

Electronic Supplementary Information

**An Ester Electrolyte for Lithium–Sulfur Batteries Capable of Ultra-Low Temperature Cycling**

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## **1 Materials Synthesis and Fabrication**

### **1.1 Preparation of SPAN material**

For SPAN cathode preparation, polyacrylonitrile (Mw = 150,000, Sigma-Aldrich) and elemental sulfur in a mass ratio of 1:4 was milled by hand to produce a homogeneous mixture. The obtained mixture was transferred into a tube furnace and then heated to 450 °C with a ramp rate of 2 °C min<sup>-1</sup>. After holding at this temperature for 6 hours, the tube furnace was allowed to cool down to room temperature.<sup>S1,S2</sup>

### **1.2 Preparation of SPAN electrode**

The prepared SPAN powder, Super-P, and PVDF (KYNAR 2800) in a mass ratio of 70:15:15 were dispersed in N methyl pyrrolidinone (NMP) solvent by a Thinky mixer. The resulted

slurry was casted on a carbon-coated Al foil and was allowed to dried in a vacuum oven at 120 °C overnight. The obtained electrode has a typical SPAN mass loading of around 1.5 mg cm<sup>-2</sup>.

## 2 Materials characterization and electrochemical tests

The morphology of the plated Li metal on Cu foil was characterized using a FEI Quanta 250 scanning electron microscopy (SEM). The SEM samples were obtained by disassembling Li||Cu cells after deposition of 1 mAh cm<sup>-2</sup> Li in 0.5 mA cm<sup>-2</sup>. Before SEM analysis, the samples were washed with MP or DEC solvent and dried at room temperature in Ar filled glovebox overnight.

In an ideal case, the thickness of plated Li metal can be calculated by the following equation:

$$h_{Li} = \frac{m_{Li}}{\rho_{Li} S_{Li}} = \frac{QM_{Li}}{nF\rho_{Li} S_{Li}}$$

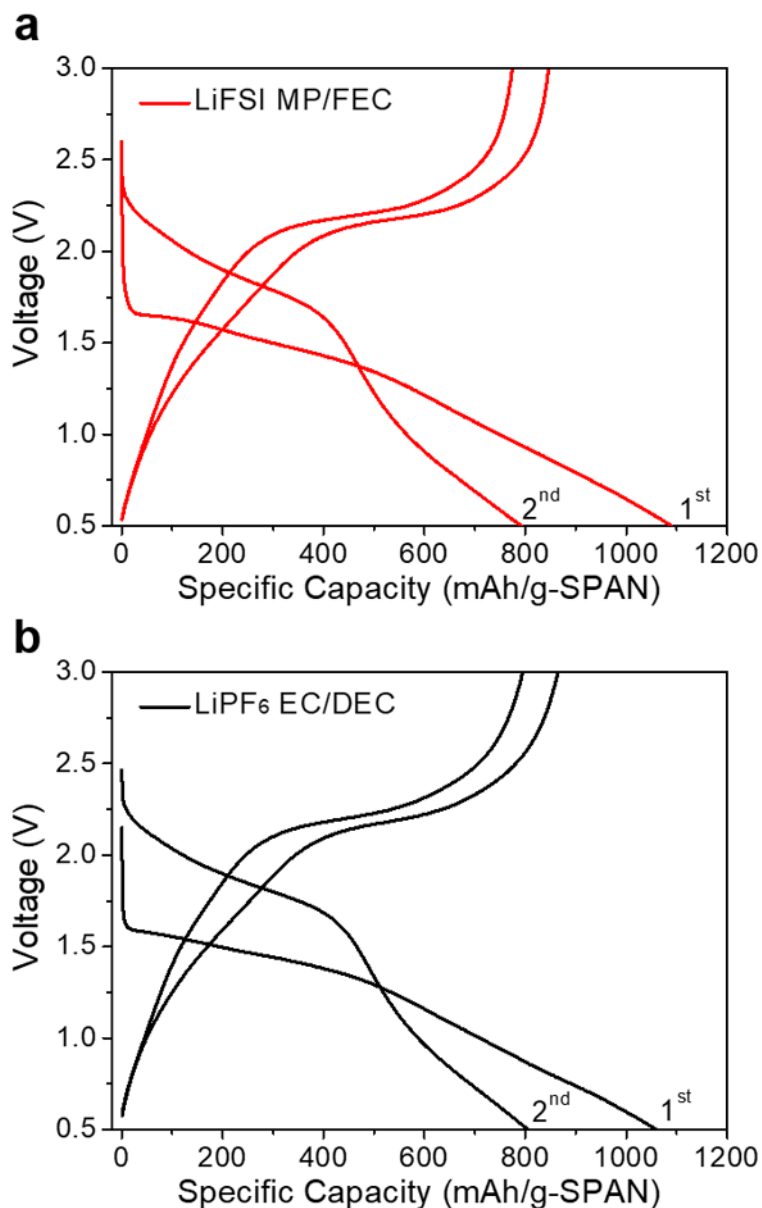
$h_{Li}$ : the thickness of plated Li metal ( $\mu\text{m}$ );  $\rho_{Li}$ : the density of nonporous Li metal ( $0.534 \text{ g cm}^{-3}$ );  $S_{Li}$  the area of plated Li metal ( $\text{cm}^2$ );  $Q$ : the amount of charge for a given amount of Li metal (mAh);  $M_{Li}$ : the molar weight of Li ( $6.94 \text{ g mol}^{-1}$ );  $n$ : the number of electrons transferred in the reaction ( $n = 1$  for Li);  $F$ : Faraday's constant ( $26.801 \text{ Ah mol}^{-1}$ ).

