Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Building a Spontaneously Formed and Self-healing Protective Layer with a F-rich Electrochemically Active Organic Molecule for Ultra-stable Li Metal Batteries

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Calculation method

To evaluate the amount of TFBQ on the cathode side, we applied the initial discharge (reduction from TFBQ to LTFBB, 60 mAh/g) specific capacity of the Super P electrode to do the calculation.
The total amount of TFBQ in one coin cell is 0.1 mol/L * 50 µL = 5 µmol.
The loading of Super P in the electrode we applied: about 0.6 mg. So the total capacity is
0.6 mg * 60 mAh/g = 36 µAh = 0.1296 Coulombs, which need 1.343 µmol electrons.
Each TFBQ can deliver 2 electrons, so the reaction consumes 0.6715 µmol of TFBQ.

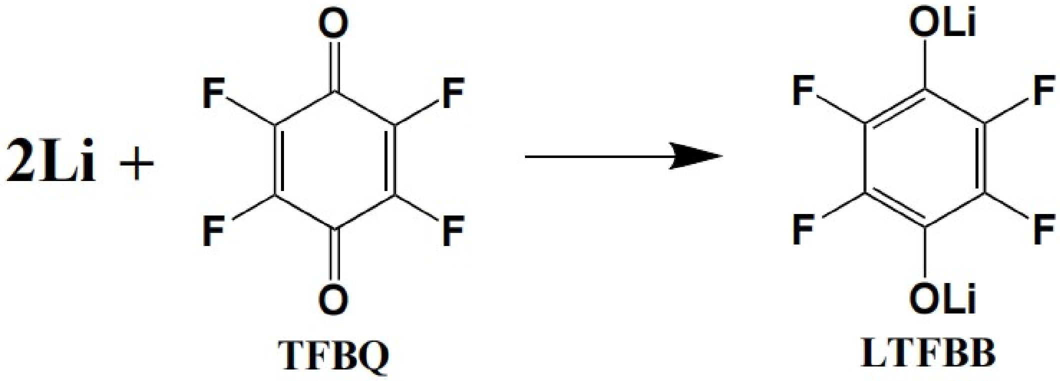

Figure S1. Mechanism of TFBQ reaction on Li metal surface.

