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Supporting information

3D-printed Al metal-organic framework/S cathode with efficient adsorption and redox conversion of polysulfides in lithium-sulfur batteries

Wen Xi,[1] Junpu Zhang,[1] Youfang Zhang,[2] Rui Wang,[1] Yansheng Gong,[1] Beibei He,[1] Huanwen Wang,[1] Jun Jin[1, 3]*

[1]*Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, China;*

[2]*Hubei Key Laboratory of Polymer Materials, Ministry of Education Key Laboratory for Green Preparation and Application of Functional Materials, School of Materials Science and Engineering, Hubei University, Wuhan 430062, China;*

[3]*Shenzhen Research Institute, China University of Geosciences, Shenzhen 518000, China.*

**Corresponding author. E-mail address: jinjun@cug.edu.cn*

Characterizations and electrochemical measurements

1. Characterizations

The morphologies and structures of samples are tested by scanning electron microscope (SEM, Hitachi SU-3500) and transmission electron microscope (TEM, FEI Talos F200S). To take optical and SEM images of the 3DP Al-MOF/S cathode, the 3D grid cathode printed on the battery shell is put into water, and the free-standing 3DP Al-MOF/S cathode is detached from the battery shell after 1 min. The X-ray diffraction (XRD) patterns of the samples are characterized on a D8-FOCUS (Bruker AXS, Panalytical) instrument with Cu Kα radiation (1.5418 Å) at 40 kV and 40 mA. The nitrogen adsorption-desorption isotherms and specific surface areas are tested on Micrometrics equipment (ASAP-2460). The X-ray photoelectron spectroscopy (XPS) spectra are collected using a Theta Probe electron spectrometer (Thermo Scientific K-Alpha).

2. Electrochemical measurements

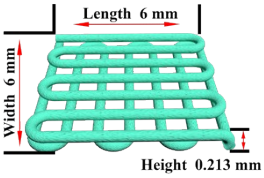
The Li-S batteries (CR 2032-type coin cells) are assembled in an Ar-filled glove box using 3DP Al-MOF/S cathode, Celgard 2400 separator, and Li anode. 20 μL of 1.0 M LiTFSI in DOL/DME (1:1 by volume) electrolyte with 1.0% $LiNO_3$ is used in the cells. The printed grid electrode area of the 3DP cathode is 0.36 cm^2, and the actual area of the 3DP cathode is 0.182 cm^2. Galvanostatic charge-discharge measurements are performed on a Land CT3001A battery tester with a voltage range from 1.7 to 2.7 V. Cyclic voltammetry (CV) curves are tested on an electrochemical workstation (CHI660E) at different scan rates in a voltage range of 1.7 - 2.8 V. Electrochemical impedance spectra (EIS) are collected on a Gamry workstation in a frequency ranging from 10^5 to 10^{-2} Hz.

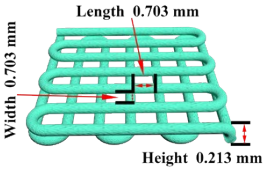
Table S1. The mass loading parameters of the 3DP Al-MOF-160/S electrode.

Electrode	Total mass (mg)	Mass of Al-MOF-160/S (mg)	Mass of sulfur (mg)	Sulfur loading (mg cm^{-2})	actual area (cm^2)
3DP Al-MOF-160/S	1.181	0.827	0.496	2.730	0.182
	1.931	1.352	0.811	4.270	
	2.214	1.550	0.930	5.120	
	6.896	4.808	2.885	15.85	

Table S2. The sizes of macropores and porosity in the 3DP electrode.

Material	3DP printing electrode			Macropores				Total volume (mm^3)	Macropore Volume (mm^3)	Porosity (%)
	Length (mm)	Width (mm)	Height (mm)	Number	Length (mm)	Width (mm)	Height (mm)			
3DP Al-MOF-160/S	6	6	0.213	36	0.703	0.703	0.213	7.668	3.790	49.4





