Supplementary Information

Phytate Lithium as Multifunctional Additive Stabilizes $LiCoO_2$ to 4.6 V

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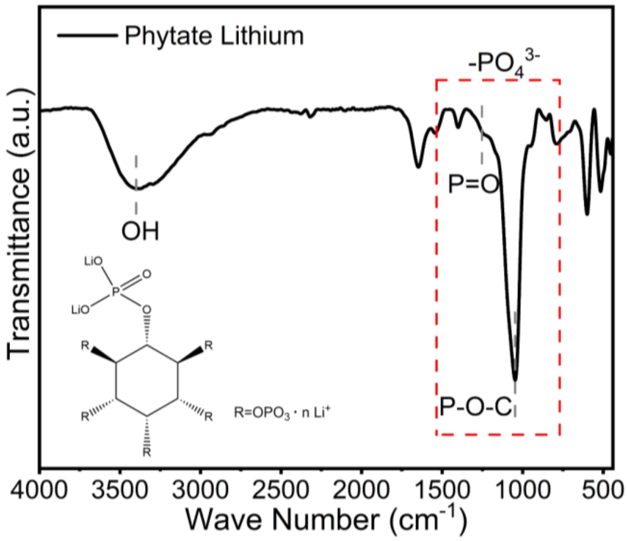

Fig. S1 The Fourier transform infrared spectrum and inserted chemical structure of phytate lithium.

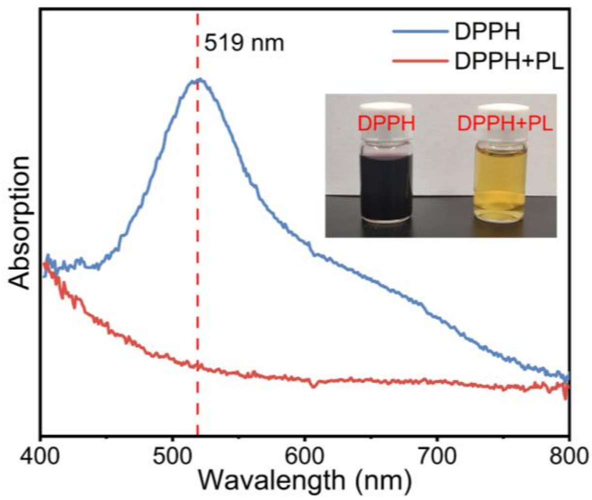

Fig. S2 The color fading (inserted) and corresponding UV absorbance spectra of DPPH (characteristic peak at 519 nm) and DPPH+PL solutions.

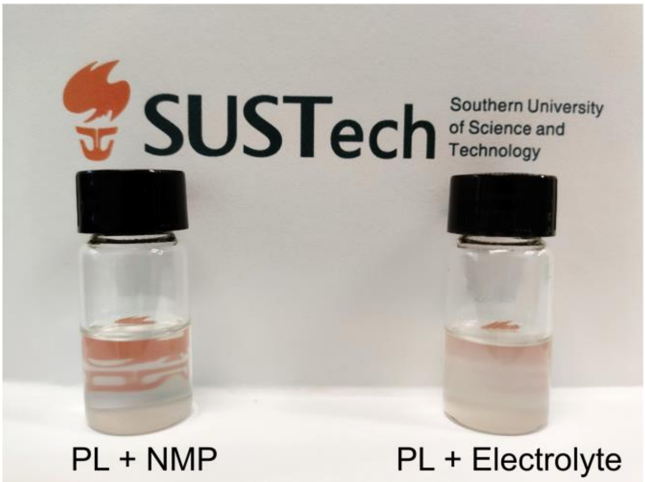

Fig. S3 Solubility test of phytate lithium (PL) in NMP and $LiPF_6$/EC/DMC/EMC electrolyte.

