Supporting Information

Surface Chemistry Regulated Gradient Multi-Component Solid Electrolyte Interphase for 460 Wh kg^{-1} Lithium Metal Pouch Cell

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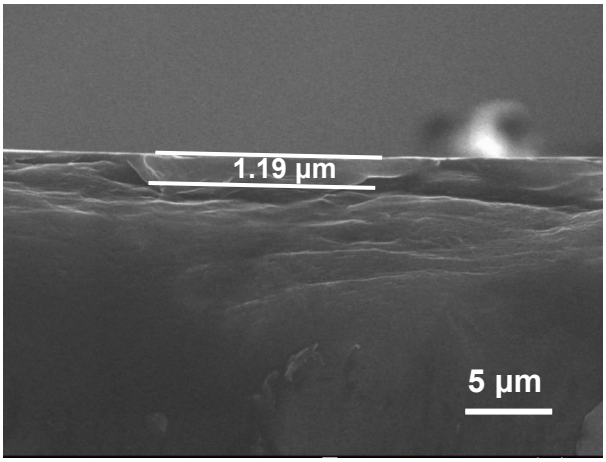

Fig. S1. Cross-sectional SEM images of DFFSA-Li.

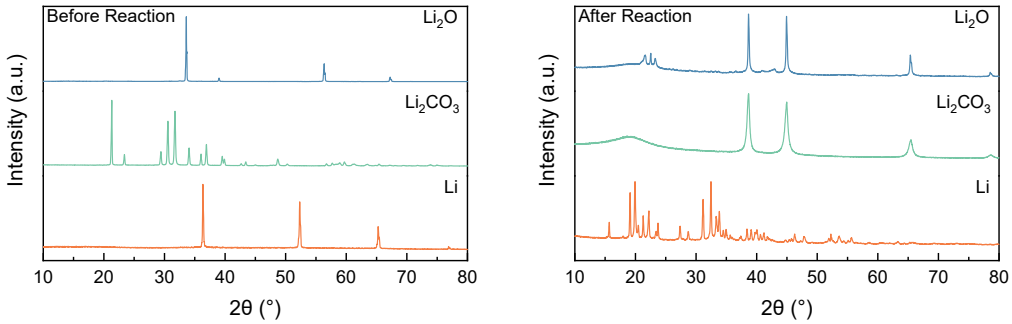

Fig. S2. XRD patterns of Li_2O, Li_2CO_3 and Li before and after reaction with excess DFFSA.

$$2C_2O_4SF_3H\ (aq) + Li_2CO_3(s) \rightarrow 3CO_2(g) + H_2O\ (l) + 2LiF\ (s) + 2SO_2(g) + CF_2{=}CF_2\ (g)$$

$$\Delta G = \mathbf{-132.03\ kcal\ mol^{-1}}$$

$$2C_2O_4SF_3H\ (aq) + Li_2O(s) \rightarrow 2CO_2(g) + H_2O\ (l) + 2LiF\ (s) + 2SO_2(g) + CF_2{=}CF_2\ (g)$$

$$\Delta G = \mathbf{-188.51\ kcal\ mol^{-1}}$$

Fig. S3. Chemical reaction of DFFSA with Li_2CO_3, Li_2O and the corresponding calculated Gibbs free energy.

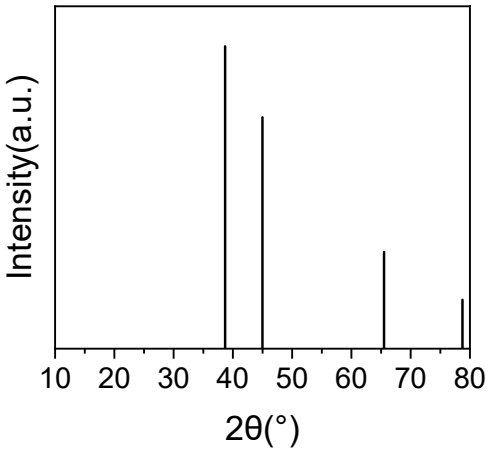

Fig. S4. XRD standard card for LiF.