Based on the above equation, the thickness of the Li metal plated on the Cu foil will be 4.8  $\mu\text{m}$  in an ideal case for 1 mAh cm<sup>-2</sup>.<sup>S3</sup>

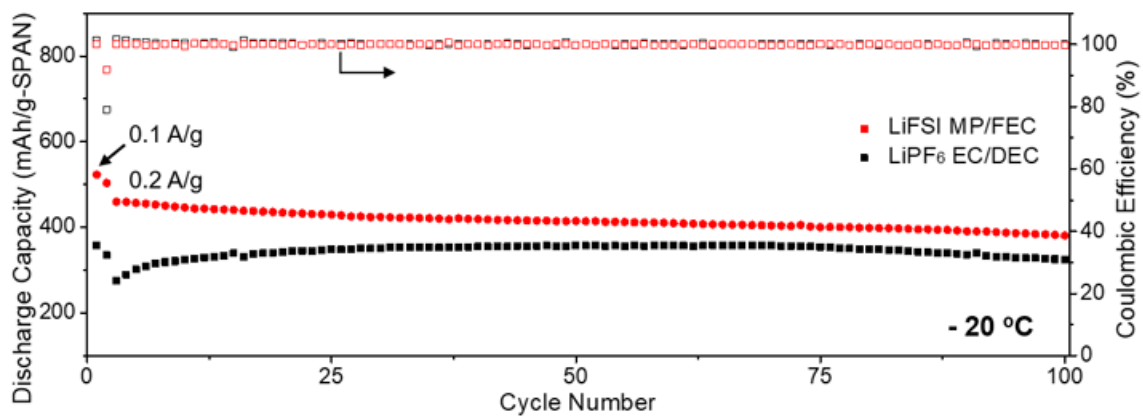
The electrochemical impedance spectroscopy (EIS) was acquired on a Metrohm Autolab potentiostat in the frequency range from 1 MHz to 10 mHz with an AC amplitude of 10 mV. The Li||Li and SPAN||SPAN symmetric cells were obtained by re-assembling corresponding electrodes from Li||SPAN half cells which cycled 5 times and then charged to 50% state of charge (SOC).

For Li||Cu cells, CR-2032 type coin cells were assembled with 7/16 inch of Li foils (China Energy Lithium Co., 99.9%), 18 mm disc of Cu foil, 25  $\mu\text{m}$  thick of Celgard membrane, and 40  $\mu\text{L}$  of electrolyte. For the Coulombic efficiency (CE) testing at room temperature, Li||Cu cells with electrolytes of interest were cycled by plating 1  $\text{mAh cm}^{-2}$  Li in 0.5  $\text{mA cm}^{-2}$  and stripping to 1.0 V. For the overpotential comparison of Li||Cu cells at various temperatures, the cells were rested at the set temperature for 5 hours and then cycled by plating 1  $\text{mAh cm}^{-2}$  of Li in 0.15  $\text{mA cm}^{-2}$  and stripping to 1.0 V (room temperature) or 2.0 V (-20  $^{\circ}\text{C}$  and -40  $^{\circ}\text{C}$ ). The fifth cycling curve was collected for the comparison of overpotentials at different temperatures.