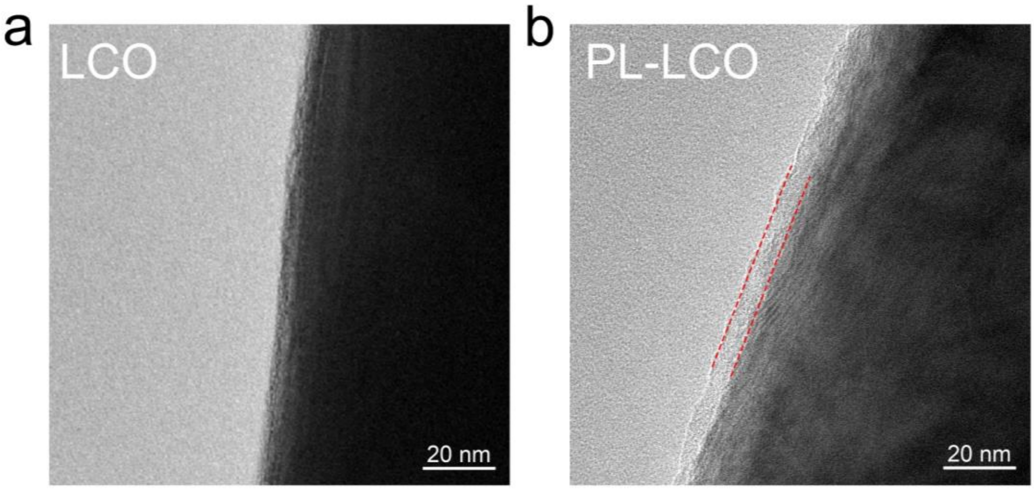

Fig. S4 TEM images of a) LCO and b) PL-LCO before cycling.

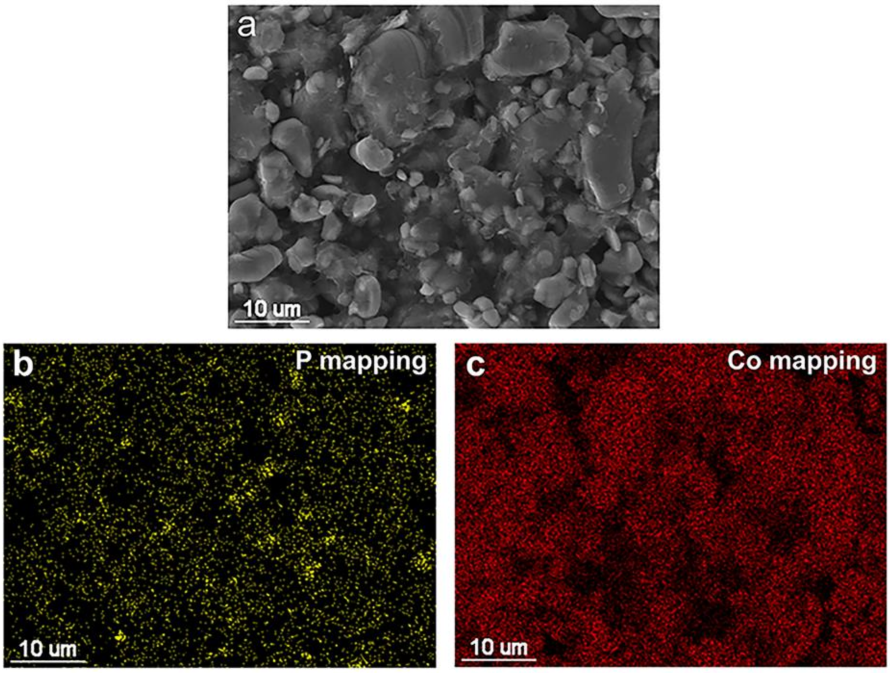

Fig. S5 a) SEM image and b-c) EDS mapping of PL-LCO cathode.

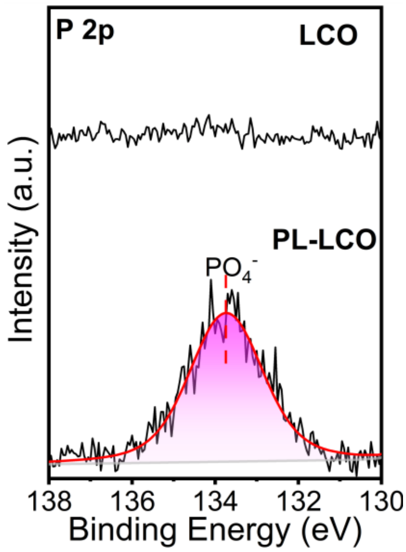

Fig. S6 P 2p XPS spectra of LCO and PL-LCO before cycling.

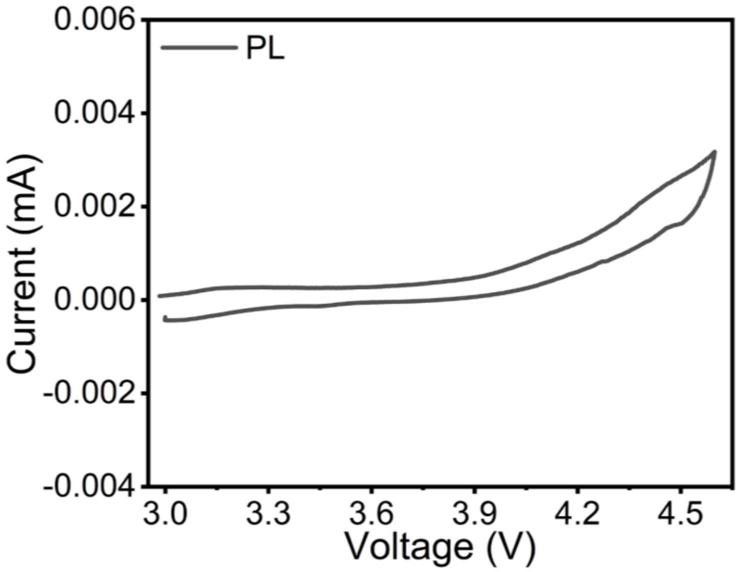

Fig. S7 CV curve of phytate lithium at the 1st cycle with a rate of 0.1 mV/s within voltage range of 3-4.6 V.

