

Two Birds with One Stone: Engineering Siloxane-Based Electrolytes for High-Performance Lithium–Sulfurized Polyacrylonitrile Batteries

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1. Experiment section

1.1 Preparation of electrolytes

Dimethoxyethane (DME), and LiFSI were purchased from DodoChem. DMMS was provided by Aladdin. The solvents were dehydrated by 4 Å molecular sieves and the LiFSI salt was dried at 80 °C overnight inside an Ar-filled glove box before use. The electrolytes were prepared by dissolving predetermined amounts of lithium salts into the solvents (DME or DMMS). The baseline carbonate electrolyte 1.0 M LiPF₆ EC/DMC (v/v=3:7) was also purchased from DodoChem. Notably, the “M” used in this paper stands for molar concentration.

1.2 Preparation of SPAN cathodes

SPAN was prepared based on our previous report with a minor modification.¹ S (Sigma-Aldrich) and PAN (Sigma-Aldrich, Mw = 150,000) powders were ball milled with a mass ratio of 4:1. The homogeneous mixture was heated at 450 °C in a tube furnace for 3 h with a ramp rate of 2 °C min⁻¹. The SPAN slurry was prepared by mixing SPAN powder, Super P, carboxymethyl cellulose, and polymerized styrene-butadiene rubber in a mass ratio of 8:1:0.5:0.5 in deionized water, which was uniformly spread on a carbon-coated aluminum foil (MTI) and dried at 80 °C under vacuum overnight. The typical mass loading of the SPAN electrode is about 2.0-2.5 mg cm⁻².

1.3 Characterization

X-ray diffraction (XRD, Bruker D8) was conducted to study the phase structure of the S, PAN, and SPAN. The chemical structure of S and SPAN and various electrolytes were analyzed by Raman spectroscopy (Raman, DXR2xi). The microstructure, morphology, and sulfur content of SPAN were examined using a scanning electron microscope (SEM, Hitachi 8100), a transmission electron microscope (TEM, JEOL 2010), and an elemental analyzer (vario Micro cube). To record the morphology of Li metal anodes and sulfur cathodes cycled using different electrolytes, all the cells were disassembled in an argon-filled glovebox (Mikrouna) with O₂ and H₂O level <0.1 ppm, and the electrodes were rinsed with pure DME to remove the impurities. The surface features of cycled electrodes were analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250 Xi, Thermo Fisher) equipped with Ar⁺ etching.

1.4 Electrochemical measurements

All coin cells (CR2025-type) were assembled in a glove box filled with argon gas. The electrochemical performance was tested using the battery testing systems (LANHE battery tester, Wuhan). The Li⁺ transference number, t_{Li^+} , was tested with a Li||Li symmetric cell with a constant voltage bias of 10 mV. The ionic conductivity of different electrolytes was measured by the electrochemical impedance spectra (EIS) taken from 0.1 Hz to 100 kHz at a current amplitude of 5 mV using a symmetric coin cell blocked with stainless steel electrodes. The specific value was calculated using Equation 1:

$$\sigma = \frac{L}{RA} \quad (1)$$

Where σ is ionic conductivity, L represents the distance between two electrodes, A is the area of stainless steel, and R is the resistance.

The electrochemical stability of the electrolyte was studied via linear sweep voltammetry (LSV) at a scanning rate of 1 mV s^{-1} . An aluminum foil was employed as the working electrode while a Li foil was used as both the counter and reference electrode. Li||Cu and Li||Li cells were assembled to evaluate the electrochemical stability between LMA and electrolytes. The modified Aurbach's protocol was used to determine the average CE (CE_{avg}) as developed by Zhang and colleagues.² Typically, 4 mAh cm^{-2} Li was first plated onto the Cu substrate and stripped away until the voltage reached 1.0 V. Subsequently, 4 mAh cm^{-2} Li (Q_i) was deposited on Cu again. Before it was fully stripped to 1.0 V, a plating and stripping step of 1 mAh cm^{-2} Li (Q_c) was cycled n times. After cycling, the residual Li (Q_s) was stripped away with a cut-off voltage of 1.0 V. The CE_{avg} was calculated according to the following Equation 2:

$$CE_{\text{avg}} = \frac{nQ_c + Q_s}{nQ_c + Q_t} \quad (2)$$

For Li||SPAN cells, a Celgard 2500 membrane filled with an electrolyte dose of $50 \mu\text{L}$ was sandwiched between the LMA and SPAN cathode. The cyclic performance and rate tests were recorded using a CHI760E electrochemical workstation between 1.0 and 3.0 V at $26 \text{ }^\circ\text{C}$. Cyclic voltammetry (CV) and EIS (with a frequency ranging from 100 kHz to 10 mHz) of Li||SPAN cells were measured using the same electrochemical workstation.

