Supporting Information for

Partially Ion-Paired Solvation Structure Design for Lithium-Sulfur Batteries under Extreme Operating Conditions

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Table S1

Materials and Methods

The preparation of electrodes

The elemental S and polyacrylonitrile (PAN, Mw = 150, 000) powders in a mass ratio of 4:1 were mixed completely by hand milling before annealing at 450 ^{o}C and Ar-filled condition for 6 h. The obtained SPAN, Super-P carbon black was added and dispersed in an NMP-based polyacrylic acid (PAA, Mw = 450, 000) solution with a mass ratio of 7/1.5/1.5. The resulting slurry was cast on carbon-coated Al foils with a SPAN mass loading of around 6 mg cm^{-1}.

The preparation of Electrolytes

Anhydrous methyl acetate (MA, Sigma), methyl propionate (MP, Sigma), methyl 3,3,3-trifluoropionate (MTFP, TCI), and methyl pentafluoropropionate (MPFP, TCI) solvents were soaked with 3 Å activated molecular zeolite before use. The selected electrolytes were prepared by dissolving per mol LiFSI salts (Lithium bis(fluorosulfonyl)imide, Gotion) in per liter solvents at ambient conditions.

Characterization

The morphology of the deposited Li on Cu foil at different temperatures was characterized via scanning electron microscopy (SEM, FEI Quanta 250). The surface information of deposited Li at various temperatures was analyzed using X-ray photoelectron spectroscopy (XPS, Kratos Analytical, Kratos AXIS Supra). Al anode source was employed at 15 kV with a step size of 1.0 eV for survey scans while a high-resolution scan for C 1s, O 1s, and F 1s regions. Raman spectra of selected electrolytes were conducted on a confocal Raman microscope (Renishaw inVia/Bruker Innova) with an excitation wavelength of 532 nm. Nuclear magnetic resonance (NMR) spectra were collected via a Varian Inova 500 MHz NMR spectrometer with an SW Probe tunable to ^{17}O and ^{7}Li. Electrolyte samples were sealed in an NMR tube in the glovebox before NMR testing. ^{7}Li NMR spectra were recorded at 194.22 MHz with a spectral width of 3884 Hz and an acquisition time of 4s for 31076 complex points using a 1s relaxation delay for 16 scans. ^{17}O NMR spectra were performed at 67.75 MHz, with a spectral width of 101652 Hz and an acquisition time of 0.2s for 40660 complex points using a 0.2s relaxation delay for 6000 scans.

Molecular dynamics (MD) simulations

MD simulations were conducted in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) using the General Amber forcefield, incorporating FSI molecule details from a prior study (S1). Simulation boxes containing approximately 500 molecules were constructed with varying ratios based on system stoichiometry to determine electrolyte structure. FSI^- and Li^+ charges were adjusted to the solvents' high-frequency dielectric properties using a documented method (S2).

For each system's ground-state structure, an initial energy minimization at 0 K (with energy and force tolerances set at 10^{-4}) was executed. Afterwards, the system underwent a gradual heating process from 0 K to room temperature at constant volume over 0.01 ns, utilizing a Langevin thermostat with a damping parameter of 100 ps. This was succeeded by 5 cycles of quench-annealing dynamics in an attempt to eliminate any meta-stable states. The temperature cycled between 298 K and 894 K, with a ramp period of 0.025 ns followed by 0.1 ns of dynamics at each temperature extreme, totaling 1.25 ns for all 5 anneal cycles. Following the annealing cycles, the system was equilibrated in the constant temperature (298 K), and constant pressure (1 bar) (NpT ensemble) for 1.5 ns. Stress resolution in the system was achieved isotropically using the Andersen barostat (pressure relaxation constant of 1 ps). Finally, 10 ns of constant volume, and constant temperature (NVT) dynamics at 298 K were performed. Radial distribution functions were obtained through the Visual Molecular Dynamics (VMD) software. Images of various solvation shells sampled from the simulation trajectory were also captured using VMD.

Electrochemical Testing

CR-2032 typed cion cells were used for the Li//Cu and Li//SPAN cells as well as the symmetric Li//Li and SPAN//SPAN cells. Before the calculation of Li CEs under selected electrolytes, a conditioning cycle by plating 4 mAh cm^{-2} Li and then stripping to 1 V at 0.5 mA cm^{-2} was performed for the formation of SEI. Another 4 mAh cm^{-2} Li was then plated. Subsequently, 10 cycles of plating/stripping 1 mAh cm^{-2} Li at 0.5 mA cm^{-2} were conducted before stripping to 1 V. The Li CEs obtained by the total stripping capacity divided by the total plating capacity. The cyclic voltammetry (CV) profiles of Li//Cu cells with selected electrolytes and a scan speed of 10 mV s^{-1} were collected using an Autolab potentiostat. The EIS curves of Li//Li and SPAN//SPAN symmetric cells were collected with an AC amplitude of 10 mV. The ionic conductivity of selected electrolytes was evaluated using a 2-electrode setup with two stainless steel spacers sandwiched PTFE washer. The electrolyte conductivity was obtained based on the following equation: $\sigma = \frac{L}{AR}$, where L and A are the area and space of the pore of the PTFE washer while R is the resistance obtained by the EIS testing at various temperatures. The Li//SPAN full cells were assembled with a high mass loading of SPAN cathodes (6 mg cm^{-2}), thin Li anode (50 μm), Celgard 2325, and selected electrolytes. For cell testing under extreme conditions, all cells were rested under target temperature for over 2 h before any galvanostatic cycling.

