

*Electronic Supplementary Information (ESI)*

Manipulating Li–S Reaction Kinetics *via*  $V_8C_7$ /Phosphorus  
Defect-Integrated Carbon Promotor

Qin Yang <sup>a</sup>, Zhuo Chen <sup>a</sup>, Zhiqin Zheng <sup>\*b</sup>, Le Chen <sup>a</sup>, Lixian Song <sup>a</sup>, Jingyu Sun <sup>\*c</sup> and  
Yingze Song <sup>\*a</sup>

<sup>a</sup> State Key Laboratory of Environment-Friendly Energy Materials, School of Materials and Science Engineering, Southwest University of Science and Technology, Mianyang, Sichuan 621010, P. R. China.

<sup>b</sup> State Key Laboratory of Environment-Friendly Energy Materials, School of Materials and Science Engineering, School of Life Sciences and Engineering, Southwest University of Science and Technology, Mianyang, Sichuan 621010, P. R. China.

<sup>c</sup> College of Energy, Soochow Institute for Energy and Materials Innovation, Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies of Jiangsu Province, Soochow University, Suzhou, Jiangsu 215006, P. R. China.

Corresponding authors: yzsong@swust.edu.cn (Y. Song), zhengzhiqin@swust.edu.cn (Z. Zheng), sunjy86@suda.edu.cn (J. Sun).

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## **1. Experimental Section**

### **1.1 Synthesis of MIL-47(V)**

The MIL-47(V) was prepared by hydrothermal method. Typically, 1.66 g *p*-phthalic acid (PTA), 1.46 g  $\text{VCl}_3$  powder were dissolved in 17 mL deionized water. Subsequently, the mixed solution was transferred into a Teflon-lined autoclave and heated under 150 °C for 96 h. After centrifugation and washed for several times to remove PTA and  $\text{VCl}_3$  residues, the pale-yellow MIL-47(V) powder was obtained.

### **1.2 Synthesis of VPC, VC, and PC electrocatalysts**

The as-prepared MIL-47(V) was successively heated at 300 °C for 0.5 h and at 1000 °C for 2 h in a tube furnace under Ar atmosphere with a heating rate of 10 °C  $\text{min}^{-1}$ . The obtained  $\text{V}_8\text{C}_7$ /carbon power was denoted as VC. To obtain VPC, VC was phosphatized by sodium hypophosphite monohydrate at 300 °C for 3 h under Ar atmosphere with a heating rate of 2 °C  $\text{min}^{-1}$ . PC was prepared by first annealing at 800 °C and then washed with HCl aqueous solution (5.0 mol  $\text{L}^{-1}$ ).

### **1.3 Preparation of S/VPC, S/VC and S/PC composites**

100 mg VPC and 300 mg sulfur were mixed and sealed into a glass vessel. Then the mixture was heated at 155 °C for 6 h under Ar atmosphere. The S/VPC composites were ground prior to use. As a control, S/VC and S/PC composites were prepared by using the same route.

### **1.4 Material characterizations**

Morphologies of samples were detected by employing a Zeiss Libra 200FE Transmission Electron Microscope and a Tescan Maia3 model 2016 Field Emission

Scanning Electron Microscope. XRD patterns of samples were achieved on a Nalytical X'Pert Pro diffractometer. Nitrogen adsorption-desorption isotherms were recorded at 77 K in N<sub>2</sub> atmosphere on a Micromeritics Autosorb-IQ Accelerated Surface Area and Porosimetry System. Square resistances were detected by four-probe resistance testing system (Suzhou Jingge Electronic Co., Ltd, ST2263). A Thermo Scientific K-Alpha+ X-ray photoelectron spectroscope was applied to probe the surface chemical compositions of samples. *UV-vis* spectra were collected on an *UV-vis* spectrometer (Shimadzu, UV1900).

## **1.5 Electrochemical measurements**

### **1.5.1 Adsorption test**

To obtain Li<sub>2</sub>S<sub>4</sub> solution (3.5 mmol L<sup>-1</sup>), the lithium sulfide and sublimed sulfur at a molar ratio of 1:3 was dissolved in 1,2-dime-thoxyethane (DME) solvent. With the same mass (10 mg), VPC, VC or PC electrocatalysts were added into the 1.5 mL Li<sub>2</sub>S<sub>4</sub> solution, respectively. The devices were placed in an argon-filled glove box.

