

## Supporting Information

# Ethyl Methyl Sulfone Co-Solvent Eliminates Macroscopic Morphological Instabilities of Lithium Metal Anode

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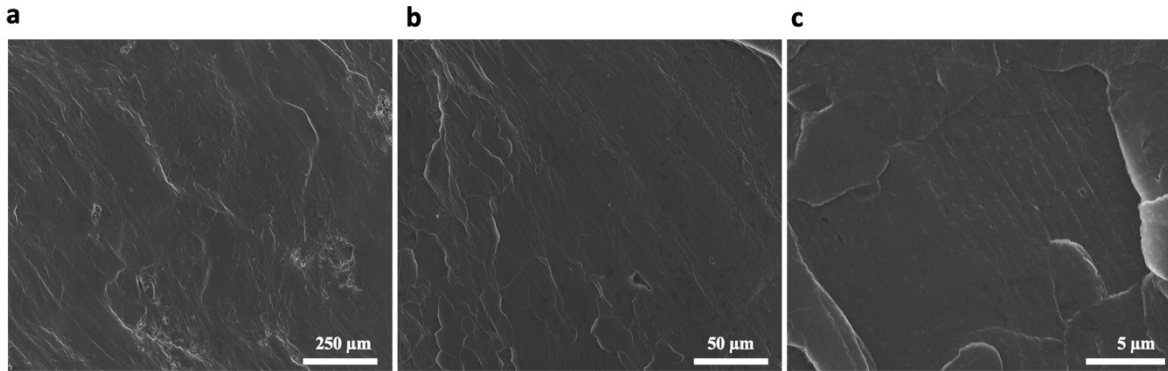
## Experimental Section

### Li || Li and Li || Cu cell fabrication

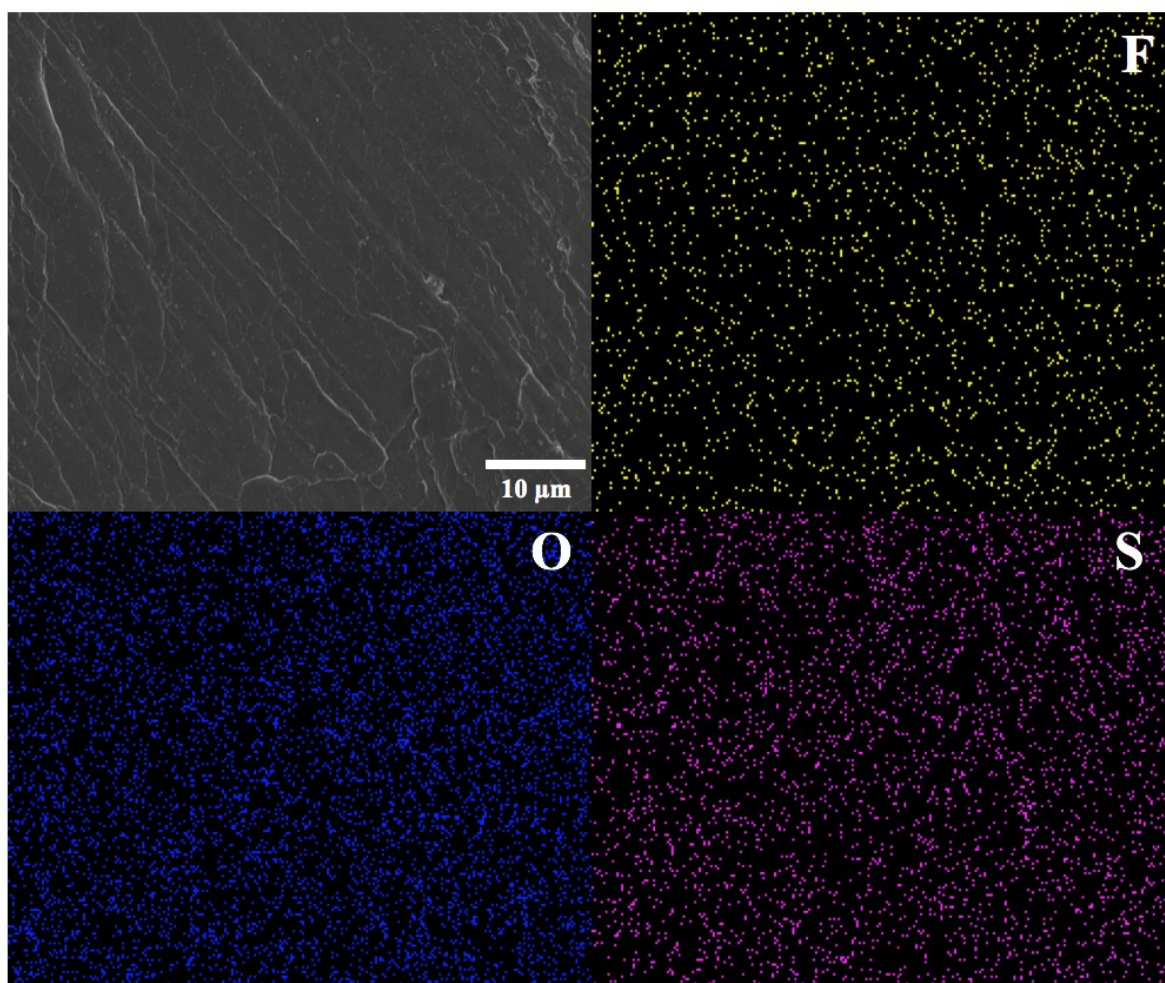
Li metal ribbon was purchased from Aldrich (0.38mm thickness, 99.9% trace metal basis) and cut into 1cm diameter disk. Cu-foil was purchased from Advent-rm and immersed in 1 M HCl solution for 10 minutes followed by washing it with DI water and isopropyl alcohol three times respectively. 2032-type coin cells were fabricated in the glove box (MBRAUN Labmaster) under Ar atmosphere that has less than 1ppm of O<sub>2</sub> and H<sub>2</sub>O. EMS was purchased from TCI America and purified by soaking lithium metal for two days. It was mixed with DOL/DME (BASF Corporation) in 1:1 volume ratio with 1 M LiTFSI (99%) that was purchased from Aldrich.

