Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Electrolyte screening studies for Li metal batteries

Jeesoo Seok[a], Na Zhang[a], Burak Ulgut[b], Aihua Jin[c], Seung-Ho Yu*[c] and Héctor D. Abruña*[a]

[a]Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States

[b]Department of Chemistry, Bilkent University, Ankara 06800, Turkey

[c]Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

E-mail: seunghoyu@korea.ac.kr, hda1@cornell.edu

Experimental

Materials. Lithium metal foil (99.9%) and lithium hexafluorophosphate ($LiPF_6$) (98%) were purchased from Alfa Aesar. Lithium perchlorate ($LiClO_4$) (99.99%), lithium bis(trifluoromethane)sulfonimide (LiTFSI) (99.95%), lithium tetrafluoroborate ($LiBF_4$) (99.99%), lithium bis(oxalato)borate (LiBOB), ethylene carbonate (EC) (≥99%), diethyl carbonate (DEC) (≥99%), 1,3-dioxolane (DOL) (99.8%), dimethyl ether (DME) (≥99%), dimethyl carbonate (DMC) (≥99.9%), propylene carbonate (≥99%) and 1-methyl-2-pyrrolidinone (NMP) (99.5%) were purchased from Sigma Aldrich. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) was purchased from Kynar Flex®. Super P Li was purchased from TIMREX®. Lithium iron phosphate (LFP) was purchased from MTI. Lithium bis(fluorosulfonyl)imide (LiFSI) (98%) was purchased from TCI. Copper electrodes were prepared from 0.006 mm thick copper metal foil (99.95+%) purchased from Goodfellow. The copper foil was soaked in sulfuric acid to remove copper oxide on the foil, washed with distilled water three times, and dried under vacuum at 60 °C for 3 h.

Electrochemical measurements. LFP electrodes were prepared via a conventional slurry-cast method by mixing LFP, super P and PVDF in NMP with a ratio of 8:1:1 (w/w). The LFP slurry was cast on a carbon coated aluminum foil. Lithium foil was punched into a disk with a diameter of half an inch in an argon-filled glove box (oxygen level was less than 0.35 ppm). The average mass loading of the active material was 1.9 (±0.1) mg/cm^2. Solvent mixtures were prepared by mixing EC and DEC (EC:DEC) or DOL and DME (DOL:DME) in a ratio of 1:1 (v/v), respectively. All electrolytes were made inside the glove box by dissolving 10 mmol of each lithium salt into 10 mL of the solvent mixture in a polypropylene container. Lithium/lithium symmetric cells (CR2032-type) were assembled in the glove box using 1.0 M $LiPF_6$ in PC or EC:DEC (1:1 v/v), 1.0 M $LiClO_4$ in PC or EC:DEC (1:1 v/v), 1.0 M LiTFSI in PC, EC:DEC (1:1 v/v) or DOL:DME (1:1 v/v), 1.0 M LiFSI in PC, EC:DEC (1:1 v/v) or DOL:DME (1:1 v/v), 1.0 M $LiBF_4$ in PC, EC:DEC (1:1 v/v), EC:PC (1:1 v/v) or EC:DMC (1:1 v/v), 1.0 M LiBOB in PC, EC:DEC (1:1 v/v), EC:PC (1:1 v/v) or EC:DMC (1:1 v/v), 0.5 M $LiPF_6$ and 0.5 M LiTFSI in PC, EC:DEC (1:1 v/v), EC:PC (1:1 v/v) or EC:DMC (1:1 v/v), or 0.5 M $LiPF_6$ and 0.5 M LiFSI in PC, EC:DEC (1:1 v/v), EC:PC (1:1 v/v), or EC:DMC (1:1 v/v). All electrochemical tests were performed using a customized battery tester (Neware, China). Li/Li symmetric cells were tested by applying constant current density of 3 mA/cm^2 for 1 h for plating/stripping cycling. Full cells were tested with the LFP electrode and the lithium disk at 1 C rate and a current density of 3 mA/cm^2 in the range of 2.5 – 4.0 V vs. Li^+/Li. Li/Cu asymmetric cells were tested by applying constant current density of 3 mA/cm^2 for 1 h for plating lithium to the copper electrode and cutting off at 1.0 V vs. Li^+/Li for stripping lithium from the plated lithium on the copper electrode. Coulombic efficiencies were calculated based on the stripping and plating times/charges.