### **1.5.2 Symmetric cells**

To form Li<sub>2</sub>S<sub>6</sub> solution (0.2 mol L<sup>-1</sup>), sulfur and lithium sulfide with a molar ratio of 5:1 were dissolved in a mixture of DME/1,3-dioxolane (DOL) solution which contains 1.0 mol L<sup>-1</sup> LiTFSI and 2 wt% LiNO<sub>3</sub>. The carbon paper was first punched into disk with a diameter of 13 mm before loading with VPC, VC or PC electrocatalysts, denoted as CP-VPC, CP-VC and CP-PC, respectively. The as-prepared electrodes were applied as the working and counter electrodes for symmetric cells and the afore-mentioned Li<sub>2</sub>S<sub>6</sub> solution (20 μL) was used as the electrolyte. And the CV tests were carried out

between  $-1$  to  $1$  V at a scan rate of  $50 \text{ mV s}^{-1}$ .

### **1.5.3 *Li<sub>2</sub>S nucleation test***

To prepare  $\text{Li}_2\text{S}_8$  solution ( $0.2 \text{ mol L}^{-1}$ ), sulfur and lithium sulfide at a molar ratio of 7:1 was mixed into tetraglyme solvent. The cathodes were prepared with the same method as the symmetric cells. All the nucleation cells were assembled by using lithium foil as the anode, the as-prepared  $\text{Li}_2\text{S}_8$  solution ( $20 \mu\text{L}$ ) as the catholyte, and  $20 \mu\text{L}$  LiTFSI solution as the anolyte. The cells were galvanostatically discharged under  $0.112 \text{ mA}$  until the potential was  $2.06 \text{ V}$  and subsequently kept potentiostatically at  $2.05 \text{ V}$  till the current reaches  $10^{-5} \text{ A}$ . The nucleation capacity of  $\text{Li}_2\text{S}$  was calculated by the integral area of the plotted curve according to Faraday's Law.

### **1.5.4 *Li<sub>2</sub>S dissociation test***

As for the  $\text{Li}_2\text{S}$  decomposition test, the cells were fabricated by following the similar procedure with the  $\text{Li}_2\text{S}$  nucleation test. To ensure the complete transformation of LiPSs into  $\text{Li}_2\text{S}$ , the dissociation tests were first performed galvanostatically at a current of  $0.112 \text{ mA}$  until the potential was below  $1.7 \text{ V}$ . Subsequently, the cells were potentiostatically charged at  $2.35 \text{ V}$  to  $10^{-5} \text{ A}$ .

### **1.5.5 *Electrochemical test***

The S/VPC, S/VC and S/PC cathodes were first obtained through the following procedure: S/VPC (S/VC or S/PC) composite, LA133 aqueous binder and super P were mixed at a mass ratio of 8:1:1 on a twin-shaft mixer to generate the cathode slurry. The as-prepared slurry was coated onto aluminum current collector and dried at  $60^\circ \text{ C}$  for 12 h under vacuum. The S/VPC (S/VC or S/PC) cathode, lithium anode, Celgard 2500

membrane, and electrolyte (1 mol L<sup>-1</sup> LiTFSI + 2 wt% LiNO<sub>3</sub> dissolved in 1,3-dioxolane DOL/DME (1:1, v/v)) were assembled into LIR 2032-type coin batteries. The electrolyte/sulfur ratio was 15.0 μL mg<sup>-1</sup><sub>S</sub> for the routine batteries and 7.0 μL mg<sup>-1</sup><sub>S</sub> for high-load batteries. The sulfur content in cathode was 60 wt%. The galvanostatic discharge and charge processes, rate capacities and cycle performances of LSBs were measured within the voltage window of 1.7–2.8 V on a Neware Battery Testing System. EIS curves in the frequency range of 10<sup>5</sup> to 10<sup>-2</sup> Hz and CV profiles were collected on a Vertex. One Electrochemical Workstation.