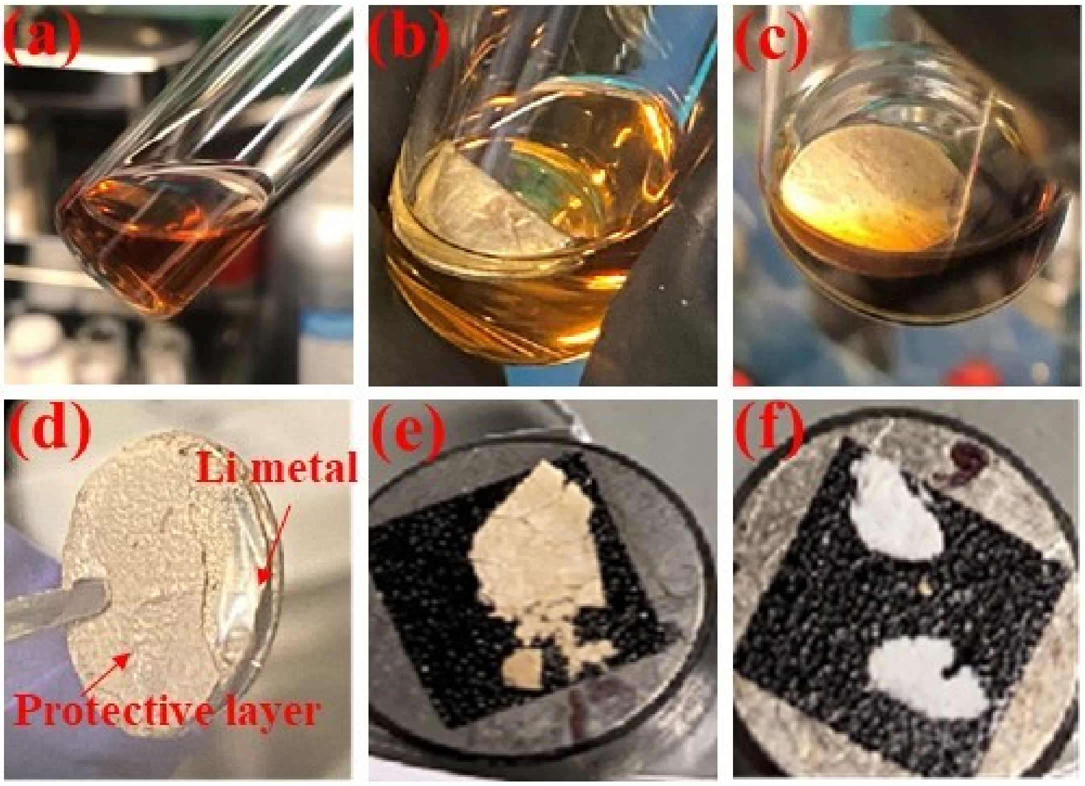

Figure S2. Images of original 0.1 M TFBQ in LDD electrolyte (a) and a Li chip immersed in the same electrolyte for 14 days (b). A control test of Li chip immersed in 0.1 M BQ for one day (c). Li metal section after cycling in 0.1 M TFBQ LDD electrolyte (d). The collected interphase from cycled Li metal with 0.1 M TFBQ LDD electrolyte (e) and LDD electrolyte (f) after 3 days.

Table S1. XPS data for element concentration corrected by relative sensitivity factors (RSF).

	Li 1s	C 1s	O 1s	F 1s	S 1s	Fe 2p3	P 1s
Li chip for A	32.7	15.14	33.43	17.64	0.02	-	1.08
Li chip for B	45.72	4.64	7.33	40.37	-	-	1.93
Li chip for C	58.63	20.07	18.33	2.94	0.03	-	-
Li chip for E	33.88	18.3	11.45	33.59	2.78	-	-
Electrode for C	17.82	41.13	16.46	21.98	0.5	2.11	-
Electrode for D	37.66	22.83	12.46	23.24	1.61	2.21	-
Electrode for F	27.23	46.44	15.59	6.73	2.48	1.54	-

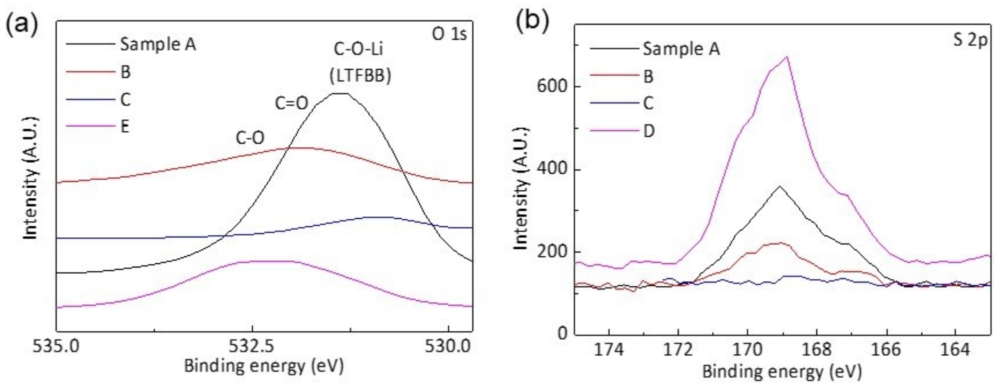

Figure S3. The XPS spectra of O 1s (a) and S 2p (b) for sample A, B, C and E.

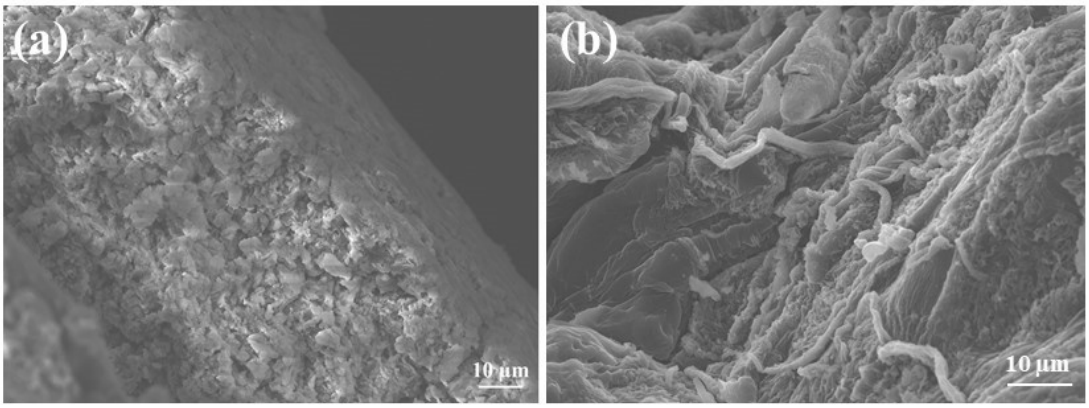

Figure S4. The cross-section of interface for cycled Li metal (a) and a specific area with Li dendrites (b).