### Characterization

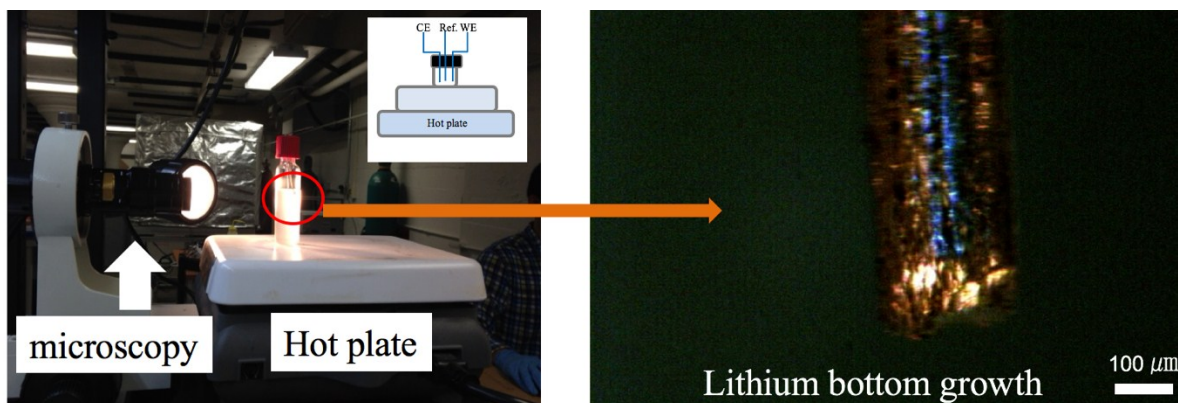
Li || Li and Li || Cu cells were cycled using the Maccor cell tester at the room temperature for overpotential measurement and Coulombic efficiency test, respectively. Cycled Li metal was harvested by disassembling coin cells for SEM and XPS analysis in the glove box. For cyclic voltammetry test, BioLogics potentiostat was used in the scan rate of 1 mV/s. Cu foil was used as working electrode and lithium foil as working/reference electrode. SEM images of the Li electrodes were obtained with Quanta 600 FEG SEM with accelerating voltage of 5 kV. XPS data was obtained by PHI Quantera Scanning ESCA. The spectrometer uses a monochromatic aluminum X-ray source with a photon energy of 1486.6eV. The energy scale of the spectrometer is calibrated with Au 4f at 84.0 eV and Cu 2p<sup>3/2</sup> at 932.7 eV. EIS impedance was measured by frequency change from 100 KHz to 10 mHz with potential amplitude of 10 mV. Sealed beaker cells are built for *in situ* optical microscopy study. Cu wire tethered lithium is connected to potentiostat for lithium deposition/stripping.