Characterizations. A potentiostat, sp-150 (Bio-Logic Science Instruments SAS, France) was used for electrochemical impedance spectroscopy (EIS). Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) data were obtained using Zeiss GeminiSEM 500 (Carl Zeiss AG, USA). X-ray photoelectron spectroscopy (XPS) was performed using Sigma Probe (ThermoFisher Scientific) using Al Kα (1486.8 eV) as X-ray source. All electrodes were directly transferred to the XPS chamber from the glovebox without air exposure. XPS spectra were calibrated based on the C–C peak to 284.60 eV via the CasaXPS software.

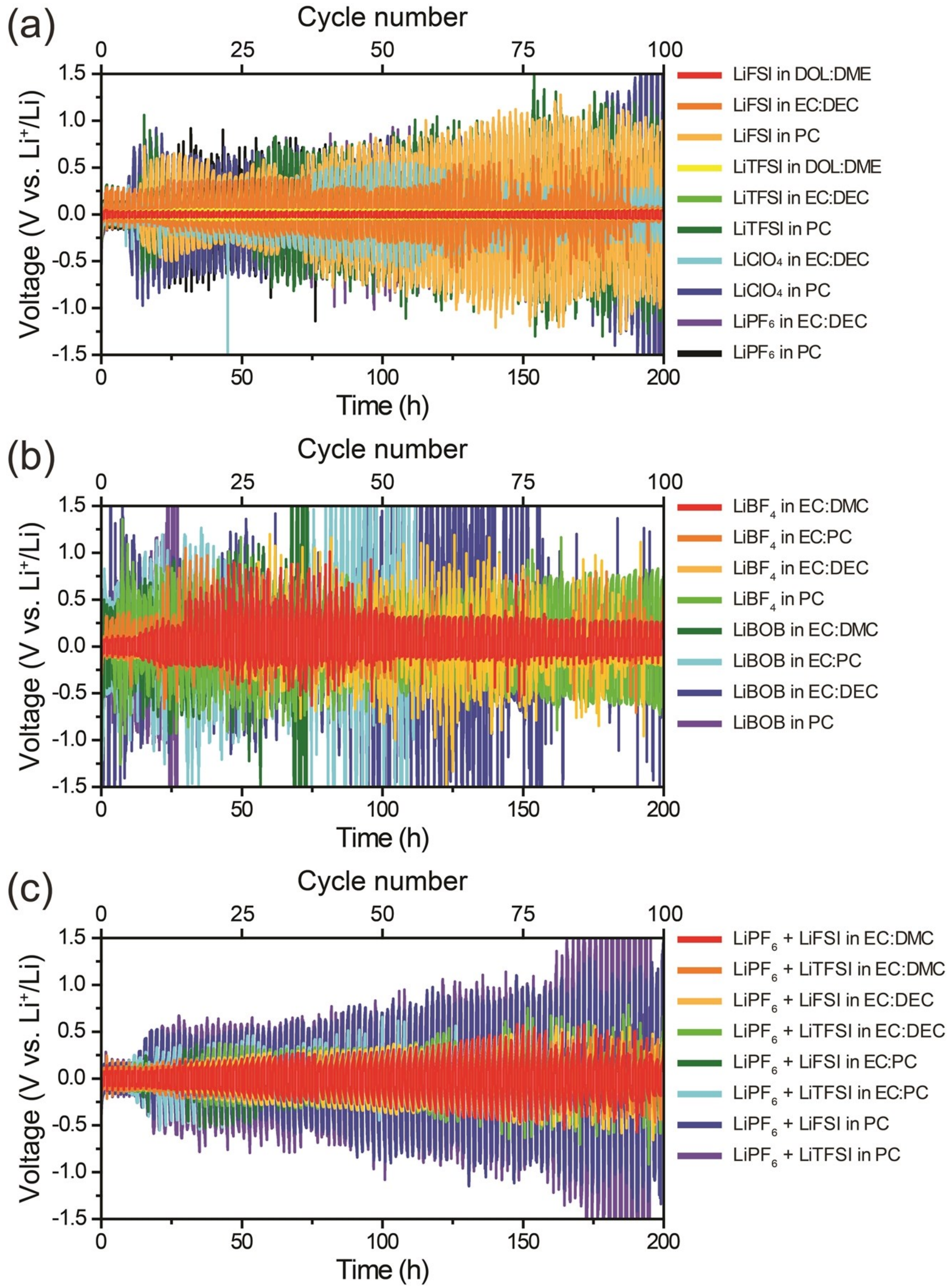

Fig. S1. Lithium plating/stripping tests in Li/Li symmetric cells with commercial lithium at a current density of 3 mA/cm^2 in (a) $LiPF_6$, $LiClO_4$, LiTFSI and LiFSI electrolytes (high resolution image of Figure 1(a)), (b) LiBOB and $LiBF_4$ electrolytes, and (c) dual salts electrolytes.

Table S1. Parameters calculated from EIS data.

	Before cycling			After cycling		
	R (Ω)	CPE Y_0 (F.$s^{1-\alpha}$)	CPE α	R (Ω)	CPE Y_0 (F.$s^{1-\alpha}$)	CPE α
$LiPF_6$ in EC:DEC	441.5	8.756×10^{-06}	0.856	42.1	5.864×10^{-05}	0.787
LiFSI In EC:DEC	157.6	6.779×10^{-06}	0.781	25.8	9.172×10^{-05}	0.767
LiFSI in DOL:DME	113.7	5.444×10^{-06}	0.851	1.5	2.454×10^{-04}	0.718