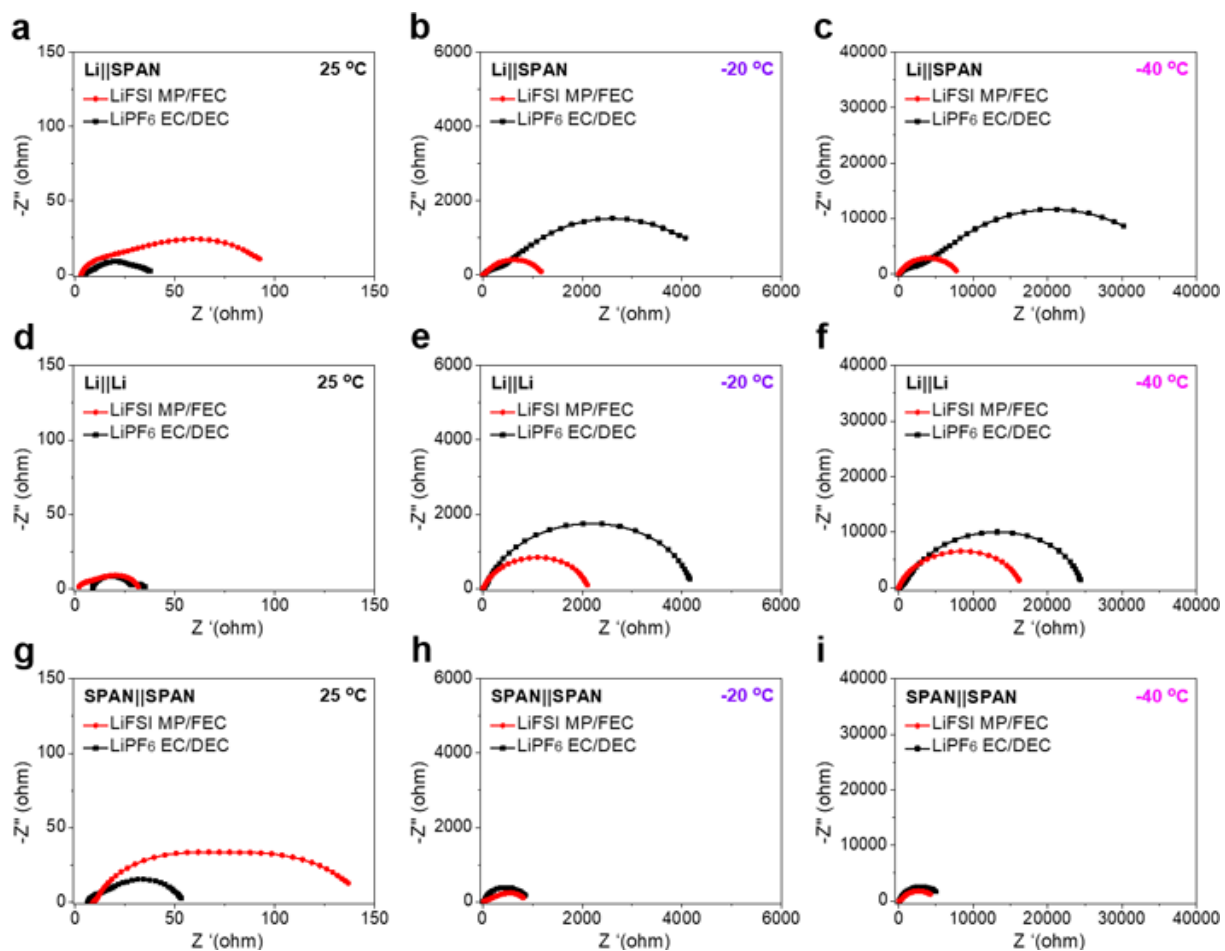
For Li||SPAN half cells, CR-2032 type coin cells were assembled with prepared SPAN cathodes (12 mm disc), Li foils, Celgard membrane (25  $\mu\text{m}$ ), and electrolyte of interest (40  $\mu\text{L}$ ). For ultra-low temperature testing, Li||SPAN cells were cycled at room temperature twice to reduce the complication that might arising from initial irreversible capacity. To ensure temperature equilibration, Li||SPAN half cells were rested in freezers (-20  $^{\circ}\text{C}$  or -40  $^{\circ}\text{C}$ ) for 5 hours before galvanostatic cycling. Their second charge-discharge curve in 0.1  $\text{A g}^{-1}$  were collected for the low-temperature performance comparison of selected electrolytes. For the long-term cycling at -40  $^{\circ}\text{C}$ , Li||SPAN half cells were conducted in 0.1  $\text{A g}^{-1}$  twice and then cycled in 0.2  $\text{A g}^{-1}$ .



