

Supporting Information

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Towards a Safe Lithium–Sulfur Battery with a Flame-Inhibiting Electrolyte and a Sulfur-Based Composite Cathode**

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Self-extinguishing time (SET) and conductivity: A cotton-ball wick was immersed in the as-prepared electrolyte to absorb 0.2–0.3 g liquid and was subsequently ignited in a fume hood, and the time for the flame to extinguish was recorded. The results were normalised against the electrolyte mass, and the SET tests were repeated at least six times. The ionic conductivities of the electrolytes with different TTFP contents were measured at room temperature using an FE30 conductivity meter and an Inlab 710 conductivity measurement cell (Mettler Toledo, Switzerland).

X-ray photoelectron spectroscopy (XPS): The cathodes were charged/discharged for three cycles and then finally charged to 3 V. The cathodes were subsequently washed with DMC three times and then dried under vacuum overnight. The surface element compositions were analysed by XPS using a Kratos Axis UltraDLD spectrometer (Kratos Analytical-A Shimadzu) with a monochromatic Al K_{α} radiation source (1486.6 eV). The analyser used hybrid magnification mode (both electrostatic and magnetic), and the take-off angle was 90°. Under slot mode, the analysis area was $700 \times 300 \mu\text{m}^2$, and the analysis-chamber pressure was less than 5×10^{-9} Torr. The binding energy was calibrated according to the C1s peak (284.8 eV) of the adventitious carbon on the analysed sample surface.

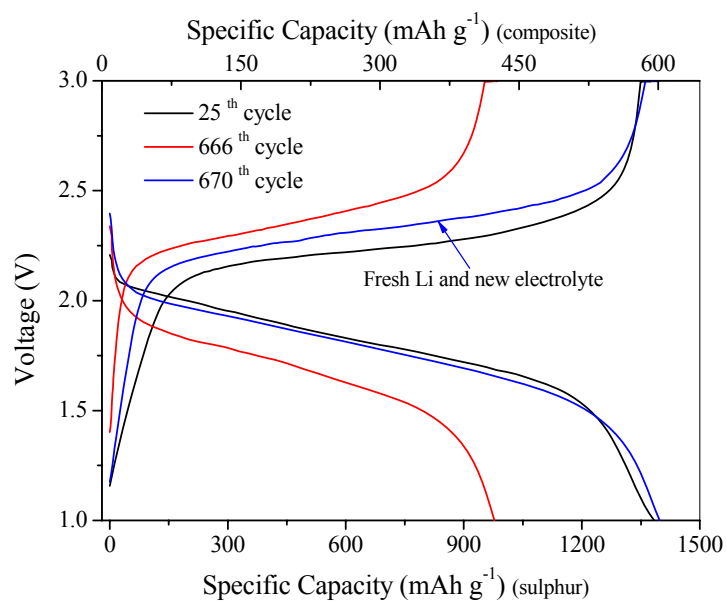


Figure S1. Charge/discharge profiles along cycling.

At 666th cycle, the pPAN@S cathode delivered only 985 mAh g⁻¹_{sulphur}. After reassembled in a new cell with fresh Li anode and new electrolyte, the capacity of the pPAN@S cathode fully recovered to its initial value of 1400 mAh g⁻¹_{sulphur}, with a slight charge voltage increment.