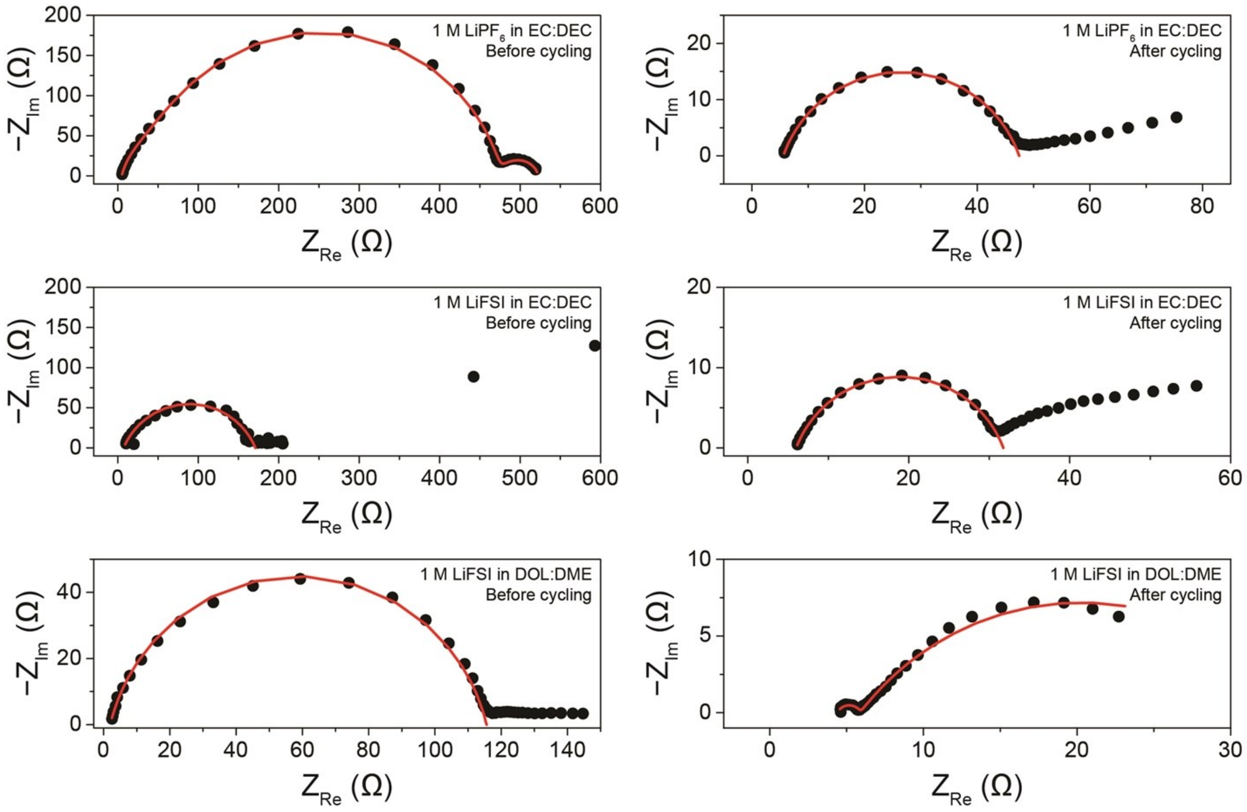

Fig. S2. Corresponding fitting data of EIS data presented in Fig. 1 (c, d). Black circles represent the actual data and red solid lines represent their fittings. The low frequency section of most