## 2. Figures

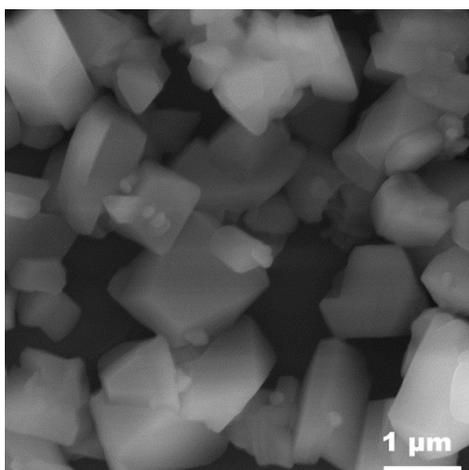


Figure S1. SEM images of MIL-47(V).

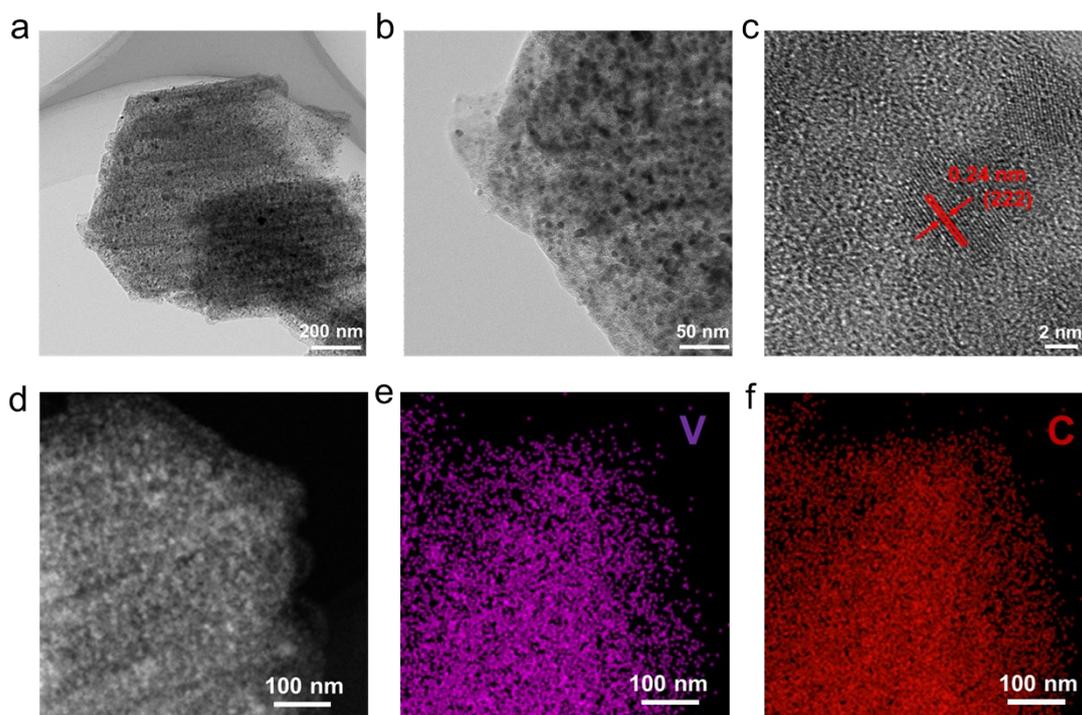


Figure S2. a, b) TEM images of VC. c) HRTEM image of VC. d–f) STEM and EDS map images of VC.