1.5 Computational methods

All the calculations were performed with density functional theory (DFT) using the B3LYP functional with the 6-311G++(d,p) basis set using the Gaussian 09 software.^{3,4} D3 dispersion corrections with zero damping were used to describe the van der Waals force.⁵ The solvation energy was defined as the difference in free energy of the solute in the solution and gas phase using the solvation model based on density (SMD).

Supporting Figures

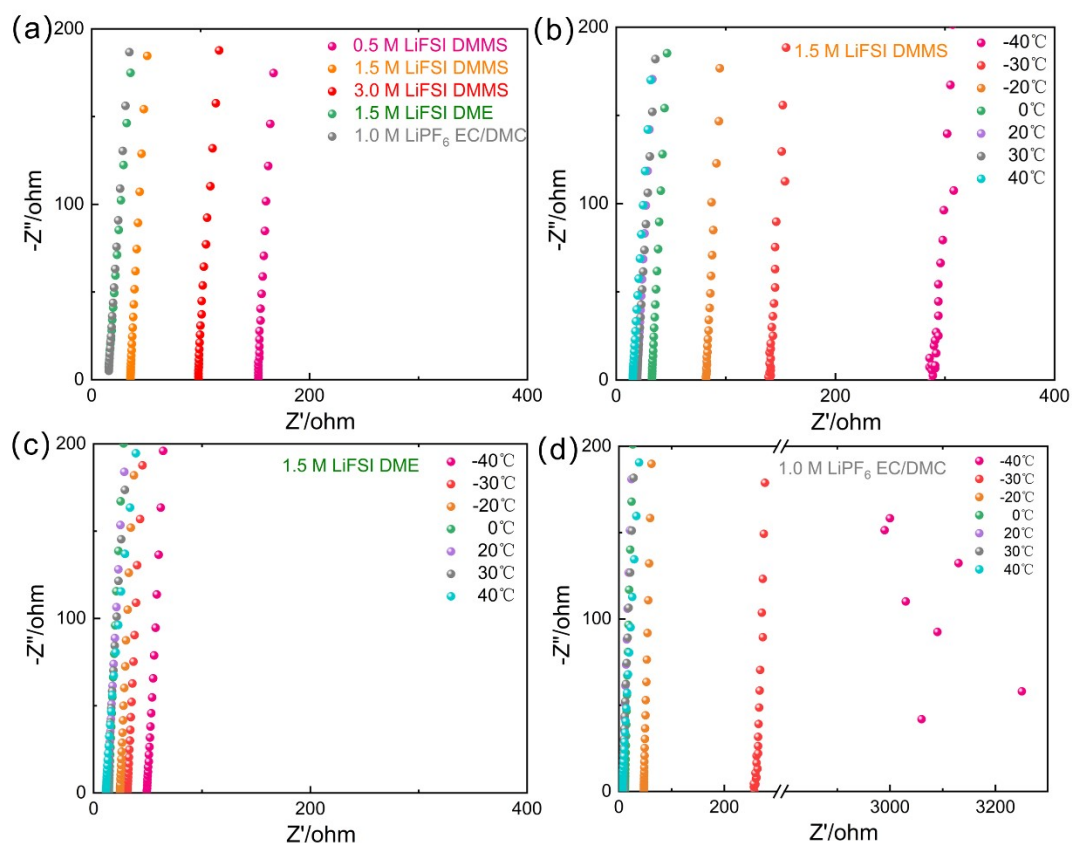


Figure S1. Nyquist plots of (a) various electrolytes at 26 °C and (b-d) 1.5 M LiFSI DMMS, 1.5 M LiFSI DME, and 1.0 M LiPF₆ EC/DMC as a function of temperature.

