Supporting Information

A Redox-Active Organic Cation for Safer High Energy Density Li-Ion Batteries

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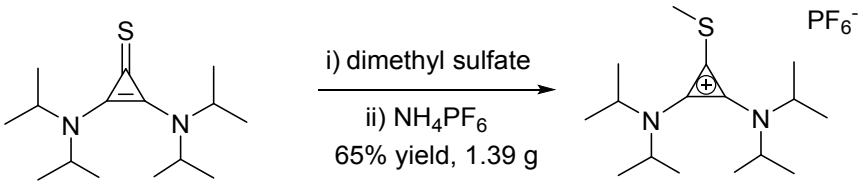
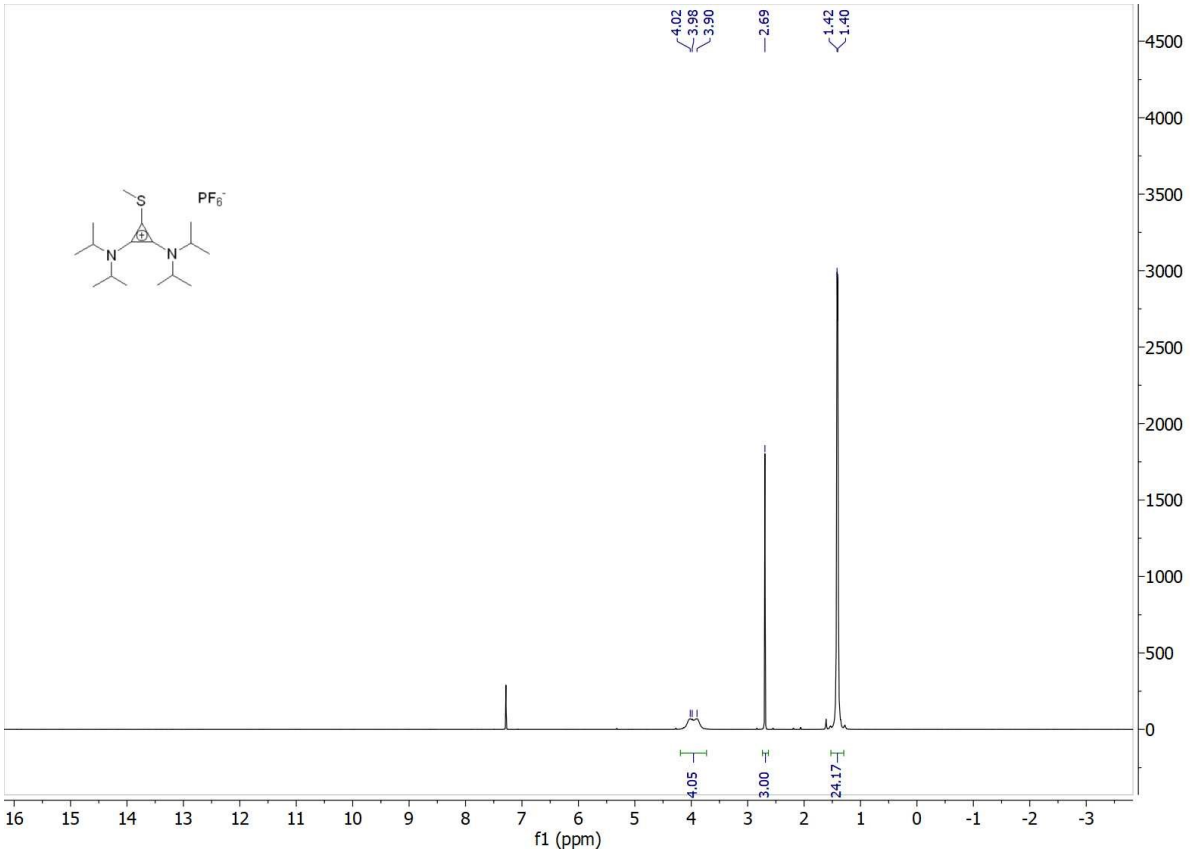
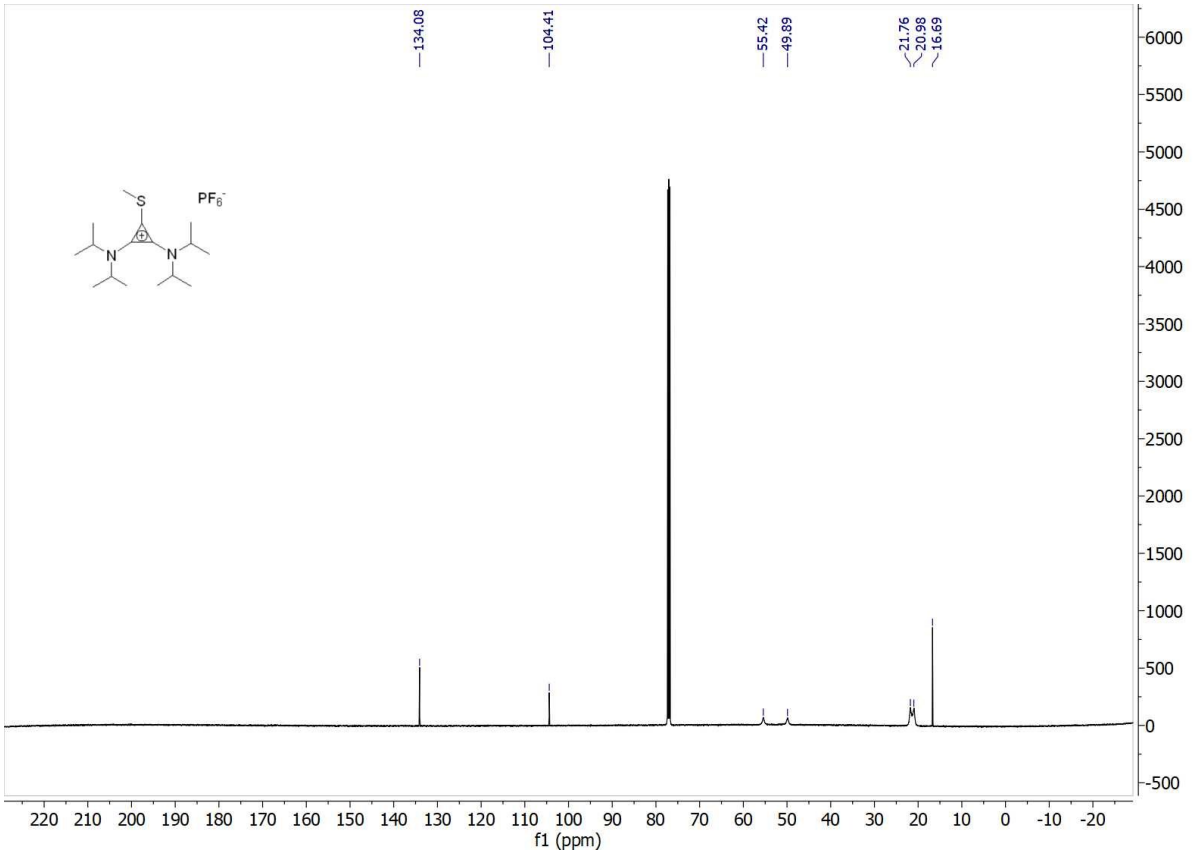
[1] These authors made equal contributions to the work