datasets were Kramers Kronig incompatible due to drift. Therefore, only the high frequency semicircle is considered for the fits and the tabulated data.

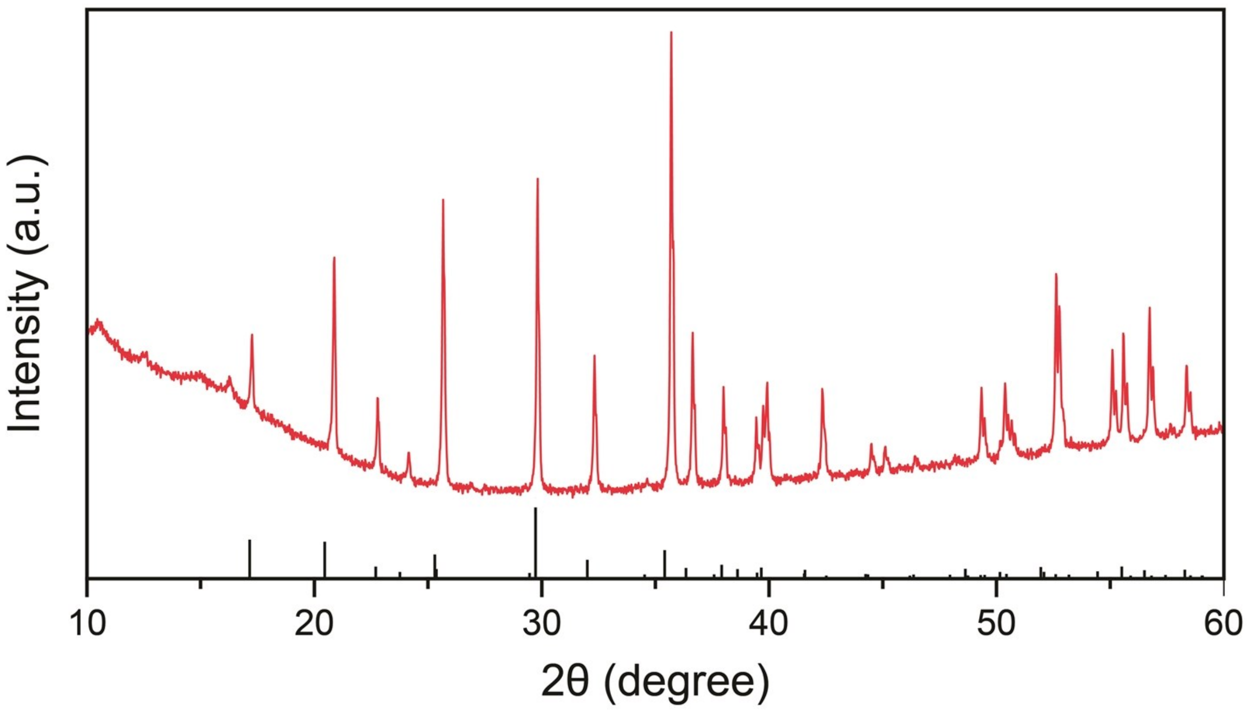

Fig. S3. Powder XRD pattern of commercial LFP.

