

Supplementary Information

Selection of suitable salt ratio.

As pre-experiment, we tried different salt ratios including LiTFSI : LiDFOB = 0.25 M : 0.75 M (named as T1D3); 0.5 M : 0.5 M (named as T1D1); and 0.75 M : 0.25 M (named as T3D1). Their cycling performance under 2.7–4.4 V is shown in **Figure S1**.

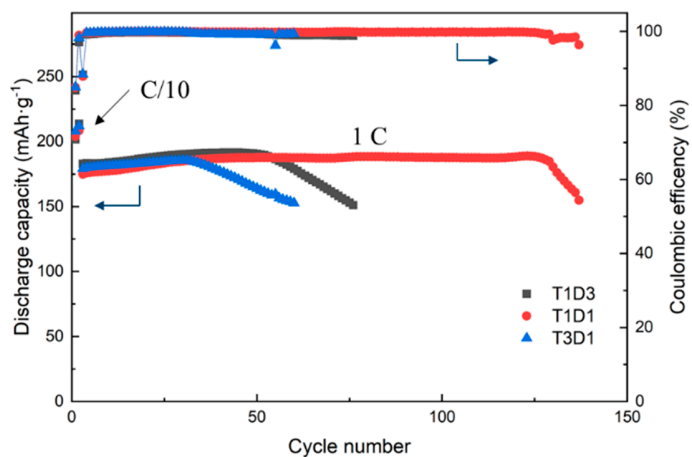


Figure S1. Cycling performance of three electrolytes with different LiTFSI to LiDFOB ratios under 2.7–4.4 V.

It can be seen from **Figure S1** that T3D1 shows the worst performance. T1D1 shows better performance than T1D3, however after around 130 cycles, it also suffers from rapid capacity loss. After adding 5.5 wt% of FEC into both T1D1 and T1D3 we get T1D1-5.5 and T1D3-5.5. A comparison of their cycling performance is shown in **Figure S2**.

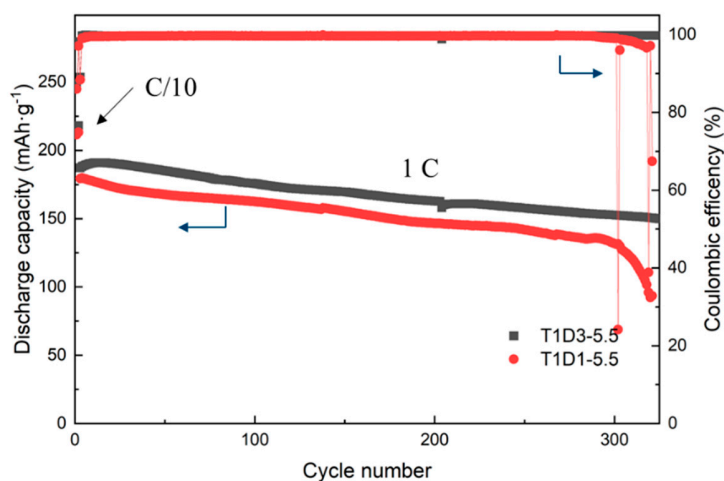


Figure S2. Cycling performance of T1D3-5.5 and T1D1-5.5 under 2.7–4.4 V.

After adding FEC, the performance of both electrolytes is improved. However, the improvement of T1D3-5.5 is more significant which even outperforms the T1D1-5.5. Thus, we chose T1D3 and T1D3-5.5 to study the synergy of dual-salt and FEC additive.

Detailed EIS fitting result.

Table S1. All the EIS fitting data of Li||NMC811 cells in three electrolytes after 2 cycles and 100 cycles.

Notation	After 2 cycles			After 100 cycles		
	Commercial	T1D3	T1D3-5.5	Commercial	T1D3	T1D3-5.5
$R_o (\Omega \cdot \text{cm}^{-2})$	2.82	3.64	4.10	16.84	5.58	5.79
CPE1-T	$5.04 \cdot 10^{-6}$	$5.07 \cdot 10^{-7}$	$3.31 \cdot 10^{-5}$	$4.32 \cdot 10^{-6}$	$7.12 \cdot 10^{-5}$	$5.99 \cdot 10^{-5}$
CPE1-P	0.91	0.66	0.73	0.85	0.67	0.65
$R_1 (\Omega \cdot \text{cm}^{-2})$	14.70	8.76	5.92	25.46	10.58	10.15
CPE2-T	$8.18 \cdot 10^{-5}$	$2.60 \cdot 10^{-4}$	$3.50 \cdot 10^{-4}$	$1.43 \cdot 10^{-4}$	$2.76 \cdot 10^{-3}$	$9.09 \cdot 10^{-3}$
CPE2-P	0.77	0.81	0.77	1.03	0.84	0.61
$R_2 (\Omega \cdot \text{cm}^{-2})$	15.47	5.20	5.54	3.25	2.65	2.30
CPE3-T	$4.94 \cdot 10^{-3}$	$6.14 \cdot 10^{-3}$	$5.71 \cdot 10^{-3}$	$4.57 \cdot 10^{-3}$	$5.67 \cdot 10^{-3}$	$4.96 \cdot 10^{-3}$
CPE3-P	0.91	0.71	0.83	0.95	0.96	0.95
$R_{CT} (\Omega \cdot \text{cm}^{-2})$	4.80	9.53	4.56	28.75	3.03	8.73
W1-R	27.63	38.94	35.37	308.7	22.73	23.58
W1-T	99.53	56.93	70.82	69454	63.03	55.26
W1-P	0.35	0.48	0.45	0.28	0.50	0.57