

## Supporting Information

### **Identifying lithium difluoro(oxalate)borate as a multifunctional electrolyte additive to enable high-voltage $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lithium-ion batteries**

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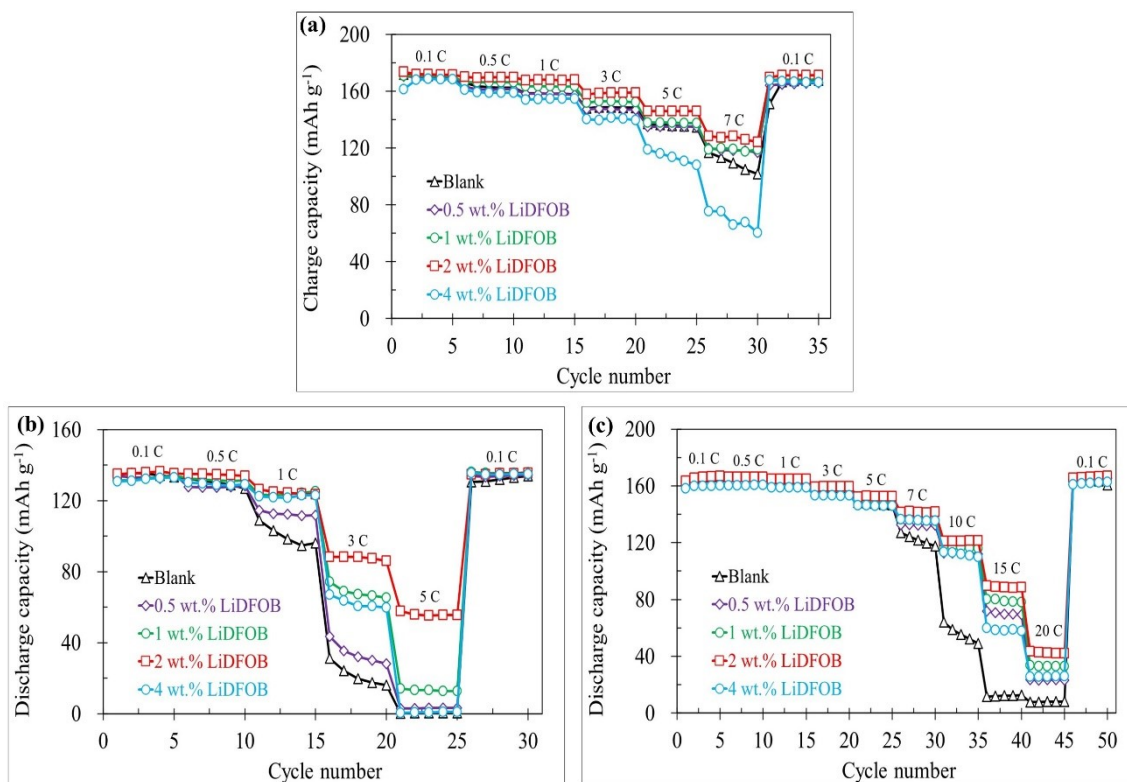
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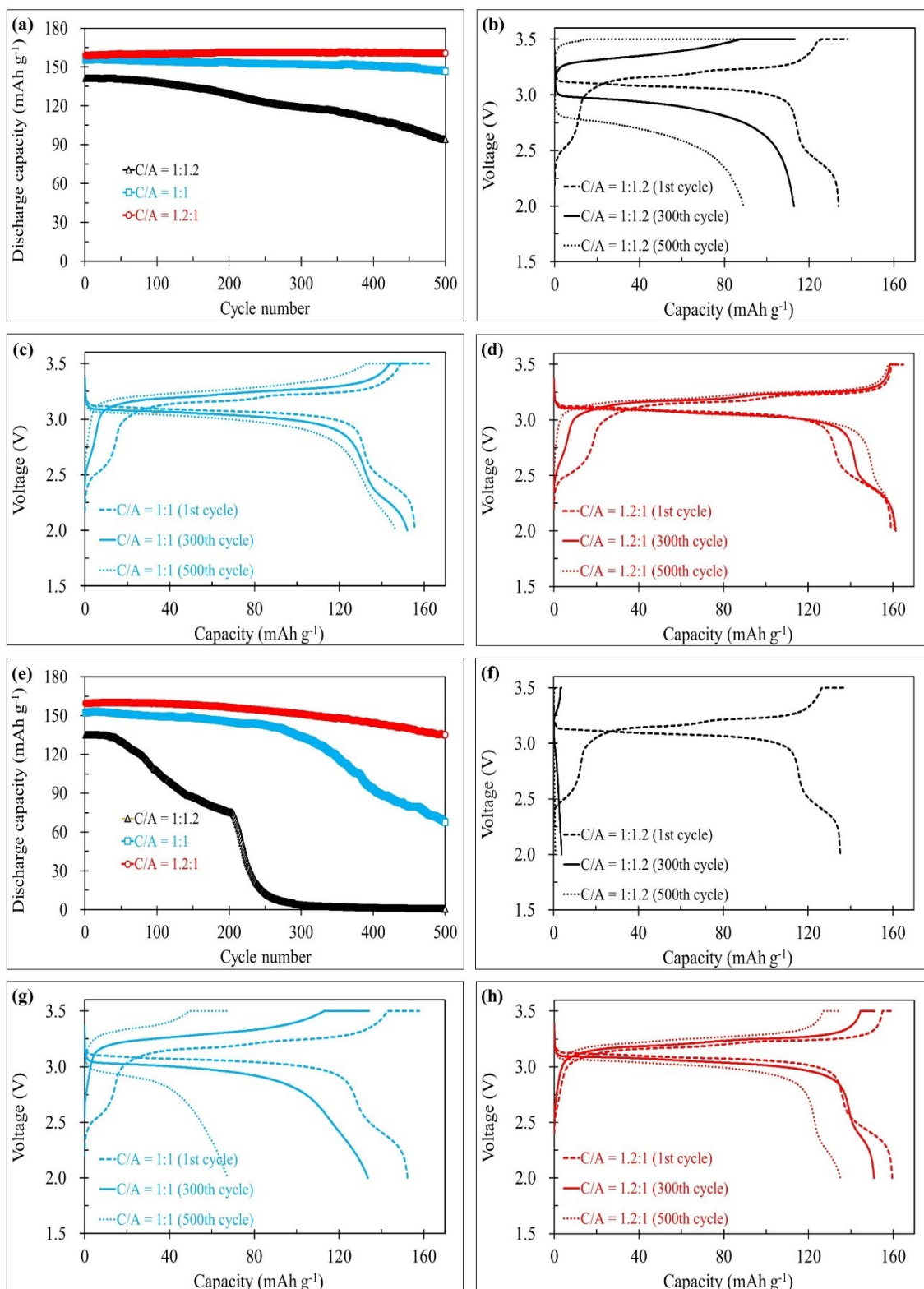