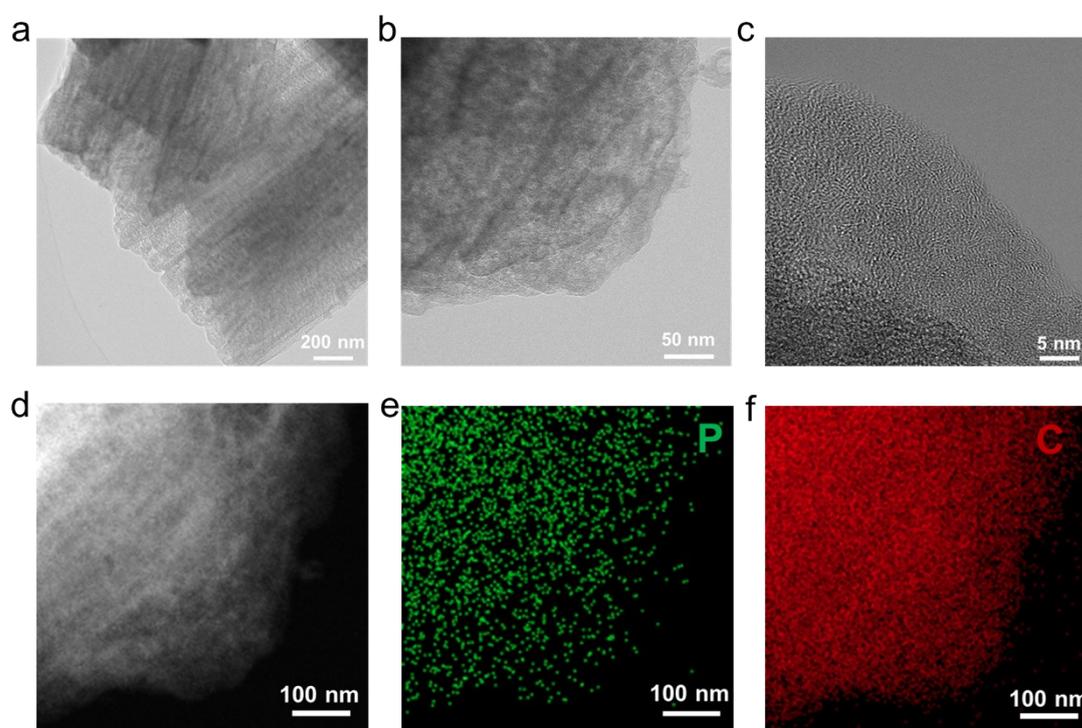


Figure S3. a, b) TEM images of PC. c) HRTEM image. d–f) STEM and EDS map

images of PC.

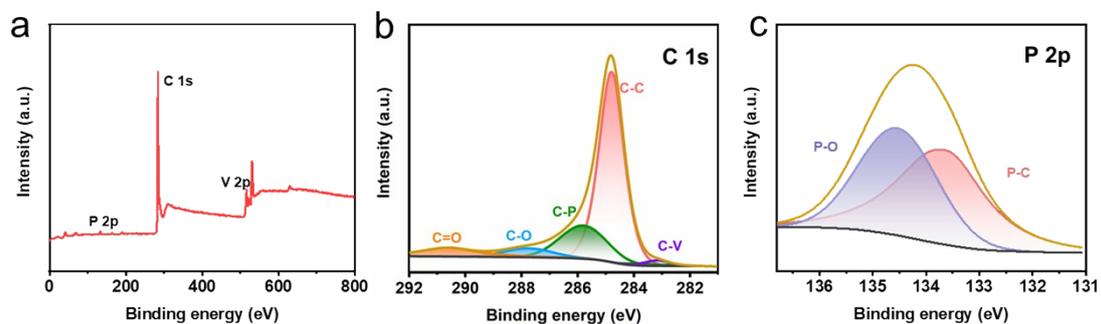


Figure S4. a) XPS survey spectrum of VPC. b) C 1s XPS spectra of VPC. c) P 2p XPS spectra of VPC.

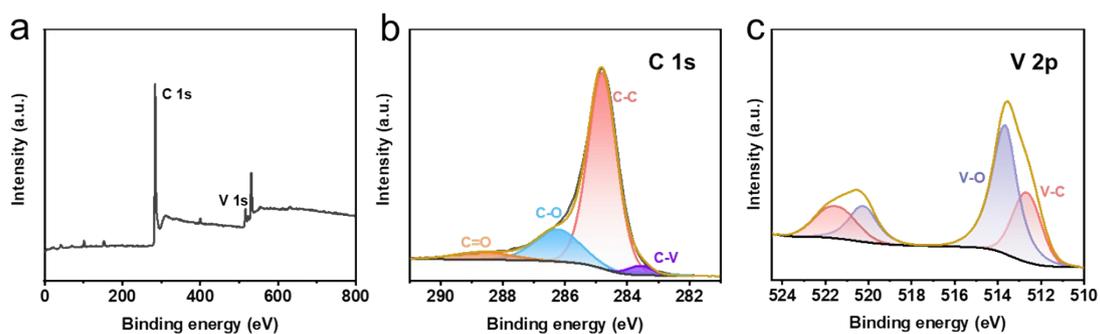


Figure S5. a) XPS survey spectrum of VC. b) C 1s XPS spectra of VC. c) V 2p XPS spectra of VC.

