Supplementary Data

Polymeric ionic conductor networks enable stable cycling of high-voltage lithium metal batteries using solid-state poly-ether electrolytes

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Table S1. Summary of parameters and chemical performance of the cathodes including the cells in this work and in previous reports.

Battery Engineering	Cathode||Li	Electrolyte Composition	LSV	Performance Cycle number–Retention Rate	Ref.
YSZ filler	NCM622||Li 2.8–4.3 V 2.8–4.6 V	LiTFSI+$LiPF_6$__DOL+YSZ (YSZ CSE)	5.6 V	800th–74% (0.5C) 60th–90% (0.5C)	1
Solvent reconstruction	NCM622||Li 3.0–4.6 V	LiFSI__DOL+LiTFSI+TTE (Hybrid-DOL/PDOL-TTE)	4.7 V	100th–88.1% (0.12C)	2
Dual–interface CEI/SEI	NCM811||Li 2.8–4.3 V NCM622||Li 2.8−4.3/4.5 V, 45 ℃	$LiPF_6$+LiTFSI+LiDFOB+$LiBF_4$__DOL	4.6 V	120th–83.1% (0.2C) 200th–82.8% (0.2C–4.3 V) 120th–86.4% (0.2C–4.5 V) 100th–86.7% (0.2C–4.5 V, 45 ℃)	3
In situ gelation	NCM622||Li 2.8–4.3 V	LiTFSI+$LiPF_6$__DME/DOL	4.6 V	100th–90.1% (0.1C)	4
TB additives	NCM622||Li 3.0–4.3 V	LiTFSI__DOL+TFB (TB–PDE)	4.8 V	200th–80% (0.5C)	5
Crosslinked polymer	NCM811||Li 2.8–4.3 V	LiTFSI__DOL/TTMAP+TFB (PTADOL)	4.6 V	150th–81.4% (0.5C)	6
LiDFOB additives	NCM622||Li 2.8–4.3 V	$LiPF_6$__EC/DEC/DMC/DOL+LiDFOB (ACPN)	–	CE~99.5% (0.2C) 200th–86% (0.5C) 120th–88.5% (1C)	7
Substrate assisted	NCM622||Li 2.8–4.3 V	LiTFSI+$LiPF_6$__DOL	5.0 V	300th–85%+(0.5C)	8
$LiPF_6$–coated separator	NCM811||Li 2.8–4.2/4.3 V	LiTFSI__DME/DOL+$LiPF_6$ coated separator (BSPE)	4.4 V	55th–99.8% (0.3C) 55th–81.3% (0.3C)	9
Nano–hierarchical	LCO||Li 3.0–4.25 V NCM811||Li 3.0–4.25 V	LiTFSI__DOL+AlI_3+$LiPF_6$+LiDFOB (SPEE)	5.7 V	200th–91.7% (0.5C) CEs>99% (0.2C)	10

Copolymer	LCO‖Li 4.2 V	LiTFSI/LiDFOB__DOL/TXE/SN (SN–CPE)	5.1 V	50th–86.4% (0.2C) ~99%	11
Hybrid solid/liquid electrolyte	(TPP mixed–) NCM622‖Li 2.8–4.2 V	$LiPF_6$__DOL/EC/DEC/DMC (HSLE)	4.6 V	100th–93% (0.5C)	12
$Al(OTf)_3$ additives	NCM622‖Li 3.0–4.2 V	LiTFSI__DOL+$Al(OTf)_3$	–	5th–96.5% (0.2C)	13
Crosslinked network	NCM811‖Li 2.8–4.2 V	LiTFSI__DOL/TMSO+TFB (PSiDOL)	5.1 V	100th–90% (0.3C)	14
Dual–function additive	LCO‖Li 3.0–4.2 V	LiTFSI__DOL+$Sn(OTf)_2$ (PDOL GPE)	4.4 V	100th: no obvious fade	15
High stable ionic conductor network”	**LCO‖Li 3.0–4.6 V 3.0–4.5 V**	**LiTFSI+$LiPF_6$__DME/DOL**	**5 V+**	**100th / 300th– 80.62% / 66.93% (0.5C–4.6 V) 600th–79.83% (0.5C–4.5 V)**	**This work**

Notes: Full name of additives for the Abbreviation in Table S1:

TFB: tris(pentafluorophenyl)borane

TPP: triphenylphosphine

TTMAP: trimethylolpropane tris[3-(2-methyl-1-aziridine) propionate]

TXE: 1,3,5-trioxane(trioxymethylene)

SN: succinonitrile

YSZ: yttrium stabilized zirconia

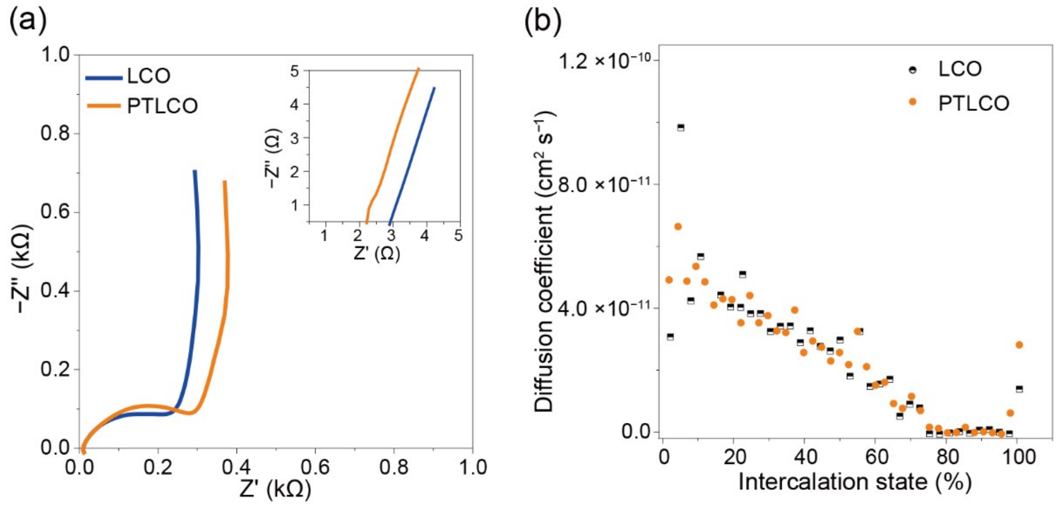

Fig. S1. Electrochemical properties. (a) EIS spectra of LCO||Li with different electrolytes. (b) Li^+ diffusion coefficient in the cathode during discharging from GITT versus intercalation state.