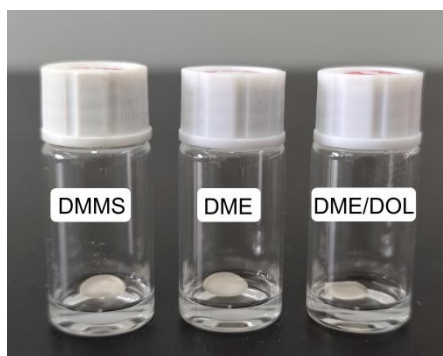


Figure S2. Photograph showing the compatibility between different solvents and Li metal.

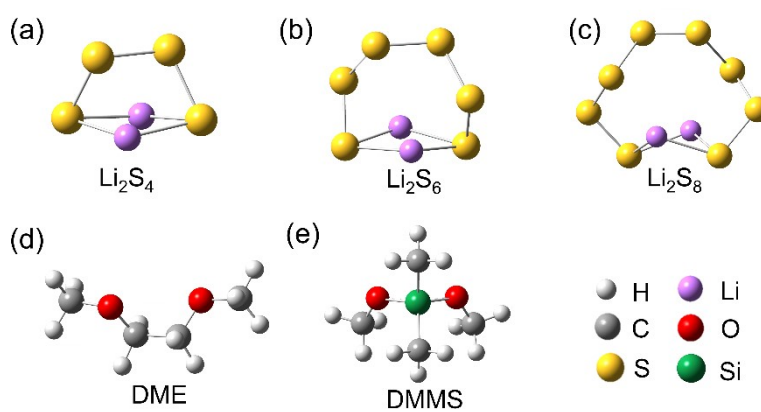


Figure S3. Optimized structures of (a) Li_2S_4 , (b) Li_2S_6 , (c) Li_2S_8 , (d) DME, and (e) DMMS.

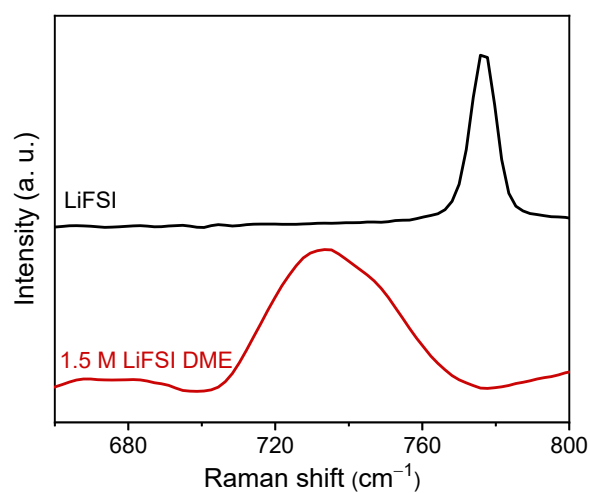


Figure S4. Raman spectra of the LiFSI salt and 1.5 M LiFSI DME electrolyte.

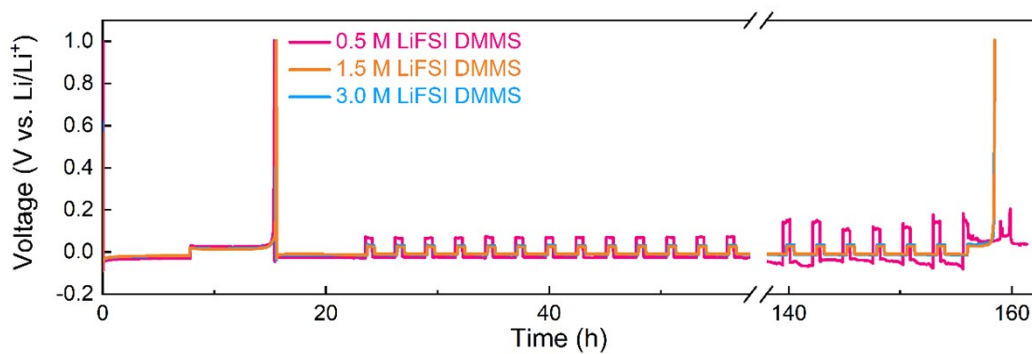


Figure S5. CE measurements of DMMS-based electrolytes using modified Aurbach's method.