Figure S1. Photographs of selected electrolytes. Photographs of 1 M LiFSI MP/FEC, 1 M LiFSI MA/FEC, 1 M LiFSI MTFP/FEC, and commercial electrolyte LP30 (1 M $LiPF_6$ EC/DMC 1/1 in vol.) at -40 ^{o}C. The LP30 is solid while others are still in a liquid state.

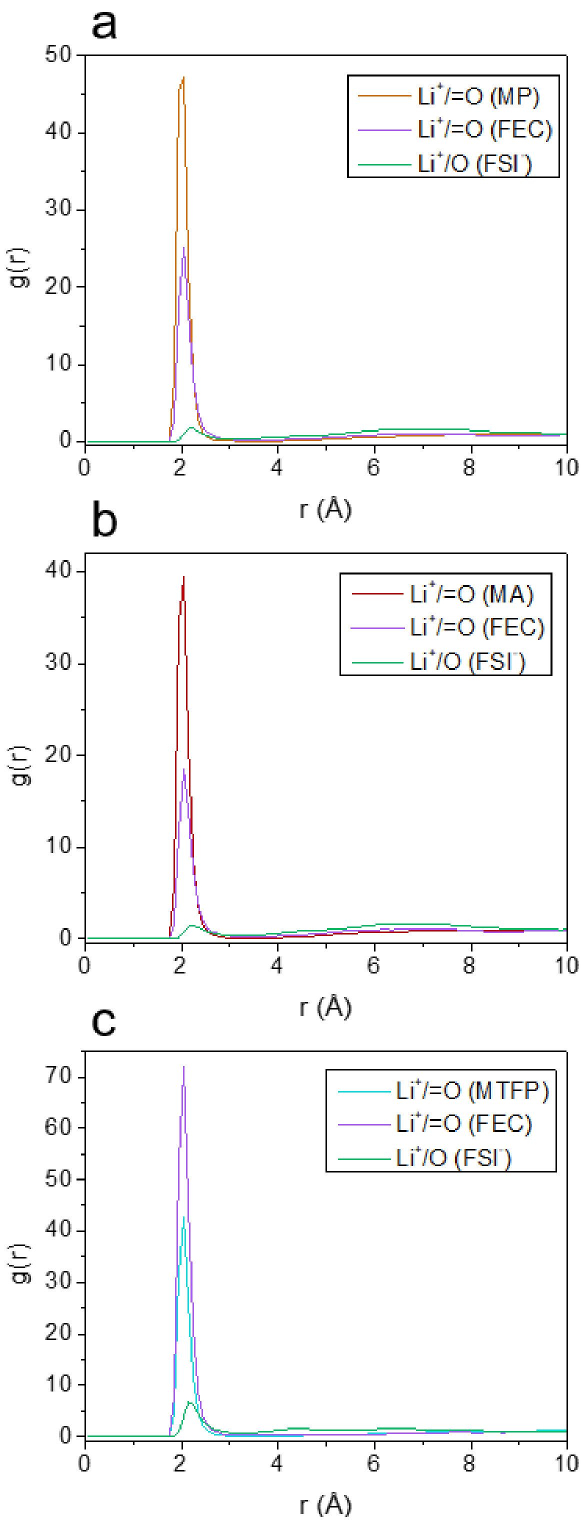


Figure S2. Li$^+$ radial distribution function obtained from MD simulations of selected electrolyte: (a) 1 M LiFSI MP/FEC, (b) 1 M LiFSI MA/FEC, and (c) 1 M LiFSI MTFP/FEC.