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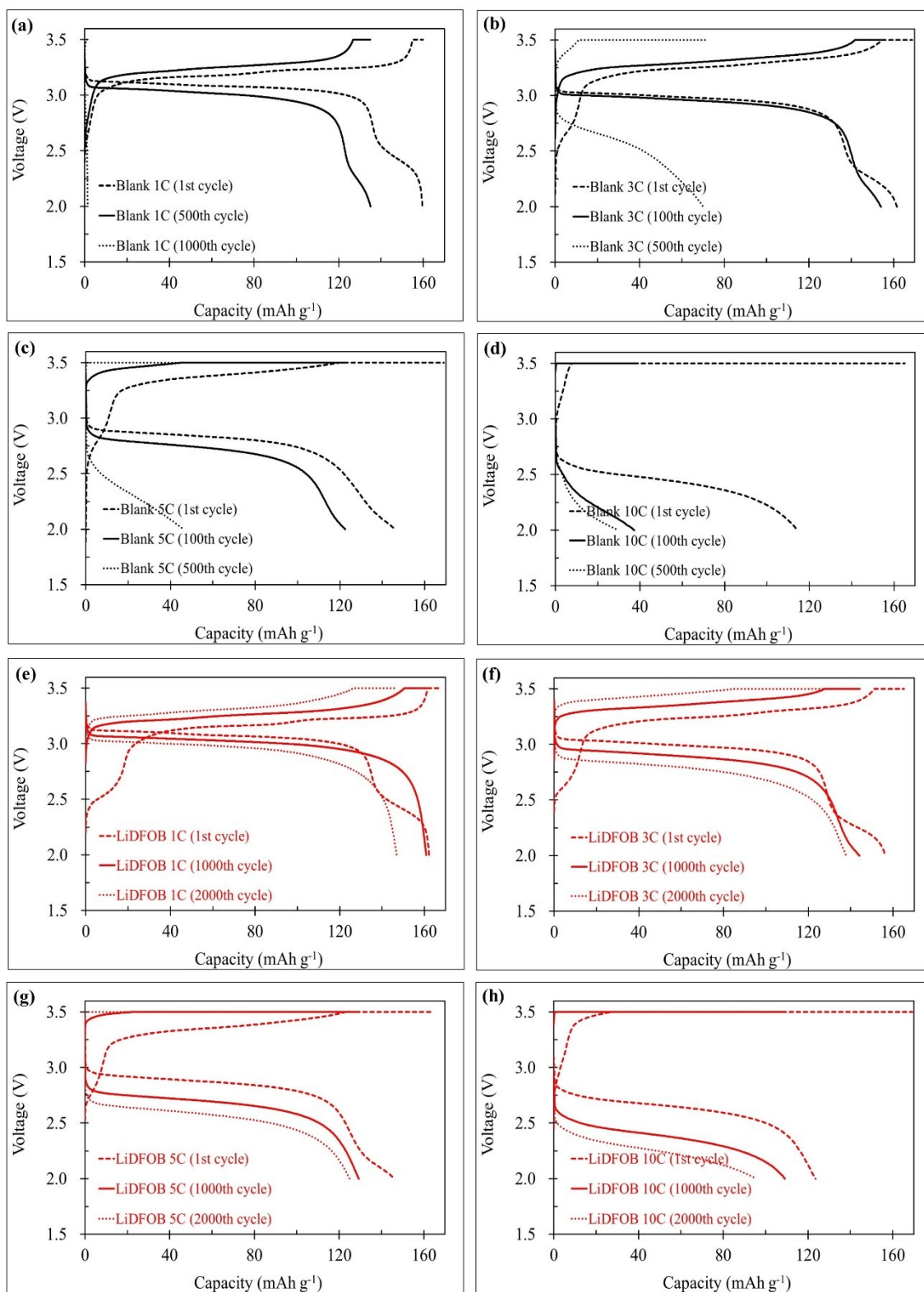
**Figure S1.** Charge/discharge capacities obtained at different currents (at each current, a same current is used for charge and discharge) with the blank and various LiDFOB-containing electrolytes for (a) the LTO electrode (Cut-off potential: 1.0 ~ 2.5 V), (b) the LNMO electrode (Cut-off potential: 3.5 ~ 4.95 V), and (c) the LNMO//LTO battery ( $C/A = 1.2:1$ . Cut-off voltage: 2.0 ~ 3.5 V).



