

I. Supporting Text

1. Materials and Methods

1.1 Raw materials

Ultrathin lithium (Li) foils (50 μm) were purchased from China Energy Lithium Co., Ltd. 1,3-dioxolane (DOL, 99.9% purity) and 1,2-dimethoxyethane (DME, 99.9% purity) were purchased from DoDoChem. Lithium bis(trifluoromethanesulfony)imide (LiTFSI) was purchased from TCI (Shanghai) Development Co., Ltd. Lithium nitrate (LiNO_3) and lithium sulfide (Li_2S) were purchased from Alpha Aesar. Sulfur (S) was purchased from Aladdin. 2-aminophenylacetonitrile (APA) was purchased from MERYER Co., Ltd. Dimethyl sulfoxide-d₆ (DMSO-d₆, 99.5% purity) was purchased from Cambridge Isotope Laboratories, Inc. All the raw materials were used without further purification.

1.2. Material characterization

Li metal anodes disassembled from Li–S batteries after cycles were cleaned by DME five times to guarantee no residual electrolyte and then dried in a glove box with H_2O and O_2 content below 0.1 ppm. During the transferring process, the samples were placed in an argon (Ar)-filled container to avert contact with air before characterization. Morphologies of Li metal anodes were characterized by a JSM 7401F (JEOL Ltd., Tokyo, Japan) scanning electron microscopy (SEM) operated at 3.0 kV. The solutions were characterized using an ultraviolet–visible (UV–vis) spectrometer (AvaSpec-ULS4096CL-EVO, Avantes, China). ^1H and ^7Li NMR spectra were recorded at 400 MHz using a Bruker AVANCE NEO 400 system at room temperature.

1.3. Battery assembly and electrochemical test

All the batteries were assembled in 2032-type coin battery configuration and tested on a LAND multichannel battery cycler at 25°C. For the Li–S batteries, a carbon/S composite (30 wt.% multi-walled carbon nanotubes and 70 wt.% S) was ball-milled with polyvinylidene fluoride at a weight ratio of 9:1 in NMP solvent, and a slurry was obtained. The slurry was cast onto Al foil and dried for 12 h at 60°C. The S cathode was cut into disks with a diameter of 13 mm. The S loading was 4.1 mg cm⁻² with an S content of 63 wt.%. The diameter of fresh Li was 15 mm. The thickness of fresh Li was 50 μm. Polypropylene (PP) membrane was used as the separator. The amount of electrolyte was controlled with an electrolyte/sulfur (E/S) ratio of 6.4 μL mg_S⁻¹. The galvanostatic cycling voltage of Li–S batteries was between 1.7–2.6 V. Li–S batteries under practical conditions were cycled at 0.1 C (1 C = 1672 mA g⁻¹) after two activation cycles at 0.05 C. For the i-Li–CP and i-Li–S batteries, the CP cathode was cut into disks with a diameter of 13 mm. The diameter of inactive Li was 15 mm. Polypropylene (PP) membrane was used as the separator. The electrolyte composed of 1.0 M LiTFSI and 2 wt.% LiNO₃ in DME/DOL (1:1, by vol.) is selected as the routine electrolyte in Li–S, i-Li–CP, and i-Li–S batteries.

The Li–S pouch cell (7 × 4 cm⁻²) was fabricated in a dry room with a dew point below –40°C. The S loading of the cathode was 7.7 mg cm⁻² for each single side. Ultrathin Li foils (50 μm for each single side) and a low E/S ratio (3.5 g_{ele} g_S⁻¹) were used. The electrolyte composed of 1.0 M LiTFSI and 5 wt.% LiNO₃ in DME/DOL (3:1, by vol.) is selected as the routine electrolyte in Li–S pouch cell. The cathodes and

anodes (double layered) were stacked layer-by-layer with a PP separator. The galvanostatic cycling voltage of the Li–S pouch cell was between 1.7–2.6 V. The pouch cell was tested at 0.05 C (1 C = 1000 mA g⁻¹) and the discharge capacity was 2.4 Ah. The total mass of the battery core (Li anode, S cathode, Cu current collector, Al current collector, separator, and tap) was 6.0 g. The mass of the electrolyte was 7.6 g. The mass of the package was 2.1 g. The energy density based on the total mass of the pouch cell was 321 Wh kg⁻¹.