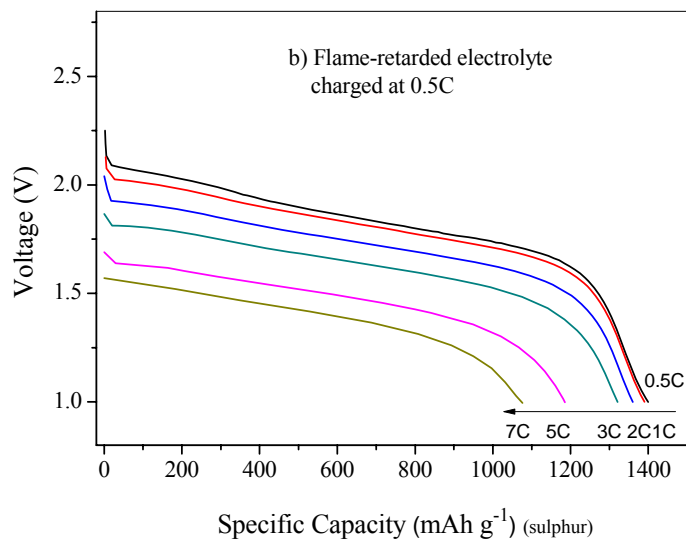
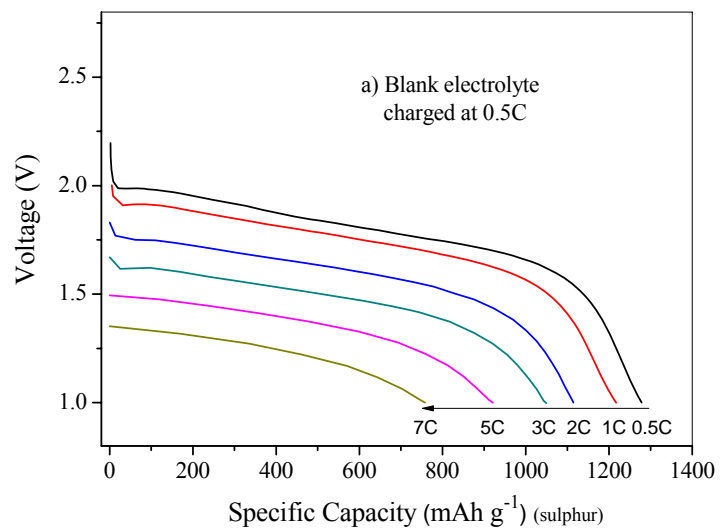


Figure S2. Discharge profiles at different rates

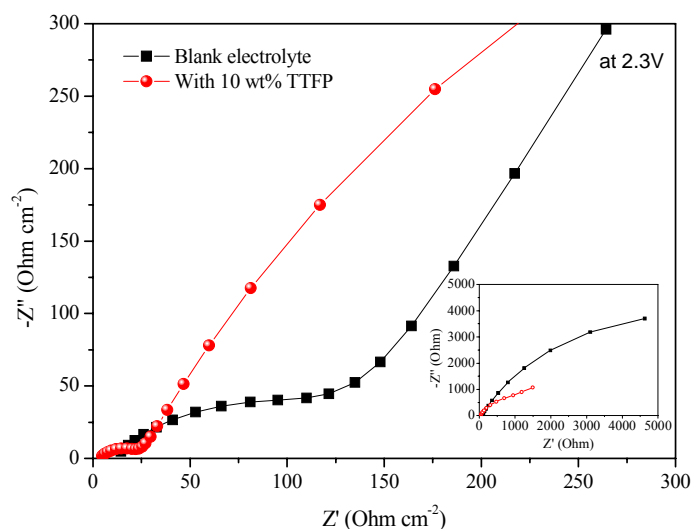


Figure S3. Impedance spectra at 2.3 V (vs. Li/Li^+)

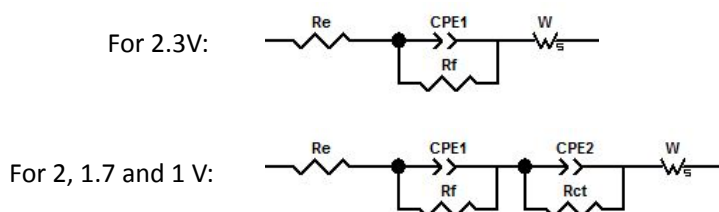


Figure S4. Equivalent circuits for EIS fitting, where R_e is the resistance of the electrolyte; R_f and CPE_1 are resistance and capacitance of the interfacial film on the electrode, corresponding to the semicircle at high frequency; R_{ct} is the charge-transfer resistance and CPE_2 represents its double-layer capacitance, corresponding to the semicircle at medium frequency; W describes the Warburg impedance related to the diffusion of Li^+ ion in the electrode materials.