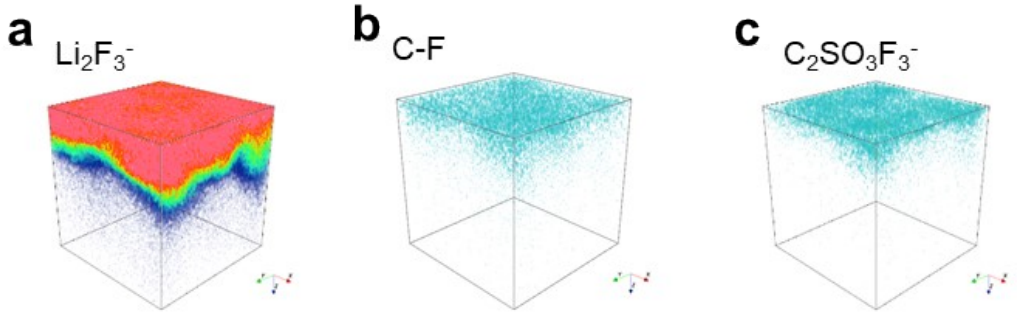

Fig. S5. The 3D overlays of the ion fragments of a) Li_2F_3-, b) C-F and c) $C_2SO_3F_3^-$.

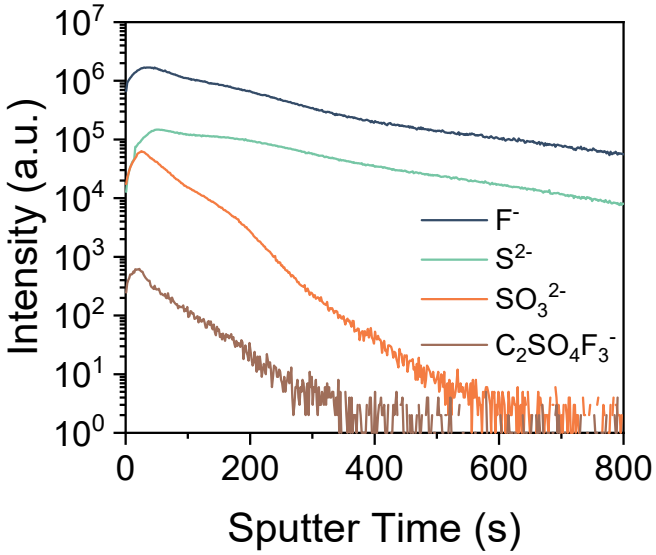

Fig. S6. The TOF-SIMS depth sputter curves of DFFSA-Li surface.

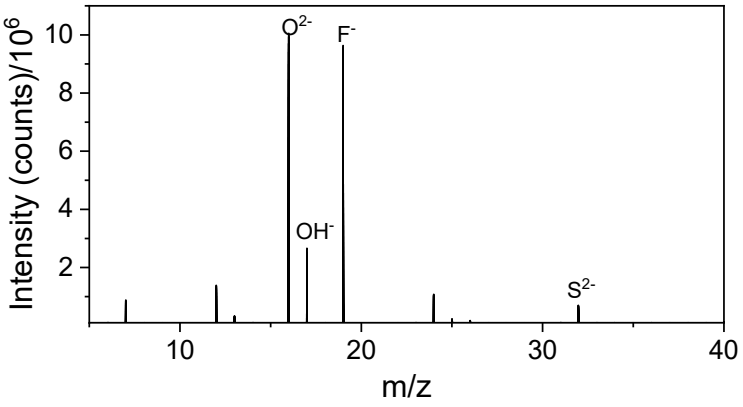

Fig. S7. Time-of-flight secondary ion mass spectrum (TOF-SIMS) of the DFFSA-Li anode.

