

Supporting Information

1-D Oriented Cross-Linking Hierarchical Porous Carbon Fibers as Sulfur Immobilizer for High Performance Lithium-Sulfur Batteries.

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Experimental Section

Synthesis of prepared CHPCF

0.42 g benzene-1,3,5-tricarboxylic acid (BTC, 2 mmol, Aladdin) and 0.96 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (4mmol, Aladdin) were firstly dissolved into 40 mL deionized water under stirring and kept for 5 minutes. After that, the mixture was transferred into a 100 mL Teflon autoclave and heated at 180 °C for 24 hours. After cooling to room temperature, the blue flocculent product was washed with deionized water and ethanol and then was collected and dried, which was labeled as Cu-MOF.

Synthesis of prepared CHPCF

The dried Cu-MOF was put into a ceramic boat and heated at 900 °C for 4 hours from room temperature with a heating rate of 3 °C min⁻¹ in an Ar filled tubular furnace. After etched Cu metal with 10 wt.% HNO_3 at room temperature for 24 hours and dried, the obtained black flocculent product (labeled as Cu-BTC) and KOH with a mass ratio of 1:4 were mixed and then was put into a nickel boat and heated to 700 °C with a heating rate of 10 °C min⁻¹ under Ar atmosphere. The temperature was kept at 700 °C for 1 hour and then was cooled to room temperature. Finally, excess 10 wt.% HNO_3 was used to neutralize KOH and further etch the Cu metal in the residue. After filtration and washed with deionized water, the collected black flocculent product was labeled as CHPCF.

Synthesis of prepared S/CHPCF

0.2 g CHPCF and 0.4 g commercial sulfur (Aldrich) was dispersed into 5 mL CS_2 under stirring at room temperature until the solvent was evaporated completely. After heated at 155 °C for 20 hour under Ar atmosphere, the obtained product was named as S/CHPCF. The sulfur content is 60 wt%.

Synthesis of prepared HKUST-1

The synthesis procedure was resulted from optimizing previous work.¹ 0.42 g BTC (2 mmol, Aladdin) and 0.96 g Cu(NO₃)₂·3H₂O (4 mmol, Aladdin) were firstly dissolved into a mixture of 20 mL deionized water and 20 mL ethanol under stirring and kept for 5 minutes. After that, the mixture was transferred into a 100 mL Teflon autoclave and heated at 120 °C for 72 hours. After cooling to room temperature, the blue powder was washed with deionized water and ethanol and then was collected and dried, which was named as HKUST-1.

Synthesis of Prepared HKC and S/HKC:

The HKC and S/HKC was prepared under the same procedure to CHPCF and S/CHPCF. The sulfur content is 60 wt% .

Materials Characterization

The scanning electron microscopy (SEM, JSM-7800F and Hitachi SU-1510) were used to observe the morphology of the samples. Transportation electron microscope (TEM, JEM-2100) and Brunauer-Emmett-Teller surface area analyzer (BET, ASPS 2020) were employed for detail pore structure studies. X-ray diffraction (XRD, DX-2700) operated at 40 kV and 30 mA with Cu-K α radiation ($\lambda=0.154$ nm) was used for crystal structure analysis and the XRD dates were collected from 3° to 70° in 2 θ at a scanning rate of 1° min⁻¹. The chemical structures of the samples were characterized by JASCO FTIR 4100 spectrometer. Each spectrum was recorded at the average rate of 48 scans with a resolution of 4 cm⁻¹, collected from 400 to 4000 cm⁻¹ in reflection mode. The elements (carbon and sulfur) distribution were measured on scanning transportation electron microscope (STEM, Tecnai G2TF20) equipped with Energy Dispersive X-Ray Spectroscopy (EDX). The ion conductivity at different temperatures was tested on a conductivity meter (METTLER TOLEDO, SG3).

Electrochemical measurements

The electrochemical performance of the electrodes with different average active sulfur loadings (0.5 mg cm⁻², 1.0 mg cm⁻², 1.7 mg cm⁻², based on geometrical area of electrodes) were tested with CR2016 coin cells, constructed in an Ar-filled glove box. 80 wt.% active materials (S/FLHPC, or S/HKC), 10 wt.% conductive carbon (KB600),

and 10 wt.% Polyvinylidene fluoride (PVDF) were first mixed with 1-methyl-2-pyrrolidinone (NMP) to form a slurry, and then casted onto aluminium foils and dried at 60 °C for 12 hours under vacuum. The cathode and the anode (lithium foil) is separated by a celgard 2325 membrane. The electrolyte is 1 M bis(trifluoromethylsulfonyl) imide (LiTFSI) in 1, 2-dimethoxymethane (DME) /1, 3-dioxolane (DOL) (1:1 v/v) with or without 5 wt.% LiNO₃ additive.