1.4. Electrolyte and inactive Li preparation

1.0 M LiTFSI dissolved in DOL/DME (v/v = 1:1) with 2 wt.% LiNO₃ was used as the blank electrolyte. 150 mM APA was added to the blank electrolyte. The mixture of S and Li₂S in the molar ratios of 1:7 and 1:5 was added in DMSO-d₆ to prepare lithium polysulfide (LiPS) electrolytes for NMR. The concentration of Li₂S₈ and Li₂S₆ was 0.5 M. Inactive Li was prepared on a copper foil by disassembling a charged-state Li–Cu battery after 10 cycles under the conditions of 1.0 mA cm⁻² and 3.0 mAh cm⁻².

II. Supporting Figures

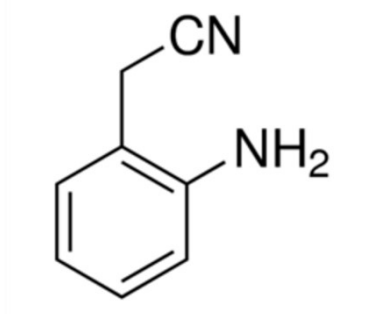


Figure S1. The chemical structure of APA.

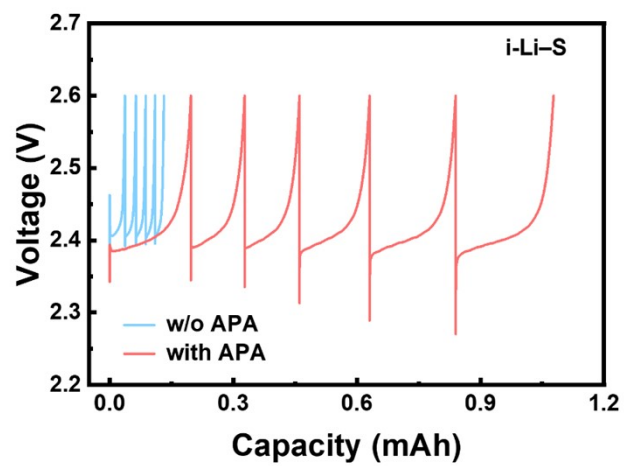


Figure S2. The galvanostatic charging test of i-Li-S batteries. Each charging interval is 5 h.

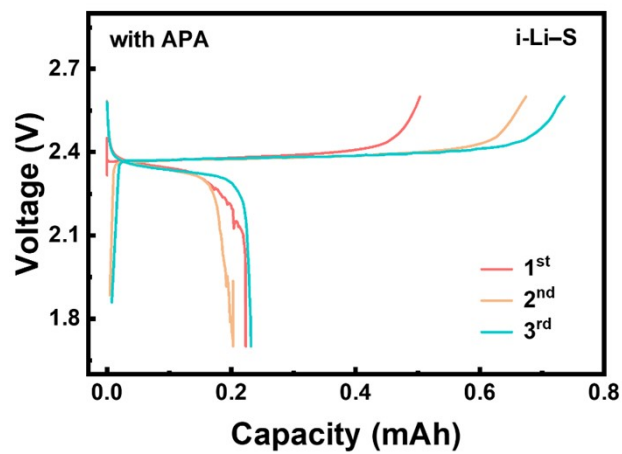


Figure S3. The voltage–capacity profiles of i-Li–S batteries with APA.

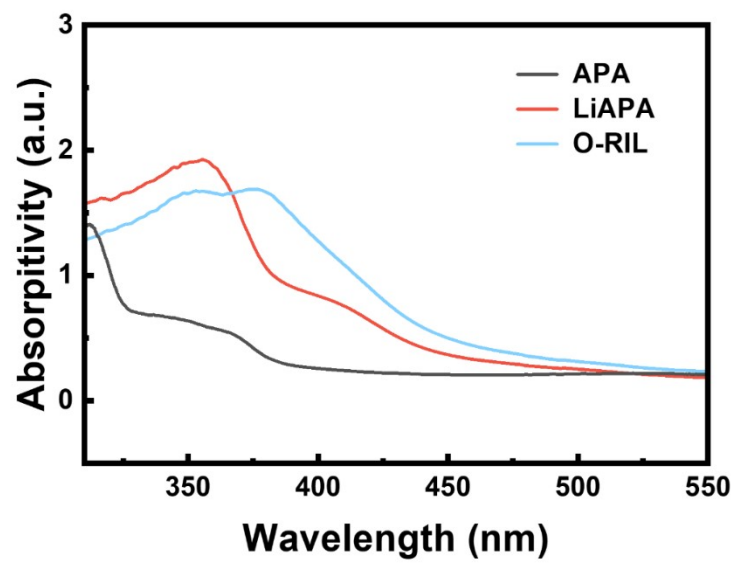


Figure S4. The UV-vis spectra tracked the evolution of APA in Li-S batteries.