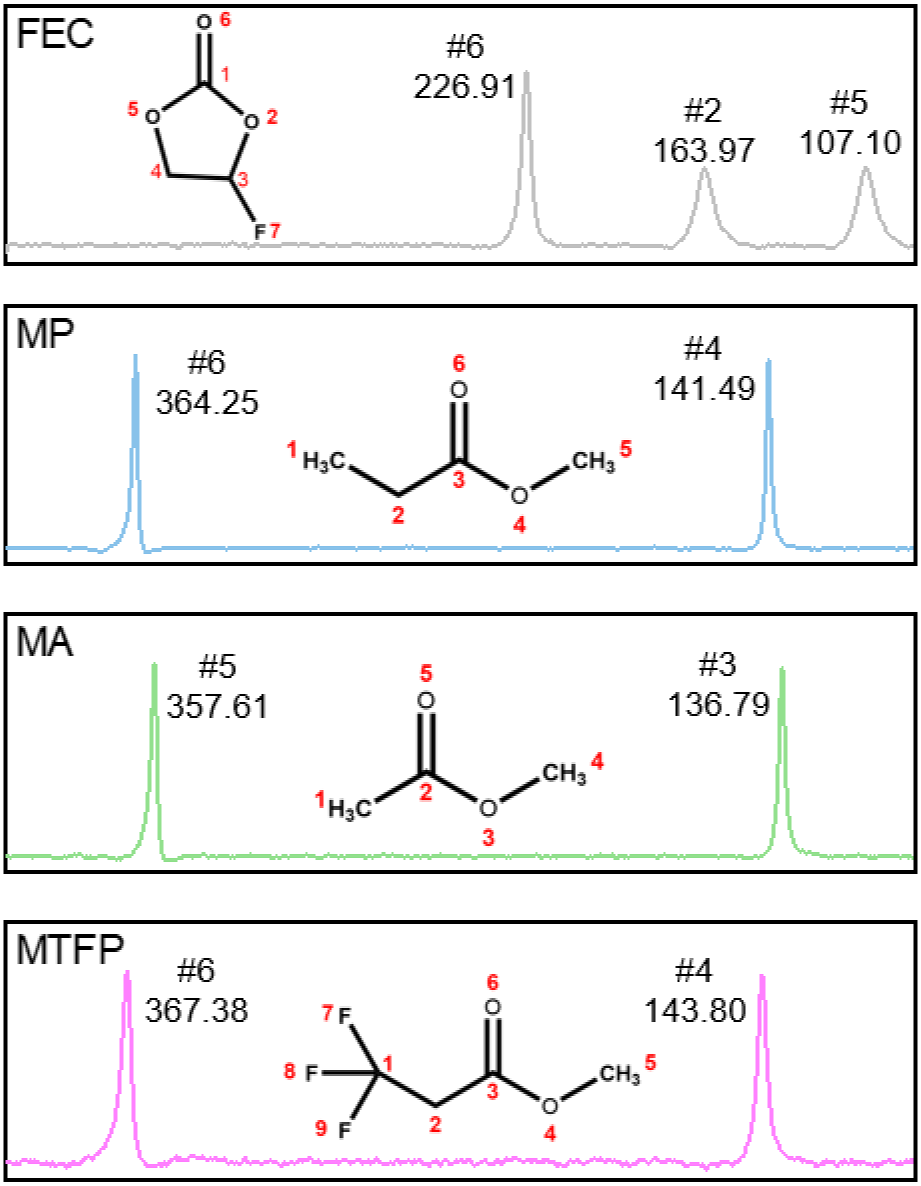


Figure S3. ^{17}O NMR spectra of FEC, MP, MA, and MTFP solvent molecules.

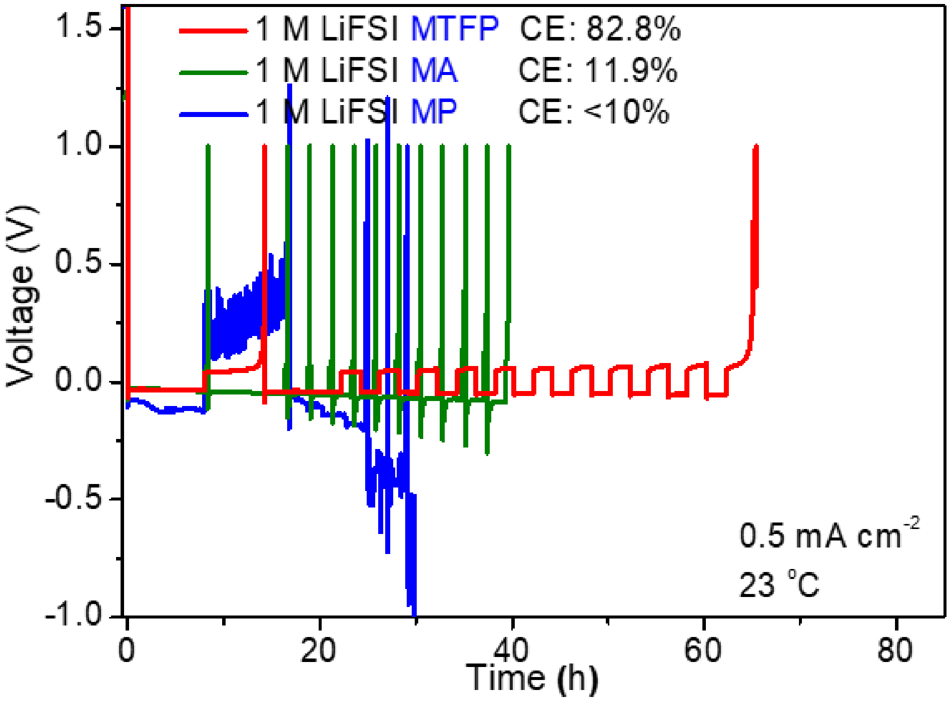


Figure S4. CE determined curves for the electrolytes of interest at ambient temperature.