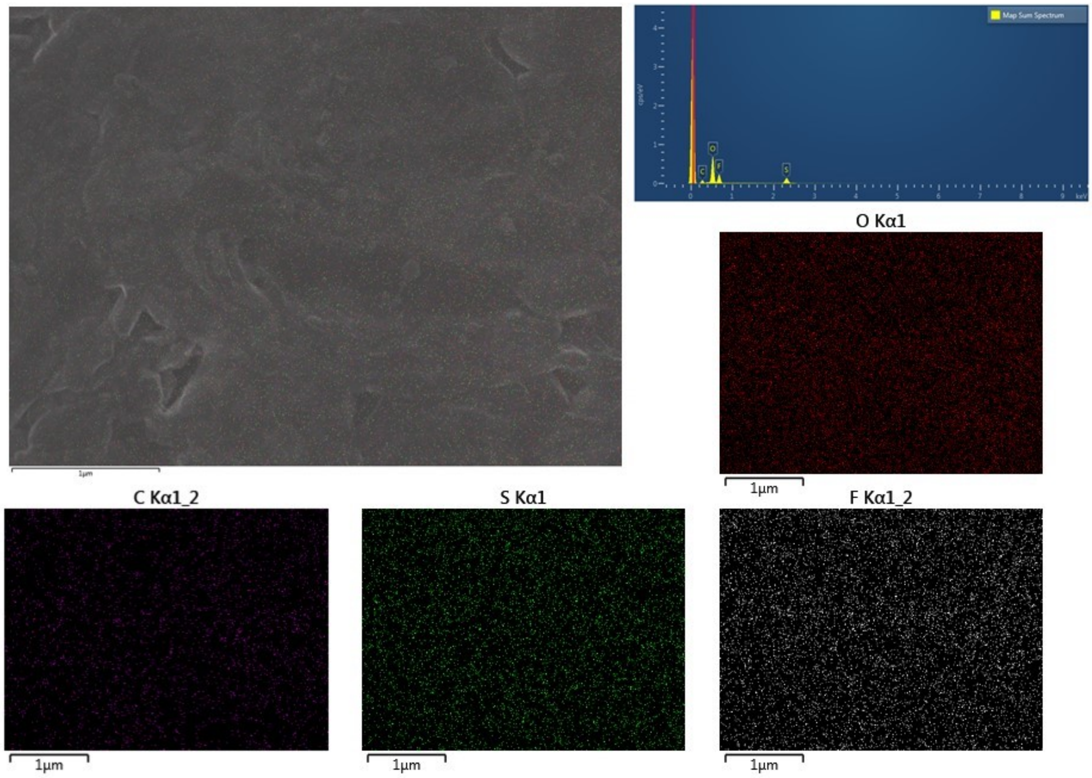

Figure S5. Multi-element EDX mapping for the protective layer in sample E.

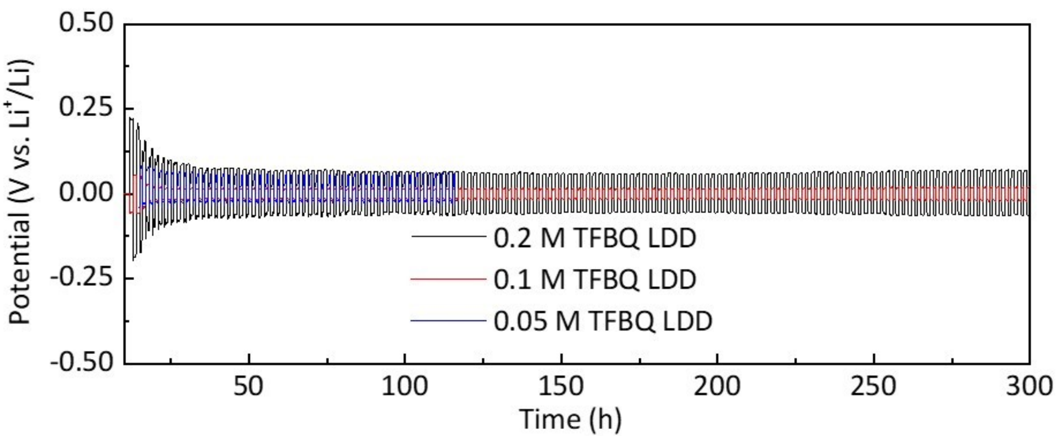

Figure S6. Li-Li symmetric cells with 0.05, 0.1 and 0.2 M TFBQ LDD electrolyte.