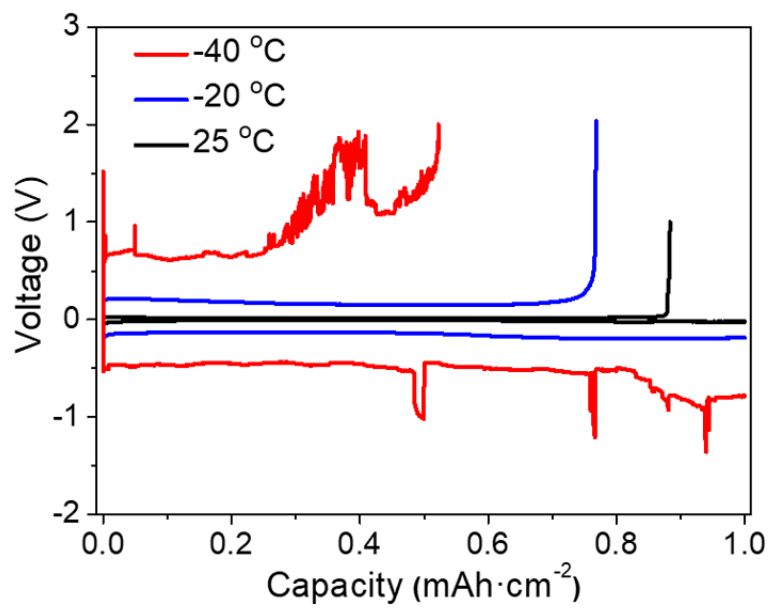
**Fig. S1** The activation process of Li||SPAN cells in selected electrolytes at  $0.1 \text{ A g}^{-1}$  and room temperature before any long-term cycling testing. The higher capacities of Li||SPAN cells during first discharge are from the parasitic reaction between  $\text{Li}^+$  and  $\text{C}=\text{N}$  bonds in SPAN, concomitantly a part of lithium ions remain in the charge products, which leads to the irreversible capacity loss.<sup>S4-S6</sup>



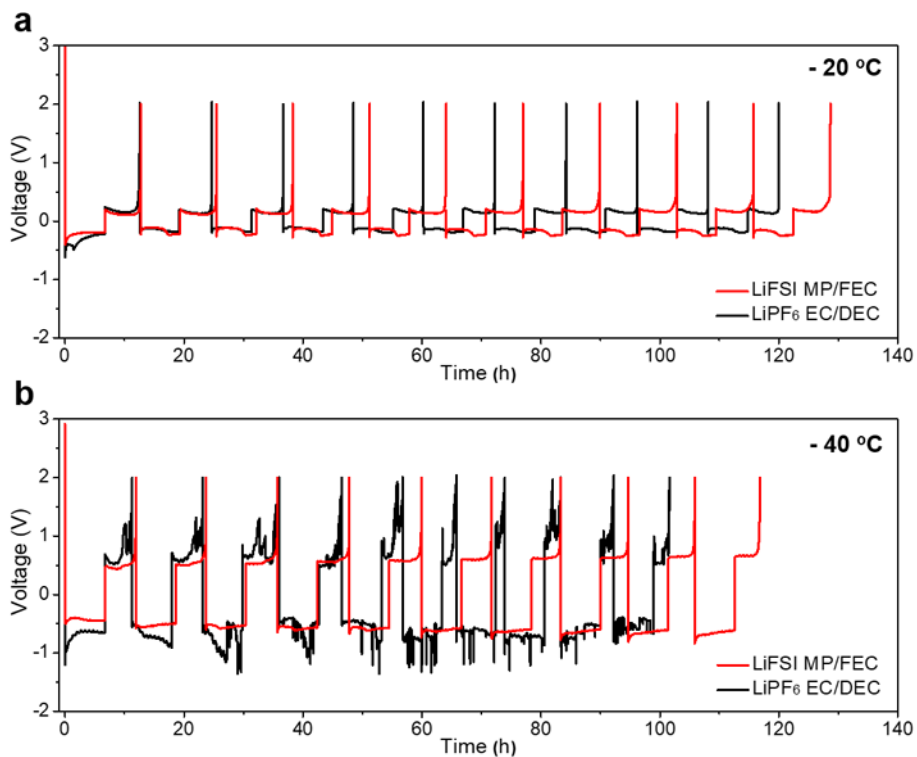
**Fig. S2** Cycling performance of Li||SPAN half cells in selected electrolytes at -20 °C and 0.2 A g<sup>-1</sup>.



**Fig. S3** EIS profiles of Li||SPAN half cells (a-c), Li||Li symmetrical cells (d-f), and SPAN||SPAN symmetric cells (g-h) at different testing temperatures in different electrolytes. The symmetrical SPAN||SPAN cell in LiFSI MP/FEC system exhibits a higher solid electrolyte interphase (SEI) impedance at room temperature than that in LiPF<sub>6</sub> EC/DEC, attributed to the formation of the dense LiF-rich SEI layers on SPAN, which may inhibit the dissolution of SPAN/polysulfide intermediates.<sup>S7,S8</sup>



**Fig. S4** Voltage curves of Li||Cu cells at 25 °C, -20 °C, and -40 °C in LiPF<sub>6</sub> EC/DEC at 0.15 mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>.



**Fig. S5** Voltage-time curves of Li||Cu cells in each electrolyte at -20 °C (a) and -40 °C (b) at 0.15 mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>.



## References

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