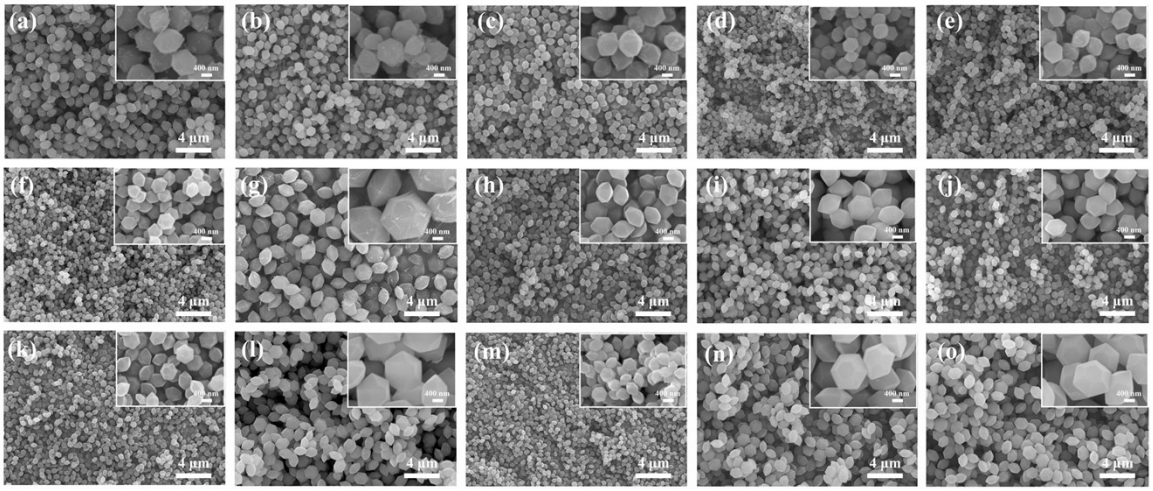


Figure S1. SEM images of the Al-MOF samples fabricated at (a)-(e) 120 ℃, (f)-(j) 140 ℃, and (k)-(o) 160 ℃ for 8, 10, 12, 14, and 16 h.

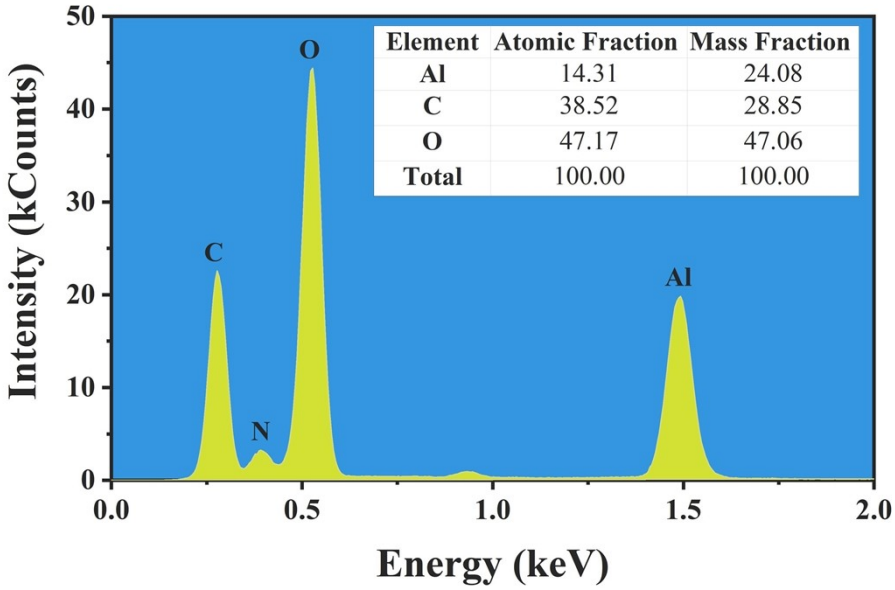


Figure S2. The TEM-EDS spectrum of Al-MOF-160.

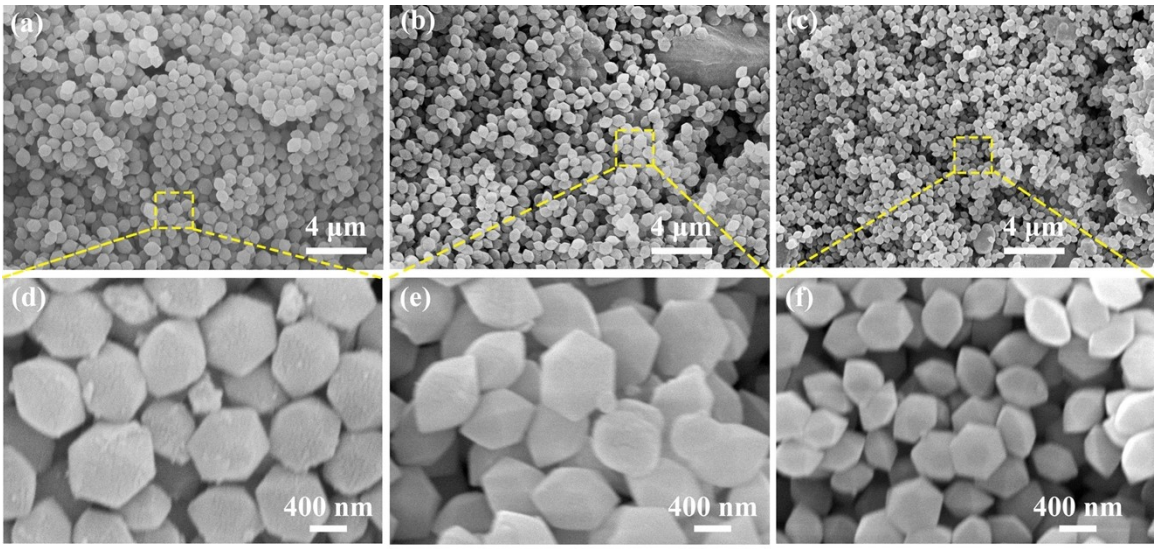


Figure S3. SEM images of (a), (d) Al-MOF-120/S, (b), (e) Al-MOF-140/S, and (c), (f) Al-MOF-160/S.