Scheme S1. The synthesize route of TDAC•PF_6 compound.





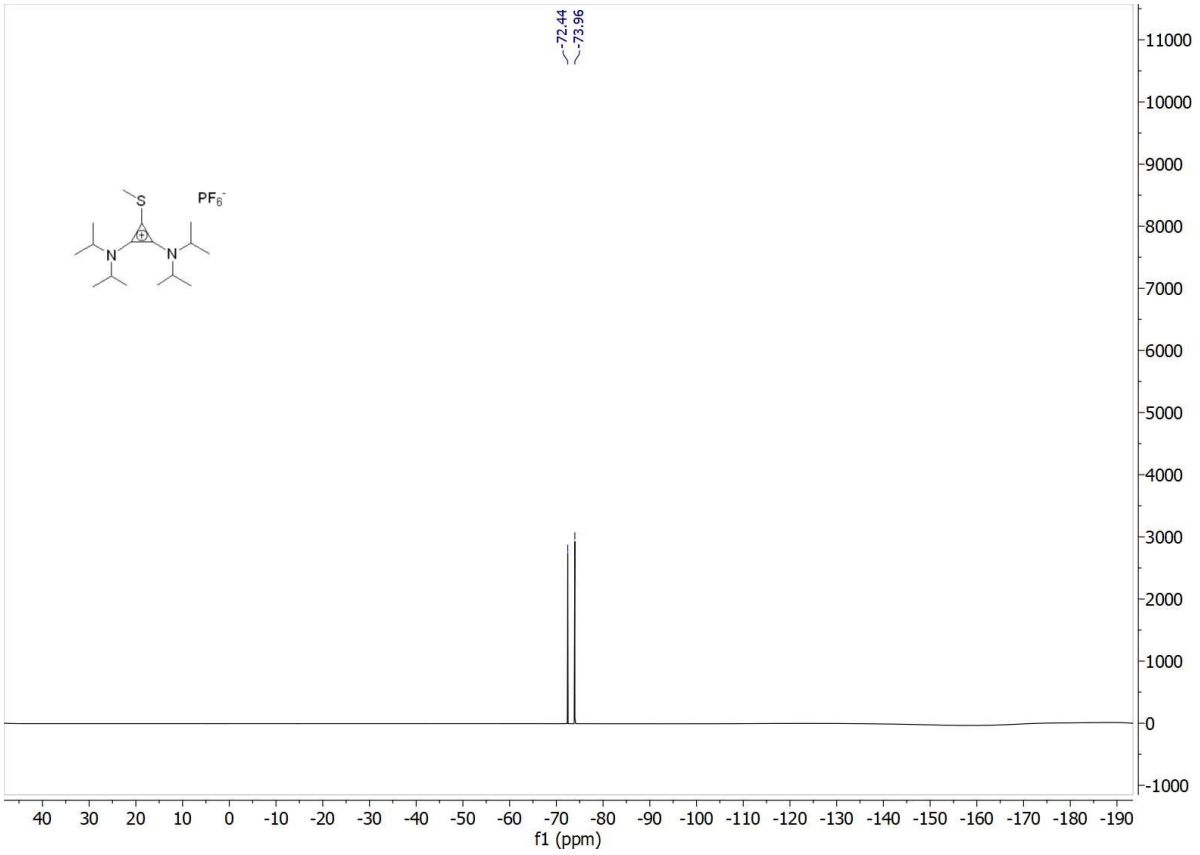


Fig. S1. The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectral data of the as-synthesized TDAC•PF_6 compound.

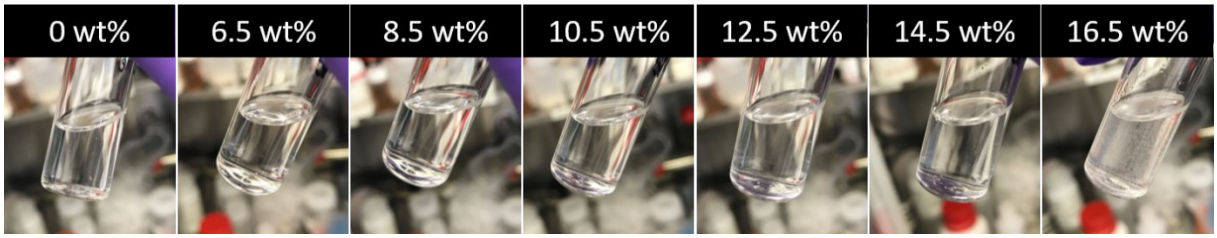


Fig. S2. Photographs of baseline electrolyte dissolved with different weight percentages of TDAC•PF_6 salt.

