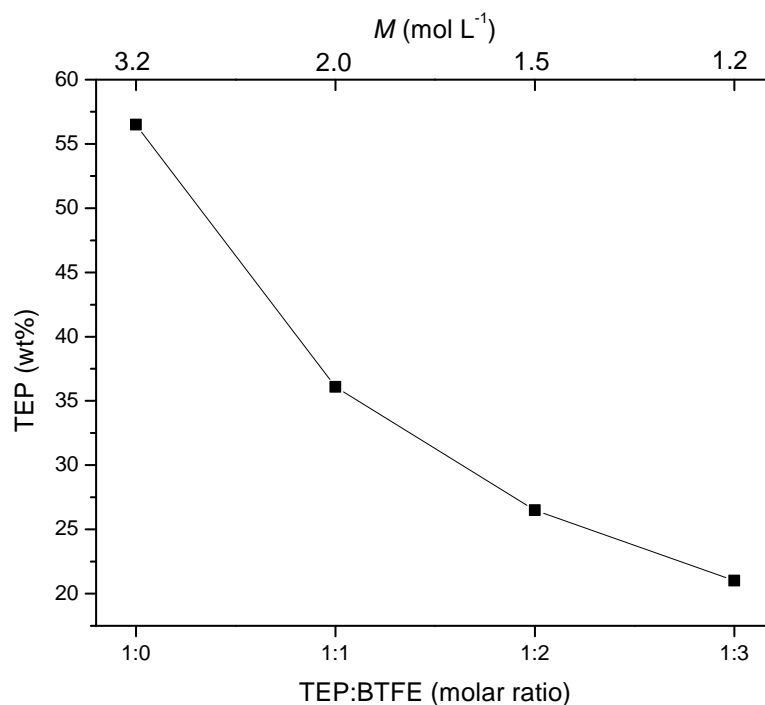# Supplemental Information

High-Efficiency Lithium Metal Batteries

with Fire-Retardant Electrolytes

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Figure S1. TEP contents in the highly concentrated electrolyte (HCE, 3.2 M LiFSI/TEP) and the locally highly concentrated electrolytes (LHCEs) with different concentrations of LiFSI produced by diluting the HCE with various amounts of BTFE.
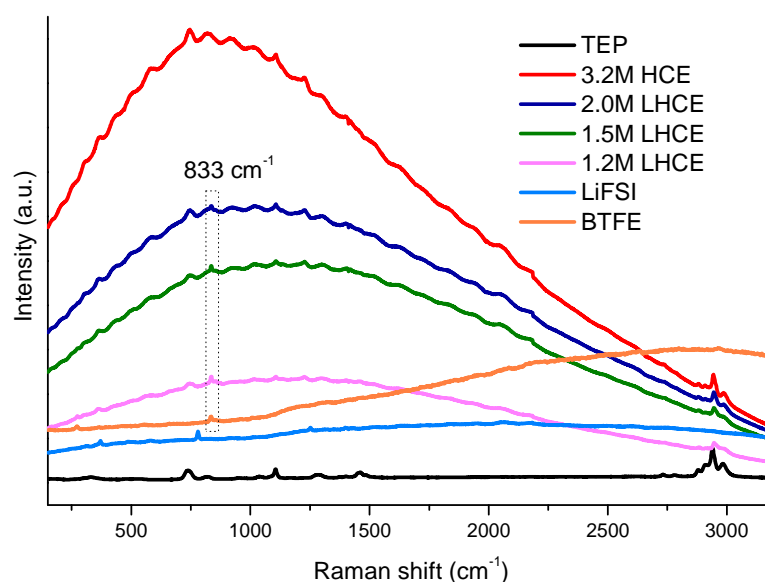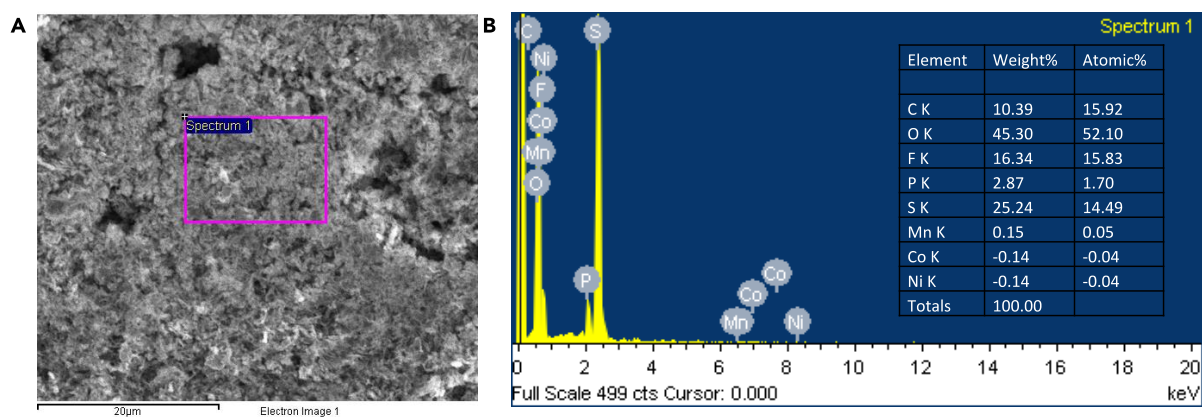