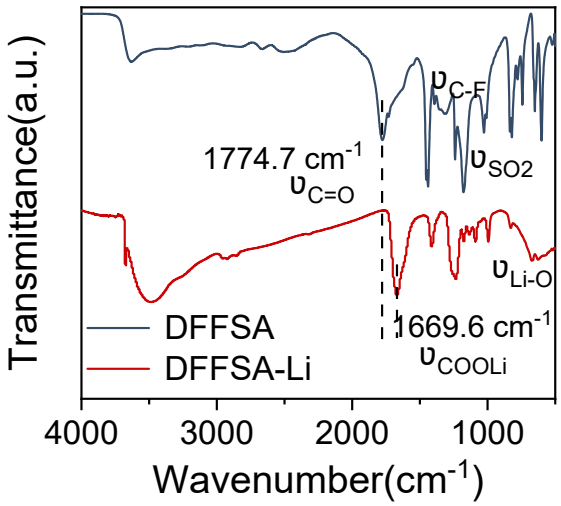

Fig. S8. Infrared spectra of DFFSA-Li and DFFSA.

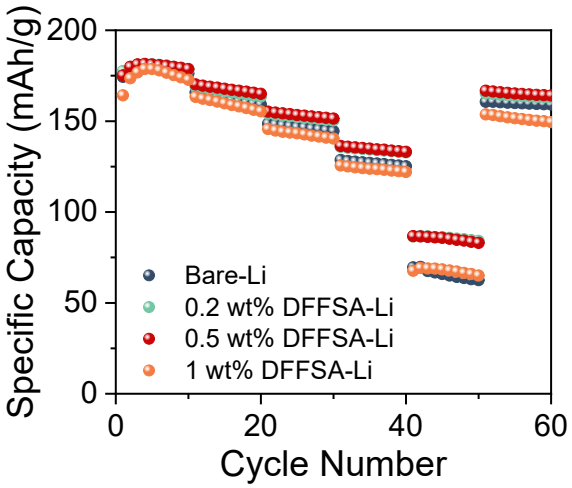

Fig. S9. Rate capability of coin cells with DFFSA-Li and Bare-Li for cycling from 0.2 to 5C.

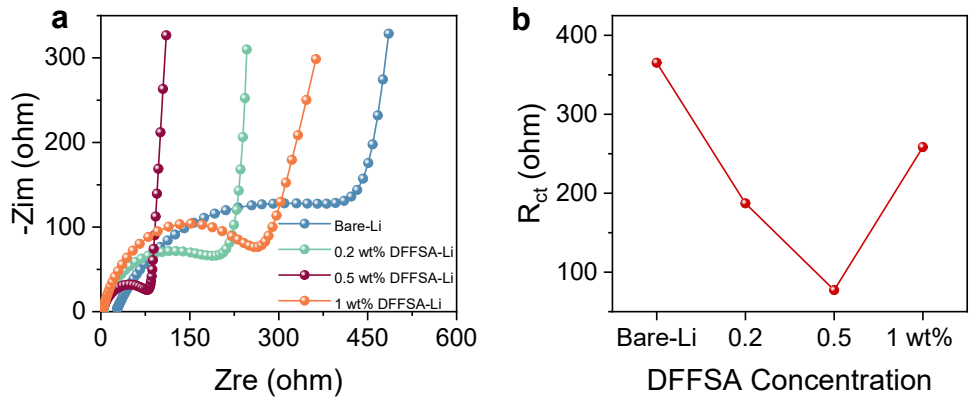

Fig. S10. Electrochemical impedance spectroscopy (EIS) tests of the Li||LCO cells with different DFFSA concentration treatment.