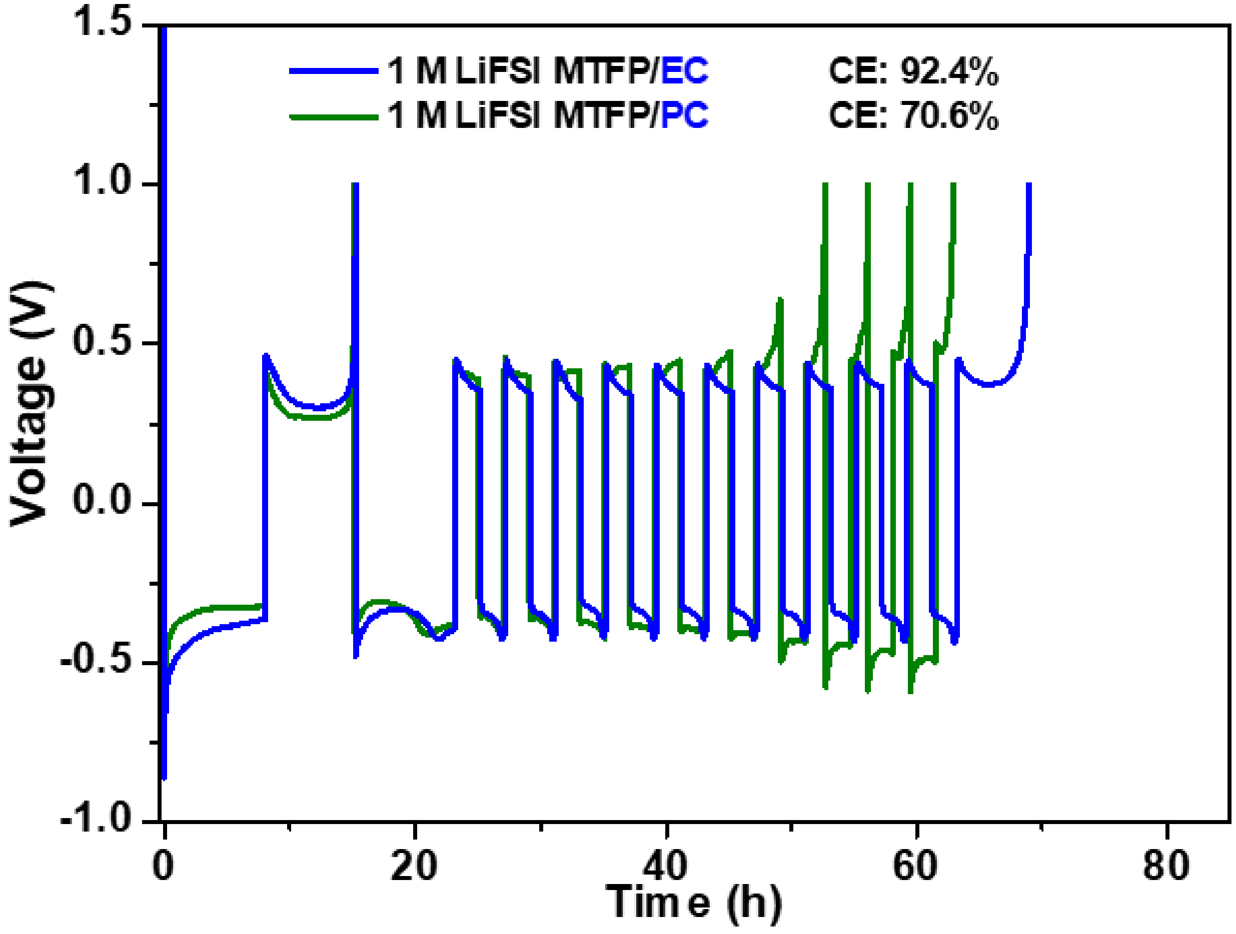


Figure S5. CE determined curves for the electrolytes of 1 M LiFSI MTFP/EC and 1 M LiFSI MTFP/PC at -40 °C.