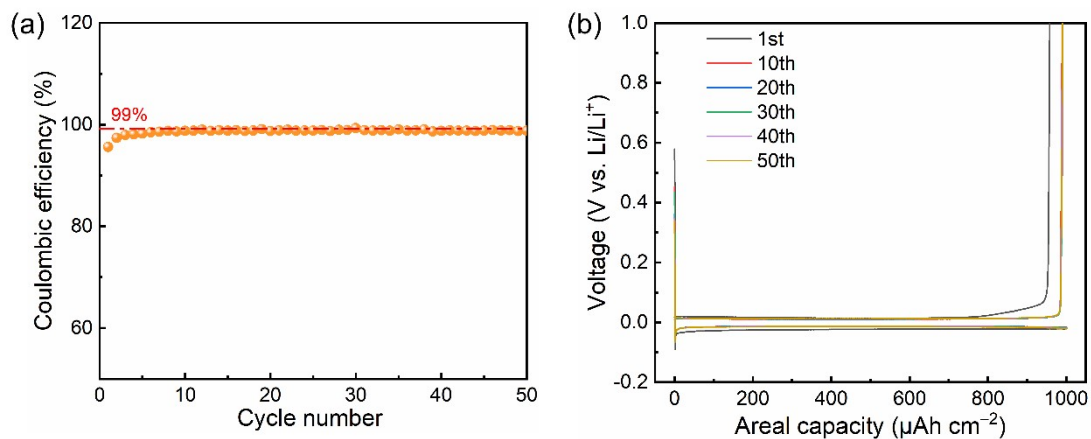


Figure S6. (a) Coulombic efficiency of Li||Cu cell using 1.5 M LiFSI DMMS electrolyte with full plating/stripping at 0.5 mA cm^{-2} for 1 mAh cm^{-2} , and (b) corresponding voltage versus areal capacity curves.

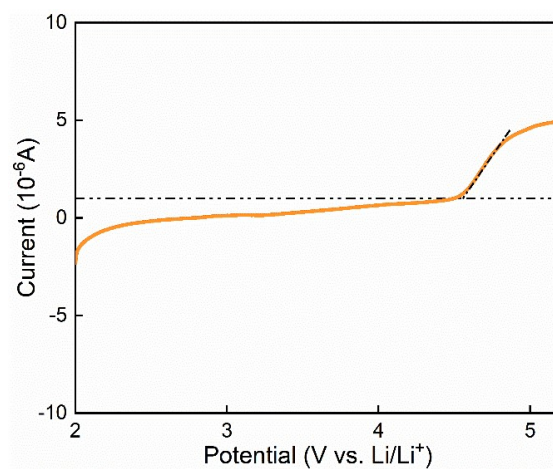


Figure S7. LSV curve of Li||Al cell using 1.5 M LiFSI DMMS electrolyte at a scan rate of 1 mV s^{-1} .