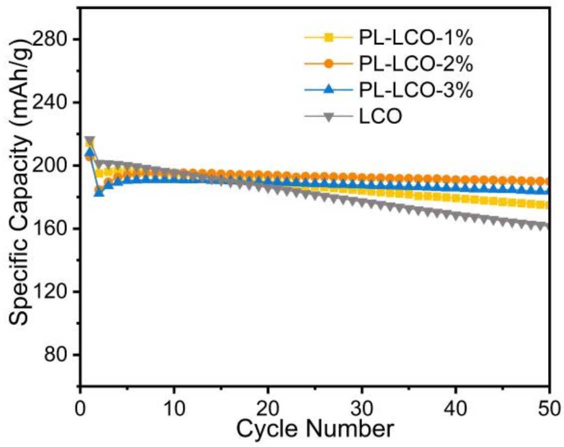

Fig. S8 Electrochemical performance of different values of PL addition.

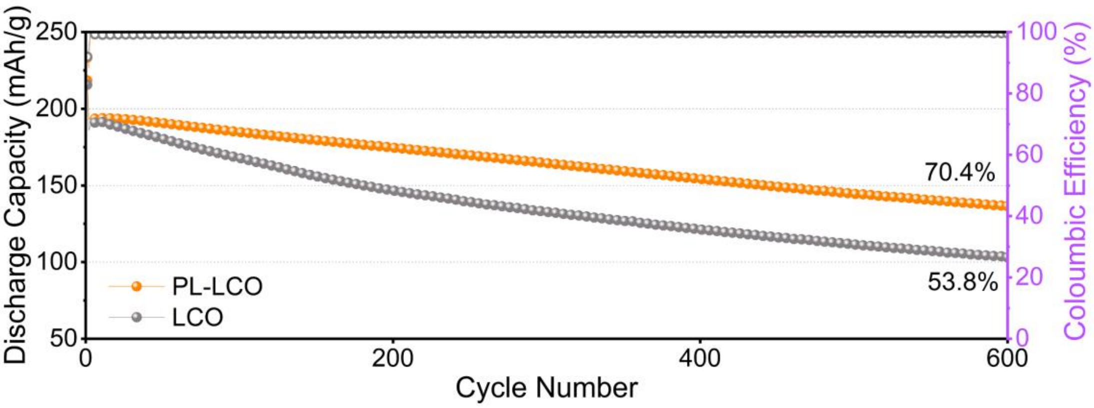

Fig. S9 Cyclic performance of PL-LCO and LCO at a high current density of 280 mA/g for 600 cycles.

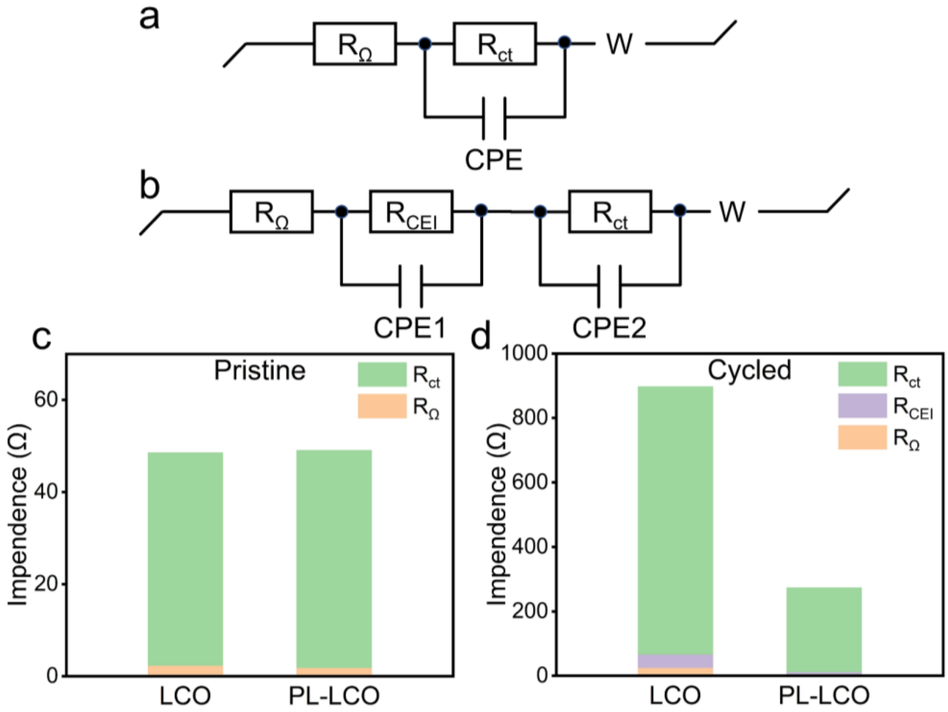

Fig. S10 The equivalent circuit models and fitted EIS data of a,c) pristine and b,d) after 200 cycles.