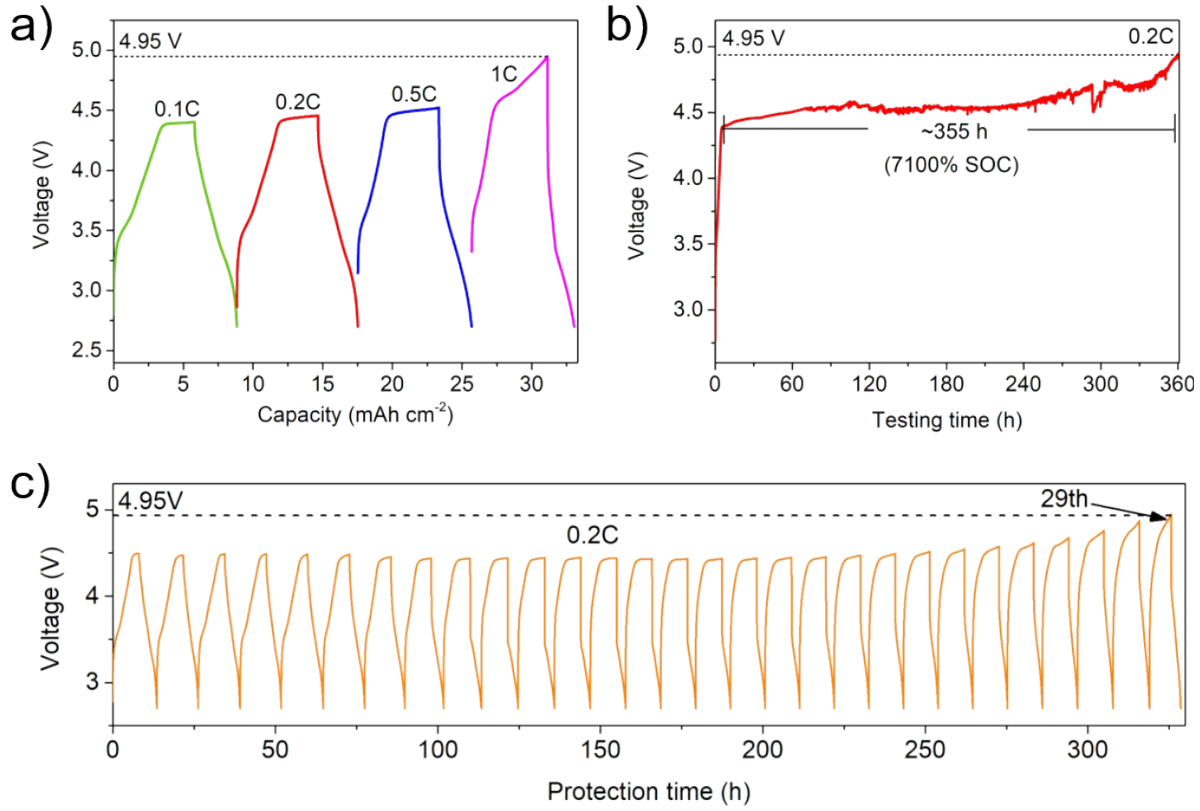


Fig. S3. Overcharge protection performance of NCA/Si-C cell with 0.2 M TDAC electrolyte. a) 100% overcharge profiles at different current rates; b) continuously charging voltage profile at 0.2 C; c) 100% overcharge cycling performance at 0.2 C.