Table S1. Electrochemical parameters at different discharge voltages

| Voltage (V) | R_e (Ω) | | R_f (Ω) | | R_{ct} (Ω) | |
|-------------|--------------------|-----------|--------------------|-----------|-----------------------|-----------|
| | Blank | →10% TTFP | Blank | →10% TTFP | Blank | →10% TTFP |
| 2.3 | 5.37 | → 3.623 | 62.717 | → 20.938 | / | |
| 2 | 5.596 | → 7.349 | 68.106 | → 27.089 | 164.956 | → 120.177 |
| 1.7 | 5.296 | → 5.081 | 72.858 | → 27.646 | 137.611 | → 29.850 |
| 1 | 6.208 | → 10.425 | 56.381 | → 40.133 | 91.150 | → 23.602 |

Table S2. Lithium ion diffusion coefficients.

| | B (slope) | | D_{Li^+} ($cm^2 s^{-1}$) | |
|-------------------|-----------|---------|------------------------------|-------------------------|
| | Cathodic | Anodic | Cathodic | Anodic |
| Blank electrolyte | 0.0224 | 0.01548 | 6.79×10^{-10} | 3.243×10^{-10} |
| With 10% TTFP | 0.07523 | 0.05827 | 9.455×10^{-9} | 5.673×10^{-9} |

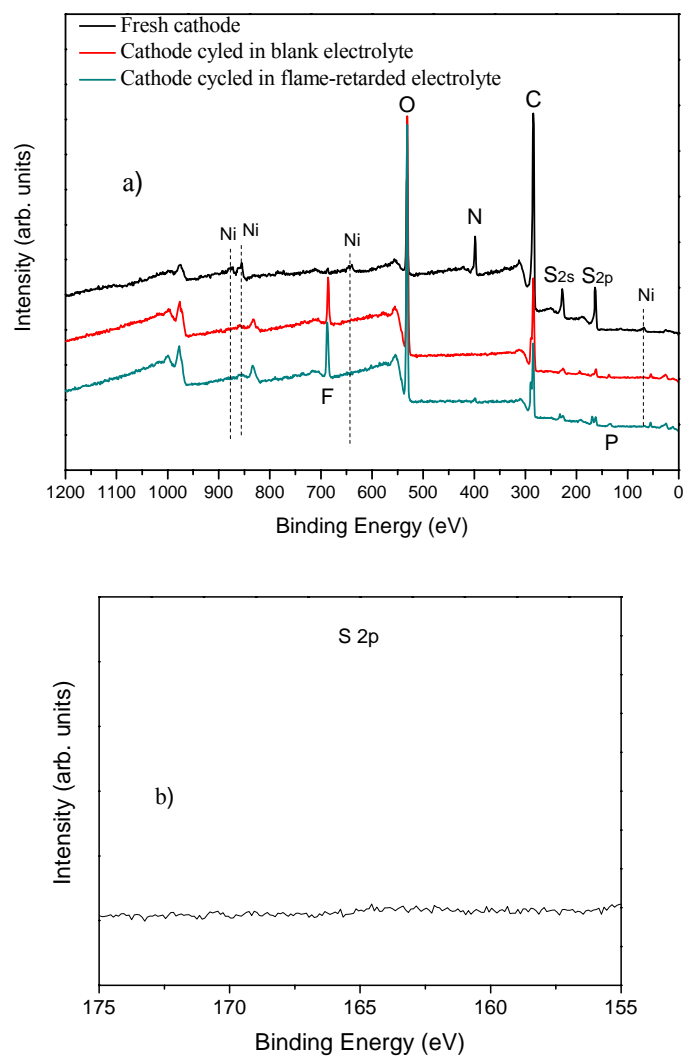


Figure S5. XPS measurements. a), Full spectra of the cathodes. Nickel foam was adopted as current collector for XPS investigations. After cycling, N spectra disappeared, indicating the interface formed during cycling, with the thickness beyond the detecting depth of XPS (several nano meters). By contrast, the weak N spectra cycled in the flame-retarded electrolyte elucidates probably a thinner interface. b), Detection of S on the cycled Li anode that was dried under vacuum directly without wash. No S on the cycled Li anode indicates no discharge product dissolution.