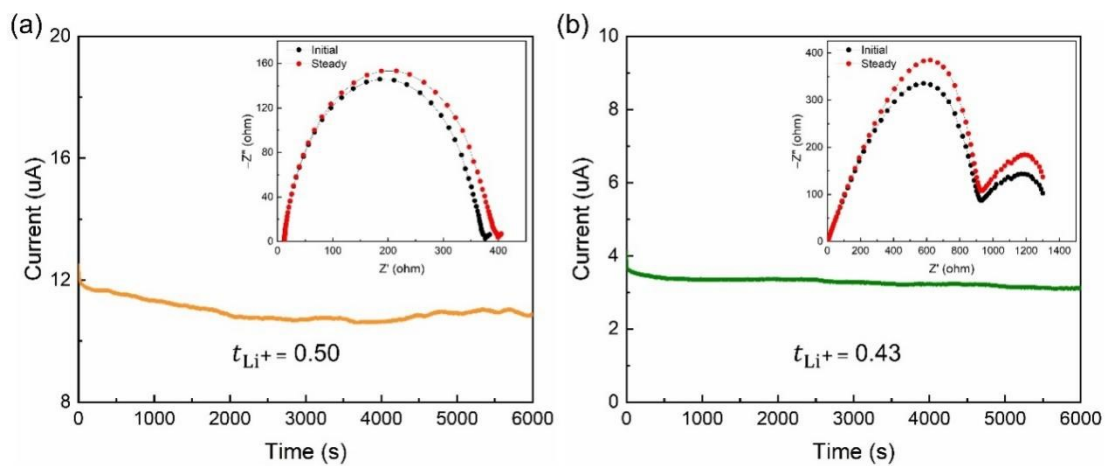


Figure S8. Chronoamperometric and Nyquist plots of symmetric Li||Li cells using (a) 1.5 M LiFSI DMMS and (b) 1.5 M LiFSI DME electrolytes.

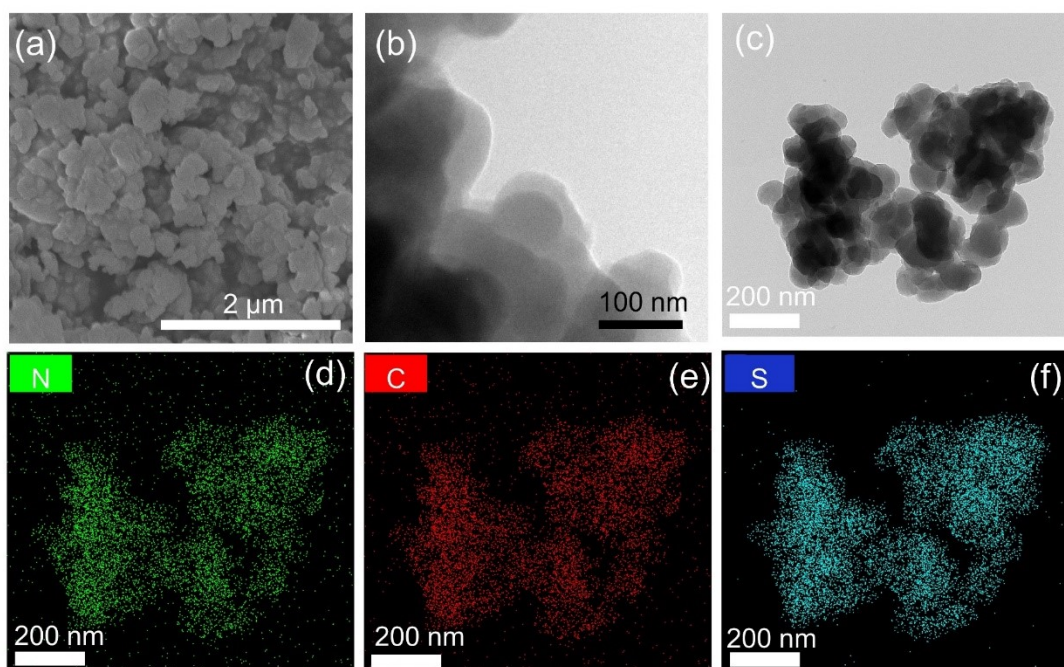


Figure S9. (a) SEM and (b) TEM images of SPAN composite, (c) TEM and (d-f) corresponding energy-dispersive X-ray spectroscopy elemental mapping of SPAN.