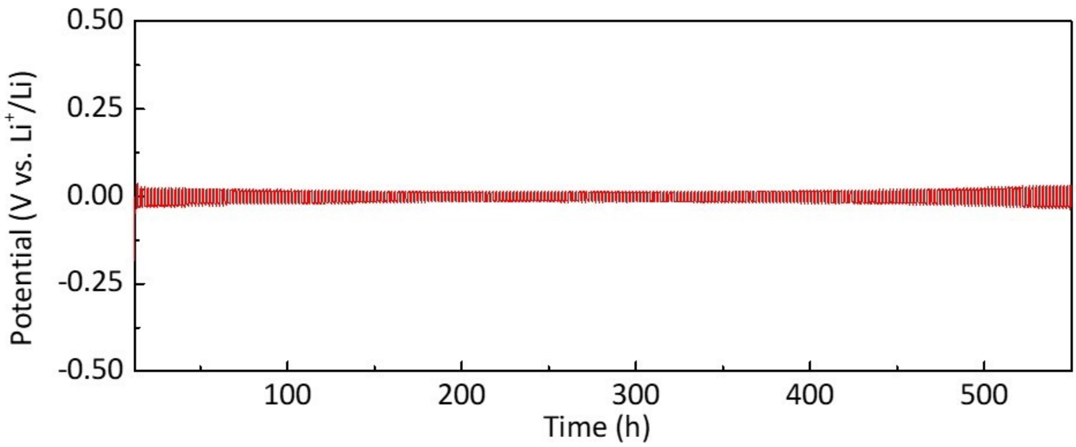

Figure S7. Li-Li symmetric cell with 0.1 M TFBQ LDD electrolyte for 175 µm Li chips.

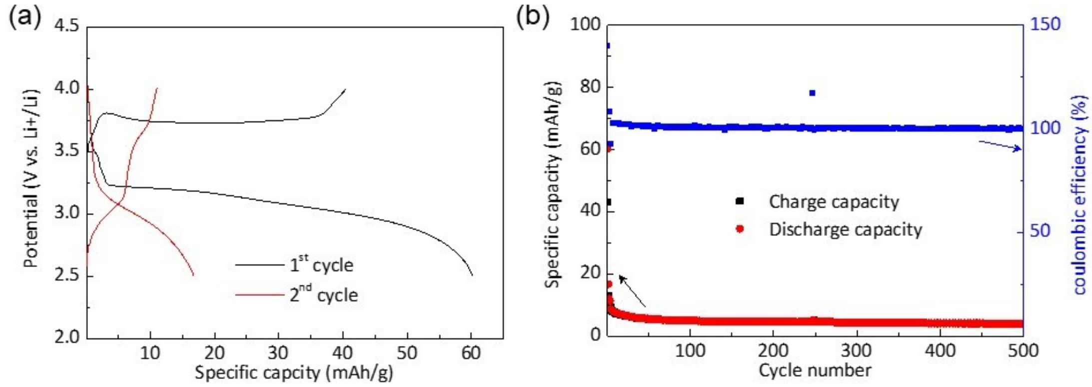

Figure S8. Charge/discharge curves (a) and cycle performance (b) of neat Super P in 0.1 M TFBQ LDD electrolyte.