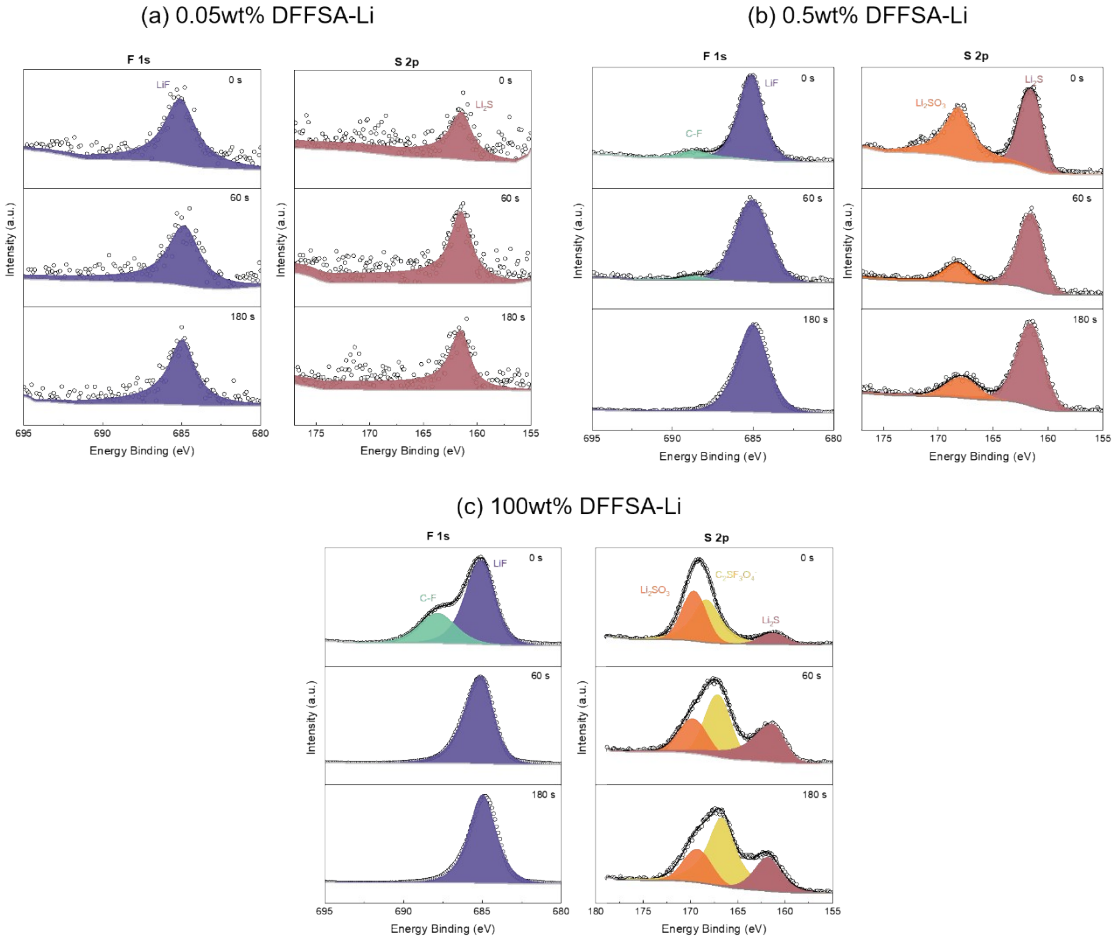

Fig. S11. Depth-dependent XPS spectra of different DFFSA concentration treatment.

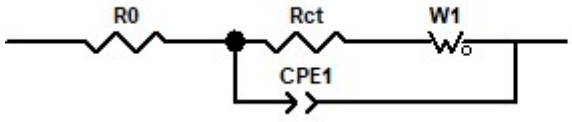

Fig. S12. Equivalent circuit diagram of the Li||LCO battery.

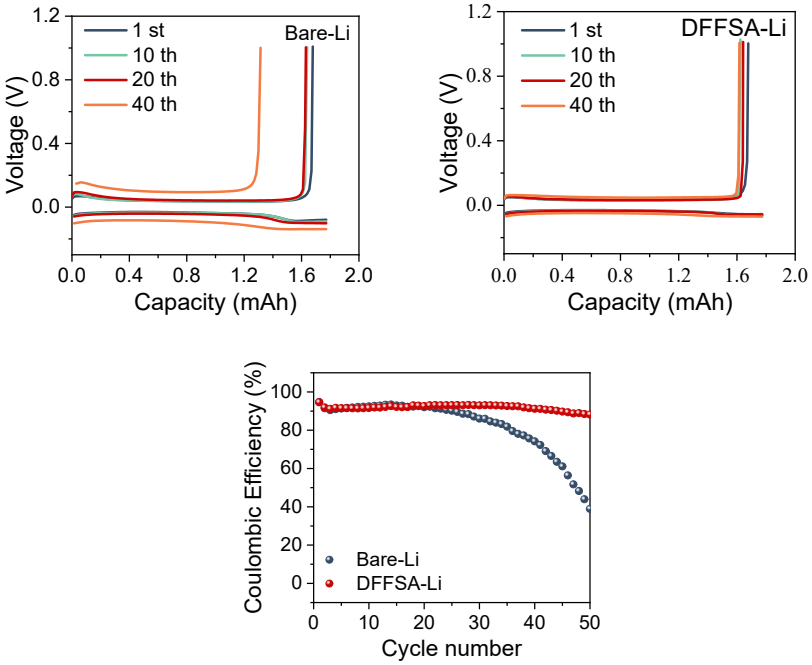

Fig. S13. Performance comparison of Bare-Li and DFFSA-Li in Li||Cu batteries.