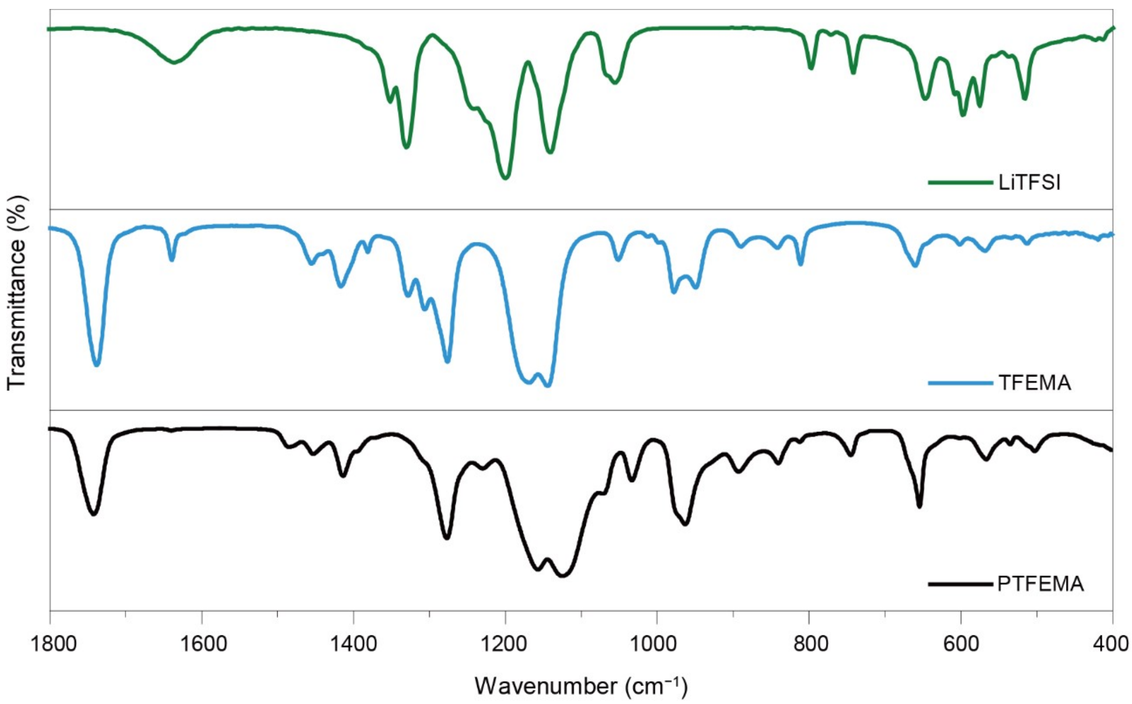

Fig. S2. FTIR spectra of LiTFSI, TFEMA, and PTFEMA.

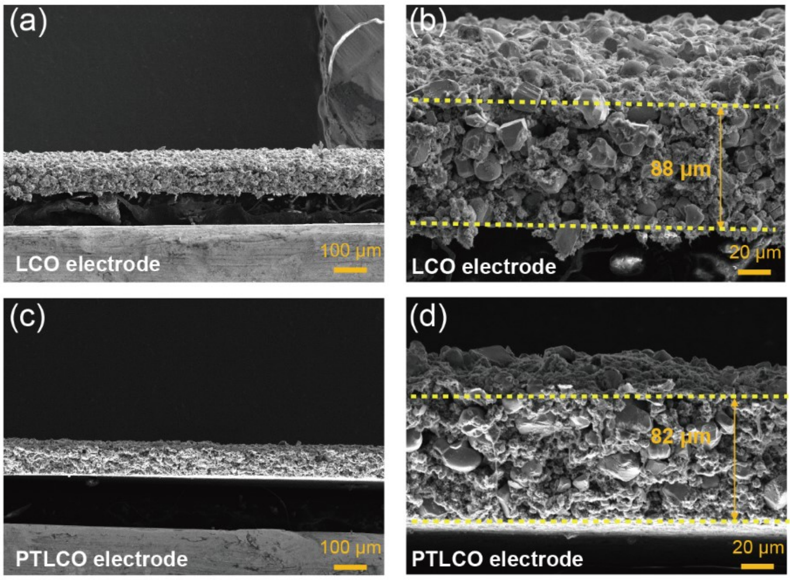

Fig. S3. Cross-sectional SEM images of the (a,b) LCO electrode and (c,d) PTLCO electrode without the Al current collector.

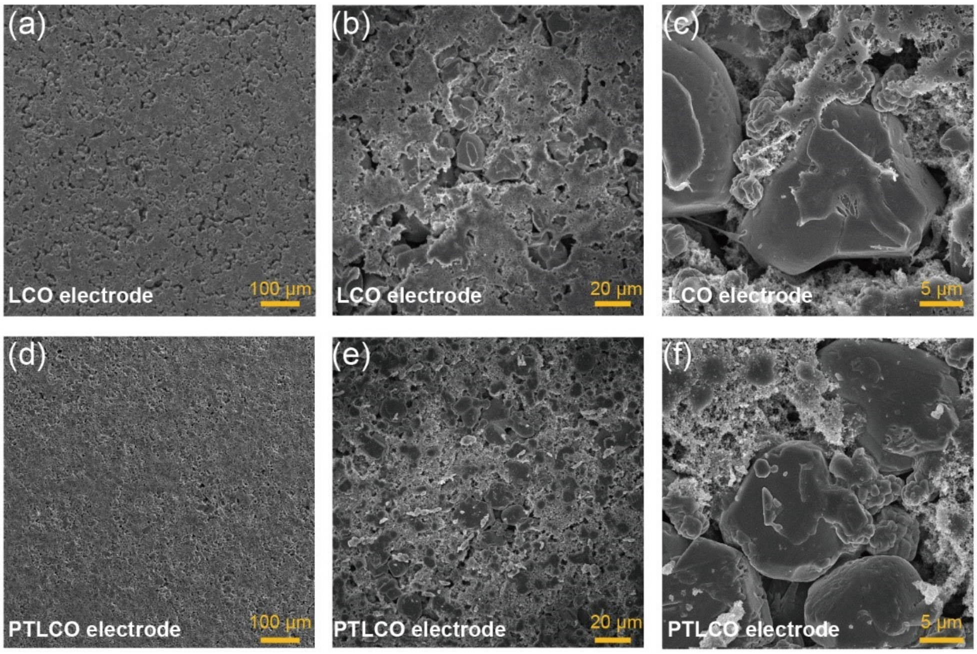

Fig. S4. SEM images from the bottom side of the (a–c) bare LCO electrode and (d–f) PTLCO electrode without the Al current collector.