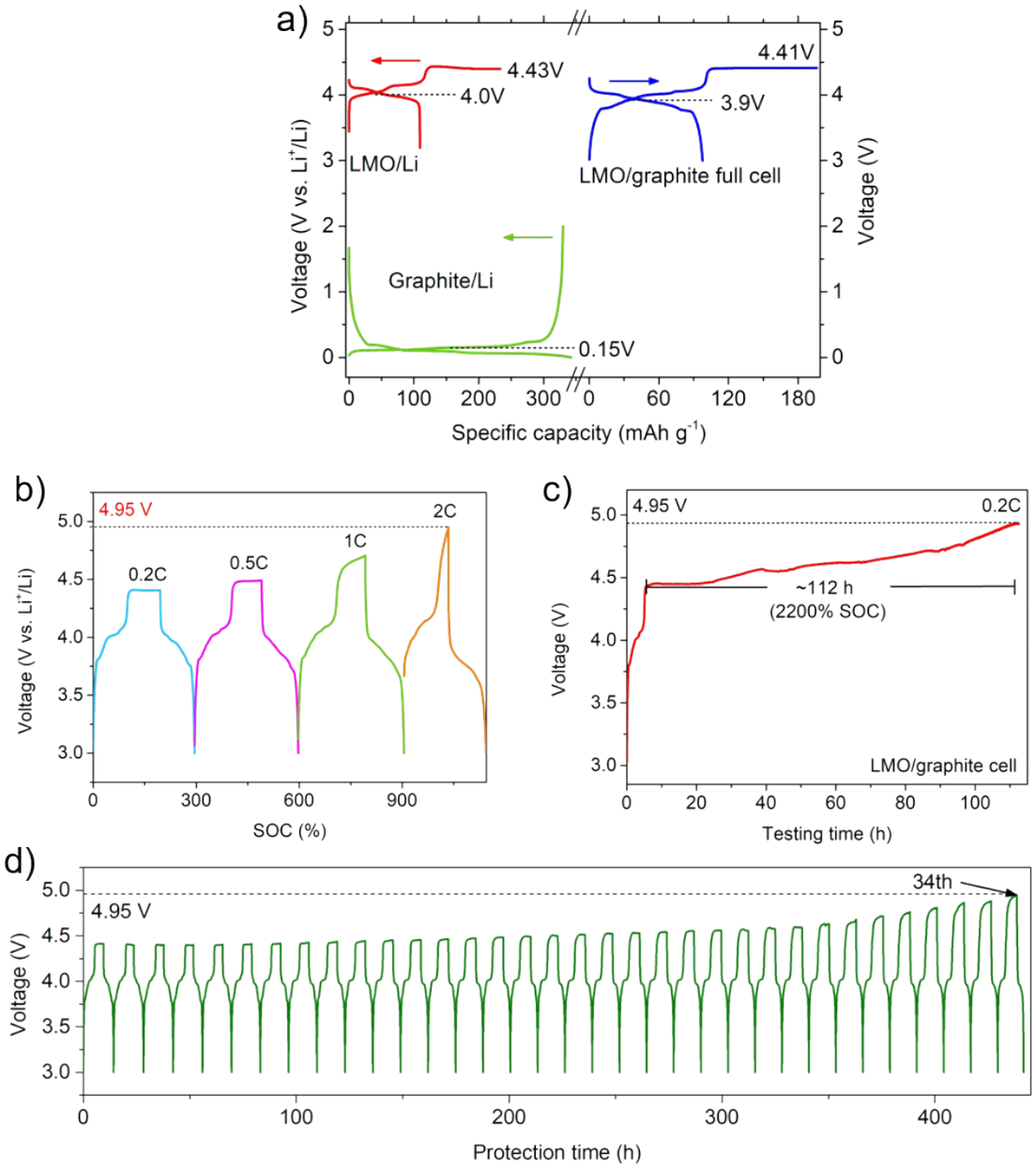


Fig. S4. Overcharge protection performance of LMO/graphite cell with 0.2 M TDAC electrolyte. a) Voltage profiles of LMO/graphite cell, LMO/Li half-cell and graphite/Li half-cell; b) 100% overcharge profiles at different current rates; c) continuously charging voltage profile at 0.2 C; d) 100% overcharge cycling performance at 0.2 C.

Note: the LMO/graphite cell can carry an utmost 2.2 mA cm^{-2} current (1 C) with 