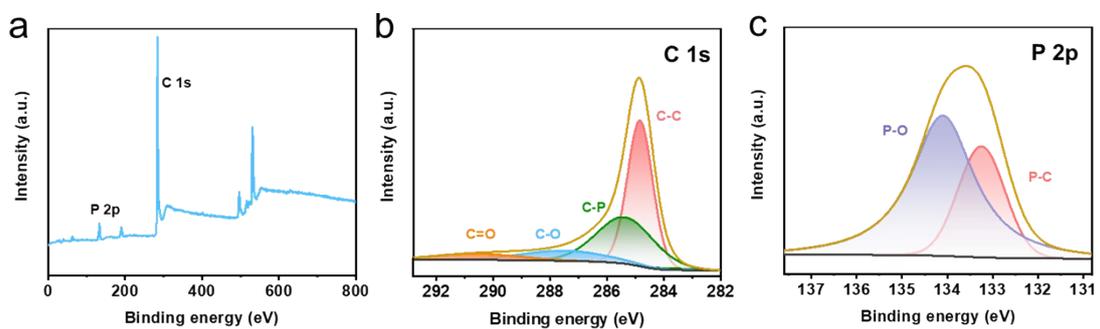


Figure S6. a) XPS survey spectrum of PC. b) C 1s XPS spectra of PC. c) P 2p XPS spectra of PC.

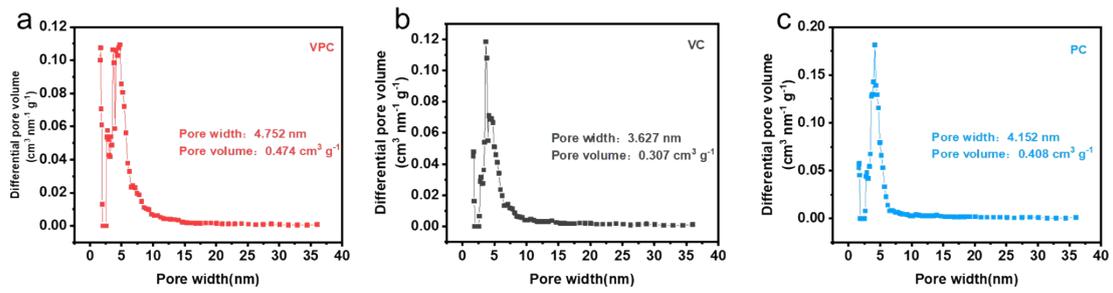


Figure S7. Pore size distribution curves of VPC, VC and PC.

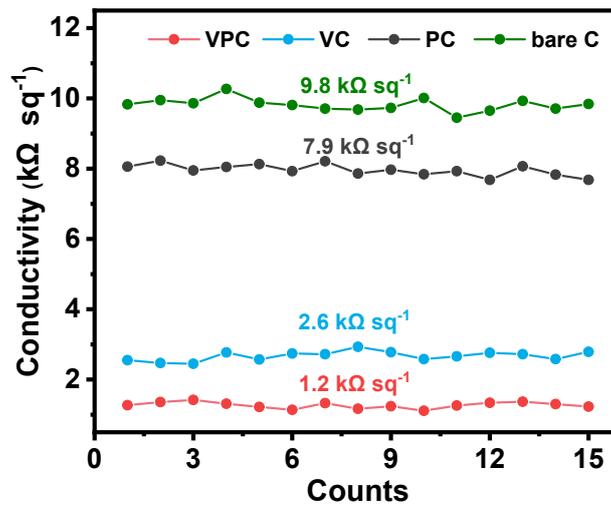


Figure S8. Square resistances of VPC, VC, PC and bare C.