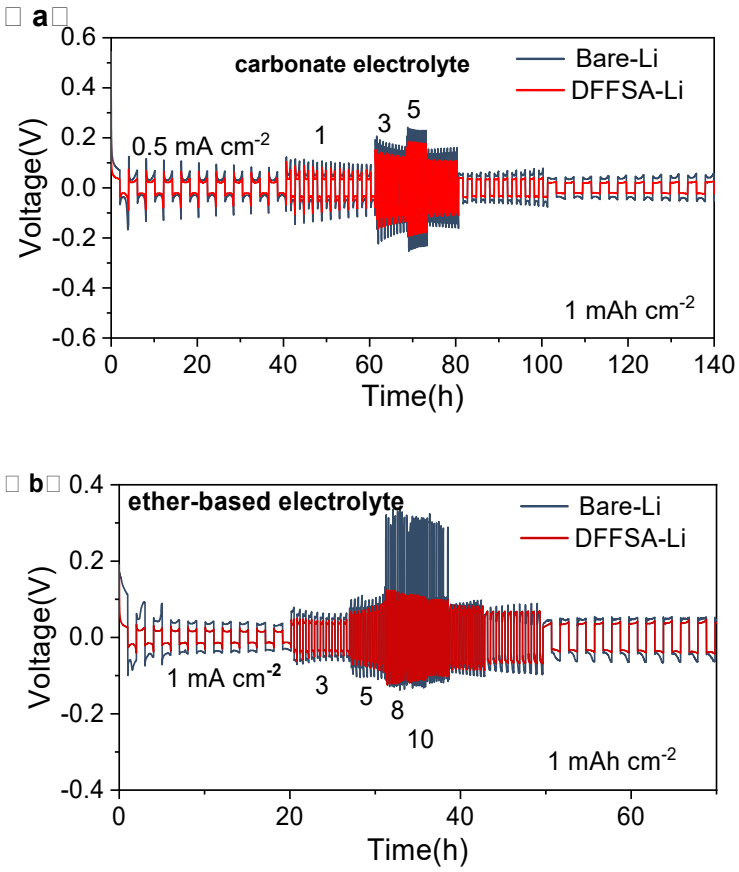

Fig. S14. Voltage profiles of the symmetric cells with Li deposition amount of 1 mA h cm^{-2} at the current density of 0.5, 1, 3 and 5 mA cm^{-2} using (a) carbonate electrolyte 1M $LiPF_6$ in EC and DEC (v/v = 3:7) with 10% FEC; (b) ether-based electrolyte 1M

LiTFSI in DOL and DME (v/v = 1:1) with 1.0wt% $LiNO_3$.