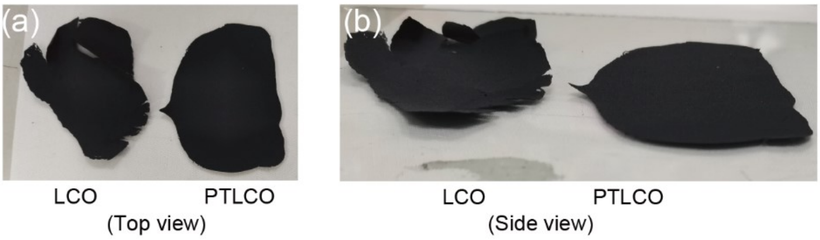

Fig. S5. Digital photos of the electrode removed from glass plate from (a) top view and (b) side view.

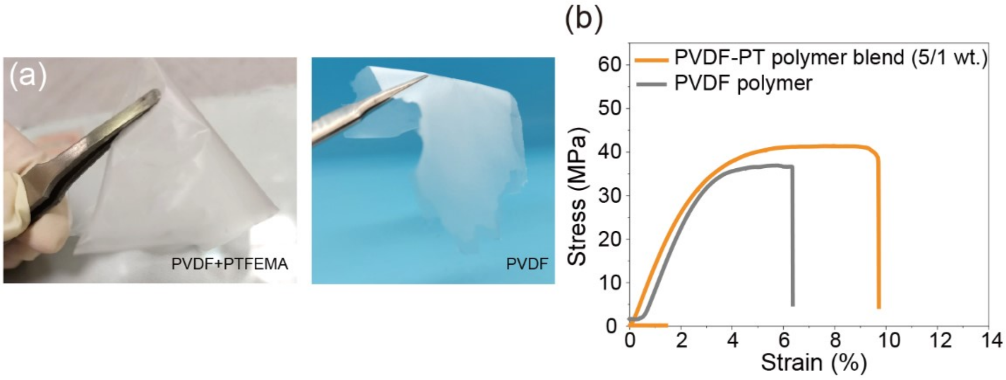

Fig. S6. Mechanical properties of the PVDF and PVDF-PT products. (a) Digital photos of polymer membranes. (b) Tensile stress-strain curves.

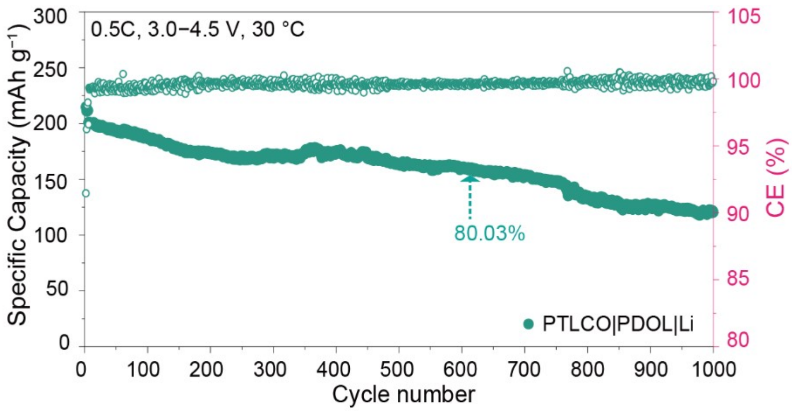

Fig. S7. Long-term cycling performance at 0.5C with a voltage range of 3.0 to 4.5 V.