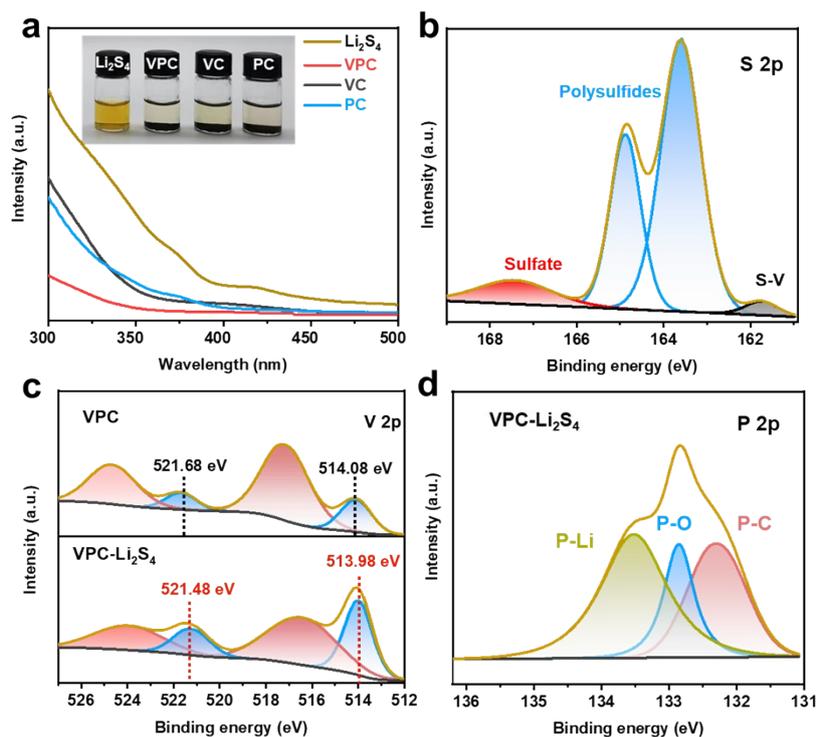


Figure S9. a) *UV-vis* absorption spectra of  $\text{Li}_2\text{S}_4$  solution after VPC, VC and VPC adsorption, the inset showing the visual  $\text{Li}_2\text{S}_4$  adsorption test. b) S 2p spectra of VPC after affinity with  $\text{Li}_2\text{S}_4$ . c) V 2p spectra of VPC before and after adsorption with  $\text{Li}_2\text{S}_4$ . d) S 2p spectra of VPC after interaction with  $\text{Li}_2\text{S}_4$ .

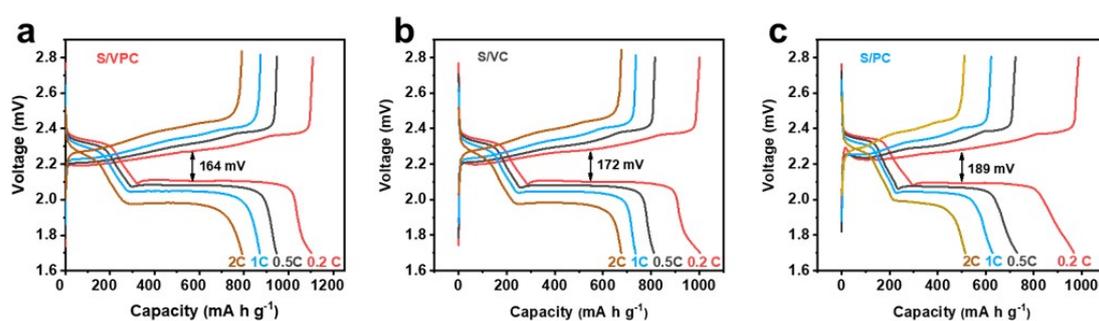


Figure S10. Galvanostatic charge-discharge profiles of S/VPC, S/VC, S/PC cathodes at various rates.