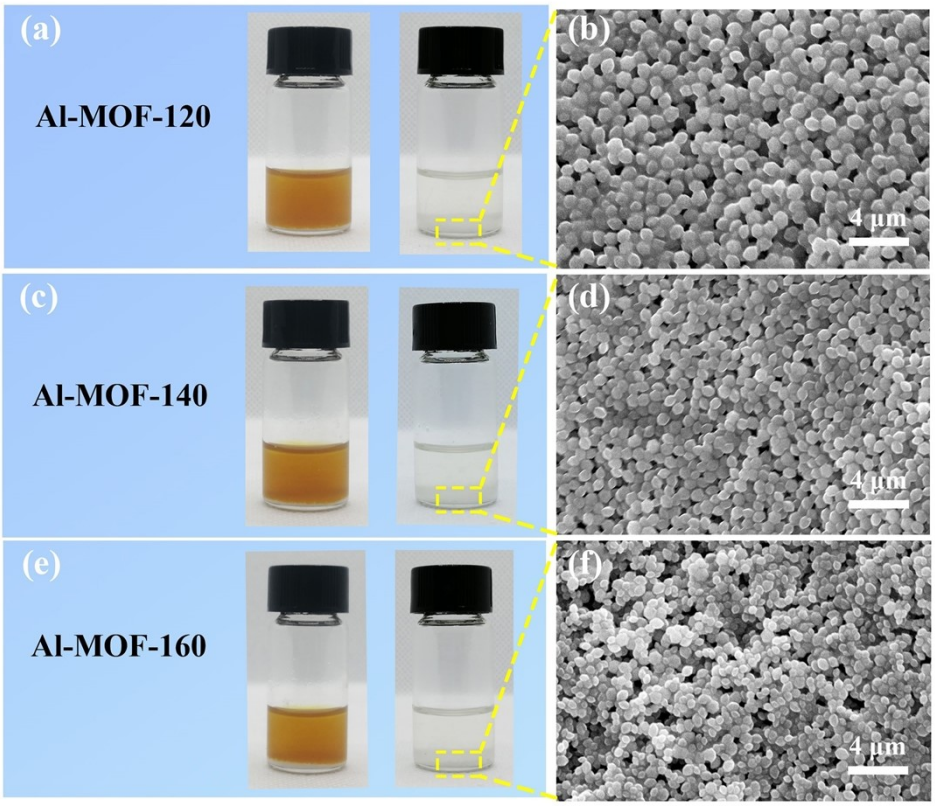


Figure S4. Visual demonstration of static Li_2S_4 adsorption properties of (a) Al-MOF-120, (c) Al-MOF-140, and (e) Al-MOF-160. The SEM images of (b) Al-MOF-120, (d) Al-MOF-140, and (f) Al-MOF-160 after Li_2S_4 adsorption.

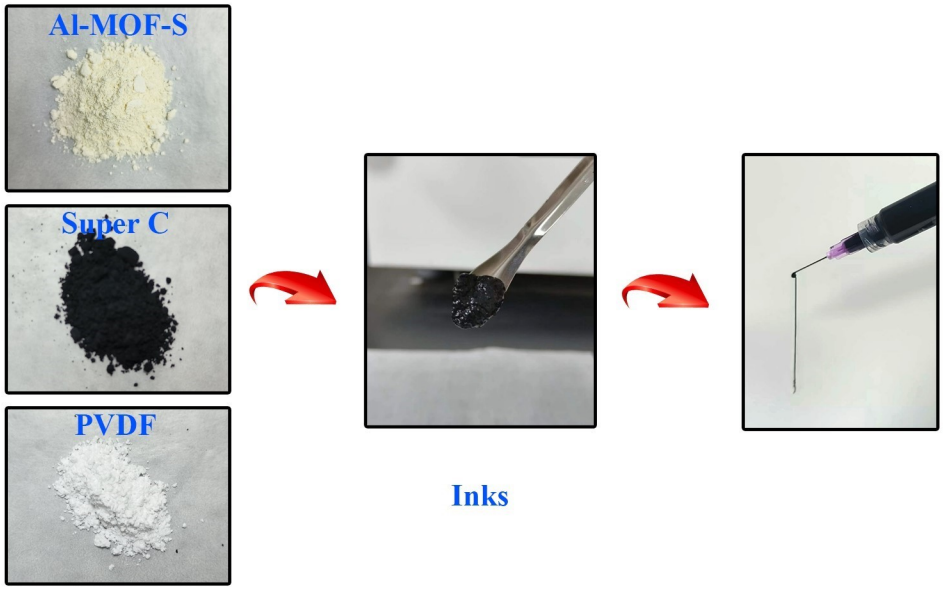


Figure S5. Schematic illustration of the 3DP ink preparation.