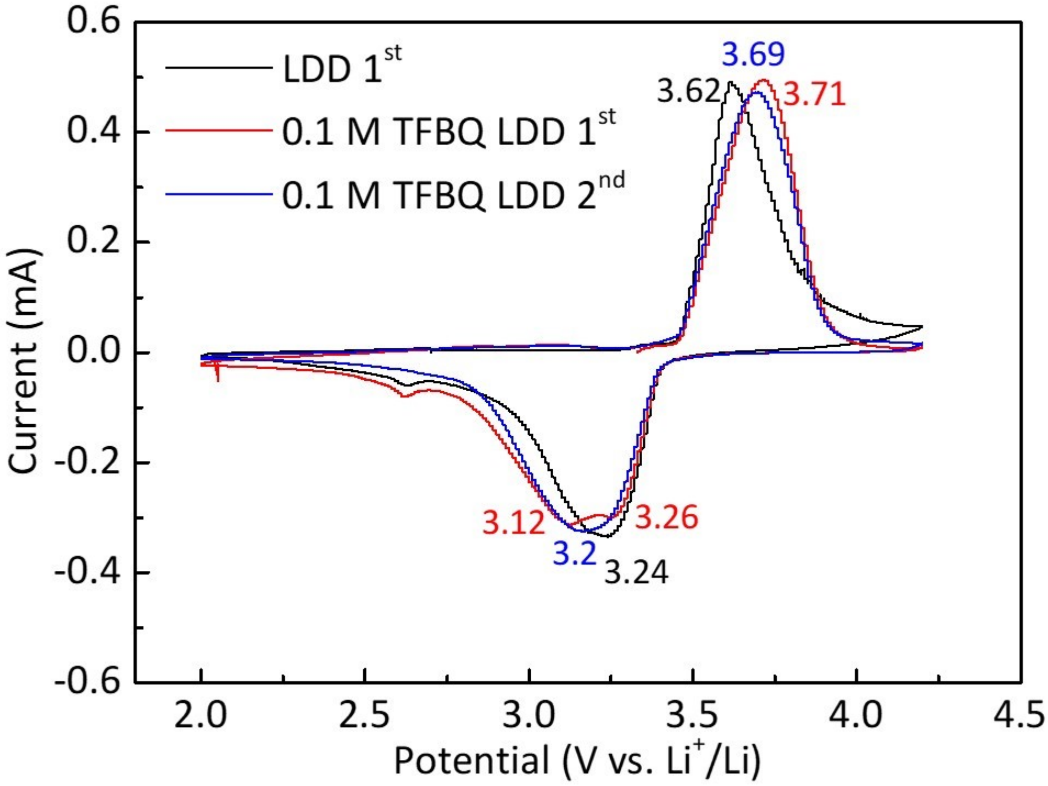

Figure S9. CV test for Li-LFP cells with LDD and 0.1 M TFBQ LDD electrolyte.