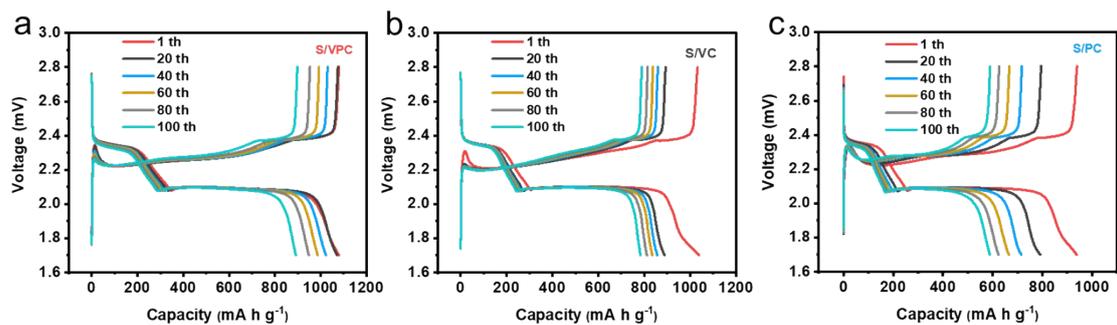


Figure S11. Galvanostatic charge-discharge profiles of S/VPC, S/VC and S/PC cathodes at 0.2 C with different cycles.

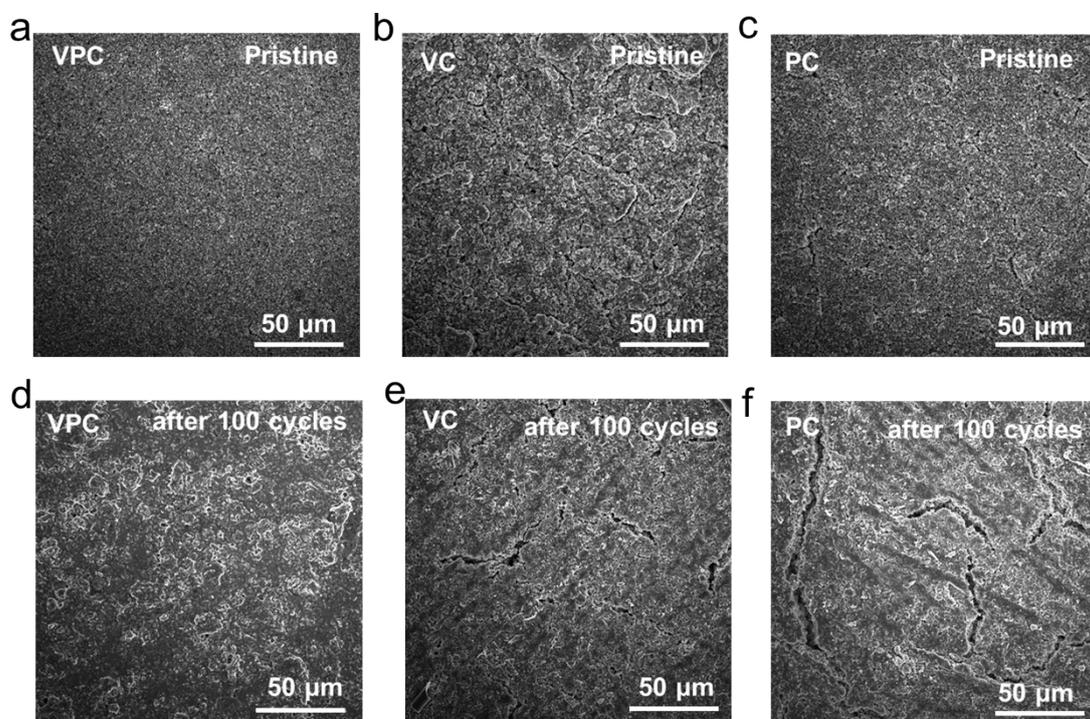


Figure S12. SEM images of S/VPC, S/VC and S/PC cathodes before and after 100 cycles at 0.2 C.