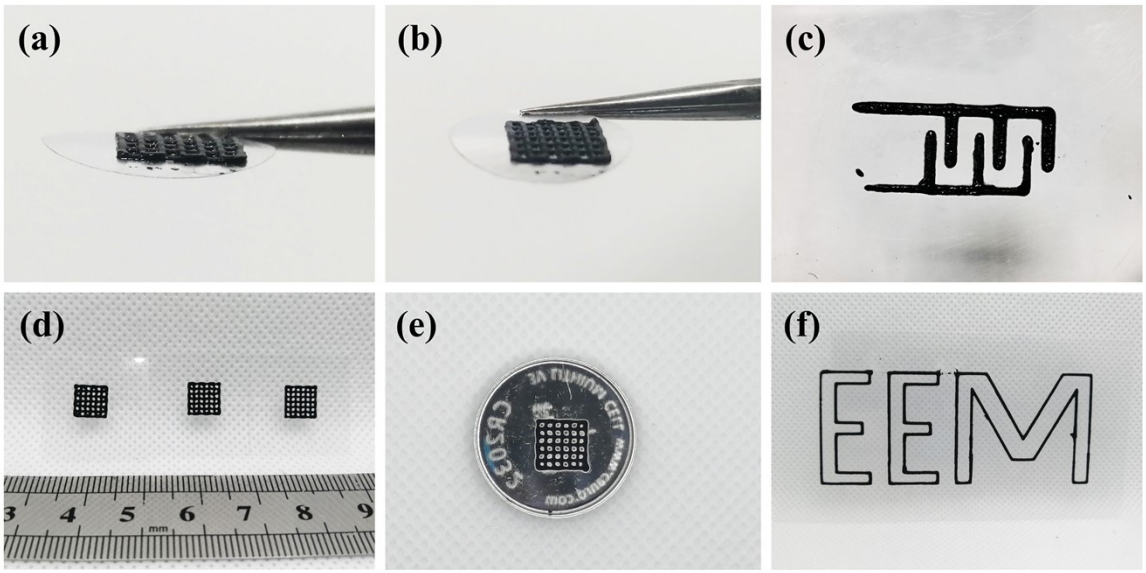


Figure S6. Various 3DP patterns printed from as-prepared Al MOF/S inks.

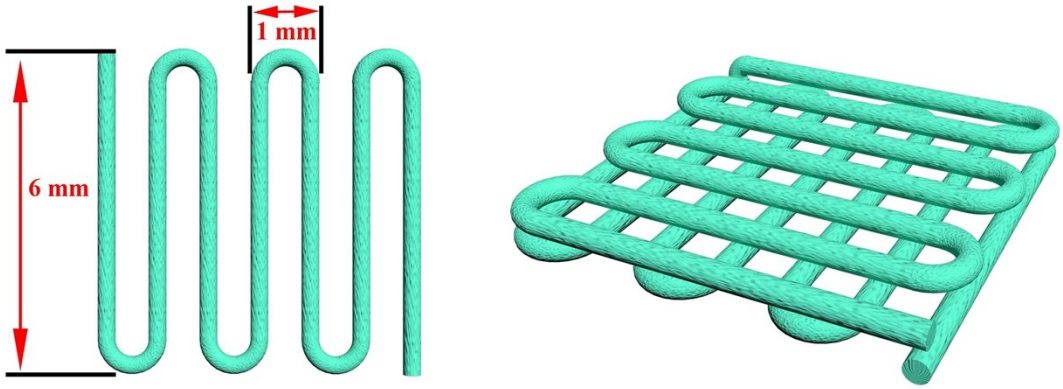


Figure S7. The printing size of the 3D-printed electrode.