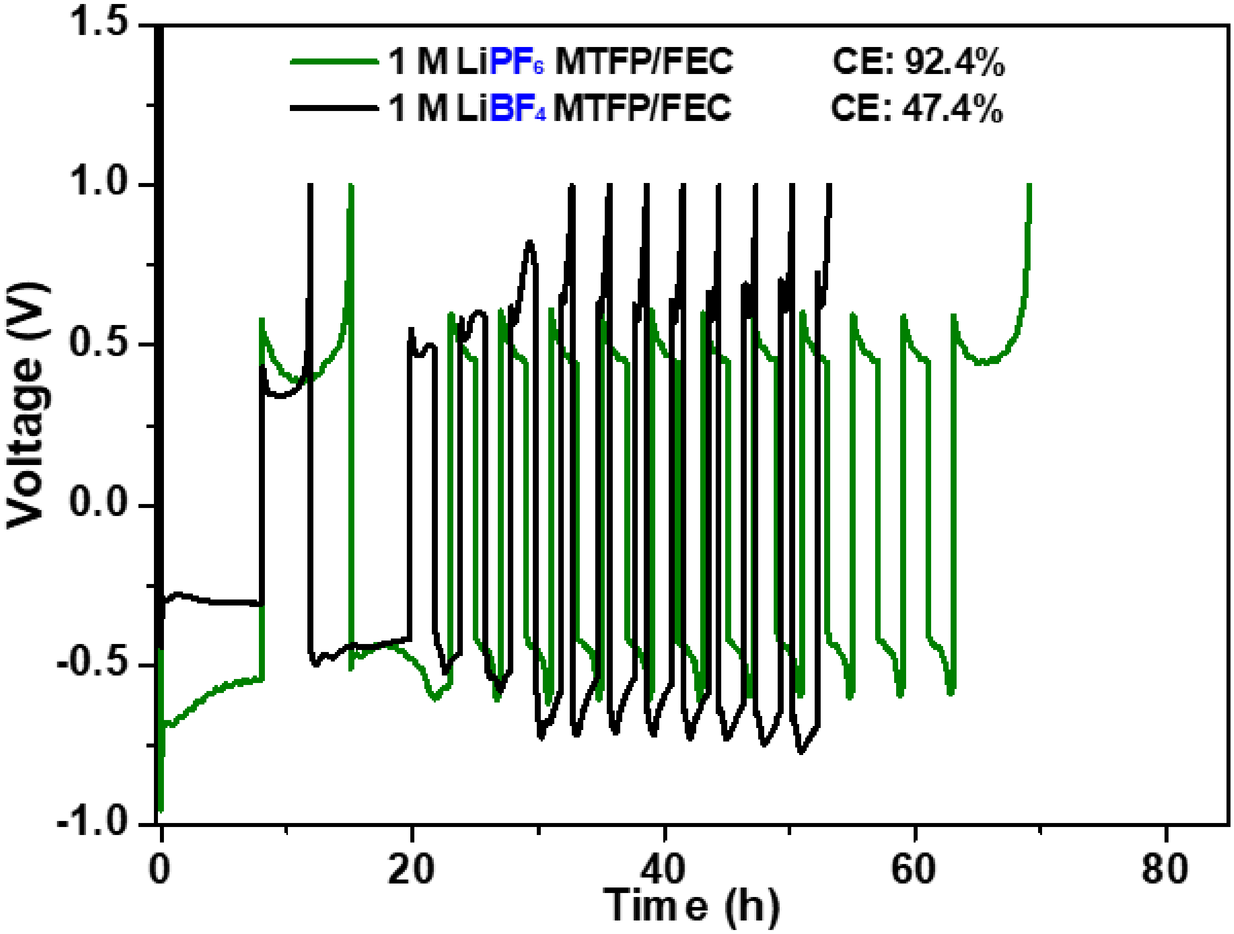


Figure S6. CE determined curves for the electrolytes of 1 M $LiPF_6$ MTFP/FEC and 1 M $LiBF_4$ MTFP/FEC at -40 ^{o}C.

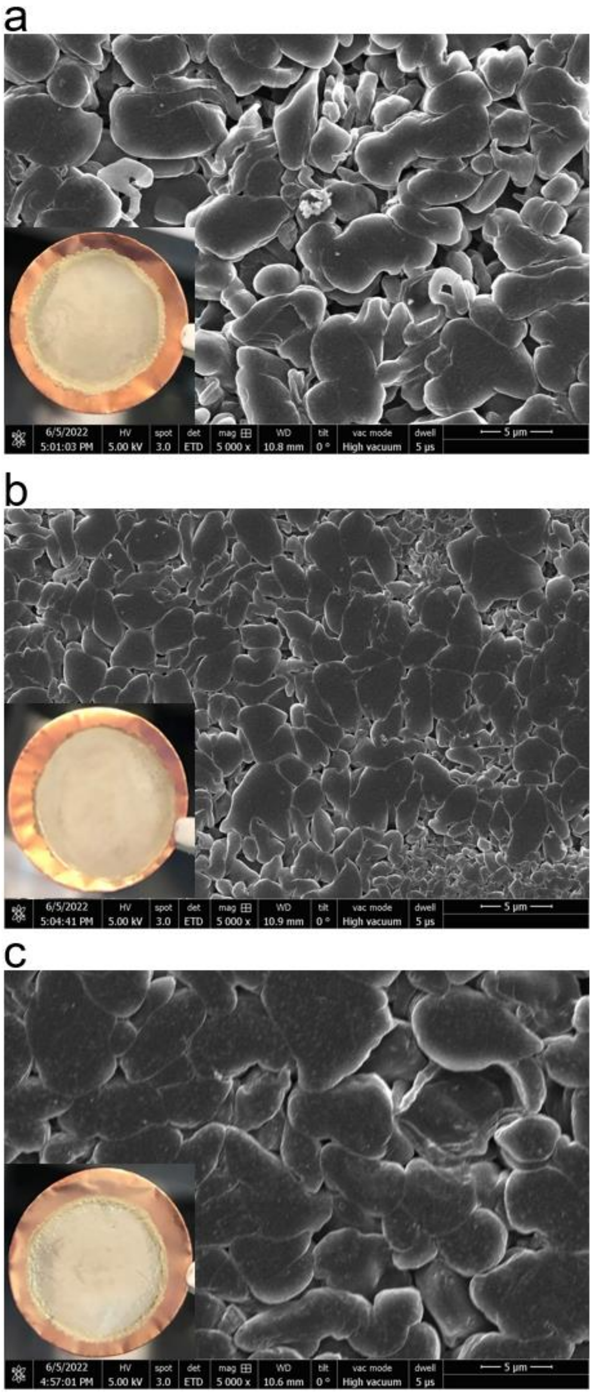


Figure S7. The SEM images of plated Li metal at 23 ^{o}C in selected electrolytes: (a) 1 M LiFSI MP/FEC, (b) 1 M LiFSI MA/FEC, and (c) 1 M LiFSI MTFP/FEC. Insets in a-c are the photographs of deposited Li on Cu foil.