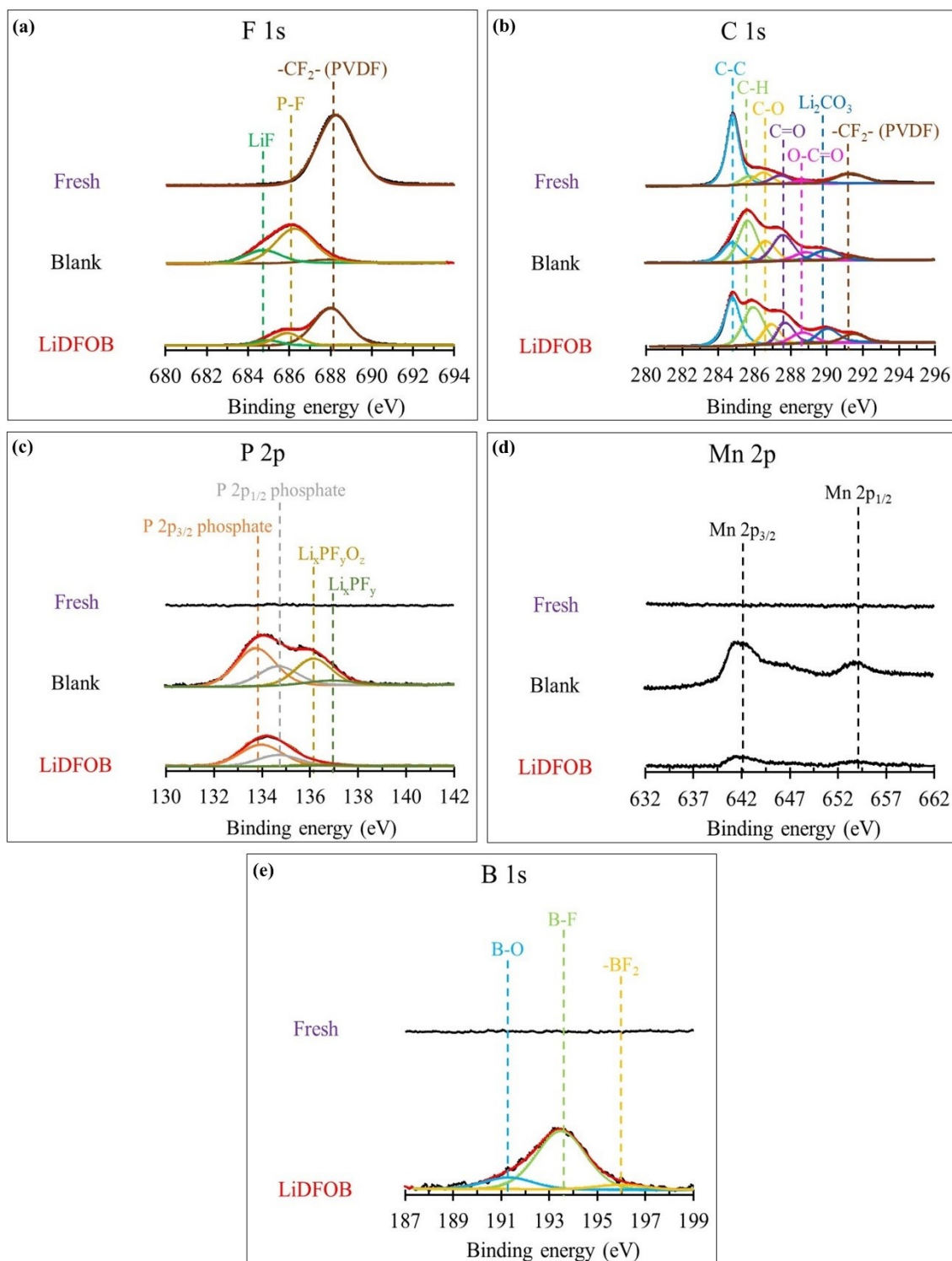
**Figure S2.** (a, e) Cycling performances and (b-d, f-h) corresponding GCD profiles of the LNMO//LTO batteries fabricated from the (a-d) 2 wt.% LiDFOB-containing and (e-h) blank