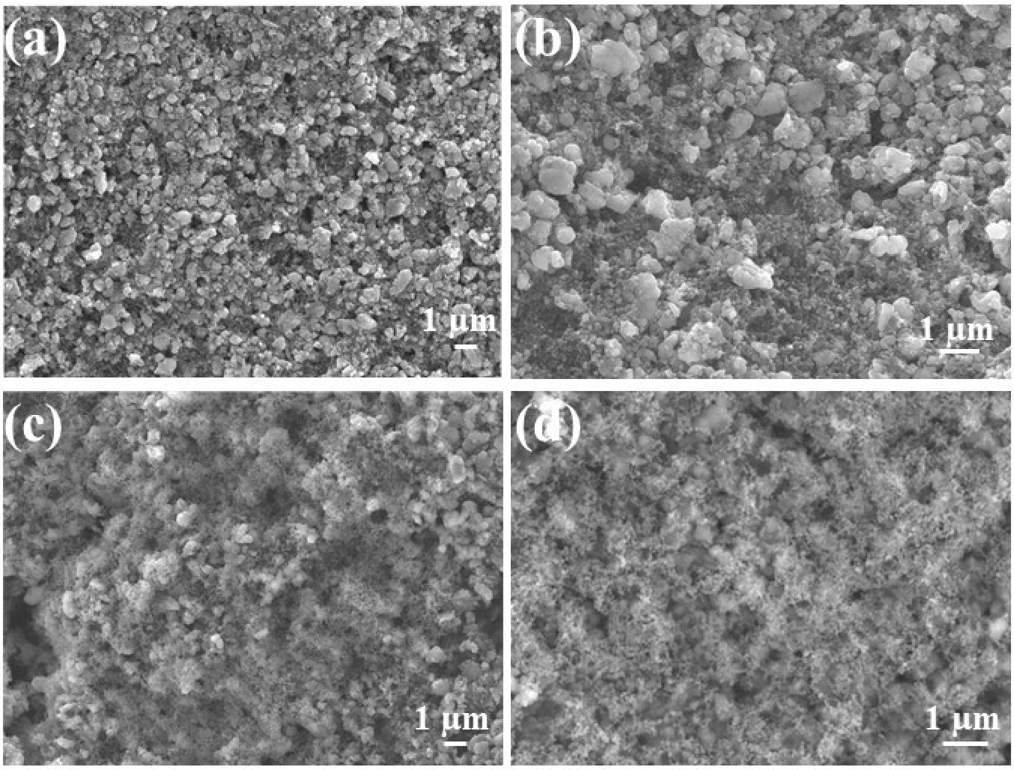

Figure S10. Surface morphology of LFP electrode before test (a), after 200 cycles under 1 C in LDD electrolyte (b), after formation (c) and after 600 cycles (d) in 0.1 M TFBQ LDD electrolyte.

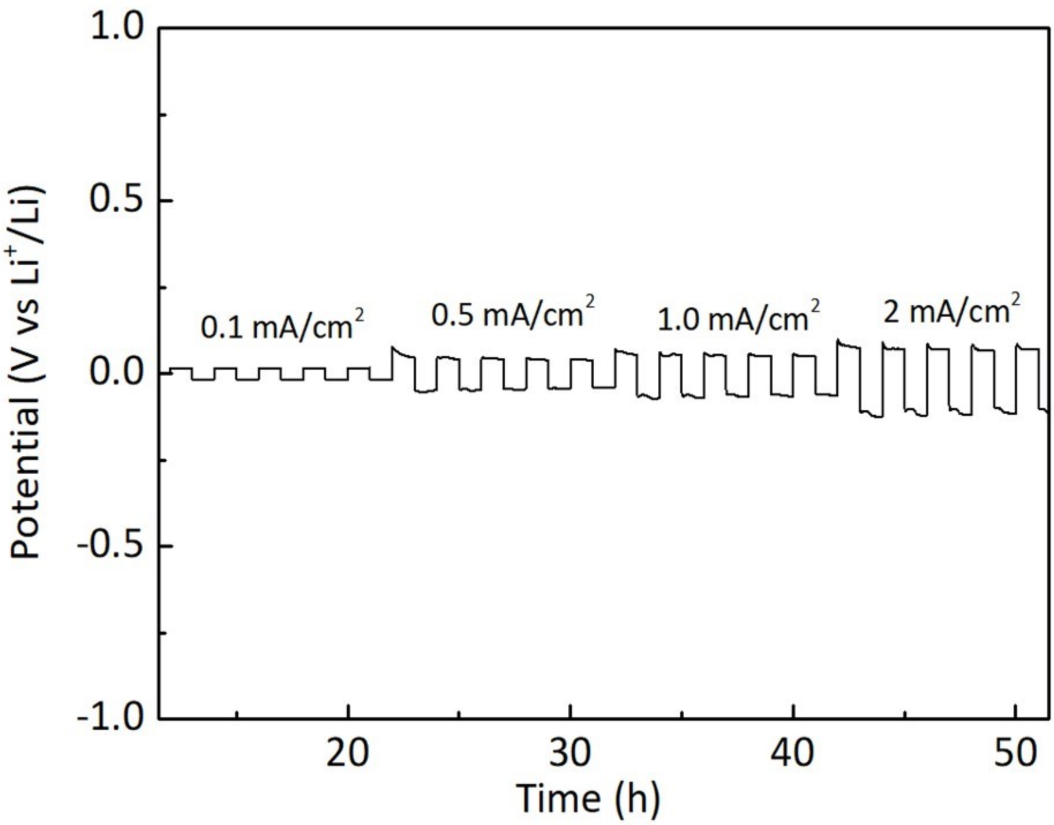

Figure S11. Rate performance for Li-Li symmetric cell with LDD electrolyte.