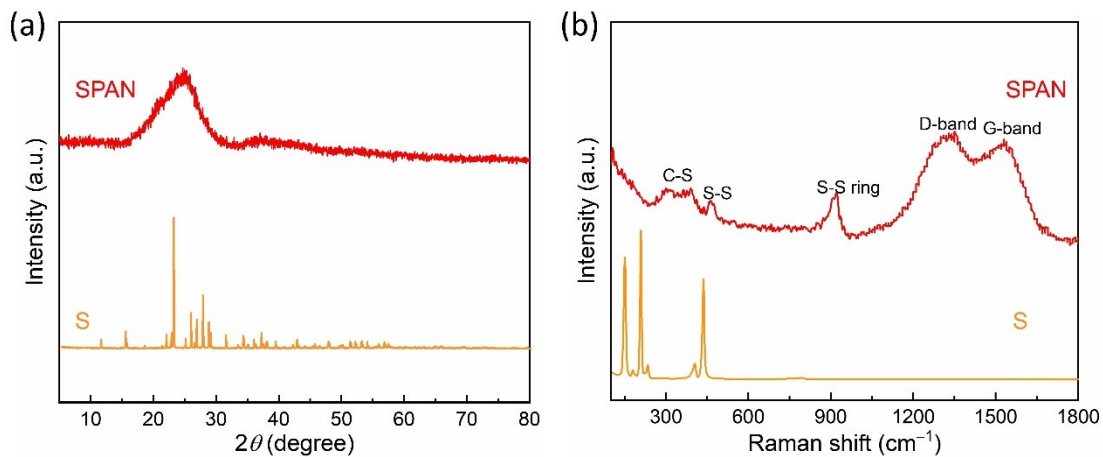


Figure S10. (a) XRD patterns and (b) Raman spectra of SPAN composite and elemental sulfur.

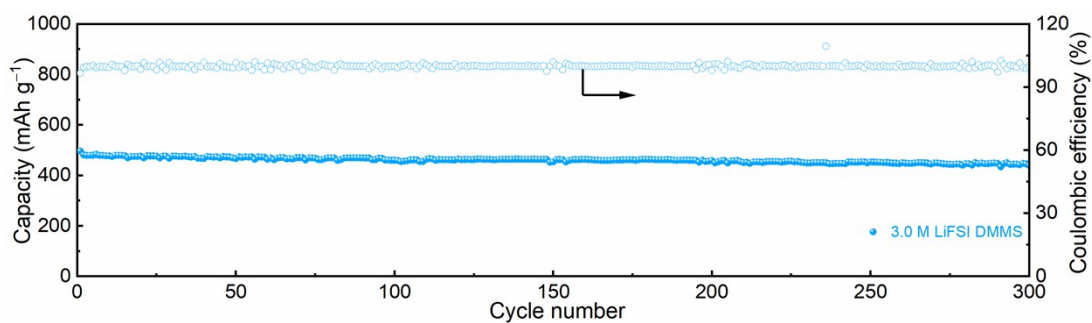


Figure S11. Cyclic performance of Li||SPAN batteries using 3.0 M LiFSI DMMS at 0.2 A g^{-1} .

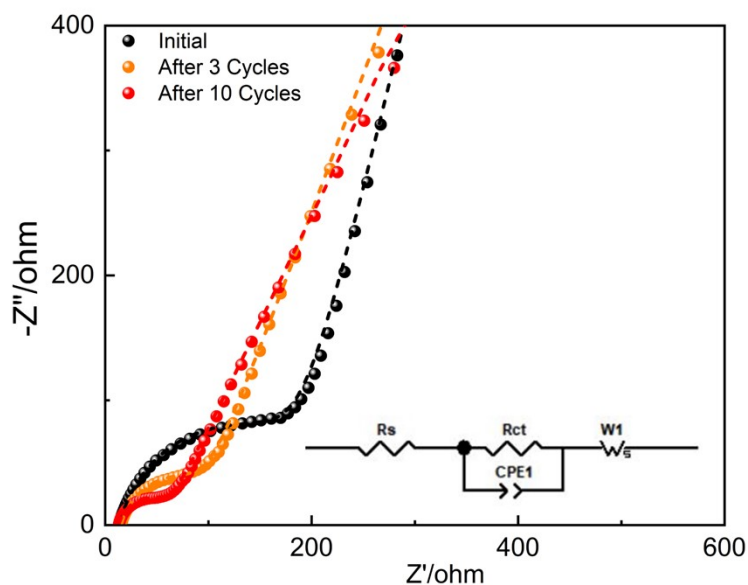


Figure S12. Nyquist plots of Li||SPAN batteries after different cycles. The inset is the equivalent circuit.