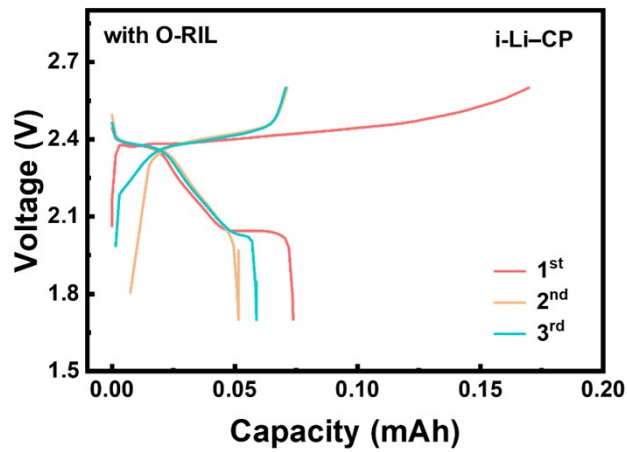


Figure S5. The voltage–capacity profiles of i-Li-CP batteries with O-RIL.

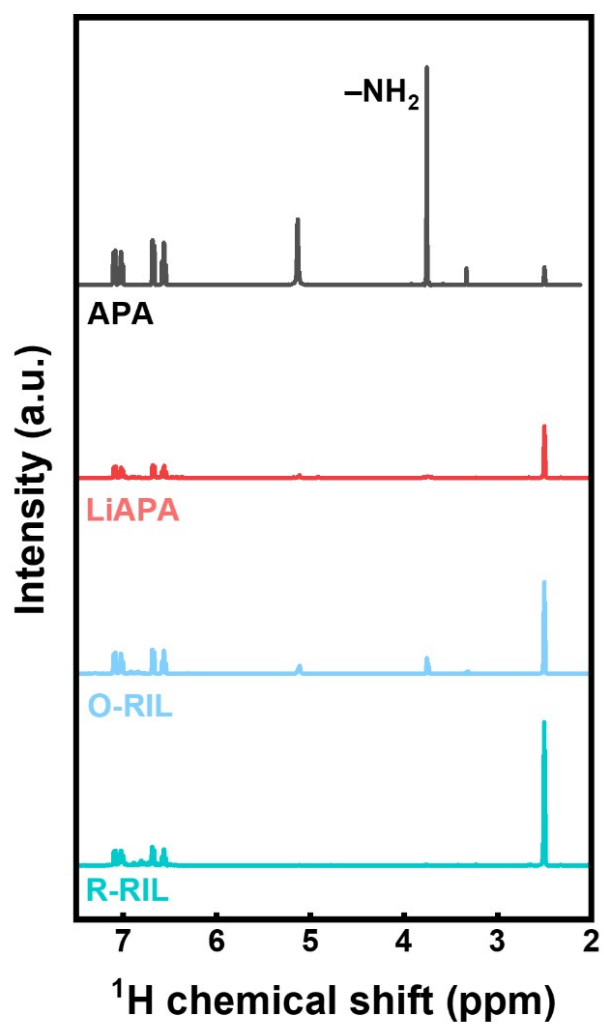


Figure S6. ^1H -NMR spectra of APA, LiAPA, O-RIL, and R-RIL.