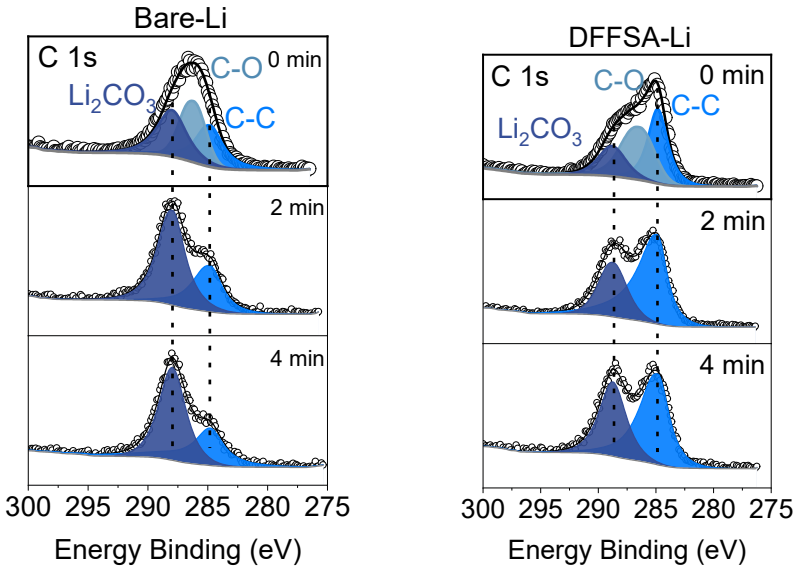

Fig. S15. XPS spectra of C 1s of Li||Li symmetric cells after 10 cycles with a)Bare-Li, b) DFFSA-Li.

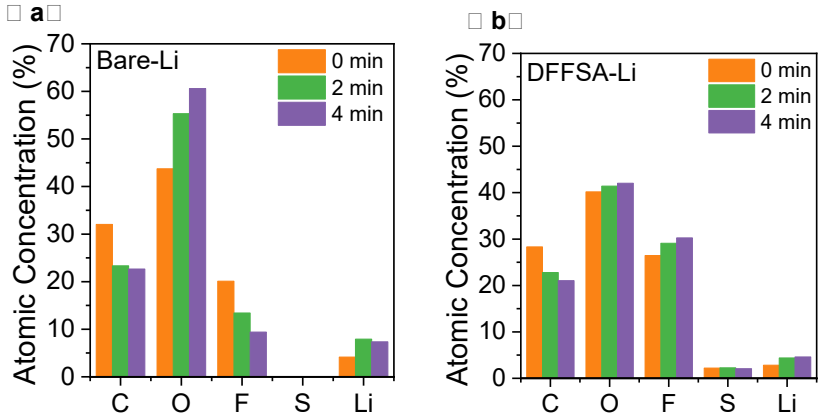

Fig. S16. Atomic composition ratios of the SEI obtained by XPS spectra for (a) Bare-Li and (b) DFFSA-Li.

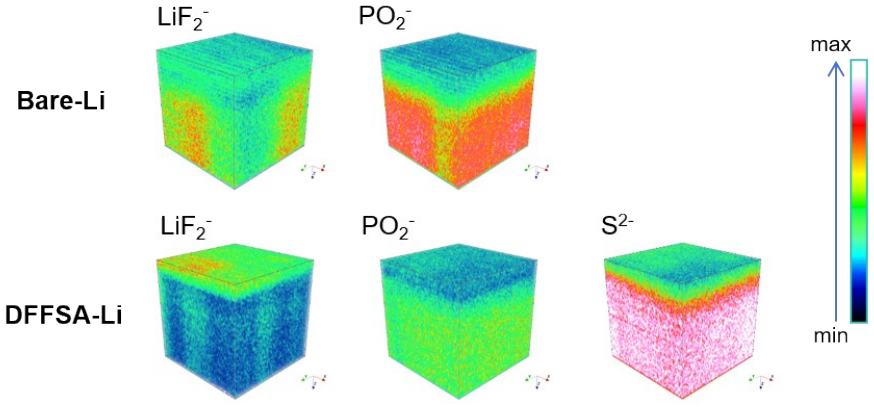

Fig. S17. TOF-SIMS results comparisons of LiF_2^- , PO_2^- and S^{2-} species in symmetric cells after 10 cycles for Bare-Li and DFFSA-Li anodes.