Table S1. The fitted EIS data of LCO and PL-LCO before and after 200 cycles.

	R_{Ω} / Ω	R_{CEI} / Ω	R_{ct} / Ω
pristine LCO	2.415	/	46.09
pristine PL-LCO	1.927	/	47.11
cycled LCO	26.12	41.25	829.8
cycled PL-LCO	2.121	11.07	259.3

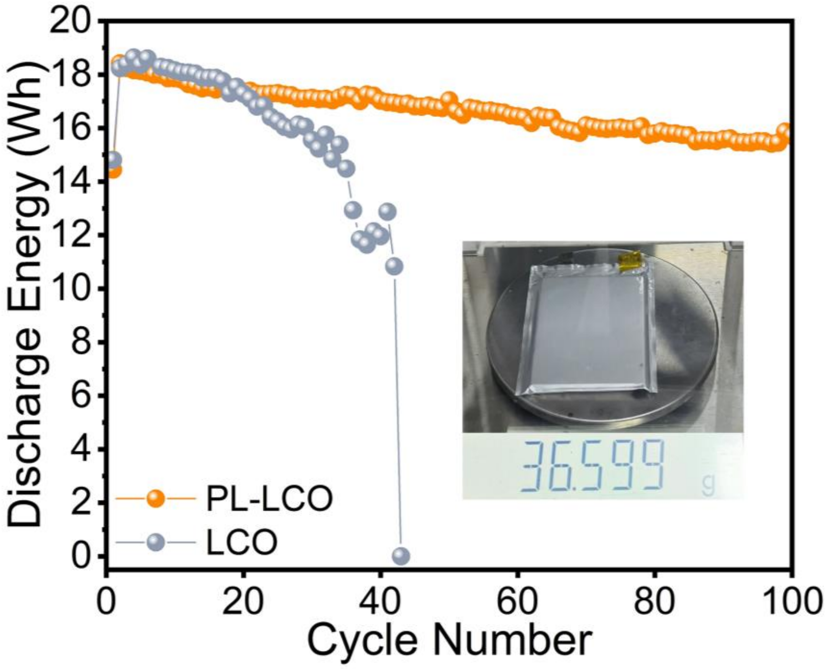

Fig. S11 Cycling performance of 503 Wh/kg PL-LCO||Li pouch cell at a current density of 100 mA/g in the voltage range of 3 – 4.6 V.

The calculation formula for specific capacity is:

$$Specific\ capacity\ (mAh/g) = capacity\ (mAh) \div mass\ of\ active\ material\ (g)$$

The calculation formula for energy density is:

$$Energy\ density\ (Wh/kg) = energy\ (Wh) \div weight\ of\ pouch\ cell\ (g)$$

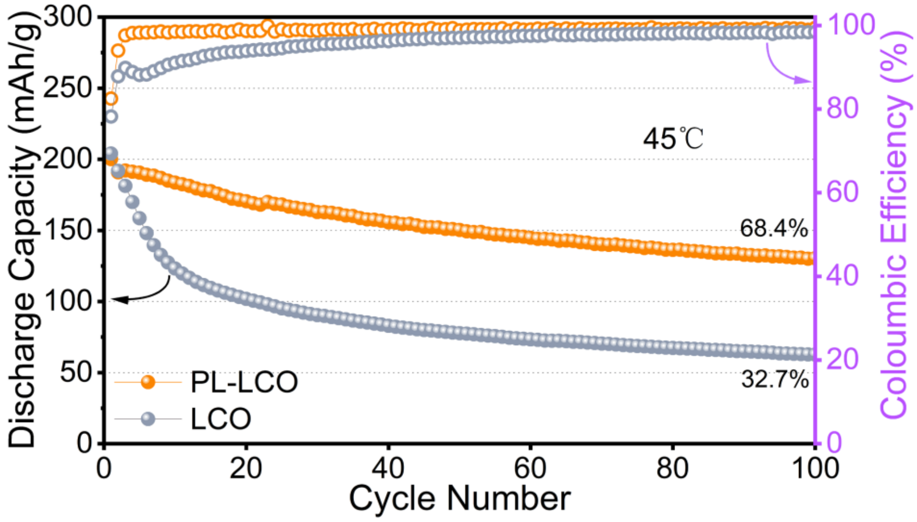

Fig. S12 Cycling performance of LCO and PL-LCO at a current density of 140 mA/g under 45 ℃.