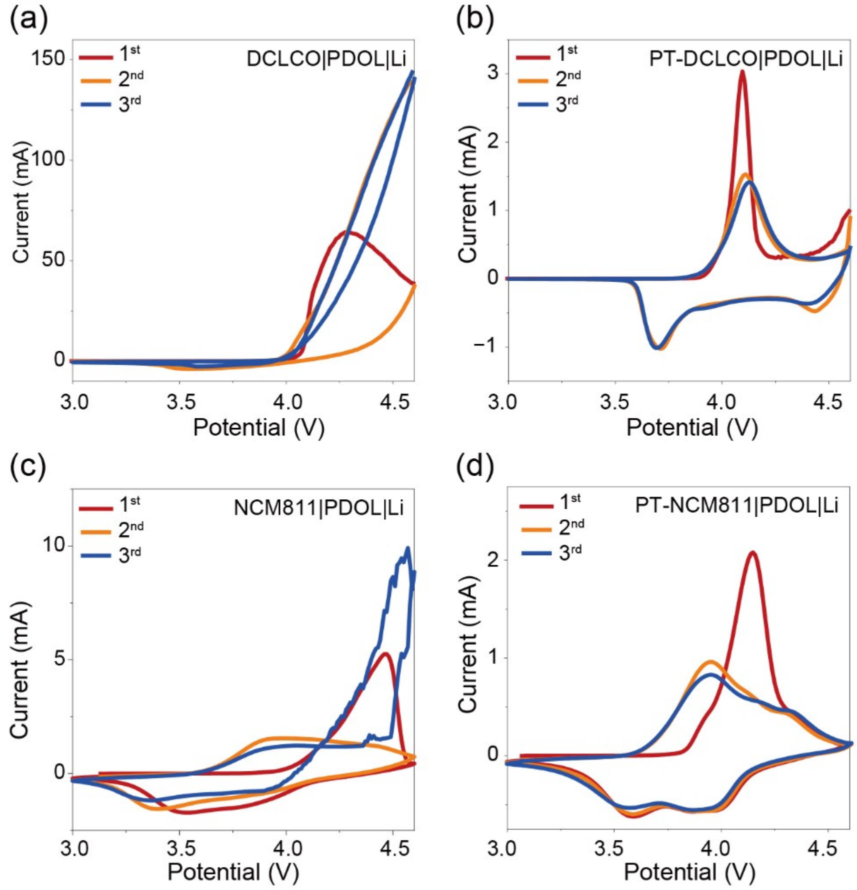

Fig. S8. CV curves for half-cell with PDOL electrolyte at the scan rate of 0.3 mV s^{-1}, with a voltage range of 2.8 to 4.6 V: a) polycrystalline LCO, b) modified polycrystalline LCO, c) NCM811, d) modified NCM811.

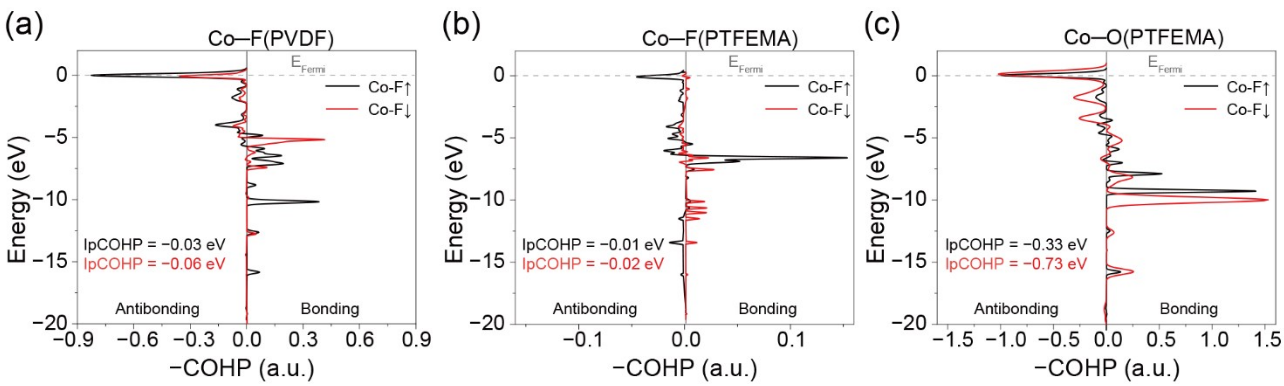

Fig. S9. Corresponding COHP. COHP Between Co *d* orbitals and (a) F(PVDF), (b) F(PTFEMA), (c) O(PTFEMA).

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