100% overcharge as displayed in Fig. S4b, endure ~112 h (equal to 2200% SOC) at 0.2 C as displayed in Fig. S4c and survive 34 cycles with 100% overcharge at 0.2 C as displayed in Fig. S4d.

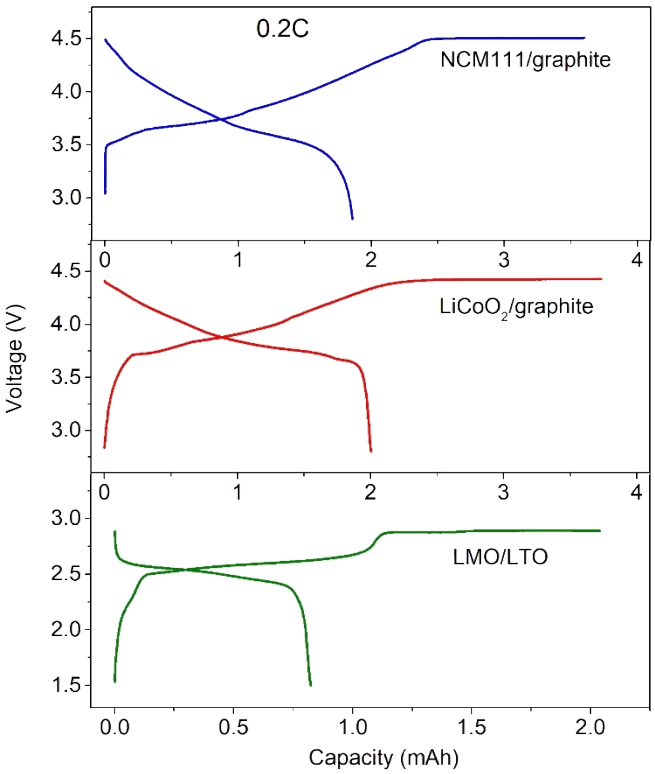
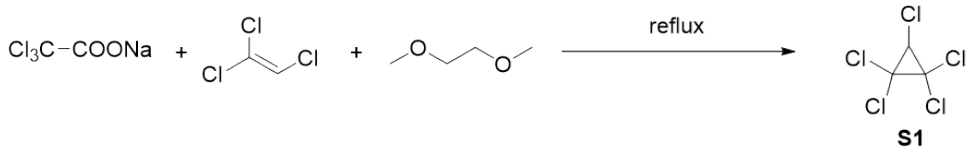


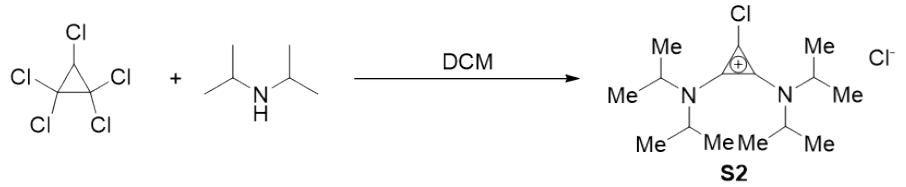
Fig. S5. Overcharge performance of NCM11/graphite cell, $LiCoO_2$/graphite and $LiMn_2O_4$/$Li_4Ti_5O_{12}$ cell with 0.2 M TDAC electrolyte at 0.2 C.