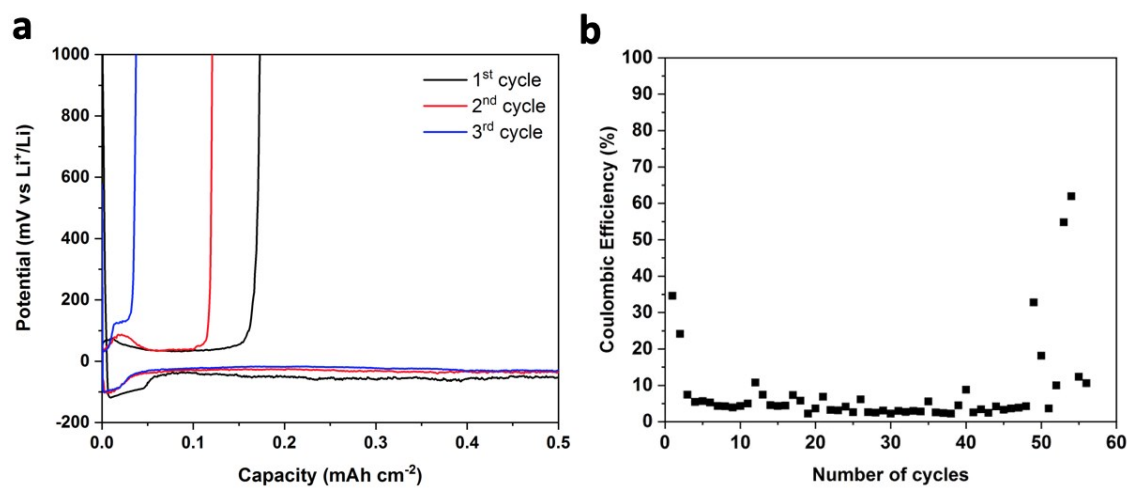
**Fig. S1.** Scanning electron microscopy (SEM) images of cycled lithium in DOL/DME/EMS electrolytes after 100 cycles at  $1.0 \text{ mA cm}^{-2}$  with a capacity of  $1.0 \text{ mAh cm}^{-2}$ . All three images show that EMS as a co-solvent can effectively suppress macroscopic morphological instabilities.



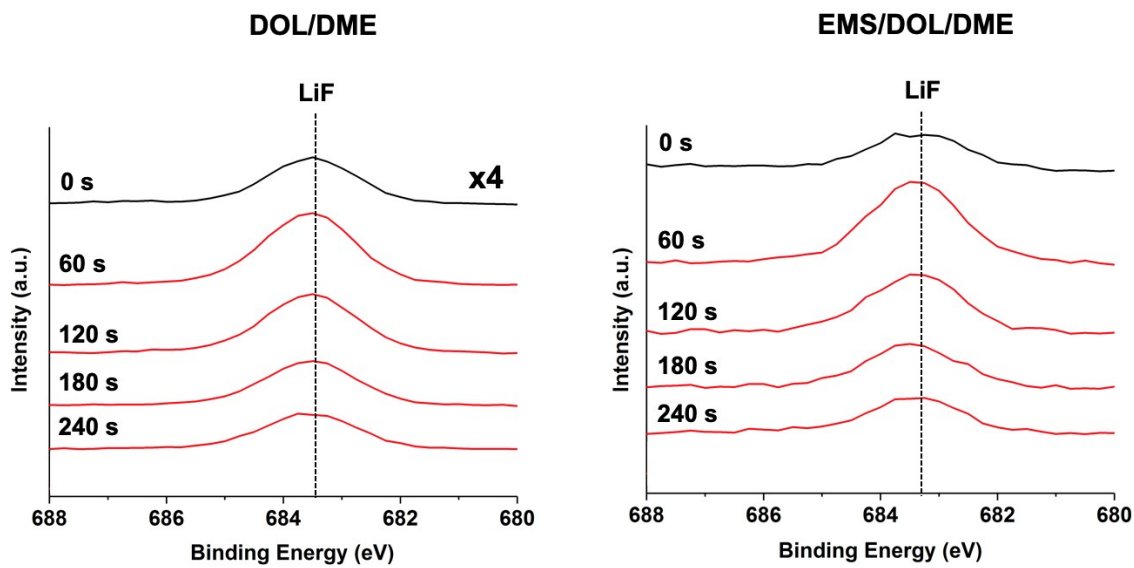
**Fig. S2.** EDX elemental mappings of the lithium surface: Fluorine, oxygen and sulfur. Before measurements, the LMA ran for 100 cycles at  $1.0 \text{ mA cm}^{-2}$  with a capacity of  $1.0 \text{ mAh cm}^{-2}$  in DOL/DME/EMS electrolyte.



**Fig. S3.** *In situ* optical microscopy setup (left panel). Inset image shows the schematic design of three electrode vial cell. Right panel represents zoomed image of lithium rod inside a vial cell. The whole setup of the optical microscopy is placed on the air table to minimize the vibration and draft for a long period during Li deposition/stripping.



**Fig. S4.** The CE test in Li || Cu cells in the EMS/DOL/DME electrolyte. (a) GCD profiles of the first three cycles. (b) Plating/stripping CE over 60 cycles at 0.5 mA cm<sup>-2</sup>. For each cycle, 0.5 mAh cm<sup>-2</sup> of lithium is plated.



**Fig. S5.** The XPS  $F_{1s}$  profiles of the cycled LMA in DOL/DME electrolyte (left) and EMS/DOL/DME electrolyte (right). Note that LiF intensity of DOL/DME shows four times stronger than EMS/DOL/DME, supporting that TFSI<sup>-</sup> anion decomposition is suppressed by the preferential decomposition of EMS.