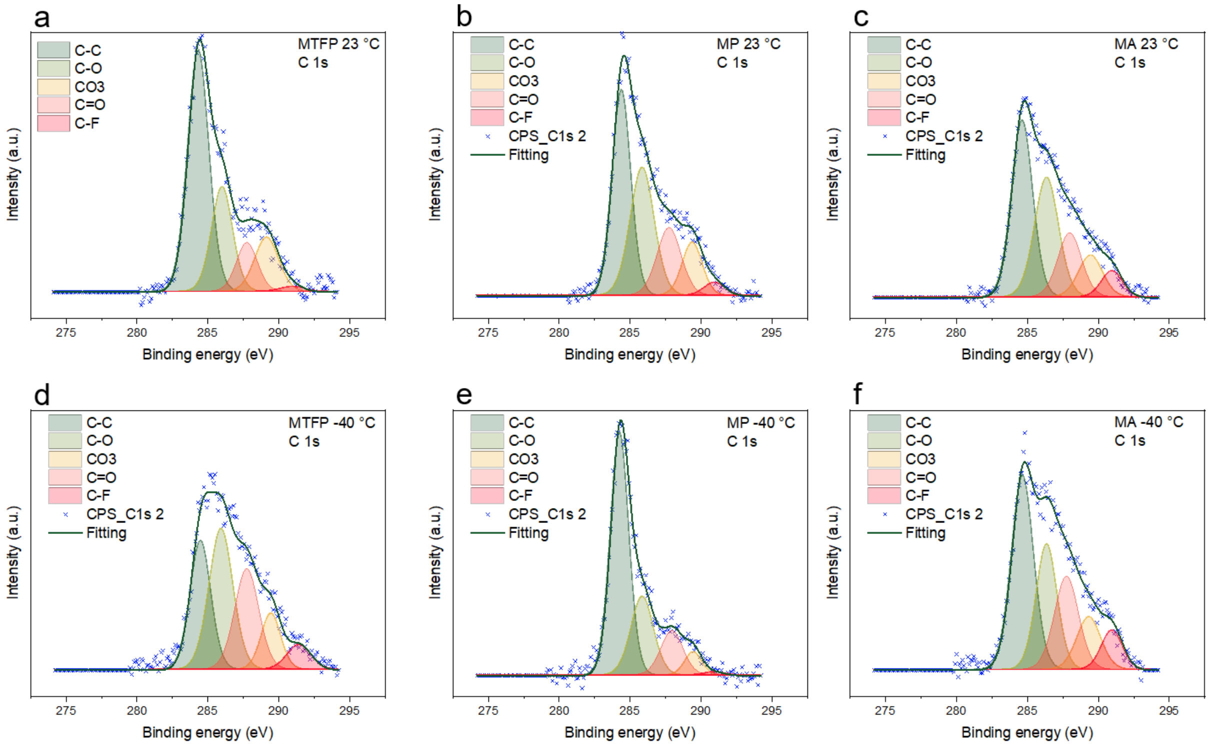


Figure S8. C 1s XPS of spectra of deposited Li metal on Cu foil obtained by disassembling the Li//Cu cells with selected electrolytes after cycling at (a-c) 23 and (d-f) -40 ^{o}C: (a, d) 1 M LiFSI MTFP/FEC, (b, e) 1 M LiFSI MP/FEC, and (c, f) 1 M LiFSI MA/FEC.