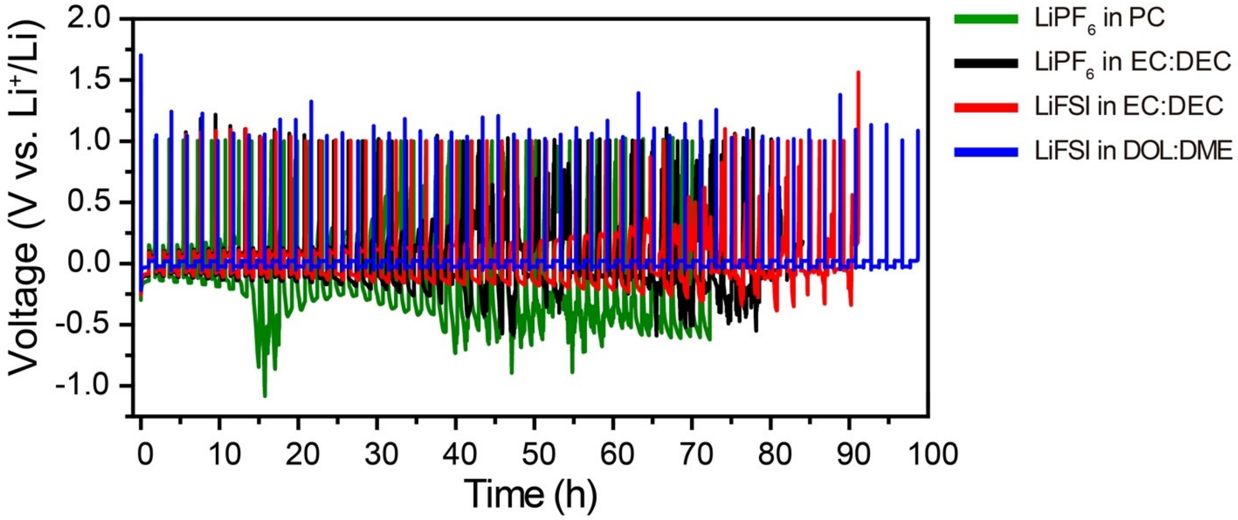

Fig. S4. Lithium plating/stripping tests in Li/Cu asymmetric cells at a current density of 3 mA/cm^2 in LiPF$_6$ in PC, LiPF$_6$ in EC:DEC, LiFSI in EC:DEC, and LiFSI in DOL:DME.

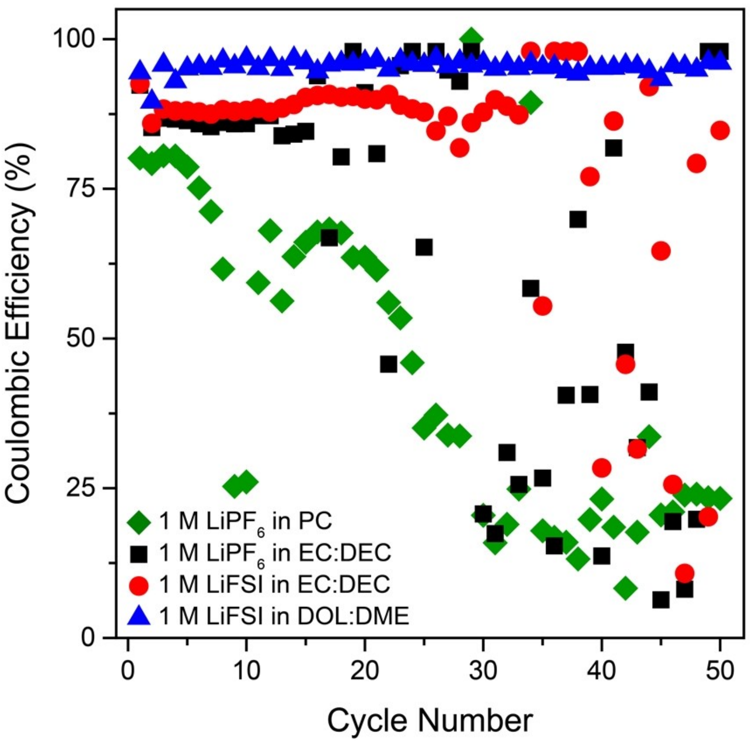

Fig. S5. Coulombic efficiencies of Li/Cu asymmetric cells cycled in different electrolytes presented in Fig. S3.