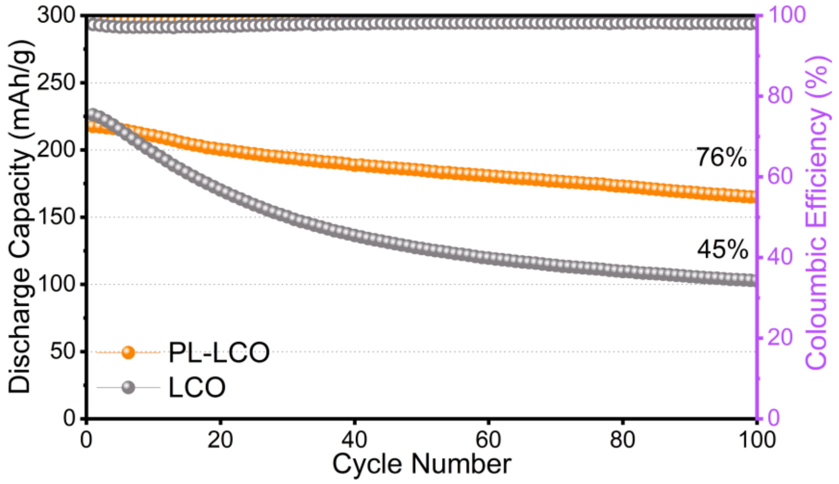

Fig. S13 Cycling performance of LCO and PL-LCO at a current density of 140 mA/g in the voltage range of 3 – 4.65 V.

Table S2. Comparison of electrochemical performance of reported 4.6 V $LiCoO_2$.

Modification strategy	Voltage range (V)	Current density (mA/g)	Initial reversible capacity (mAh/g)	Capacity retention	Ref
$Li_4Mn_5O_{12}$ coating	3-4.5	135	180.7	83% (300th)	1
Ti, F doping	3-4.6	137	185.6	82.5% (100th)	2
Ti, Mg, Al doping	3-4.6	137	202.3	86% (100th)	3
Ni, Ti, Mg doping	2.7-4.6	175	180	67% (100th)	4
Al, Nb, W doping	2.7-4.6	90	193.8	77.9% (100th)	5
Mg doping	3-4.6	270	188	84% (100th)	6
Al, F, Mg doping	3-4.6	137	202.6	88.4% (300th)	7
O vacancy and V doping	3-4.6	270	170	84% (100th)	8
LATP coating	3-4.6	137	204.2	88.3% (100th)	9
LAF coating	3-4.6	137	200	81.8% (200th)	10
AlZnO coating	3-4.6	185	183.9	65.7% (500th)	11
3-TPIC electrolyte additive	3-4.6	100	186	81% (150th)	12
VC and KBF_4 dual additive	3-4.6	274	182	91.1% (300th)	13
MMD electrolyte additive	3-4.6	200	198.8	83.5% (200th)	14
DSL binder	2.8-4.6	137	192.7	93.4% (100th)	15
This work	**3-4.6**	**140**	**195.7**	**89.4% (200th)**	
		280	**195**	**70.3% (600th)**	
	3 - 4.65	**140**	**217.5**	**75.9% (100th)**	

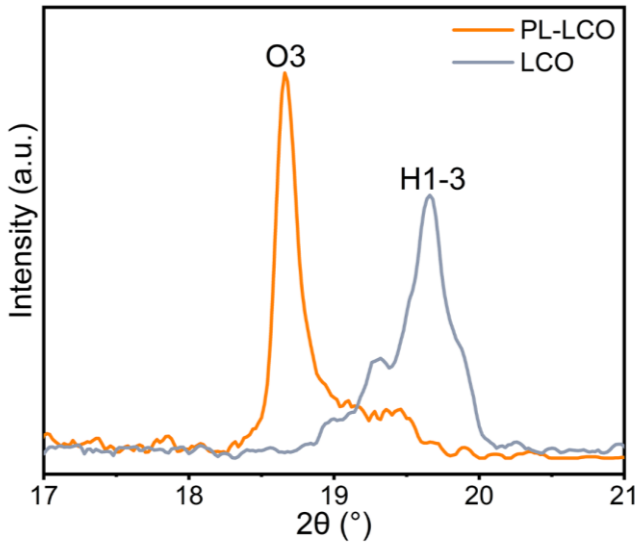

Fig. S14 (003) XRD peak of PL-LCO and LCO at 4.6 V after CV charging until limit current decrease to beneath 0.01 mA.