electrolytes with various C/A ratios. Cut-off voltage: 2.0 ~ 3.5 V. Charge/discharge current: 1

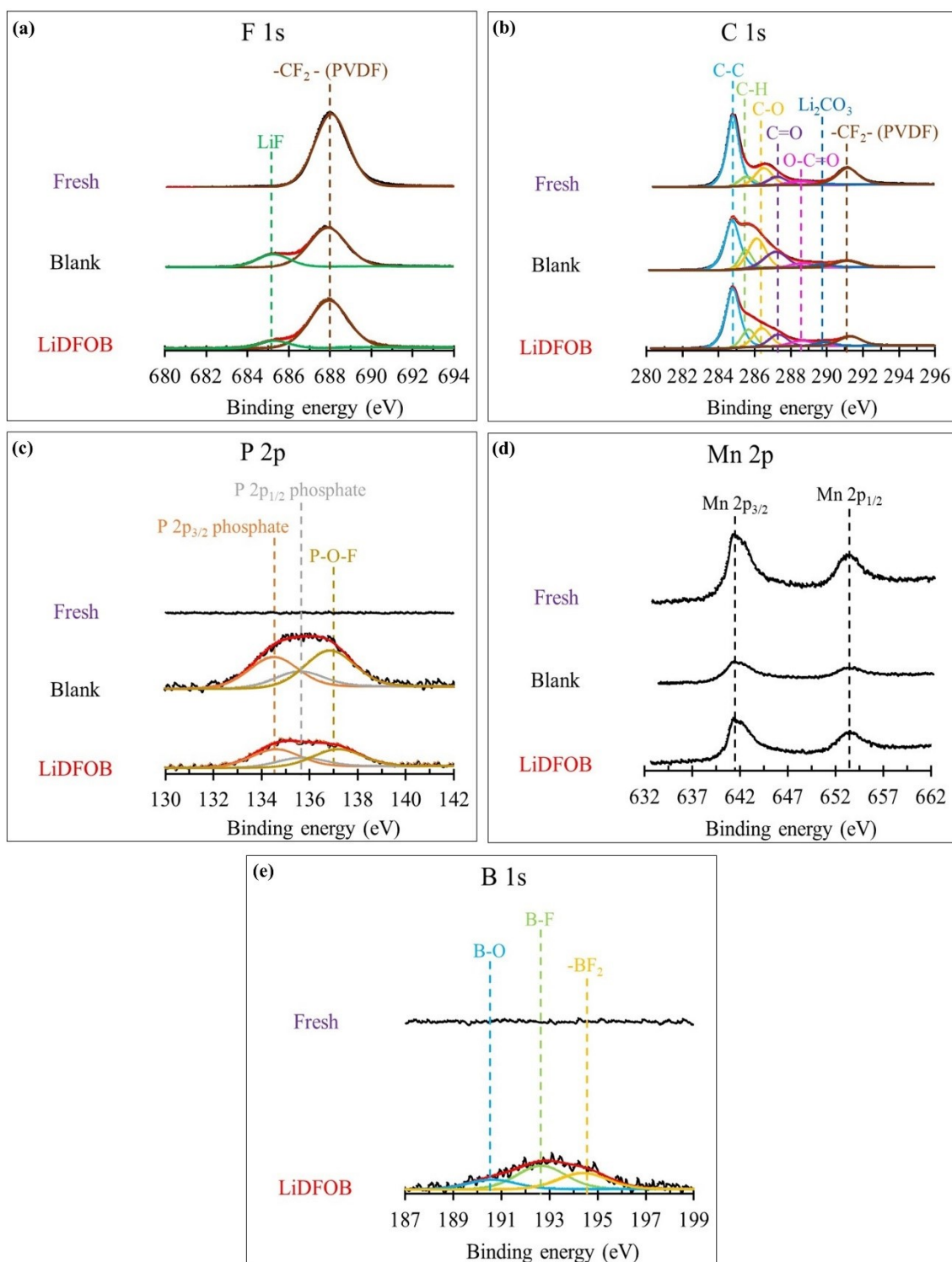
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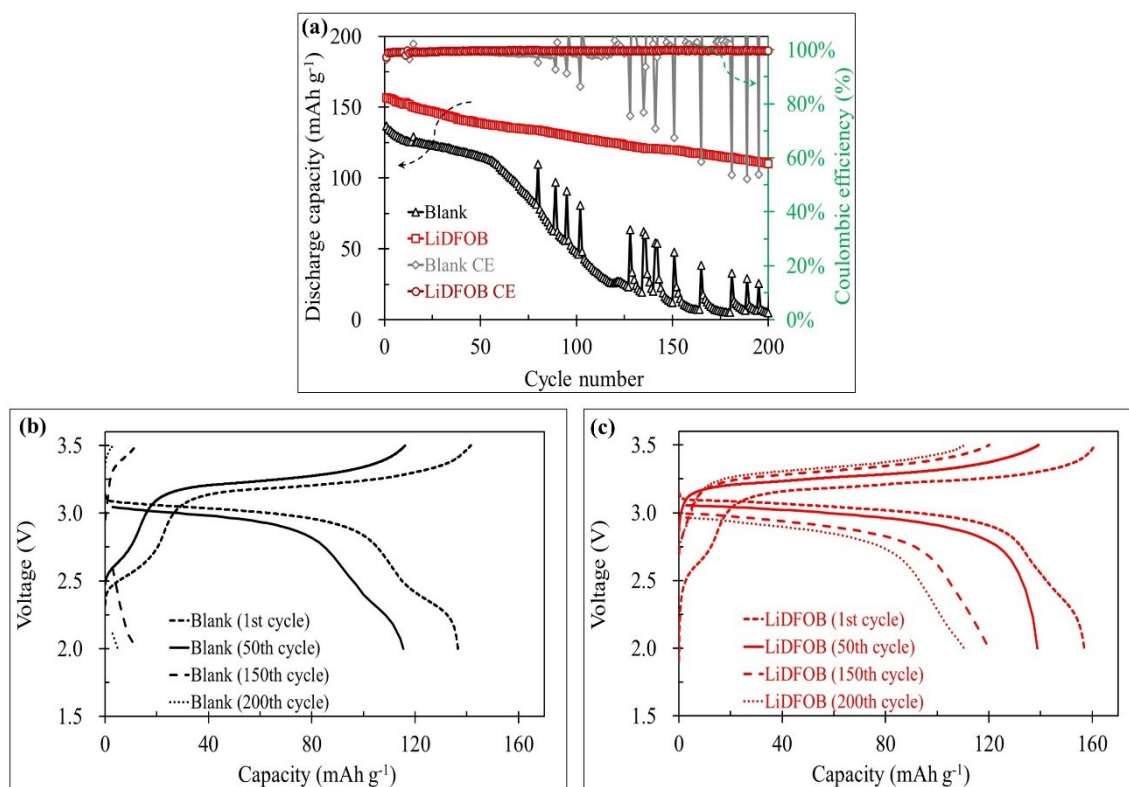
**Figure S3.** GCD profiles of the LNMO//LTO batteries of Figure 5 fabricated from the (a-d) blank and (e-h) 2 wt.% LiDFOB-containing electrolytes upon charge/discharge at (a, e) 1 C, (b, f) 3 C, (c, g) 5 C, and (d, h) 10 C, respectively.