Figure S2. Wide scale Raman spectra of pure TEP, pure BTFE, LiFSI, the HCE, and LHCEs with different LiFSI salt concentrations and TEP/BTFE molar ratios.
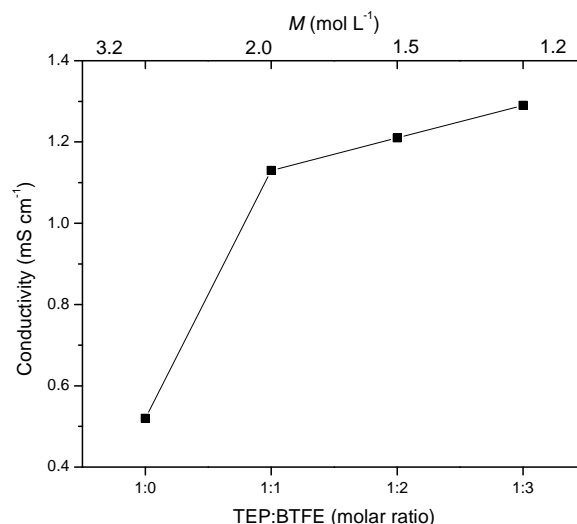
Figure S3. Ionic conductivity (25°C) of the HCE (3.2 M LiFSI/TEP) and the LHCEs with different concentrations of LiFSI produced by diluting the HCE with various amounts of BTFE.
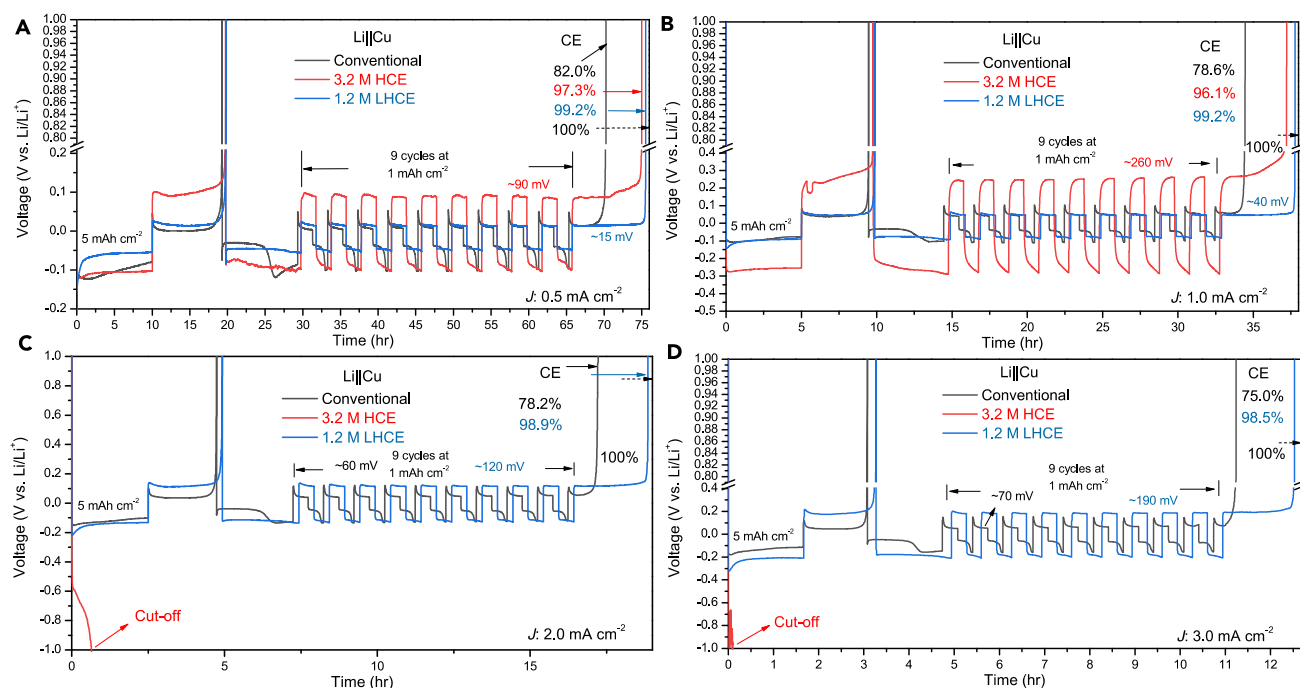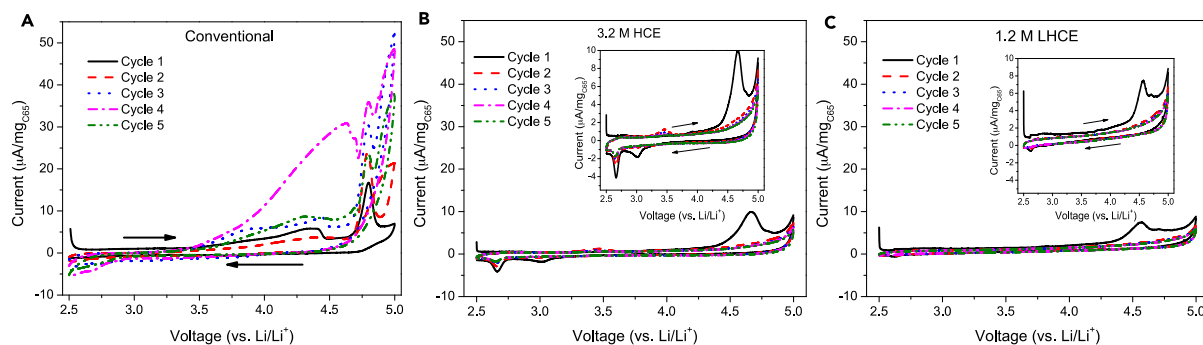