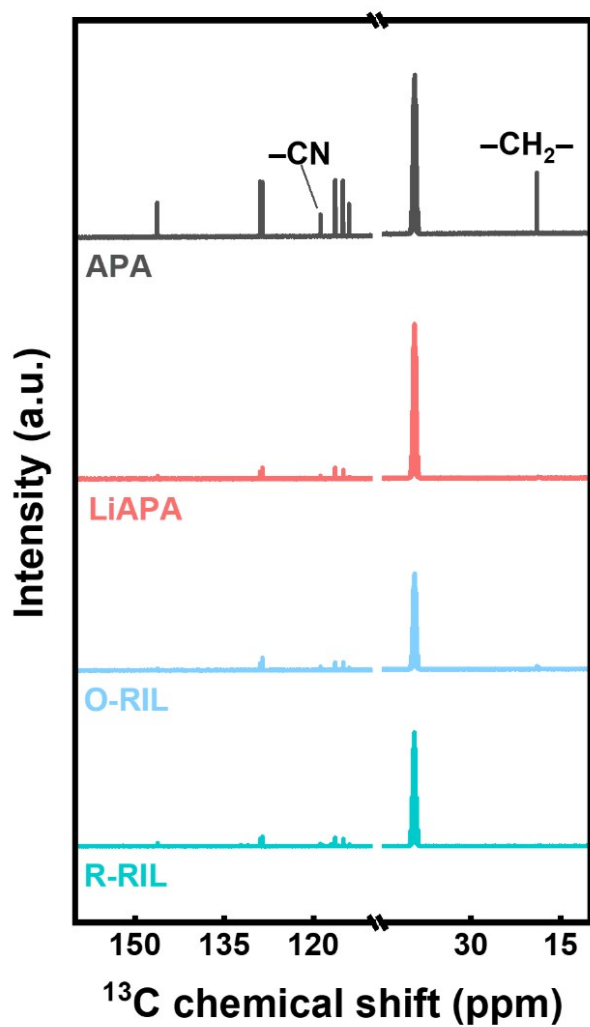


Figure S7. ^{13}C -NMR spectra of APA, LiAPA, O-RIL, and R-RIL.

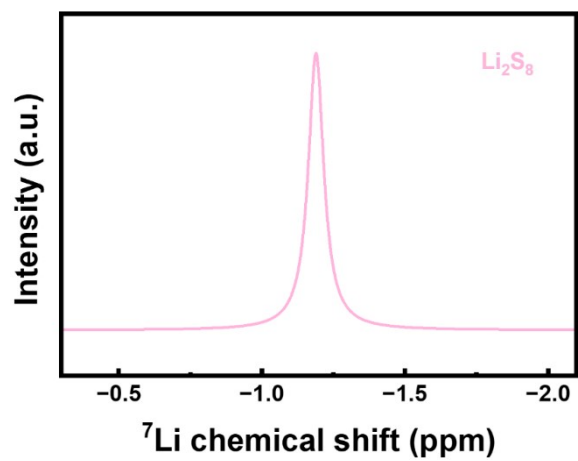


Figure S8. ${}^7\text{Li}$ -NMR spectra of Li_2S_8 in DMSO-d_6 .

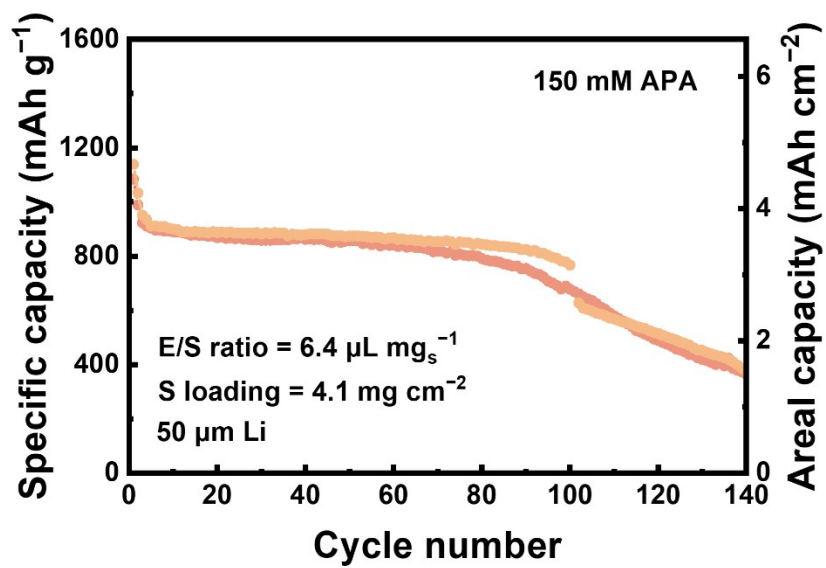


Figure S9. The electrochemical performance of Li-S batteries of the other two parallel samples with 150 mM APA.