The electrochemical impedance spectroscopy (EIS) measurement was conducted at open-circuit condition with a frequency range from 3.0×10⁶ Hz to 1.0×10⁻² Hz with the amplitude of 10 mV on a Solartron 1287 electrochemical work station. The charge-discharge test was carried out using a LAND CT-2001A system with voltages arrange from 1.0 V (without LiNO₃ in electrolyte) or 1.7 V (with 5 wt.% LiNO₃ in electrolyte) to 2.8 V at different temperatures (25°C, 0°C, -20°C) in a constant temperature box. Except special emphasis, all of measurements and tests are based on the electrodes with a sulfur loading of 0.5 mg cm⁻². The specific capacities mentioned in this article were calculated based on sulfur. The voltage mentioned in this article were respected to Li⁺/Li (vs. Li⁺/Li).

Electrolyte uptake

The electrolyte uptake of the S/HKC and S/CHPCF electrodes were determined by our early work with minor emendation.² The dried electrodes were immersed in 1 M LiTFSI dissolved in a 1:1 (v/v) mixture of DME and DOL electrolyte for 24 hours at room temperature. Then measured the electrodes' weight again after quickly wiping out the surface electrolyte. The electrolyte uptake of the membranes can be calculated based on the weight difference between the dried and swollen samples by the equation as follows:

$$\text{Electrolyte uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}} - W_{\text{Al foil}}} \quad (1)$$

Where W_{wet} , W_{dry} , $W_{\text{Al foil}}$ are weight of wet elcectrodes, dry eloelectrodes and Al foil.

Electronic conductivity

The electronic conductivity of HKC, CHPCF, S/HKC and S/CHPCF composite were

measured by the previous report with modification.³ A self-designed instrument as illustrated in Fig. 8a, the powder samples were put into the insulated mould without any additional pressure but only the self-weight of the pillar. The pillar and slice in both sides are made of stainless steel which also act as the electrodes for the measurement of conductivity. The resistance (R) of the samples was determined by a digital multi-meter (Fluke 15 B). The bulk conductivity was calculated by the following equation:

$$\kappa = L / RA \quad (2)$$

Where L and A are the thickness and sectional area of the pressed samples.

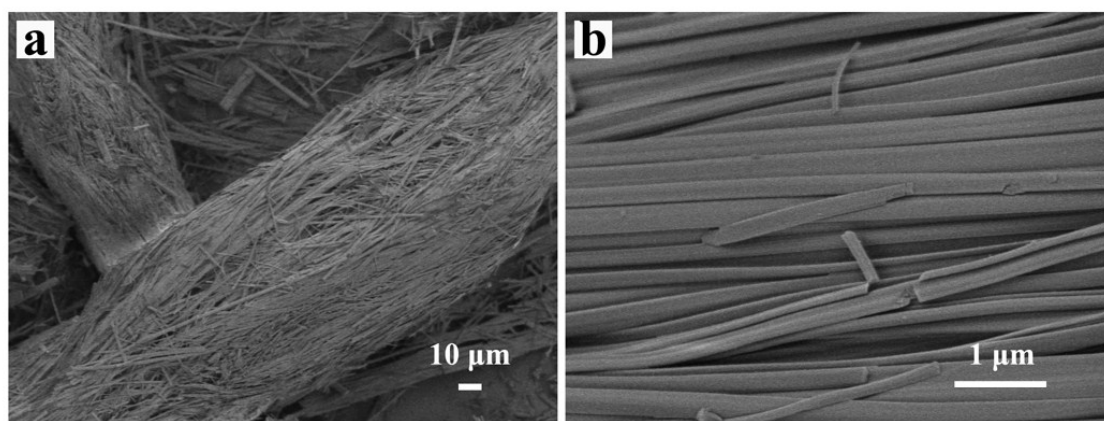


Fig. S1. SEM images of Cu-BTC at different magnification.

