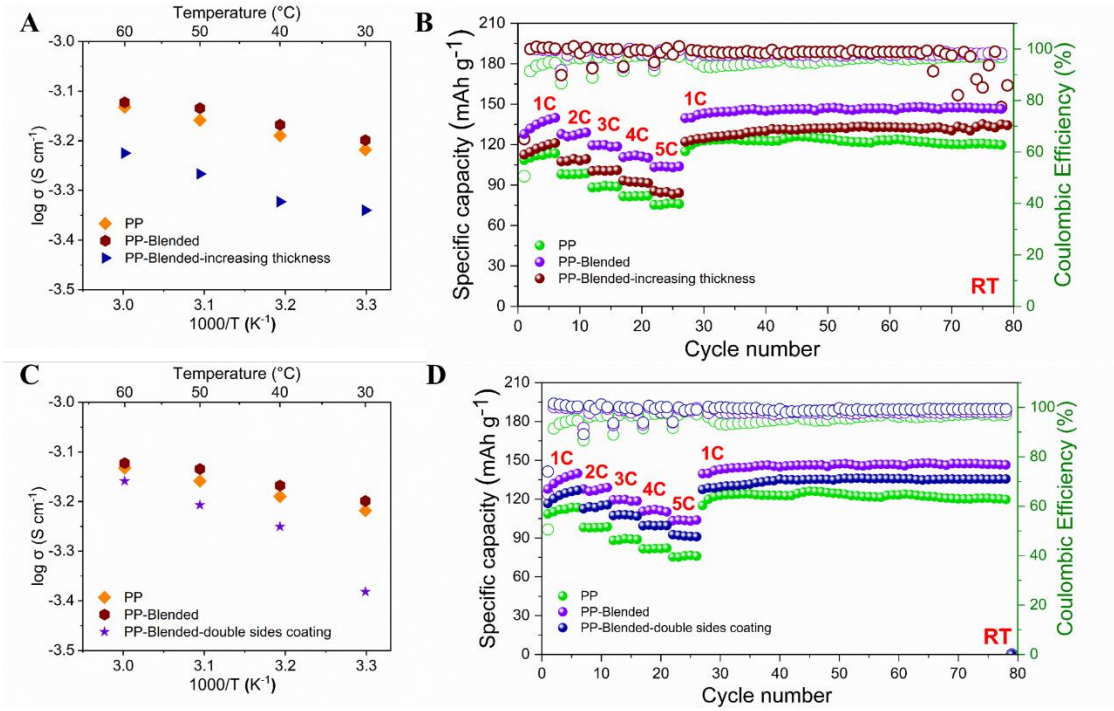
Supplementary Figure 10. Top-view SEM images of Li anode assembled with PP separator (A) and PP-Blended PEO_{60w}/PCL_{5w} (B) separator after lithium plating/striping for 100 h at 0.5 mA cm^{-2}.

Supplementary Table 1. The t_{Li^+} with different coating materials.

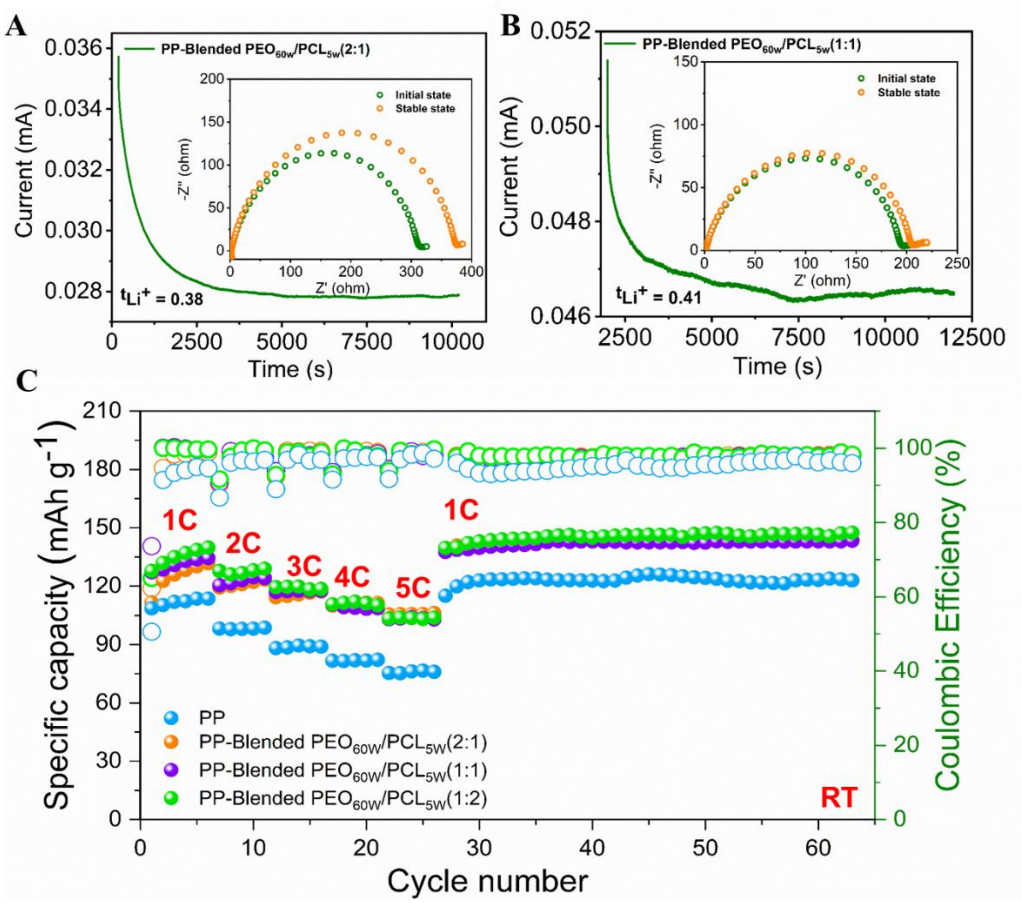
Entry	Coating materials	t_{Li^+}	Ref
1	PEO+PAA+PEI	0.48	DOI:10.1021/acssuschemeng.7b02502
2	TA/PEI	0.44	DOI:10.1016/j.electacta.2018.03.099
3	TiO_2	0.5	DOI:10.1016/j.apsusc.2020.148661
4	PVDF+LLZTO	0.66	DOI:10.1016/j.ensm.2019.12.022
This work	PEO/PCL	0.46	
This work	PCL	0.63	