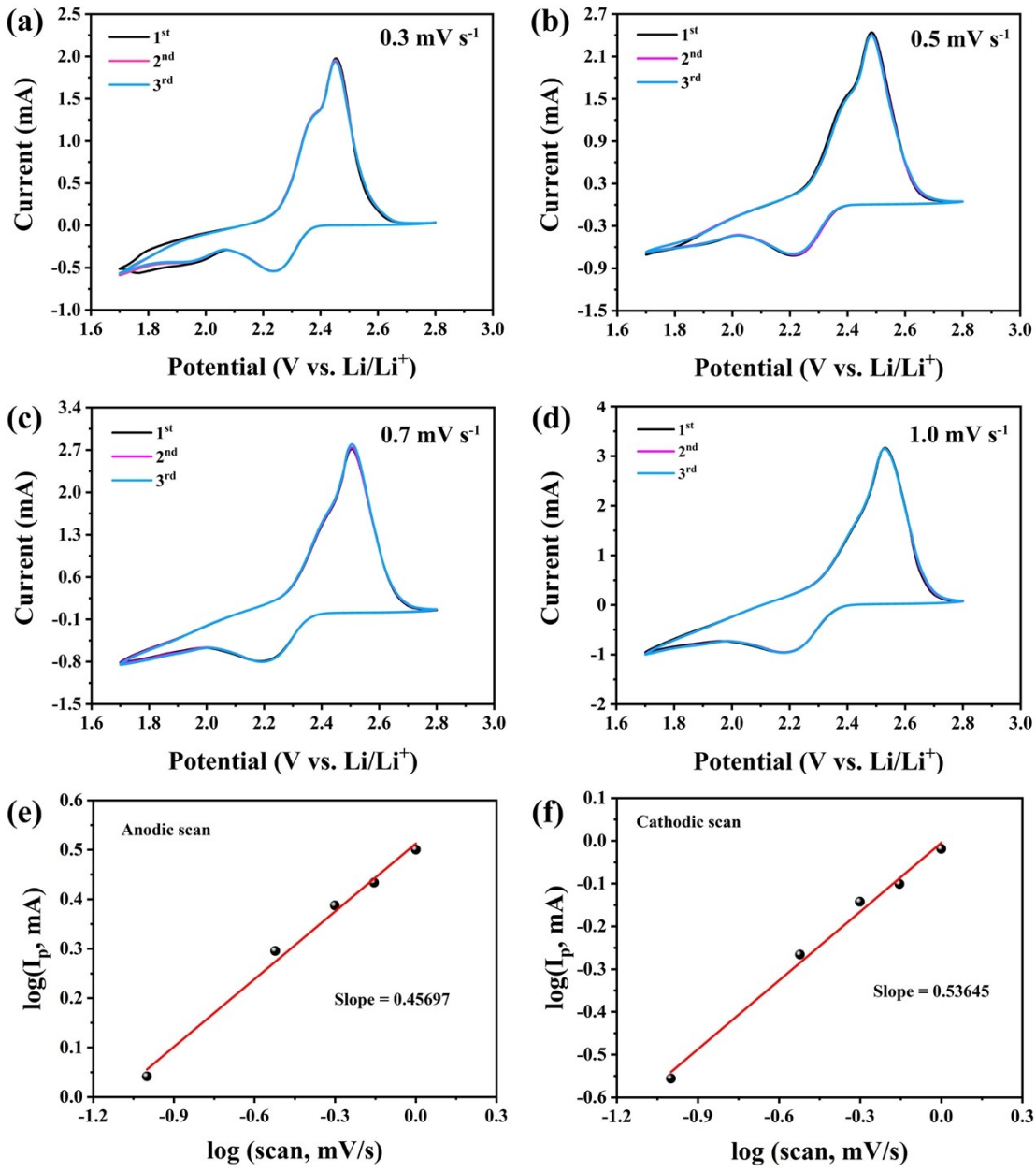


Figure S8. (a)-(d) CV curves of 3DP Al-MOF-160/S at different scan rates (0.3, 0.5, 0.7, and 1.0 mV s^{-1}). (e)-(f) The determination of the *b*-value using the relationship between current intensity and scan rate.

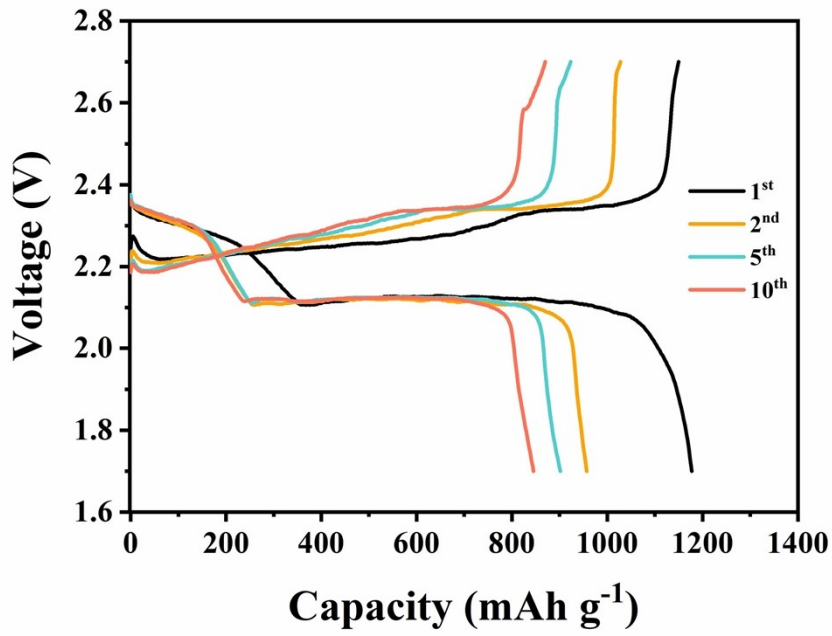


Figure S9. The charging-discharging profiles of the 3DP Al-MOF-160/S cathode at 0.1 C.