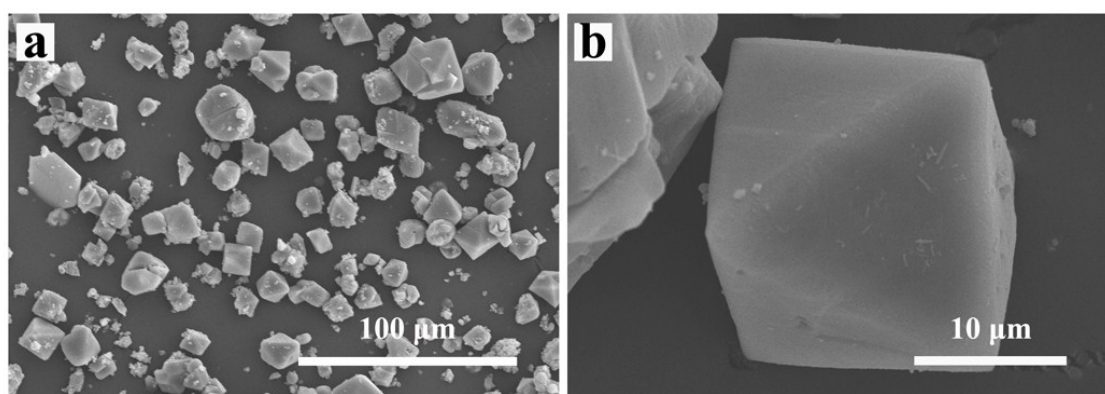


Fig. S2. SEM images of HKUST-1 at different magnification.

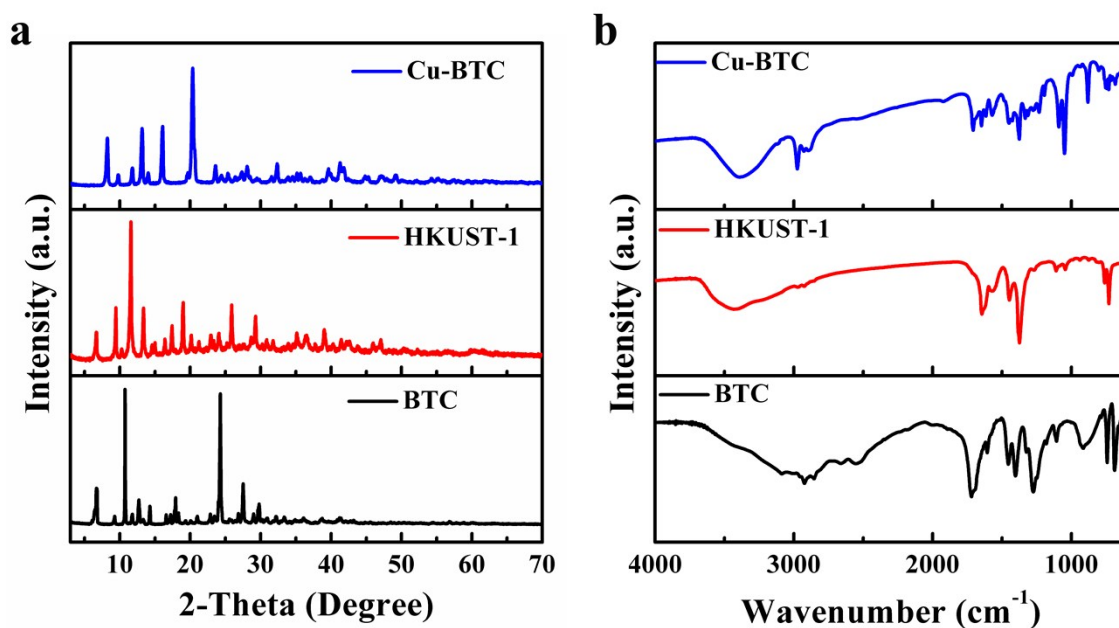


Fig. S3.(a) XRD patterns and (b) FTIR curves of BTC, HUSKT-1 and Cu-BTC.