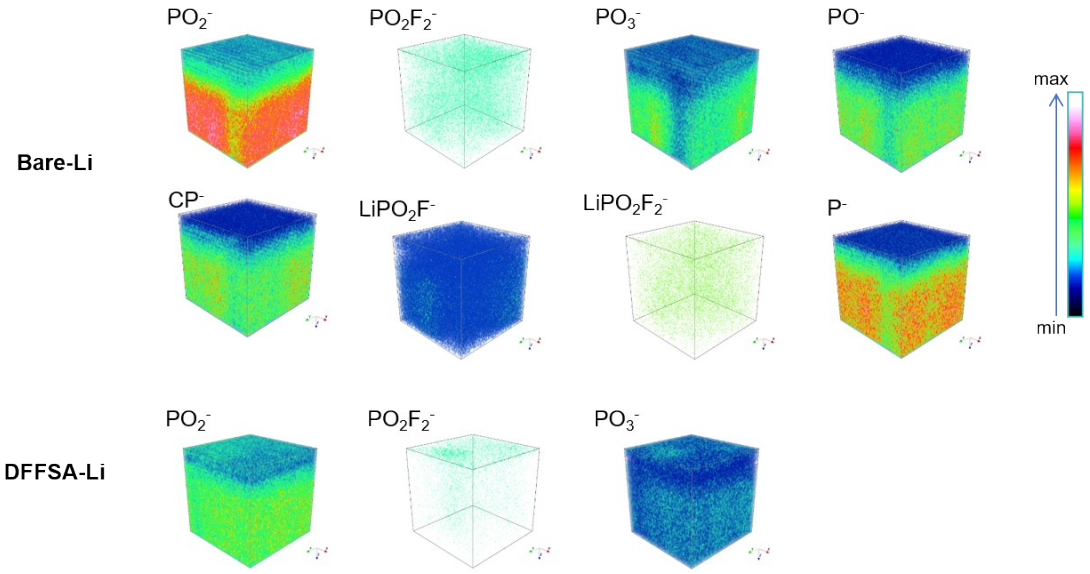

Fig. S18. TOF-SIMS results of P-containing species in symmetric cells after 10 cycles for Bare-Li and DFFSA-Li anodes.

Table S1. The detailed parameters of the DFFSA-Li||LCO and Bare-Li||LCO pouch cells.

	Cell parameters				
Cathode	Cathode Materials	$LiCoO_2$			
	Areal density (mg cm^{-2})	51.6	51.6	51.6	51.6
	Proportion of active materials (%)	96.34	96.34	96.34	96.34
	Electrode length (mm)	60	60	60	60
	Electrode width (mm)	20	20	20	20
	LCO wight (mg)	597	621	651	622
Anode	Anode Materials	Bare-Li		DFFSA-Li	
	Li thickness (μm)	100	50	100	50
	N/P ratio	2.24	1.12	2.24	1.12
Electrolyte	Weight (g)	0.5	0.5	0.5	0.5

Table S2. The detailed parameters of a high-energy DFFSA-Li||NCM811 pouch cell.

Cell component	Cell parameters	Value
Cathode	Materials	NCM811
	Area weight (each side, mg cm^{-2})	19.5
	Area capacity (each side, mAh cm^{-2})	3.9
	Electrode length (mm)	69
	Electrode width (mm)	51
	NCM811 wight (g)	1.34
	The wight of Al foil + NCM811 (g)	1.5
	Number	20
Anode	Materials	DFFSA-Li
	Number	21
	Li thickness (double side, μm)	50
	Area capacity (each side, mAh cm^{-2})	5
	N/P ratio	1.28
Electrolyte	E/C ratio (g/Ah)	1.6
	Weight (g)	8.78
Pouch cell	Total weight (g)	47.29
	Theoretical capacity (Ah)	5.49
	First circulating capacity (Wh)	21.84
	Energy density (Wh/kg)	461.6

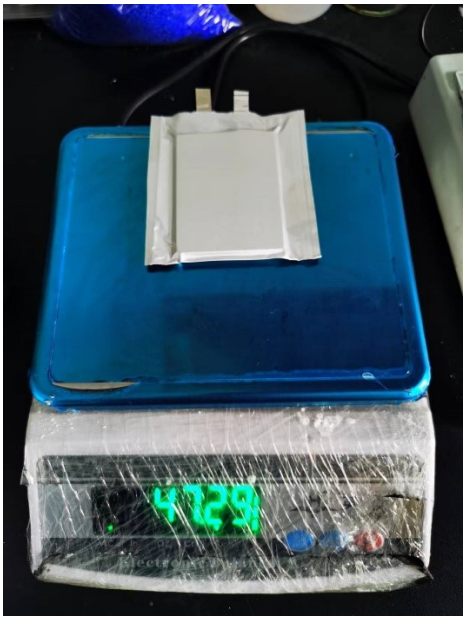

Fig. S19. The weighing mass of the DFFSA-Li||NCM811 pouch cell.