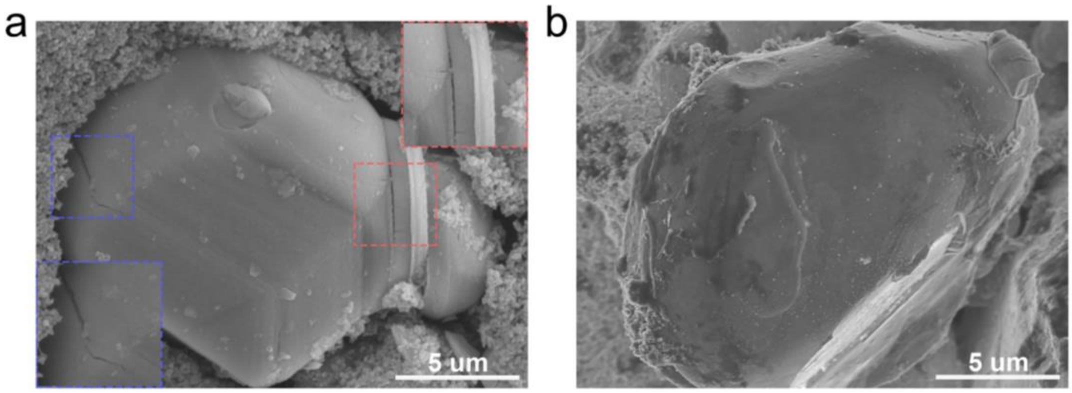

Fig. S15 SEM images of a) LCO and b) PL-LCO after 50 cycles.

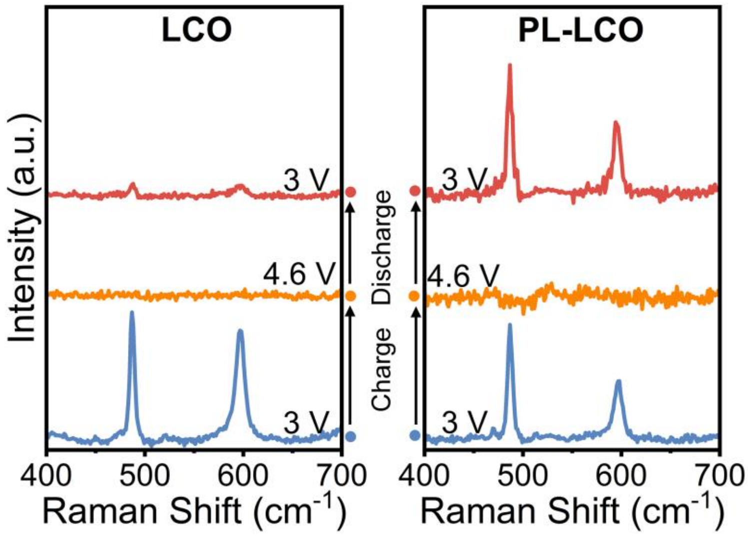

Fig. S16 The selected curves of the E_g and A_{1g} vibrational peaks of LCO and PL-LCO at different voltages.