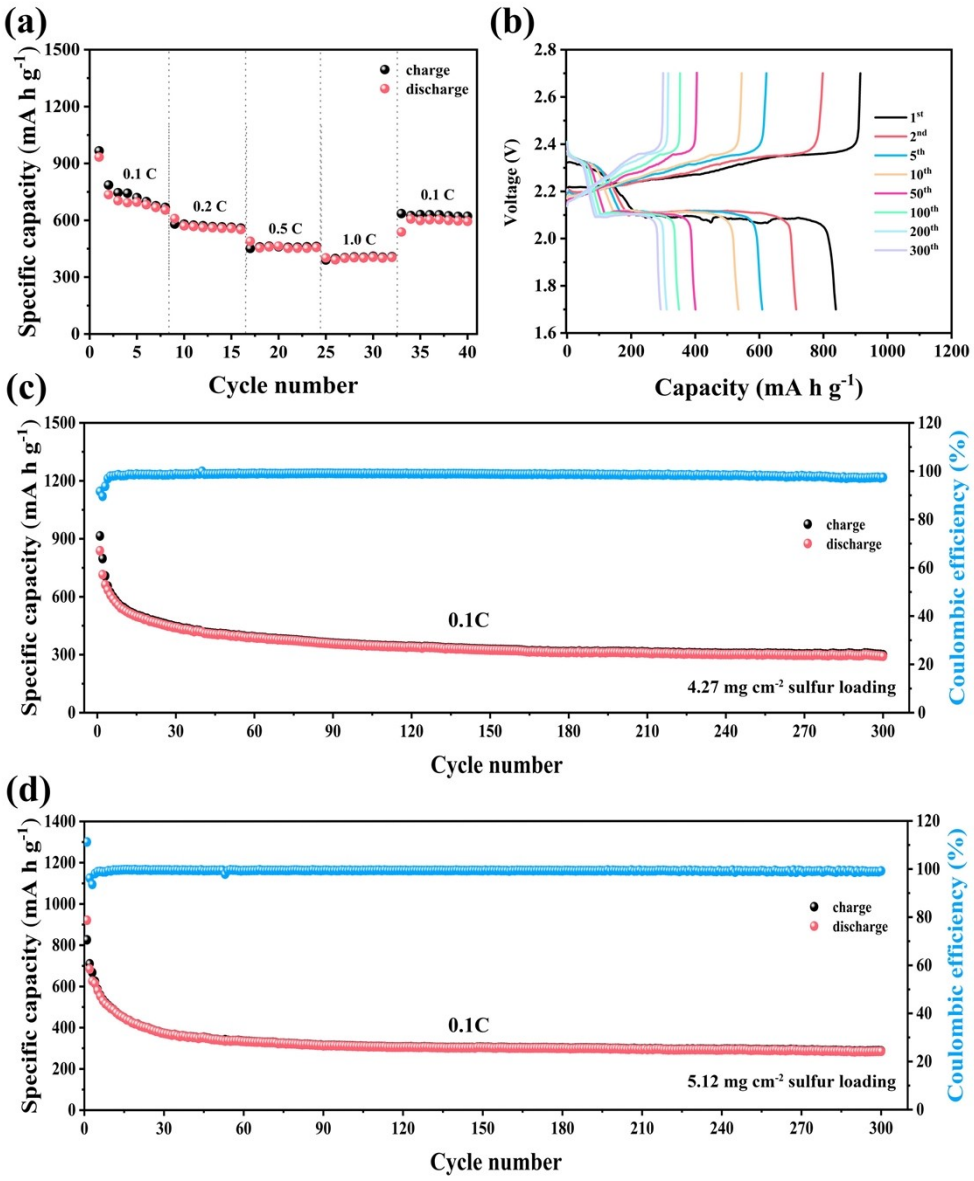


Figure S10. (a) Rate capabilities at various rates (0.1, 0.2, 0.5, 1.0, and 0.1 C), (b) charging/discharging profiles at select cycles, (c) cycling performance of 3DP Al-MOF-160/S at 0.1 C with sulfur loading of 4.27 mg cm^{-2}, and (d) cycling performance of 3DP Al-MOF-160/S at 0.1 C with sulfur loading of 5.12 mg cm^{-2}.