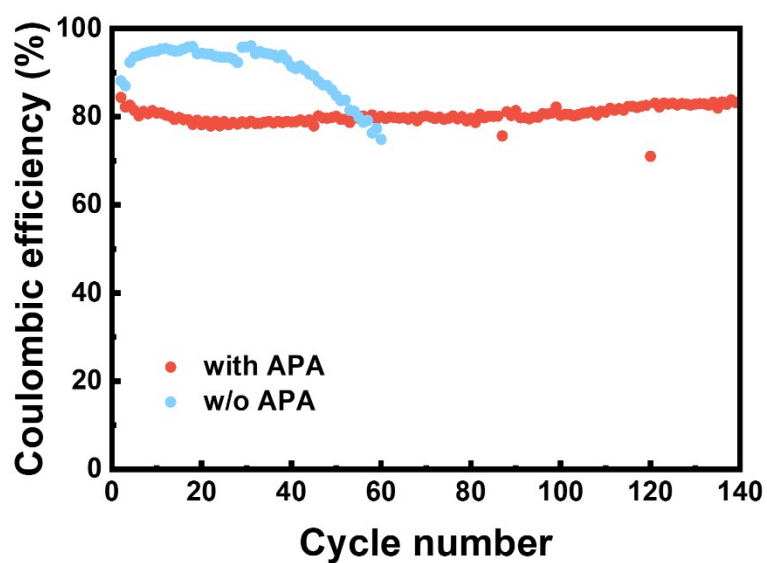


Figure S10. Coulombic efficiency of Li–S batteries with and without the organic polysulfide redox at 0.1 C under practical conditions with a high loading S cathode (4.1 mg cm^{-2}), a low E/S ratio ($6.4 \text{ } \mu\text{L mg}_S^{-1}$), and an ultrathin Li anode ($50 \text{ } \mu\text{m}$).

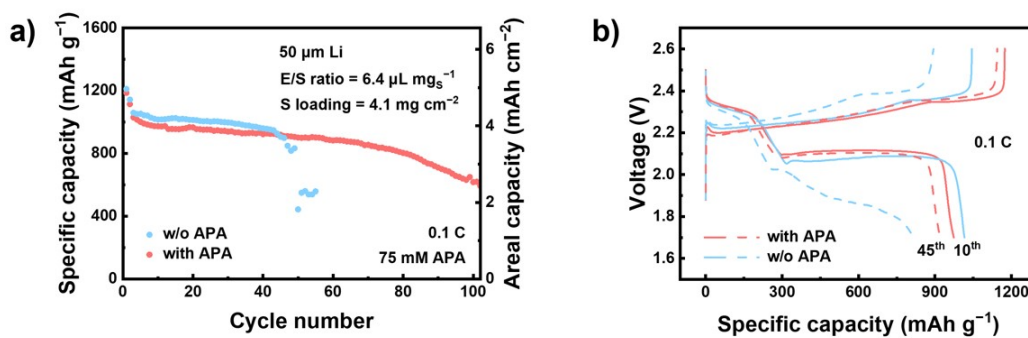


Figure S11. Electrochemical performance of Li-S batteries with 75 mM APA. a) The cycling performance of Li-S batteries at 0.1 C under practical conditions with a high loading S cathode (4.1 mg cm^{-2}), a low electrolyte/sulfur ratio (E/S ratio = $6.4 \mu\text{L mg}_\text{S}^{-1}$), and an ultrathin Li anode ($50 \mu\text{m}$). b) The galvanostatic discharge-charge profiles at the 10th and the 45th cycle.

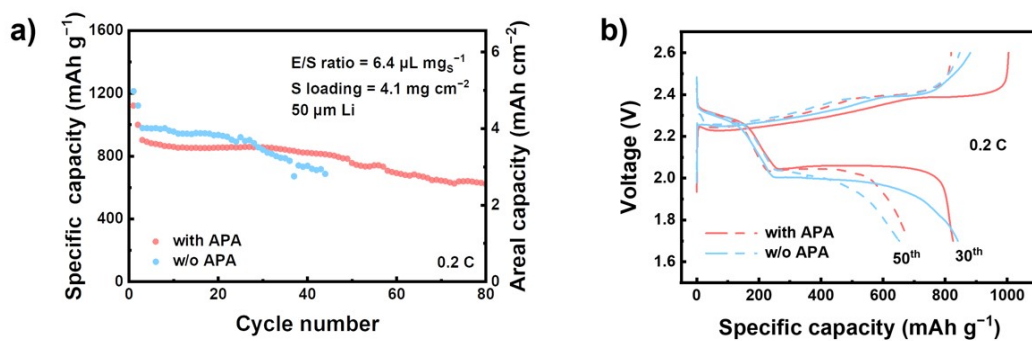


Figure S12. The electrochemical performance of Li-S batteries with 150 mM APA at 0.2 C. a) The cycling performance of Li-S batteries at 0.2 C under practical conditions with a high loading S cathode (4.1 mg cm^{-2}), a low E/S ratio ($6.4 \mu\text{L mg}_s^{-1}$), and an ultrathin Li anode ($50 \mu\text{m}$). b) The galvanostatic discharge-charge profiles at the 30th and the 50th cycle.