Figure S4. Accurate measurement of coulombic efficiency (CE) for Li metal anodes in different electrolytes at current densities (denoted J) of (A) 0.5, (B) 1.0, (C) 2.0, and (D) 3.0 mA cm^{-2} using Li‖Cu coin cells was done using the following procedure: 1) Perform one initial formation cycle with Li plating of 5 mAh cm^{-2} on Cu (or terminate the test if overpotential <-1 V) and stripping to 1 V; 2) Plate 5 mAh cm^{-2} Li on Cu as Li reservoir; 3) Repeatedly strip/plate Li with 1 mAh cm^{-2} (or strip to 1 V if overpotential >1 V is needed to strip Li with 1 mAh cm^{-2}) for 9 cycles; 4) Strip all Li to 1 V. Average CE is calculated by dividing the total stripping capacity by the total plating capacity after the formation cycle.

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Element	Weight%	Atomic%
C K	10.39	15.92
O K	45.30	52.10
F K	16.34	15.83
P K	2.87	1.70
S K	25.24	14.49
Mn K	0.15	0.05
Co K	-0.14	-0.04
Ni K	-0.14	-0.04
Totals	100.00	

Figure S5. (A) SEM image and (B) EDS spectrum of Li from a Li‖NMC622 cell using the 1.2 M LHCE cycled more than 300 times, with inset showing the detailed contents of different elements. A porous solid electrolyte interphase (SEI) layer on the surface of a Li metal anode with negligible amount of P compared to O, F, and S was observed from EDS, suggesting an FSI-derived SEI. In addition, negligible amounts of Mn, Co, and Ni were observed, indicating no transition metal dissolution loss from the NMC622 cathode in the LHCE.
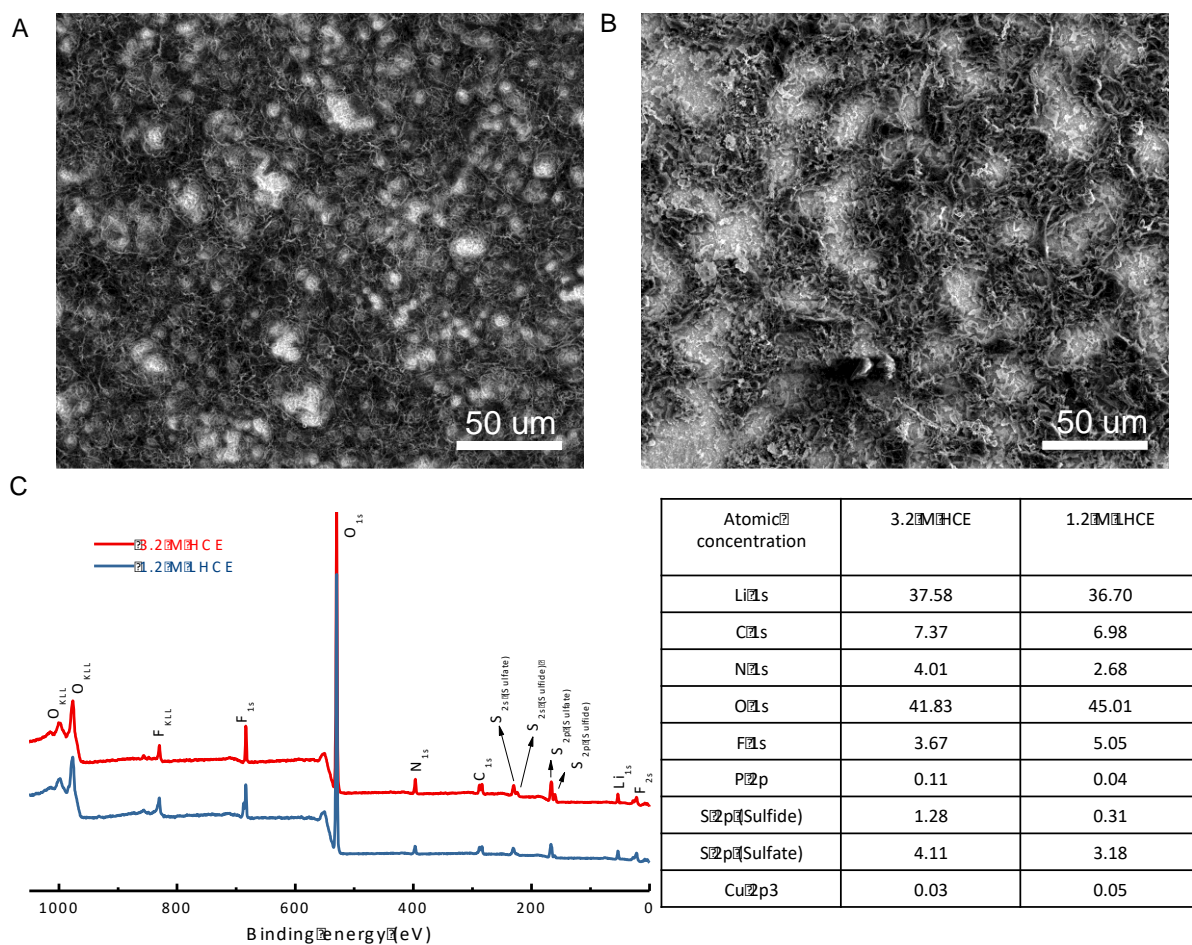
Figure S6. (A and B) SEM images and (C) wide-scan XPS and quantification of different components of SEI on Cu substrate collected by disassembly of Li‖Cu cells (after fully plating and stripping Li (to 1 V) at a current density of 0.5 mA/cm^2 with capacity of 5 mAh/cm^2 in the 3.2 M HCE (A) and 1.2 M LHCE (B) in glovebox and rinsed with DMC followed by drying under vacuum.

| Atomic concentration	3.2 M HCE	1.2 M LHCE
Li 1s	37.58	36.70
C 1s	7.37	6.98
N 1s	4.01	2.68
O 1s	41.83	45.01
F 1s	3.67	5.05
P 2p	0.11	0.04
S 2p (Sulfide)	1.28	0.31
S 2p (Sulfate)	4.11	3.18
Cu 2p3	0.03	0.05