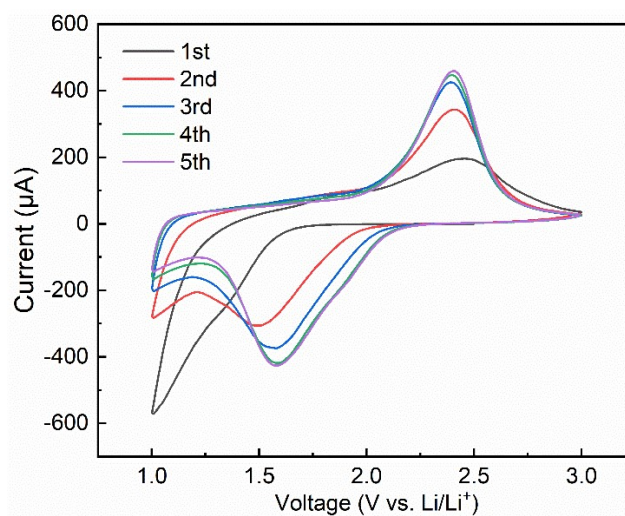


Figure S13. CV curves of Li||SPAN cell at a scan rate of 0.2 mV s^{-1} .

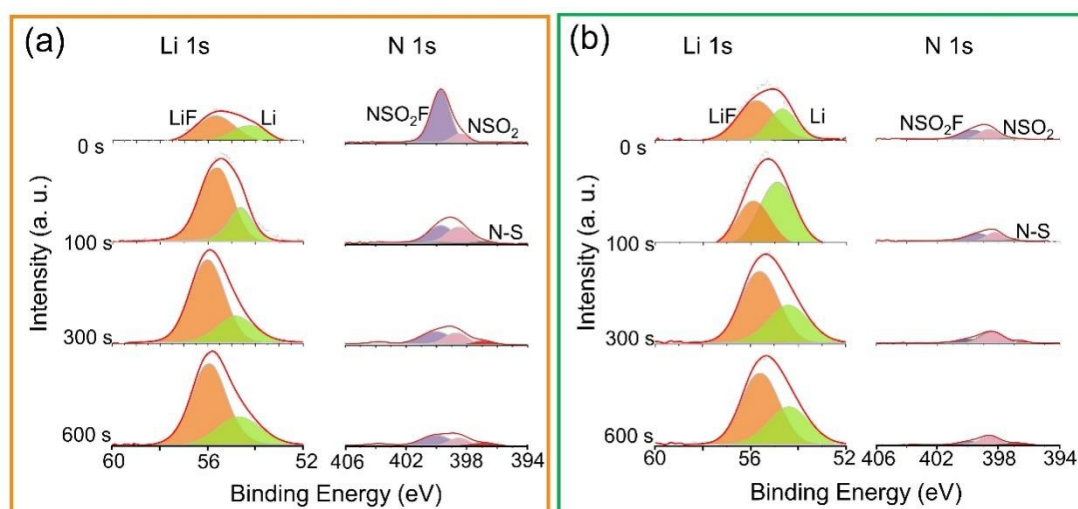


Figure S14. Depth-profiling XPS (Li 1s and N 1s) of the SEIs formed on Li anodes cycled using electrolytes of (a) 1.5 M LiFSI DMMS and (b) 1.5 M LiFSI DME.

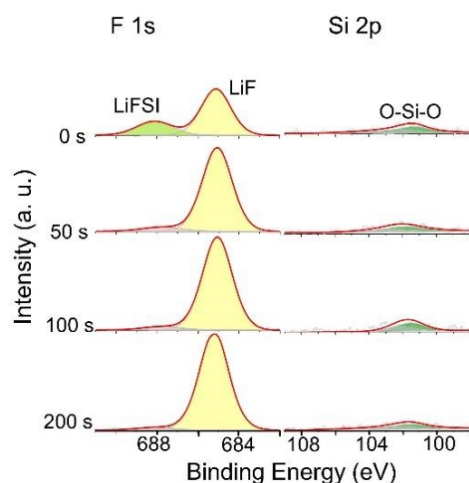


Figure S15. Depth-profiling XPS (F 1s and Si 2p) of the SEIs formed on SPAN cathode using 1.5 M LiFSI DMMS electrolyte.

Table S1. Results of elemental analysis of the SPAN composite

Sample	Mass fraction (wt.%)			
	H	N	C	S
SPAN	0.43	15.5	41.4	37.8

References

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- 2 B. D. Adams, J. Zheng, X. Ren, W. Xu and J.-G. Zhang, *Adv. Energy Mater.*, 2018, **8**, 1702097.
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- 4 M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, Gaussian 09, Revision a. 02 Gaussian, Inc., Wallingford, CT 200, 2009.
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