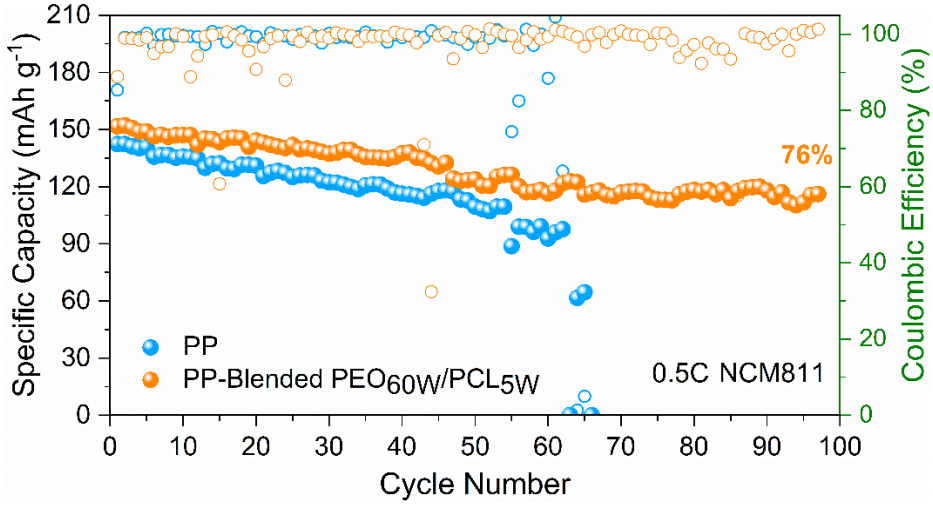
Supplementary Figure 11. Cycle stability of the cells with PP-PCL_{5w} separator and PP-PCL_{5w} (PCL:LiTFSI = 8:1) separator.



Supplementary Figure 12. (A) Temperature dependence of ionic conductivity of PP, PP- PP-Blended and PP-Blended-increasing thickness separators; (B) C-rate capability of the cells with PP, PP-Blended and PP-Blended-increasing thickness separators; (C) Temperature dependence of ionic conductivity of PP, PP- PP-Blended and PP-Blended-double sides coating separators; (D) C-rate capability of the cells with PP, PP-Blended and PP-Blended-double sides coating separators.



Supplementary Figure 13. Chronoamperometry profile of the Li/Li symmetric cells with PP-blended PEO_{60w}/PCL_{5w} (2:1) separator (A) and PP-blended PEO_{60w}/PCL_{5w} (1:1) separator (B) under a polarization potential of 10 mV and the EIS before and after the polarization (insert); (C) C-rate capability of the cells with PP, PP-blended PEO_{60w}/PCL_{5w} (2:1), PP-blended PEO_{60w}/PCL_{5w} (1:1) and PP-blended PEO_{60w}/PCL_{5w} (1:2) separators.



Supplementary Figure 14. Cycle stability of the cells with PP and PP-blended PEO_{60w}/PCL_{5w} separators paired with NCM811 cathode.

Supplementary Table 2. Performance comparation of different coating materials.

Entry	Coating materials	Basement separator	σ (mS cm^{-1} RT)	Capacity (RT 1C)	Capacity retention rate （1C）	Ref
1	PEO+OPIC	PE	-	134.4 mAh·g^{-1} (Li/LFP)	76.2% after 200 cycles	DOI:10.1016/j.matlet.2022.133511
2	PEO+DAPTMS +polycatechol	PE	1.17	124.5 mAh·g^{-1} (Li/LCO)	82% after 300 cycles	DOI:10.1016/j.memsci.2020.118886
3	PI	PP	0.36	172.3mAh·g^{-1} (Li/NCM)	80.1% after 200 cycles	DOI:10.1016/j.cej.2022.136314
4	PVDF	PP	0.59	133 mAh·g^{-1} (Li/LCO)	99.1% after 50 cycles	DOI:10.1016/j.jelechem.2017.01.016
This work	PEO/PCL	PP	0.63	144 mAh·g^{-1} (Li/LFP)	77% after 800 cycles	
This work	PCL	PP	0.59	134 mAh·g^{-1} (Li/LFP)	80% after 800 cycles	