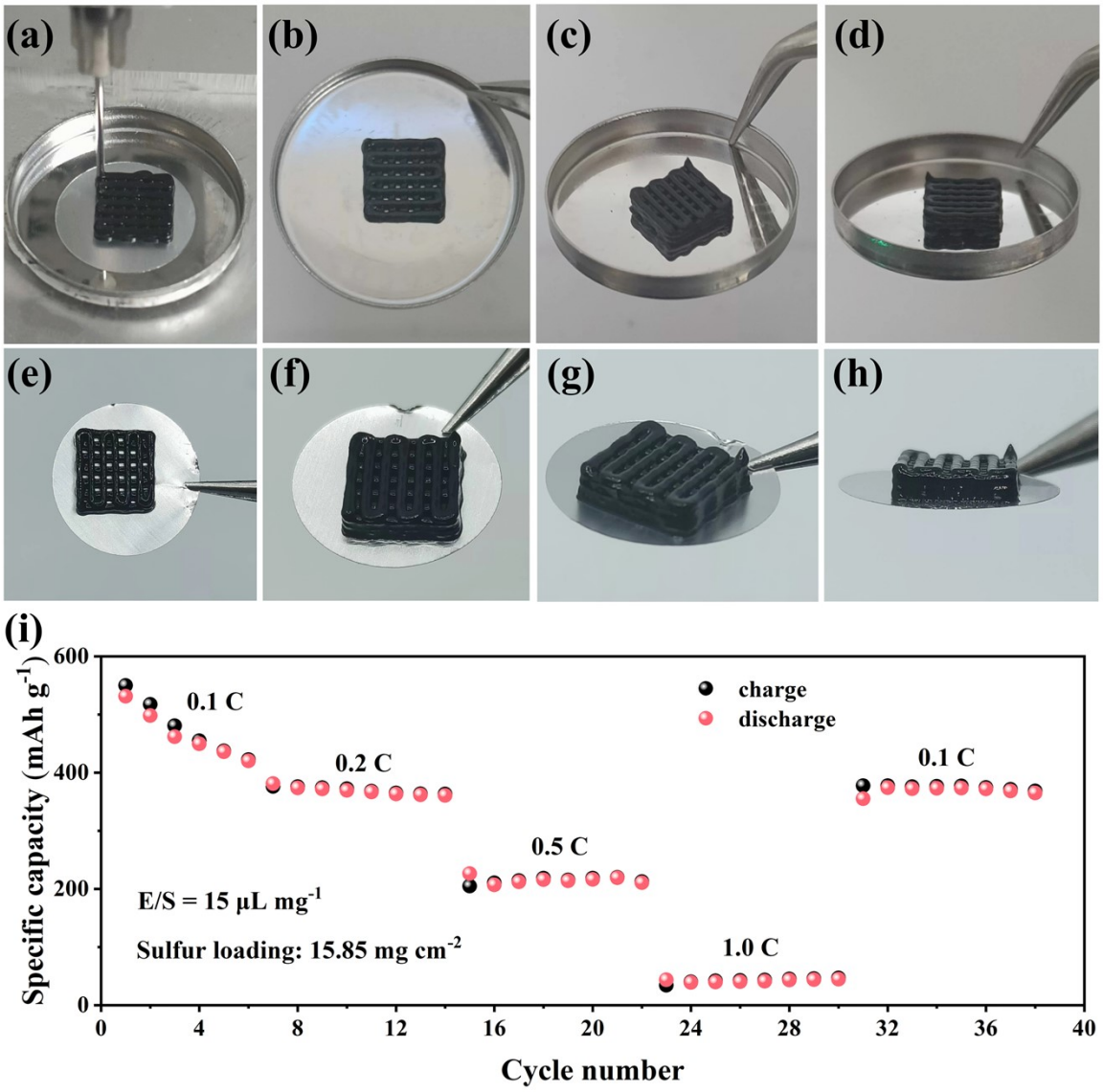


Figure S11. (a)-(h) Optical images of the 3DP Al-MOF-160/S cathode with high sulfur loading of 15.85 mg cm^{-2}. (i) Rate performance of the 3DP Al-MOF-160/S cathode with sulfur loading of 15.85 mg cm^{-2} at 0.1, 0.2, 0.5, 1.0, and 0.1 C.