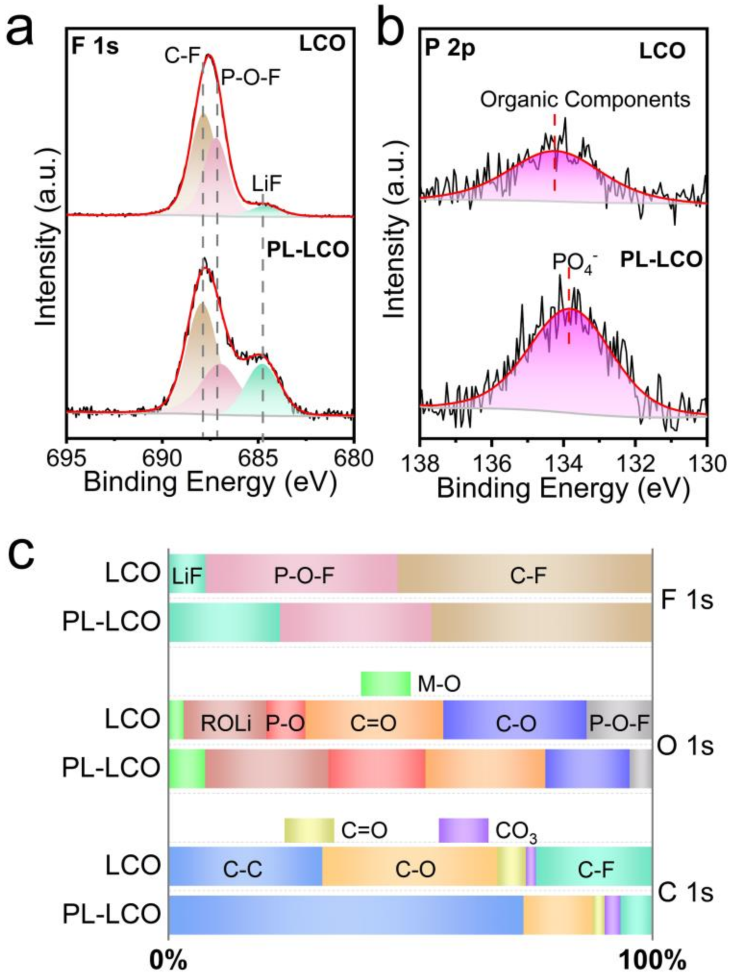

Fig. S17 a) F 1s and b) P 2p XPS spectra of and c) the quantified chemical components of the interface layer of cycled LCO and PL-LCO after 50 cycles.

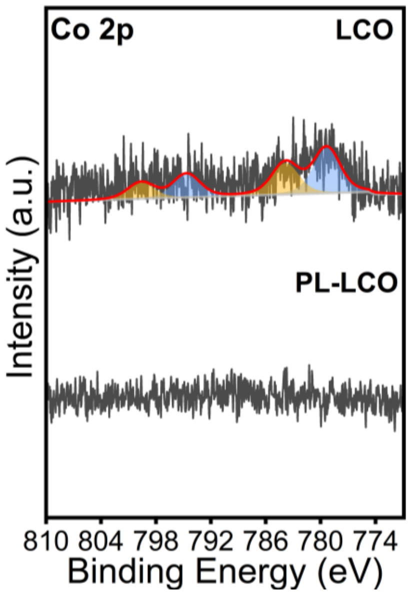

Fig. S18 Co 2p XPS spectra collected on lithium anode of LCO and PL-LCO cells after 50 cycles.

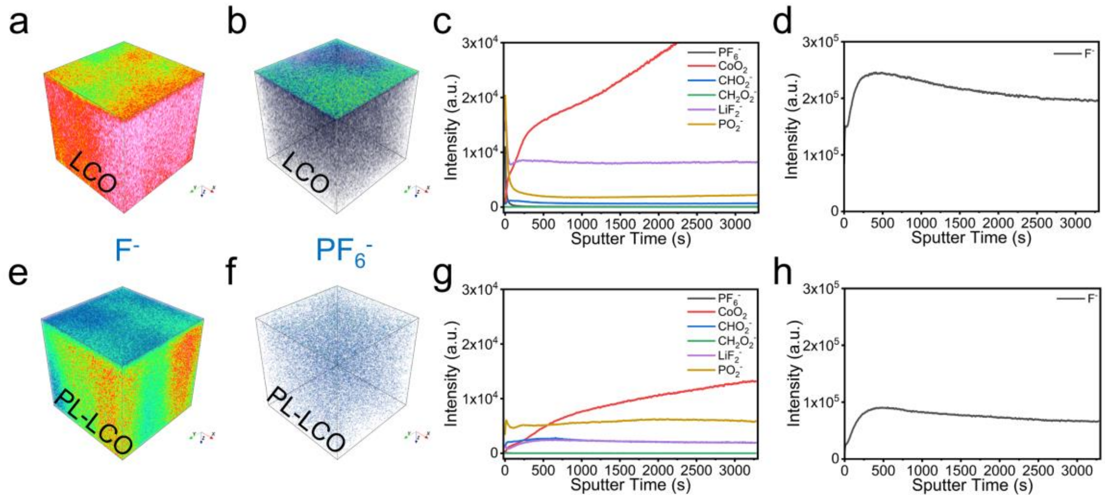

Fig. S19 The 3D reconstruction of F^- and PF_6^- fragments at the a-b) LCO and e-f) PL-LCO cathode surface after 50 cycles. The TOF-SIMS normalized depth profiles of different fragments constituting the CEI of c-d) LCO and g-h) PL-LCO.