**Figure S4.** (a) F 1s XPS, (b) C 1s XPS, (c) P 2p XPS, (d) Mn 2p XPS, and (e) B 1s XPS spectra of the fresh and cycled LTO anodes of the LNMO//LTO batteries fabricated from the blank and 2 wt.% LiDFOB-containing electrolytes. C/A = 1.2:1. Cut-off voltage: 2.0 ~ 3.5 V. Charge/discharge current: 1 C. Cycle number: 600.



**Figure S5.** (a) F 1s XPS, (b) C 1s XPS, (c) P 2p XPS, (d) Mn 2p XPS, and (e) B 1s XPS spectra of the fresh and cycled LNMO cathodes of the LNMO//LTO batteries fabricated from the blank and 2 wt.% LiDFOB-containing electrolytes. C/A = 1.2:1. Cut-off voltage: 2.0 ~ 3.5 V. Charge/discharge current: 1 C. Cycle number: 600.



**Figure S6.** (a) Cycling performances and (b, c) corresponding GCD profiles of the LNMO//LTO batteries fabricated from the (b) blank and (c) 2 wt.% LiDFOB-containing electrolytes. C/A = 1.2:1. Cut-off voltage: 2.0 ~ 3.5 V. Charge/discharge current: 1 C. Temperature: 55 °C.



**Table S1.** Performance comparison of LNMO//LTO batteries between the present work and the relevant literature results.

Research focus	Electrolyte	Mass loading of electrodes (mg cm <sup>-2</sup> )	Cut-off voltage (V)	Rate capability	Room-temperature cycling stability	High-temperature cycling stability	Energy density (Wh kg <sup>-1</sup> )	Power density (kW kg <sup>-1</sup> )	Reference
Electrolyte additive	2 wt.% LiDFOB / 1 M LiPF <sub>6</sub> / EC:DMC:EMC (1:1:1)	Cathode: 12 Anode: 8	2.0-3.5	0.1 C capacity: 166.2 mAh g <sup>-1</sup> 1 C/0.1 C retention: 99.2% 3 C/0.1 C retention: 96.0% 5 C/0.1 C retention: 91.8% 10 C/0.1 C retention: 73.0%	1 C 2000th-cycle retention: 90.9% 3 C 2000th-cycle retention: 88.1% 5 C 2000th-cycle retention: 85.6% 10 C 2000th-cycle retention: 77.3%	55°C / 1 C 200th-cycle retention: 70.3%	523.6	10.8	This work
LTO anode	1 M LiPF <sub>6</sub> / EC:DEC (1:1)	Anode: 3.0-3.5	1.7-3.4	0.5 C capacity: 126.0 mAh g <sup>-1</sup> 1 C/0.5 C retention: 95.2% 2 C/0.5 C retention: 88.9% 5 C/0.5 C retention: 75.4% 10 C/0.5 C retention: 64.3%	3 C 1000th-cycle retention: 93.4%	—	396.9*	—	[34]