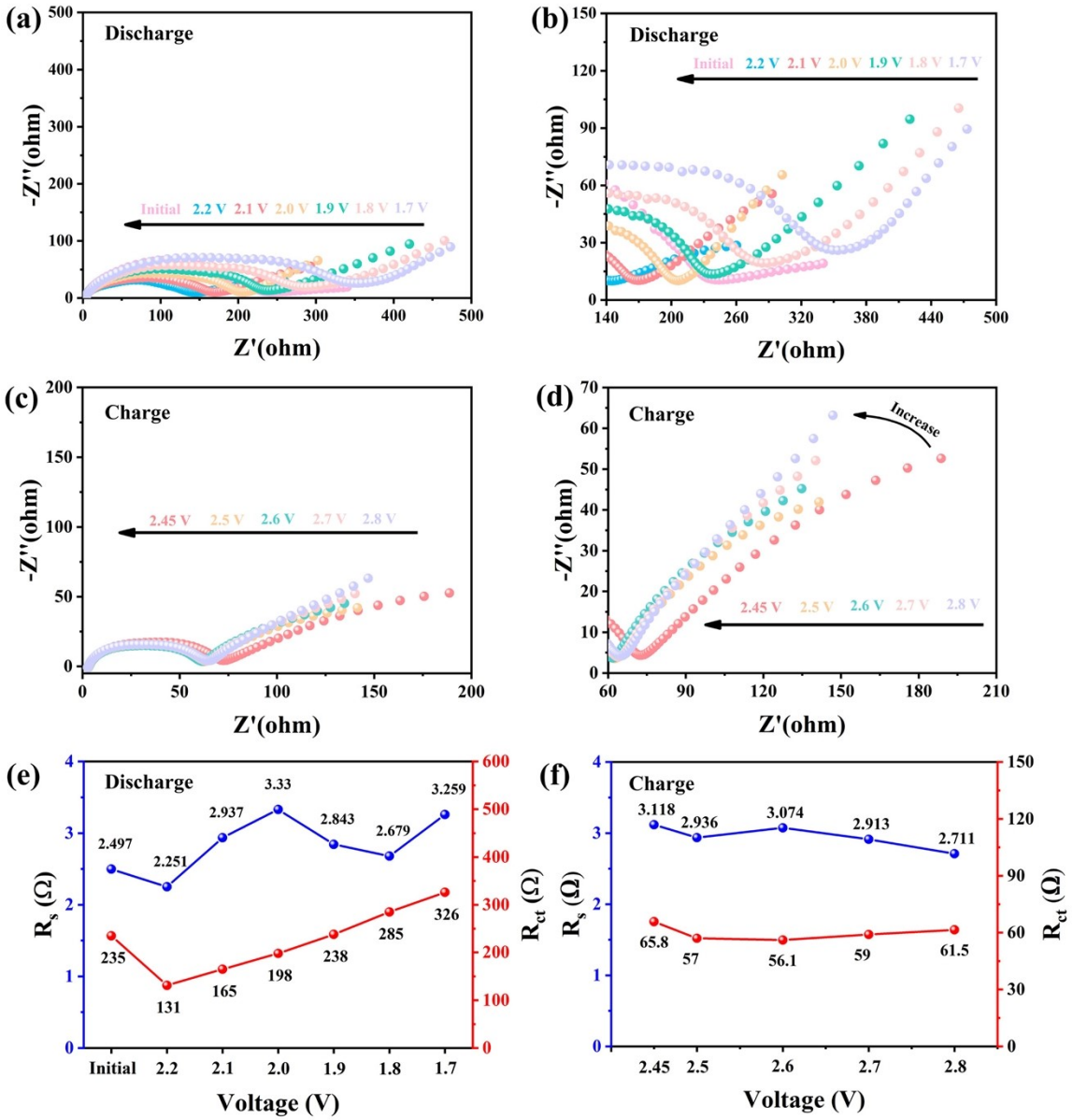


Figure S12. (a)-(d) Change of slope during the discharging and charging processes. (e)-(f) The changes of R_s and R_{ct} in the equivalent circuit diagram during discharging and charging processes.

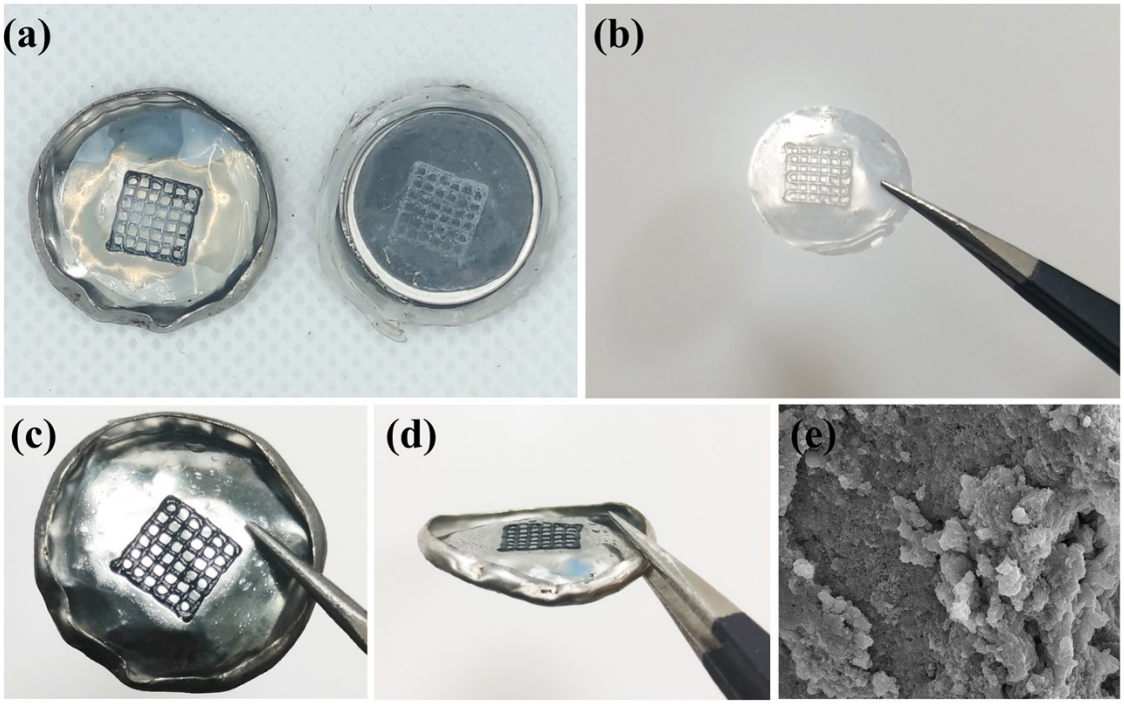


Figure S13. (a)-(d) Optical images of the 3DP Al-MOF-160/S cathode after cycling. (e) SEM image of the 3DP Al-MOF-160/S cathode after cycling.