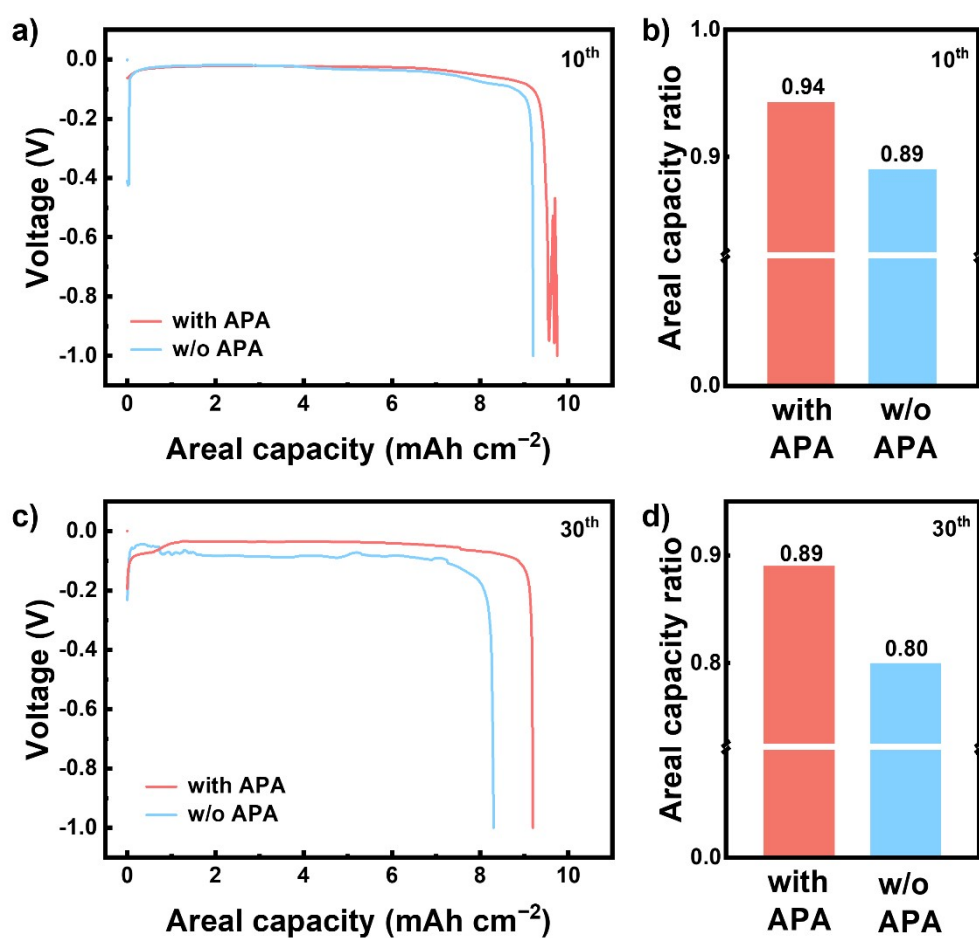


Figure S13. a) Determination of residual active Li in Li-S batteries with and w/o APA after (a) 10 and (b) 30 cycles. b) The areal capacity ratio between cycled Li anodes after (a) 10 and (b) 30 cycles and fresh Li anodes. The cycled Li anode after washing by DME solvent and Li foil were assembled to achieve Li | Li cells, and then the cell was discharged at 1.0 mA cm⁻² to measure the remaining active Li in the cycled Li anode.