LTO anode	1 M LiPF <sub>6</sub> / EC:DMC:EMC (1:1:1)	Anode: 2.87	2.0-3.45	0.1 C capacity: 131.2 mAh g <sup>-1</sup> 1 C/0.1 C retention: 96.9% 2 C/0.1 C retention: 93.8% 5 C/0.1 C retention: 89.2% 10 C/0.1 C retention: 83.2%	5 C 500th-cycle retention: 97.3%	—	413.3*	—	[35]
LTO anode	1 M LiPF <sub>6</sub> / EC:DEC (1:1)	Cathode: 1.3-1.9 Anode: 1.3-1.9	1.6-3.4	0.5 C capacity: 128.0 mAh g <sup>-1</sup> 1 C/0.5 C retention: 92.2% 2 C/0.5 C retention: 85.9% 5 C/0.5 C retention: 78.1% 10 C/0.5 C retention: 69.5%	5 C 500th-cycle retention: 89.5%	—	403.2*	—	[36]
LTO anode	1 M LiPF <sub>6</sub> / EC:DEC:DMC:EMC (1:1:1:3)	—	2.0-3.5	0.1 C capacity: 164.8 mAh g <sup>-1</sup> 1 C/0.1 C retention: 82.3% 3 C/0.1 C retention: 59.2% 5 C/0.1 C retention: 28.2%	—	—	519.1*	—	[37]

LNMO cathode	1 M LiPF <sub>6</sub> / EC:DMC (1:1)	—	—	—	1 C 200th-cycle retention: 92.4%	—	—	—	[38]
LNMO cathode	1 M LiPF <sub>6</sub> / EC:DMC (1:1)	Cathode: 2.0	2.0-3.5	0.1 C capacity: 129.4 mAh g <sup>-1</sup> 1 C/0.1 C retention: 68.1% 2 C/0.1 C retention: 61.3% 5 C/0.1 C retention: 45.7%	1 C 100th-cycle retention: 85.2%	55°C / 2 C 100th-cycle retention: 88.9%	407.6*	—	[39]
LNMO cathode	1 M LiPF <sub>6</sub> / EC:DMC (1:1)	Cathode: 3.5	2.0-3.5	—	1 C 200th-cycle retention: 97.6%	—	—	—	[40]
LNMO cathode	1 M LiPF <sub>6</sub> / FEC:DEC (1:4)	—	2.0-3.5	—	1 C 100th-cycle retention: 93.4%	—	—	—	[41]
LTO anode and LNMO cathode	1 M LiPF <sub>6</sub> / EC:DMC (1:1)	—	2.0-4.0	—	1 C 200th-cycle retention: 87.0%	—	—	—	[42]
LTO anode and LNMO cathode	1 M LiPF <sub>6</sub> / EC:DMC (1:1)	—	2.0-3.5	—	1 C 200th-cycle retention: 94.0%	—	—	—	[43]
Electrolyte solvent	1.2 M LiPF <sub>6</sub> / F-AEC:F-EMC:F-EPE (2:6:2)	—	2.0-3.45	—	0.5 C 200th-cycle retention: almost 100%	—	—	—	[44]
Electrolyte solvent	1M LiPF <sub>6</sub> / PC:HFE (8:2)	—	2.0-3.5	0.1 C capacity: 152.0 mAh g <sup>-1</sup> 1 C/0.1 C retention:	1 C 200th-cycle retention: 92.5%	—	478.8*	—	[45]

				96.7% 6 C/0.1 C retention: 80.9%					
Electrolyte solvent	1 M LiPF <sub>6</sub> / TMP:FEPE (8:2)	—	2.0-3.5	0.1 C capacity: 140.8 mAh g <sup>-1</sup> 4 C/0.1 C retention: 49.2%	1 C 118th-cycle retention: 98.5%	—	443.5*	—	[46]
Electrolyte additive	1 wt.% LiO-t-C <sub>4</sub> F <sub>9</sub> / 1 M LiPF <sub>6</sub> / EC:DMC (1:1)	—	1.5-3.5	—	0.05 C 50th-cycle retention: 98.5%	—	—	—	[47]
Electrolyte additive	1 wt.% FEC / 1 M LiPF <sub>6</sub> / EC:DEC (1:1)	Cathode: 11.8	1.5-3.5	0.1 C capacity: 128.0 mAh g <sup>-1</sup> 1 C/0.1 C retention: 85.2% 5 C/0.1 C retention: 78.1%	1 C 500th-cycle retention: 48.3%	55°C / 0.5 C 100th-cycle retention: 13.0%	403.2*	—	[48]
Electrolyte solvent/salt	0.7 M LiTFSI / MMMPyrTFSI	Cathode: 2.9-3.5 Anode: 2.9-3.5	1.4-3.4	—	—	40°C / 0.5 C 50th-cycle retention: 68.6% 60°C / 0.5 C 50th-cycle retention: 74.1%	—	—	[49]
Electrolyte solvent/salt/additive	2 % FEC / 2 M LiBF <sub>4</sub> / GBL:AND (1:1)	—	2.0-3.5	0.1 C capacity: 120.2 mAh g <sup>-1</sup> 1 C/0.1 C retention:	1 C 100th-cycle retention: 84.0%	—	378.6*	—	[50]