S1

usage	300 g	500 mL	145 mL		60 g, 17% yield
price	5 kg / $ 278 (Alfa Aesar)	4 L / $ 65 (Oakwood)	4 L / $ 158 (Oakwood)		
cost	$ 17	$ 8	$ 6	$10 for electricity and work-up	Sum: $ 41

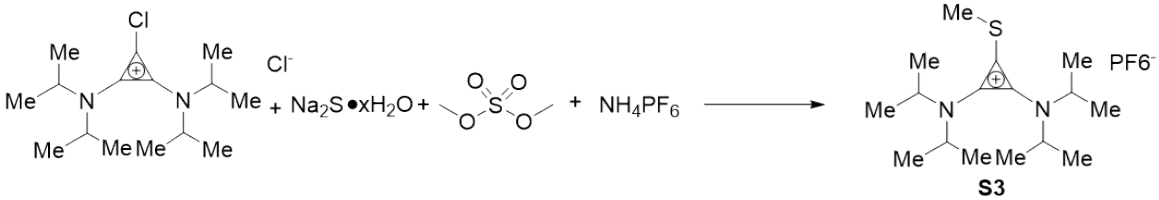
S1 = $ 0.7 per gram



S2

usage	15 g	79 mL	500 mL	13.8 g, 64% yield
price	1 g / $0.7	4 L / $ 68 (Oakwood)		
cost	$ 11	$ 1	$10 for electricity and work-up	Sum: $ 22

S2 = $ 1.6 per gram



S3

usage	2 g	1 g	1 mL	2 g	1.39 g, 65% yield
price	1 g / $ 1.6	2.5 kg / $ 82.3 (Aldrich)	3 kg / $ 123 (Oakwood)	500 g / $ 115 (Oakwood)	
cost	$ 3		$5 for electricity, other chemicals and work-up		Sum: $ 8

S3 = $ 5.8 per gram

Fig. S6. The cost calculation of the TDAC compound. Please bear in mind, this is a very new proprietary compound which has not been commercialized and mass produced yet. The cost estimated is on the lab scale NOT on mass production level e.g. the overhead, logistics etc. are not included, neither does the quantity discount.

Table S1. Performance summary of state-of-the-art redox shuttles for 4V-class cathodes.

Shuttle additives	Cell chemistry	Cell capacity	Concentration	Overcharge current	Protection cycles	Ref.
1#	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/Li half-cell	2 mAh	0.4 M	0.2 mA cm^{-2}	7	1
2#	$LiMn_2O_4$/Li half-cell	0.83 mAh cm^{-2}	0.01 M	0.083 mA cm^{-2}	11	2
	$Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$/Li half-cell	0.83 mAh cm^{-2}	0.01 M	0.083 mA cm^{-2}	9	
3#	$LiMn_2O_4$/MCMB full cell	1 mAh cm^{-2}	0.15 M	0.1 mA cm^{-2}	95	3
4#	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/graphite full cell	2 mAh cm^{-2}	0.05 M	0.2 mA cm^{-2}	16	4
5#	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/graphite full cell	2.2 mAh cm^{-2}	0.2 M	0.44 mA cm^{-2}	54	this work
	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/silicon-carbon full cell	3 mAh cm^{-2}	0.2 M	0.6 mA cm^{-2}	29	

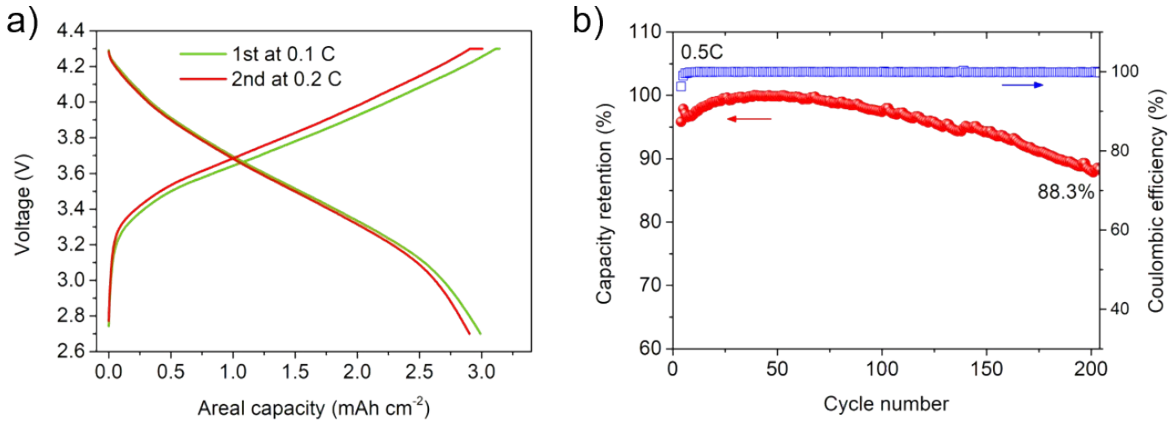


Fig. S7. a) The first two formation cycles and b) cycling performance of NCA/Si-C cell in 0.2 M TDAC electrolyte between 2.7-4.3 V.