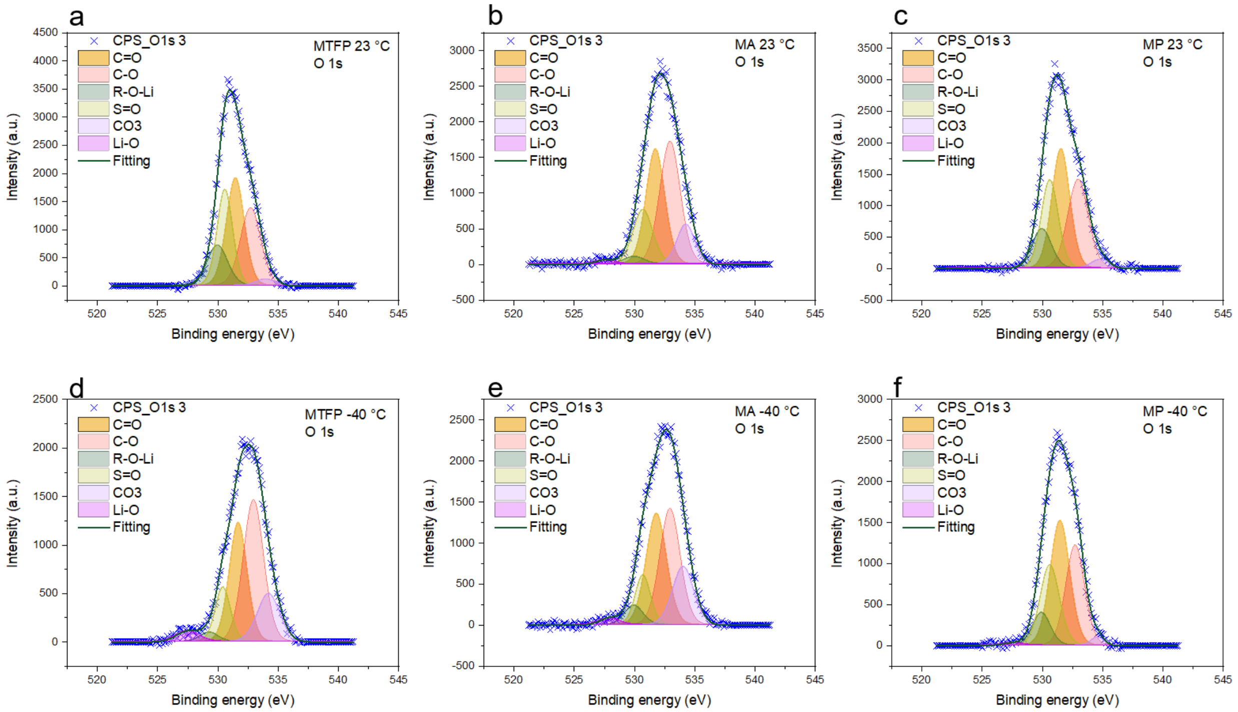


Figure S9. O 1s XPS of spectra of deposited Li metal on Cu foil obtained by disassembling the Li//Cu cells with selected electrolytes after cycling at (a-c) 23 and (d-f) -40 ^{o}C: (a, d) 1 M LiFSI MTFP/FEC, (b, e) 1 M LiFSI MP/FEC, and (c, f) 1 M LiFSI MA/FEC.

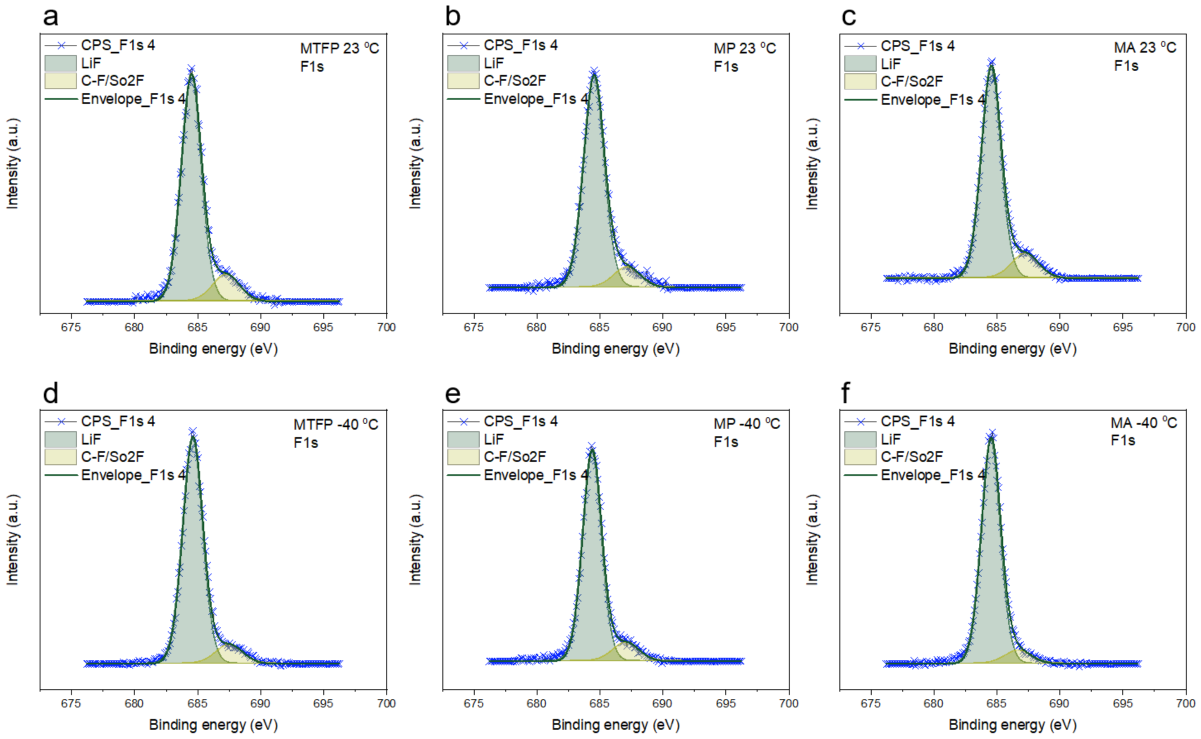


Figure S10. F 1s XPS of spectra of deposited Li metal on Cu foil obtained by disassembling the Li//Cu cells with selected electrolytes after cycling at (a-c) 23 and (d-f) -40 °C: (a, d) 1 M LiFSI MTFP/FEC, (b, e) 1 M LiFSI MP/FEC, and (c, f) 1 M LiFSI MA/FEC.