				74.9% 2 C/0.1 C retention: 60.8% 5 C/0.1 C retention: 45.8%					
Polymer electrolyte	LiPF <sub>6</sub> / PAMM	Anode: 1.96	2.0-3.5	0.1 C capacity: 129.0 mAh g <sup>-1</sup> 5 C/0.1 C retention: 38.6%	1 C 100th-cycle retention: 88.4%	55°C / 1 C 23rd-cycle retention: 71.2%	406.4*	—	[51]
Aqueous electrolyte	1 mol LiTFSI / 0.5 mol TMS / 1 mol Water	Cathode: 2.73 Anode: 1.29	2.0-3.5	—	3 C 150th-cycle retention: 62.4% 6 C 300th-cycle retention: 64.3%	—	408.0*	—	[52]
Aqueous-nonaqueous hybrid electrolyte	(21 M LiTFSI in water) : (1 mol LiTFSI / 1.2 mol DMC) = 1:1 by mass	Cathode: 8 Anode: 4	2.0-3.5	0.5 C capacity: 162.1 mAh g <sup>-1</sup> 1 C/0.5 C retention: 94.4% 4 C/0.5 C retention: 75.9% 6 C/0.5 C retention: 58.0%	0.5 C 200th-cycle retention: 89.4% 6 C 1000th-cycle retention: 76.0%	—	510.6*	—	[53]
Current collector	1 M LiPF <sub>6</sub> / EC:DMC (1:1)	—	2.0-3.4	0.1 C capacity: 115.0 mAh g <sup>-1</sup> 1 C/0.1 C retention: 95.6% 3 C/0.1 C retention: 89.2% 5 C/0.1 C retention:	1 C 500th-cycle retention: 98.5% 5 C 500th-cycle retention: 95.5% 10 C 500th-cycle retention: 84.7%	—	362.2*	—	[54]

				83.8% 8 C/0.1 C retention: 76.9% Charge: 0.1 C					
Separator	1 M LiPF <sub>6</sub> / EC:DEC (1:1)	Cathode: 3.4 Anode: 2.6	2.0-3.5	—	1 C 100th-cycle retention: 98.1%	—	—	—	[55]

\*Energy density is calculated based on the active material mass of the determining electrode (LTO anode or LNMO cathode) and the discharge capacity and voltage (3.15 V) of the battery.

**Table S2.** EIS parameters of the LTO electrodes measured in Figure 2e.

Condition	Parameter	Electrolyte	
		Blank	2 wt.% LiDFOB-containing
After activated at 0.1 C for 5 cycles	$R_s$ ( $\Omega$ )	7.38	2.89
	$R_f$ ( $\Omega$ )	27.47	10.28
	$R_{ct}$ ( $\Omega$ )	93.91	79.74
	Slope of low-frequency tail	0.94	1.17

**Table S3.** EIS parameters of the LNMO electrodes measured in Figure 3e.

Condition	Parameter	Electrolyte	
		Blank	2 wt.% LiDFOB-containing
After activated at 0.1 C for 5 cycles	$R_s$ ( $\Omega$ )	8.35	5.71
	$R_f$ ( $\Omega$ )	169.80	147.80
	$R_{ct}$ ( $\Omega$ )	10.86	2.42
	Slope of low-frequency tail	0.35	0.75



**Table S4.** EIS parameters of the LNMO//LTO batteries measured in Figures 5a, e.

Condition	Parameter	Electrolyte	
		Blank	2 wt.% LiDFOB-containing
After activated at 0.1 C for 5 cycles	$R_s$ ( $\Omega$ )	3.26	2.25
	$R_f$ ( $\Omega$ )	34.92	24.41
	$R_{ct}$ ( $\Omega$ )	6.73	3.41
	Slope of low-frequency tail	1.09	1.48
After cycled at 1 C for 600 cycles	$R_s$ ( $\Omega$ )	5.20	2.31
	$R_f$ ( $\Omega$ )	72.03	32.95
	$R_{ct}$ ( $\Omega$ )	22.34	6.41
	Slope of low-frequency tail	0.82	1.20