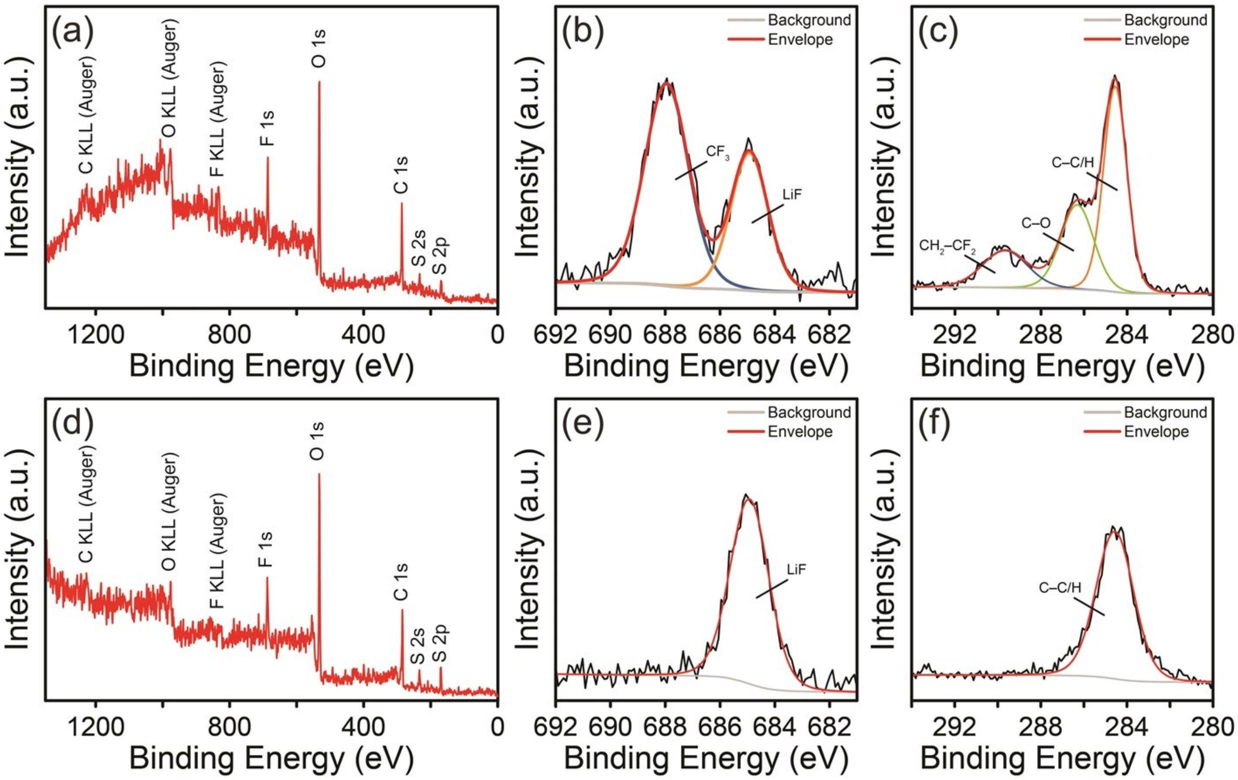

Fig. S6. XPS spectra of (a) a survey scan, and high resolution scans of (b) F 1s and (c) C 1s of top of lithium electrode after 30 cycles in Li/Li symmetric cells in LiFSI in EC:DEC and (d) a survey scan, and high resolution scans of (e) F 1s and (f) C 1s of top of lithium electrode after 30 cycles in Li/Li symmetric cells in LiFSI in DOL:DME.