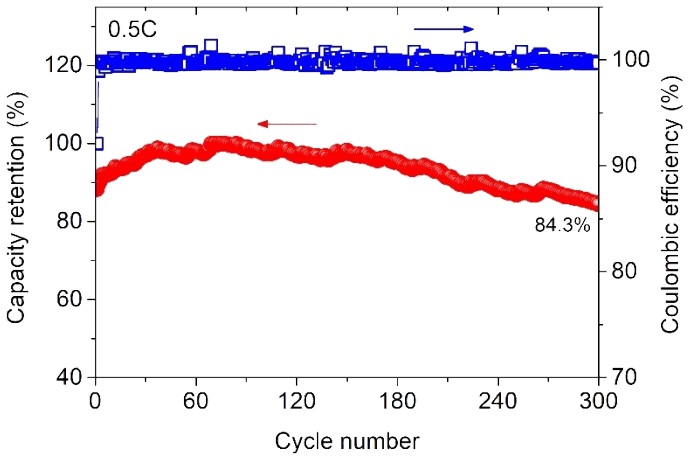


Fig. S8. Cycling performance of LMO/graphite cell in 0.2 M TDAC electrolyte between 3-4.3 V.

Note: The LMO/graphite cell with TDAC containing electrolyte remains at 84.3% capacity with a nearly 100% CE after 300 cycles.

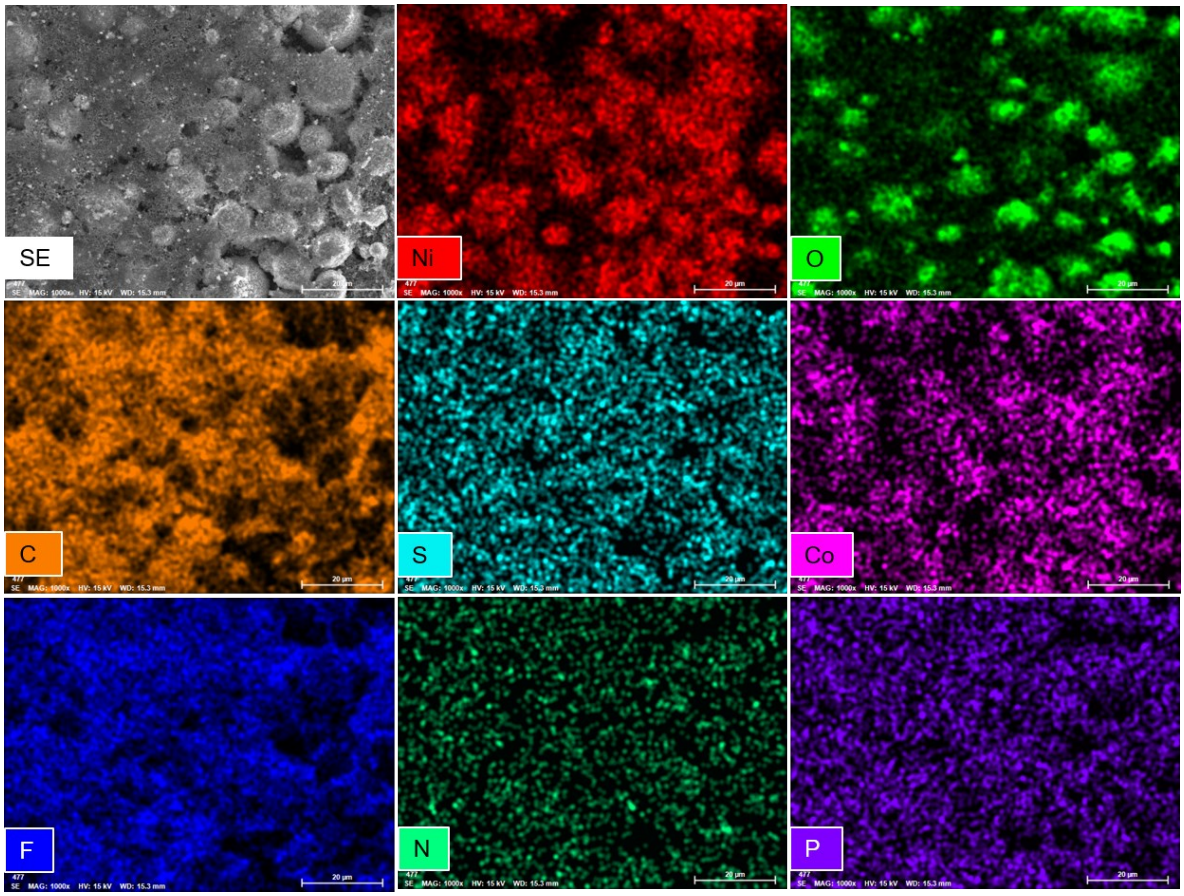


Fig. S9. Elemental mapping images of the reclaimed NCA cathode after overcharge.