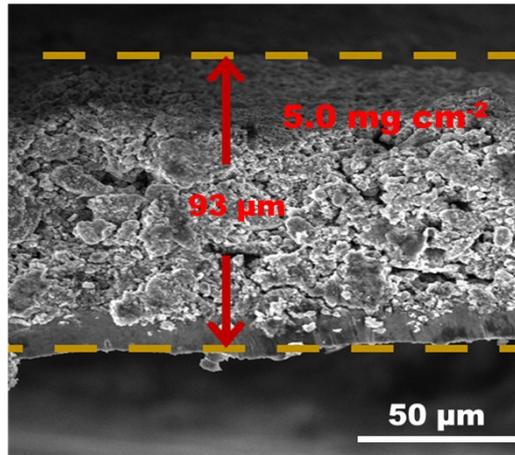


Figure S13. Cross-sectional SEM image of S/VPC cathode with a sulfur loading of 5.0 mg cm<sup>-2</sup>.

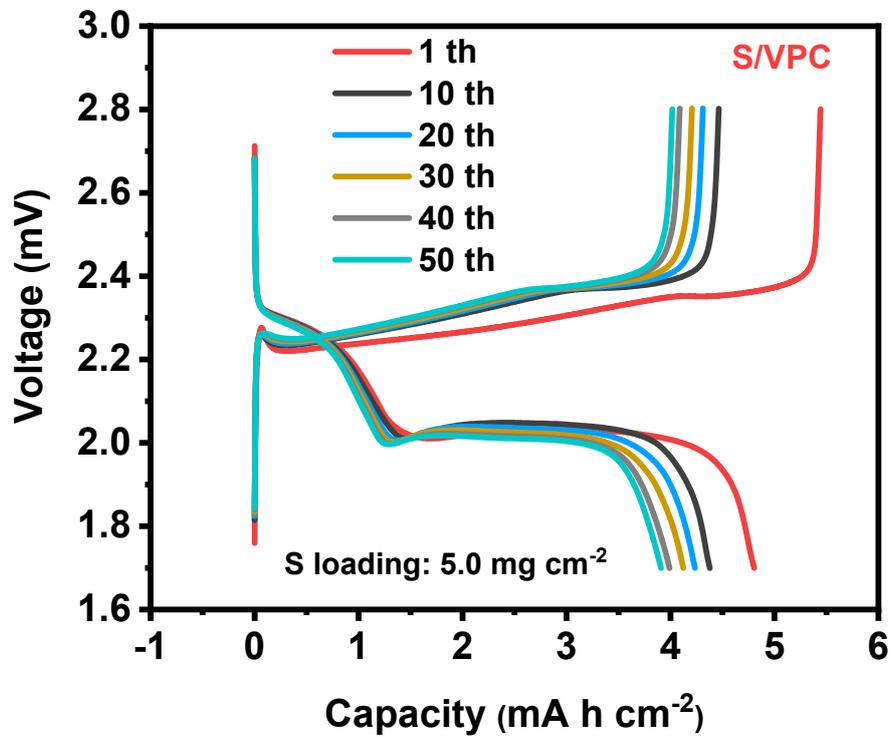


Figure S14. Galvanostatic charge-discharge profiles of S/VPC cathode with a sulfur loading of 5.0 mg cm<sup>-2</sup> at 0.2 C.

Table S1. Comparison of battery performances on high-sulfur-load LSBs between this works and other reported studies.

Electrocatalyst	Sulfur loading (mg cm <sup>-2</sup> )	Rate (C)	Areal Capacity (mA h cm <sup>-2</sup> )	Retention (%)	Ref.
<b>VPC</b>	<b>5.0</b>	<b>0.2</b>	<b>4.8</b>	<b>81.2</b>	<b>This work</b>
V <sub>2</sub> O <sub>3</sub> /V <sub>8</sub> C <sub>7</sub>	4.2	0.2	3.9	81.1	1
VN-NBs	5.4	0.5	5.8	74.2	2
NPCNA	~3.5	0.2	3.3	68	3
V <sub>2</sub> O <sub>3</sub> -VN	3.95	0.2	3.95	71.6	4
HCMs	4.84	0.2	4.0	77.5	5
CNTP	4.0	0.5	5.6	45.2	6
V <sub>2</sub> O <sub>3</sub>	3.7	0.2	4.2	60.1	7
VN	3.8	0.2	4.2	64.2	8
NCNF	4.5	0.05	~5.5	40	9
VN	4.2	0.2	4.7	71.2	10

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