Figure S7. Cyclic voltammetry studies of the anodic corrosion of Al and the high-voltage stability of (A) the conventional 1.0 M LiPF$_6$ electrolyte, (B) 3.2 M HCE and (C) 1.2 M LHCE. The current was specified based on the mass of Super C65 carbon for comparison.
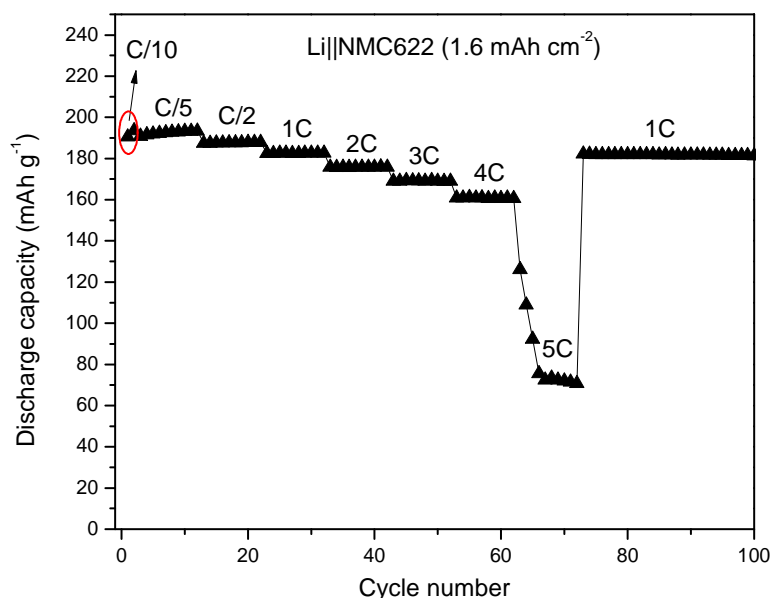
Figure S8. Rate capability of Li||NMC622 battery charged at constant C/3 rate and discharged at different C rates after two formation cycles at C/10 charge and discharge in the 1.2 M LHCE. 1C equals 180 mA g^{-1} of NMC622 or ~1.6 mA cm^{-2}.
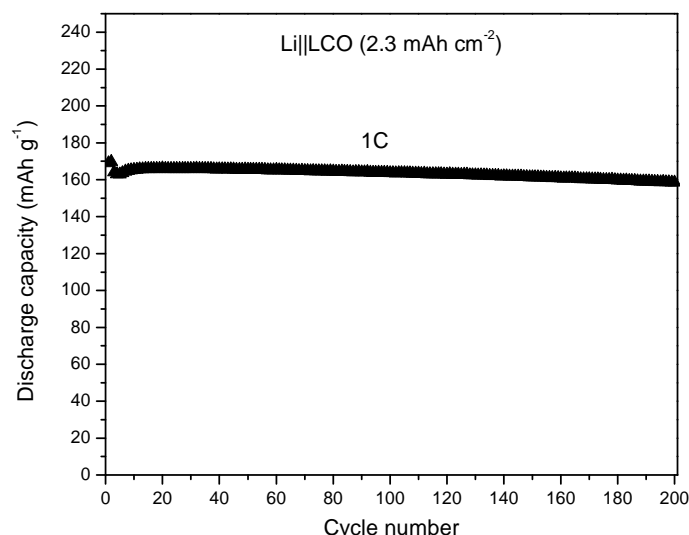
Figure S9. Cycling performance of Li‖LiCoO$_2$ (LCO) battery charged at constant C/3 rate and discharged at 1C between 2.8 and 4.4 V after two formation cycles in the 1.2 M LHCE at C/10 at 30°C. Constant voltage charge (4.4 V) until the current dropped below C/20) was applied after the formation cycles. 1C equals 160 mA g^{-1} of LCO. The LCO electrode was provided by Argonne National Laboratory's Cell Analysis, Modeling, and Prototyping (CAMP) Facility.
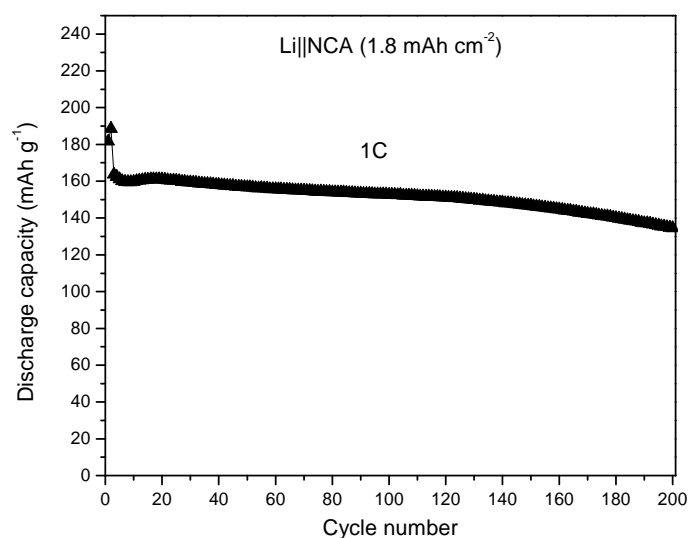
Figure S10. Cycling performance of Li‖ LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) battery charged at constant C/3 rate and discharged at 1 C between 2.8-4.4 V after two formation cycles at C/10 in the 1.2 M LHCE at 30°C. Constant voltage charge (4.4 V until the current dropped below C/20) was applied after the formation cycles. 1C equals 190 mA g^{-1} of NCA. The NCA electrode was provided by Saft America.