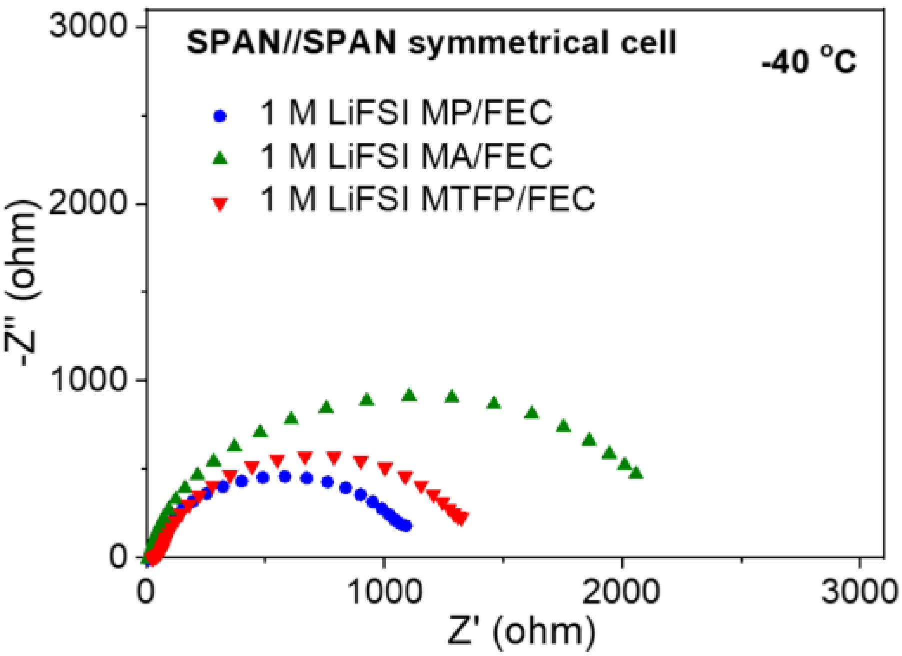
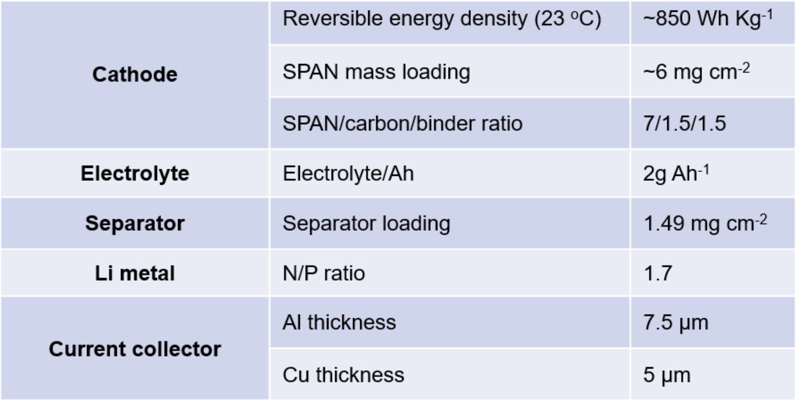


Figure S11. EIS profiles of SPAN||SPAN symmetrical cells collected at -40 ^{o}C in selected electrolytes of 1 M LiFSI MP/FEC, 1 M LiFSI MA/FEC, and 1 M LiFSI MTFP/FEC.

Table S1 The parameters for the projection of stack energy density based on the 18, 650 cylinder cell model by Betz et al.[S3]



Cathode	Reversible energy density (23 °C)	~850 Wh Kg^{-1}
	SPAN mass loading	~6 mg cm^{-2}
	SPAN/carbon/binder ratio	7/1.5/1.5
Electrolyte	Electrolyte/Ah	2g Ah^{-1}
Separator	Separator loading	1.49 mg cm^{-2}
Li metal	N/P ratio	1.7
Current collector	Al thickness	7.5 μm
	Cu thickness	5 μm

References

S1. A. S. Gouveia, C. E. Bernardes, L. C. Tomé, E. I. Lozinskaya, Y. S. Vygodskii, *Phys. Chem. Chem. Phys.* **2017**, *19*, 29617-29624.

S2. C. Park, M. Kanduč, R. Chudoba, A. Ronneburg, S. Risse, M. Ballauff, J. Dzubiella, *J. Power Sources* **2018**, *373*, 70-78.

S3. J. Betz, G. Bieker, P. Meister, T. Placke, M. Winter, R. Schmuch, *Adv. Energy Mater.* **2019**, *9*, 1803170