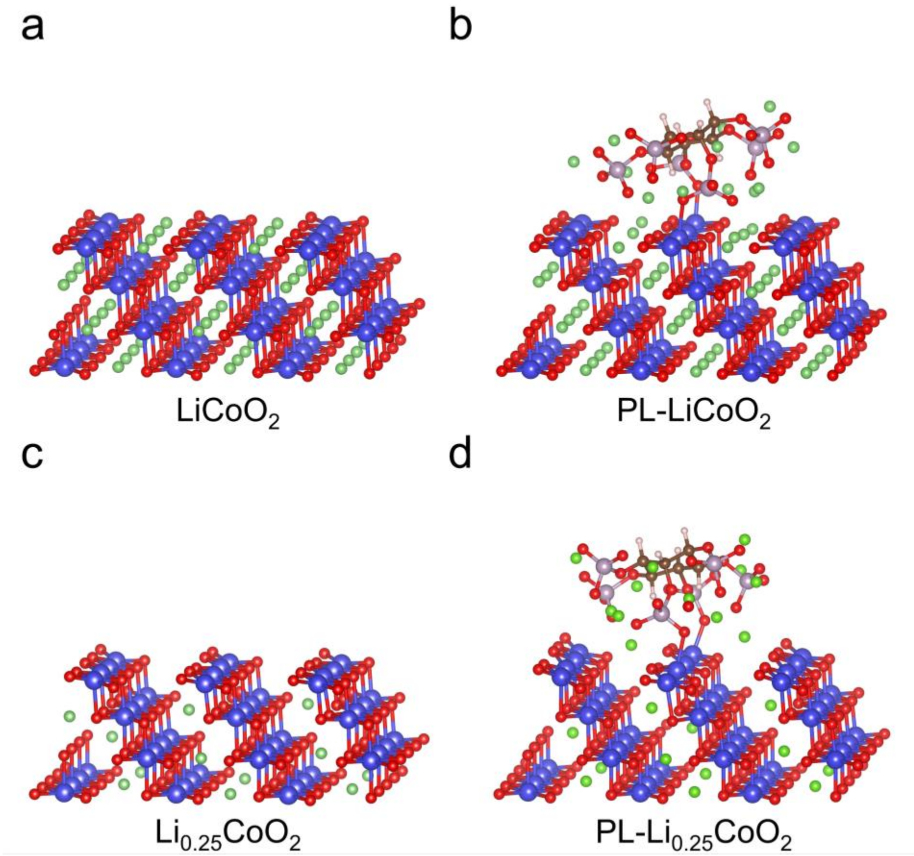

Fig. S20 The simplified (104) surface models of $LiCoO_2$ and PL-$LiCoO_2$ at a-b) pristine state; $Li_{0.25}CoO_2$ and PL-$Li_{0.25}CoO_2$ at c-d) deep delithiation state.

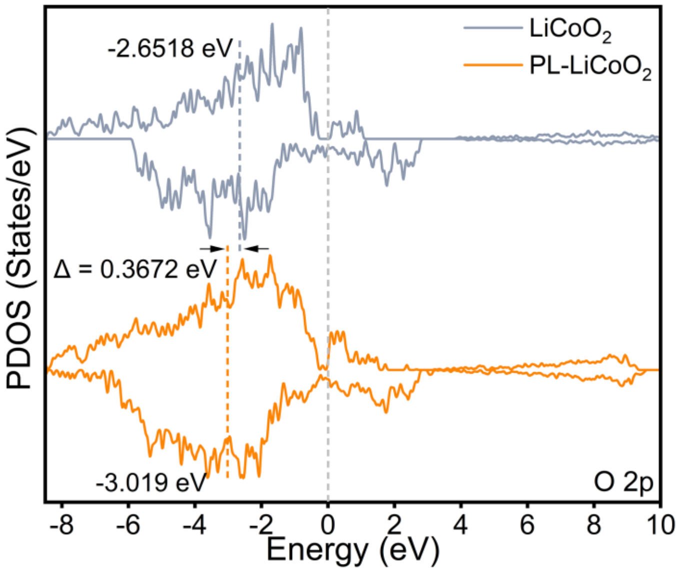

Fig. S21 Projected density of states (PDOS) of oxygen for $LiCoO_2$ and PL-$LiCoO_2$ of (104) slab at pristine state.

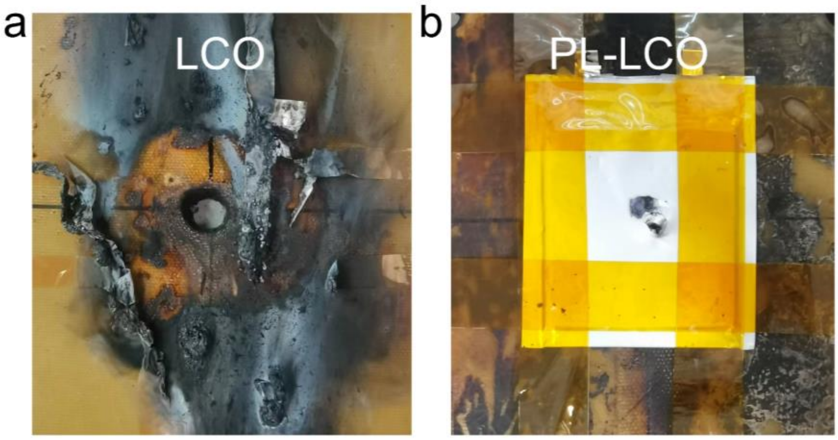

Fig. S22 Piercing experiment of a) LCO||Li and b) PL-LCO||Li pouch cells after 100 cycles.

Reference

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