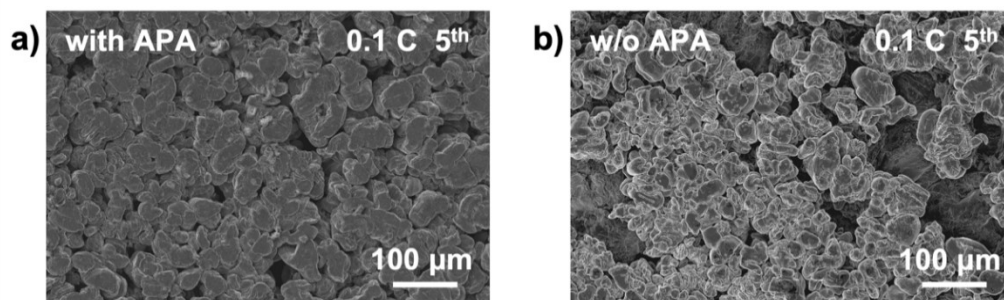


Figure S14. Li deposition morphologies in Li-S batteries a) with APA and b) without APA after 5 cycles at 0.1 C.

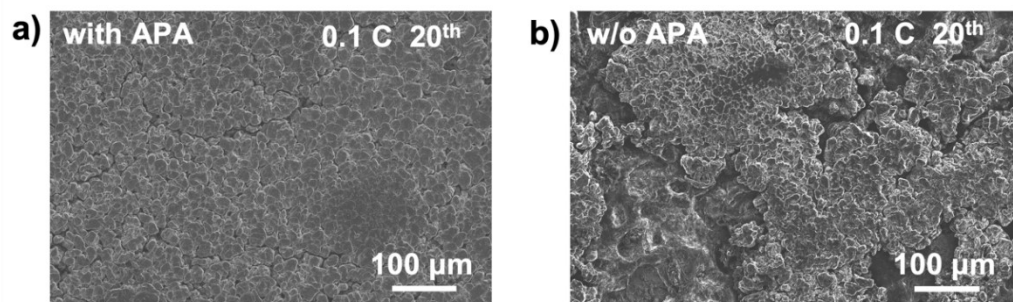


Figure S15. Li deposition morphologies in Li-S batteries a) with APA and b) without APA after 20 cycles at 0.1 C.

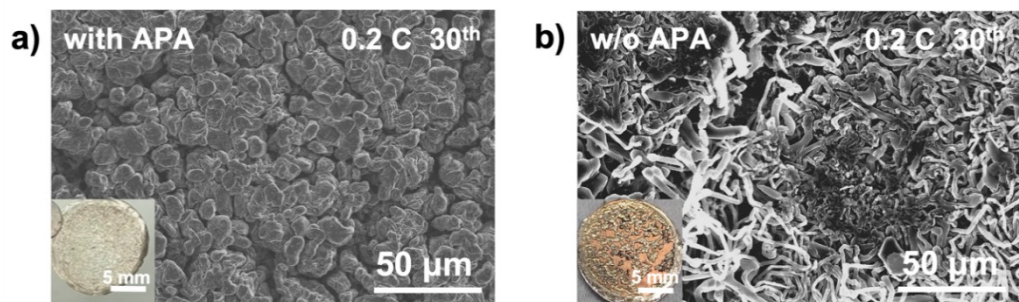


Figure S16. Li deposition morphologies in Li-S batteries a) with APA and b) without APA after 30 cycles at 0.2 C.

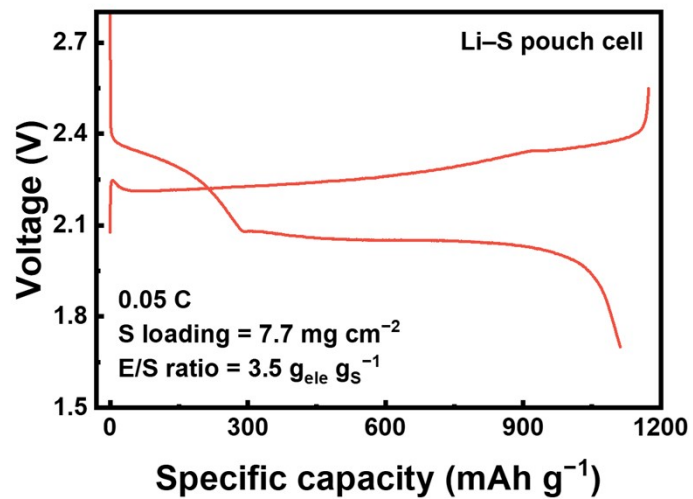


Figure S17. The voltage–specific capacity profiles of the Li–S pouch cell at the first cycle.