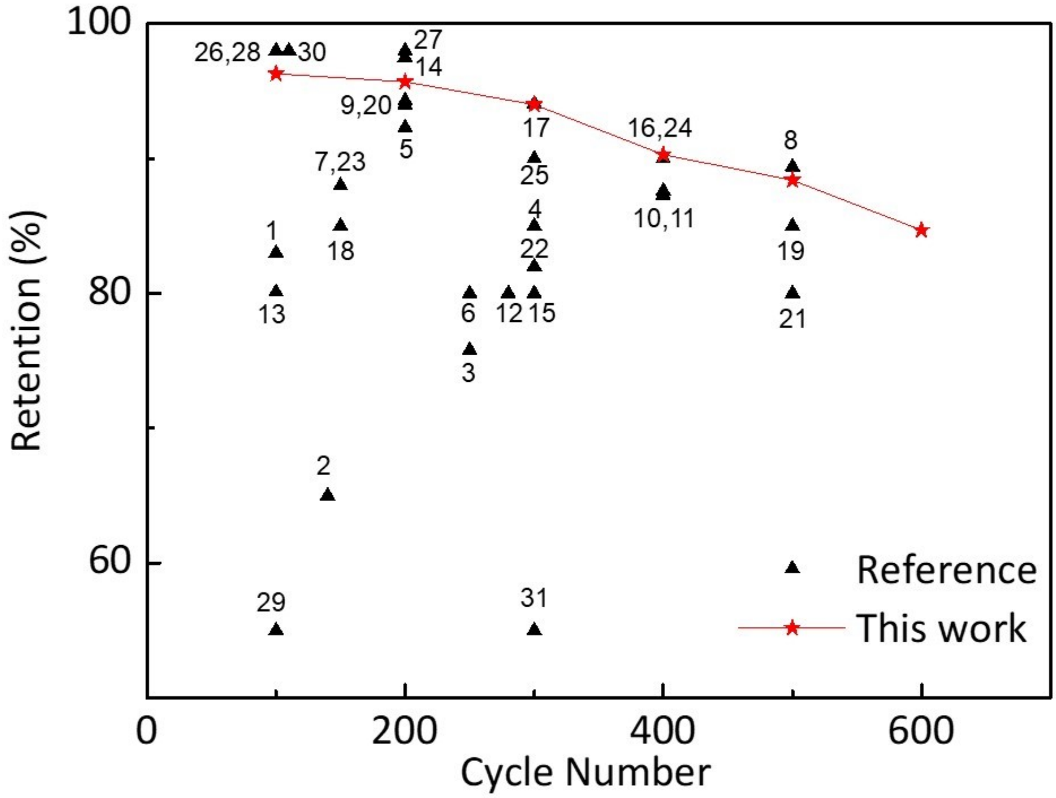

Figure S12. Specific energy delivered for Li-LFP battery reported.

Table S2. Comparison of the cycle performance for recent Li-LFP full cells.

Reference	Cycle number	Retention (%)	Current density	Journal
This work	100/200/300/ 400/500/600	96.3/95.7/94.0/ 90.3/88.4/84.7	1 C	This work
1	100	83	0.25 C	*Adv. Energy Mater.*
2	140	65	1 C	*Adv. Mater.*
3	250	75.8	1 C	*Adv. Funct. Mater.*
4	300	85	1 C	*Adv. Funct. Mater.*
5	200	92.3	0.5 C	*Adv. Mater.*
6	250	80	0.5 C	*Adv. Funct. Mater.*
7	150	88	0.5 C	*Energy Storage Mater.*
8	500	89.4	0.5 C	*ACS Energy Lett.*
9	200	94	0.2 C	*Nano Energy*
10	400	87.6	1 C	*Energy Storage Mater.*
11	400	87.3	0.5 C	*Nano Energy*
12	280	80	0.2 C	*Angew. Chem. Int. Ed.*
13	100	80.1	1 C	*Adv. Energy Mater.*
14	200	97.5	0.5 C	*Adv. Mater.*
15	300	80	0.5 C	*Adv. Mater.*
16	400	90	0.5 C	*Joule*
17	300	94.08	1 C	*Energy Storage Mater.*
18	150	85	0.5 C	*Adv. Funct. Mater.*
19	500	85	0.5 C	*Energy Storage Mater.*
20	200	94.3	0.5 C	*Adv. Energy Mater.*
21	500	80	0.5 C	*Nat. Commun.*
22	300	82	1 C	*Nat. Commun.*
23	150	88	0.5 C	*Nat. Commun.*
24	400	90	0.079 C charge/ 0.263 C discharge	*Nat. Energy.*
25	300	90	0.2 C charge/ 0.6 C discharge	*Adv. Funct. Mater.*
26	100	98	1 C	*Nano Energy*
27	200	98	0.2 C	*J. Am. Chem. Soc.*
28	100	98	1 C	*Angew. Chem. Int. Ed.*
29	100	55	0.33 C	*Adv. Mater.*
30	110	98.9	-	*Adv. Mater.*
31	300	55	0.5 C	*Adv. Mater.*

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