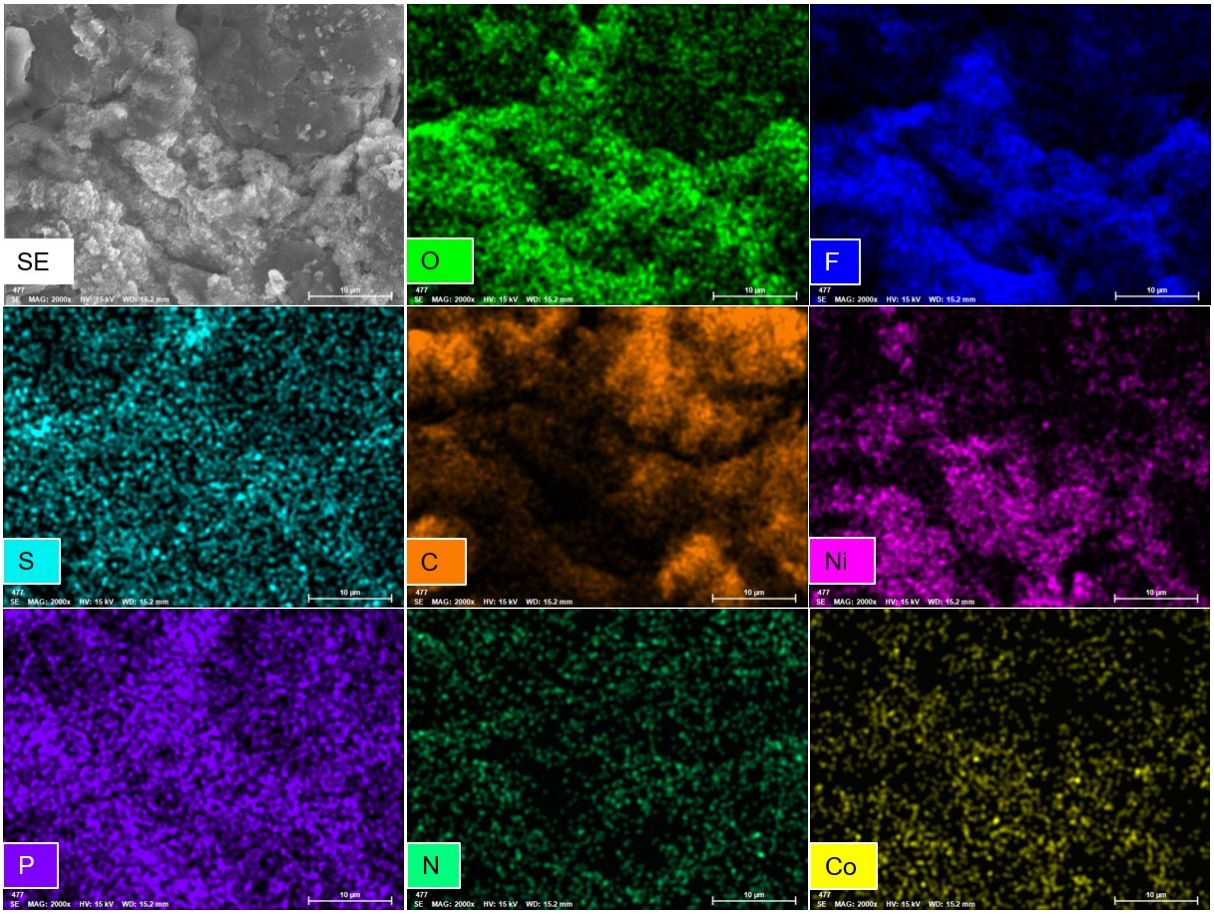


Fig. S10. Elemental mapping images of the reclaimed graphite anode after overcharge.

Reference

1. W. Weng, J. Huang, I. A. Shkrob, L. Zhang, Z. Zhang, *Adv. Energy Mater.* 2016, **6**, 1600795.
2. L. Zhang, Z. Zhang, H. Wu, K. Amine, *Energy & Environ. Sci.* 2011, **4**, 2858-2862.
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4. A. P. Kaur, M. D. Casselman, C. F. Elliott, S. R. Parkin, C. Risko, S. A. Odom, *J. Mater. Chem. A* 2016, **4**, 5410-5414.