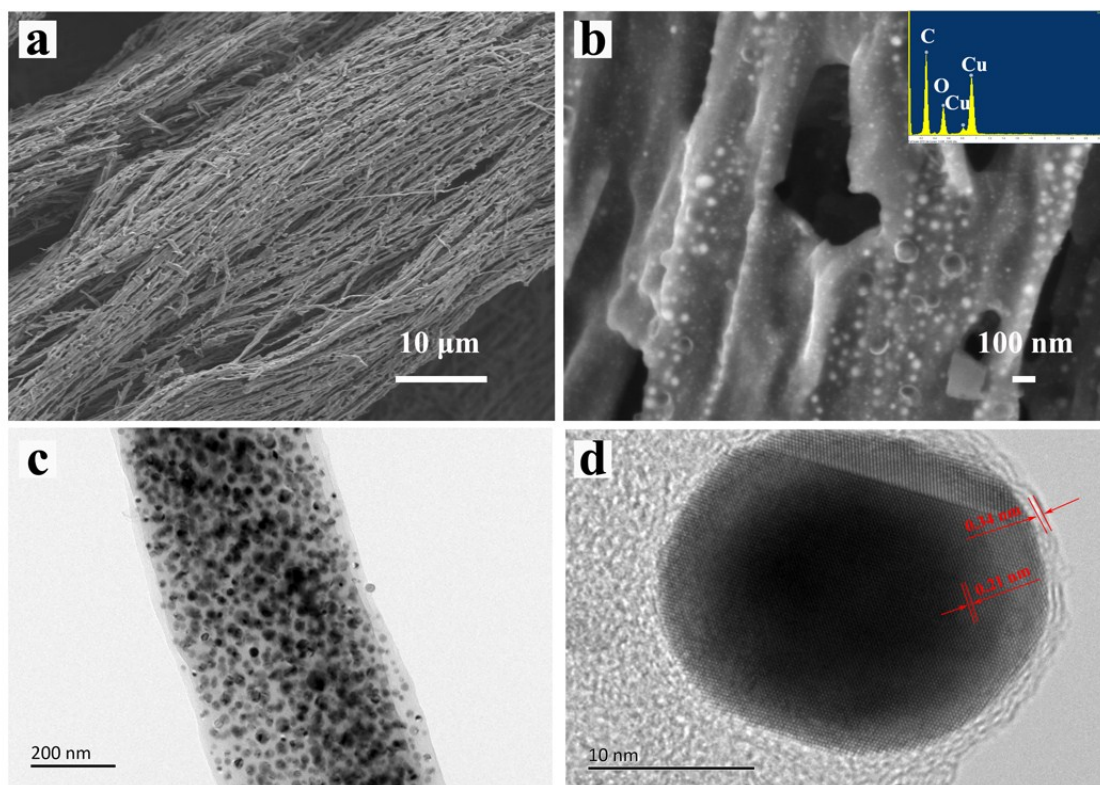


Fig. S4. (a)~(b) SEM images (inset of (b) is corresponding EDX) and (c)~(d) TEM images of Cu-BTC-C at different magnification.

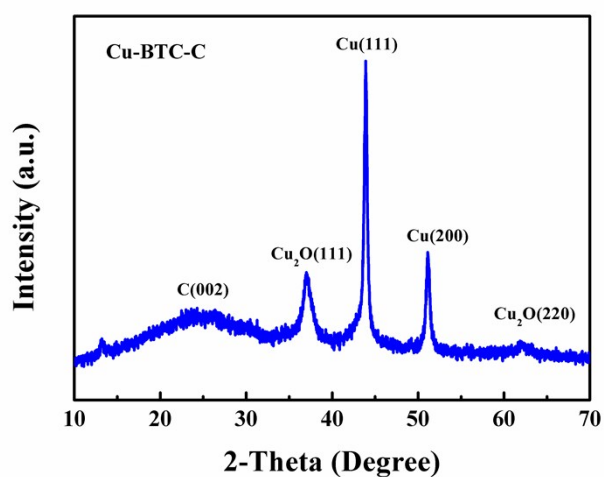


Fig. S5. XRD pattern of Cu-BTC-C.

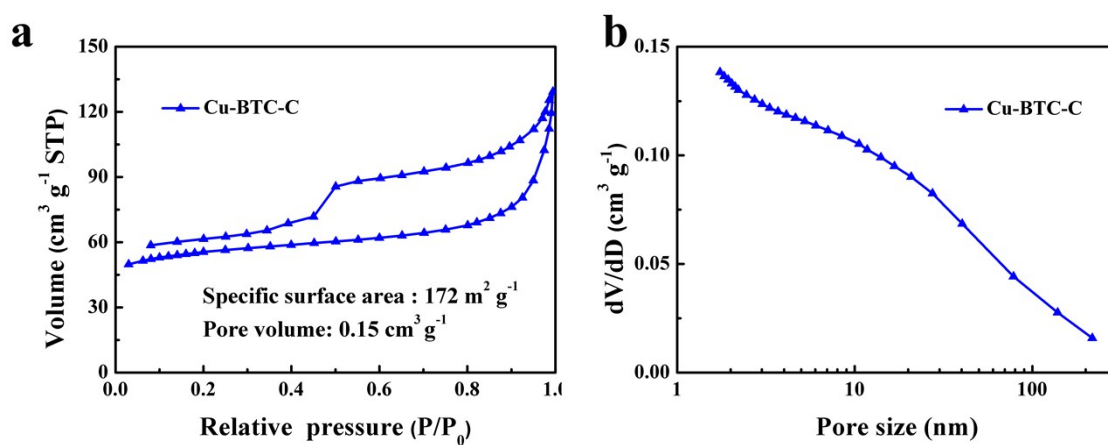


Fig. S6. (a) Nitrogen adsorption—desorption isotherms and (b) pore size distribution curves of Cu-BTC-C.

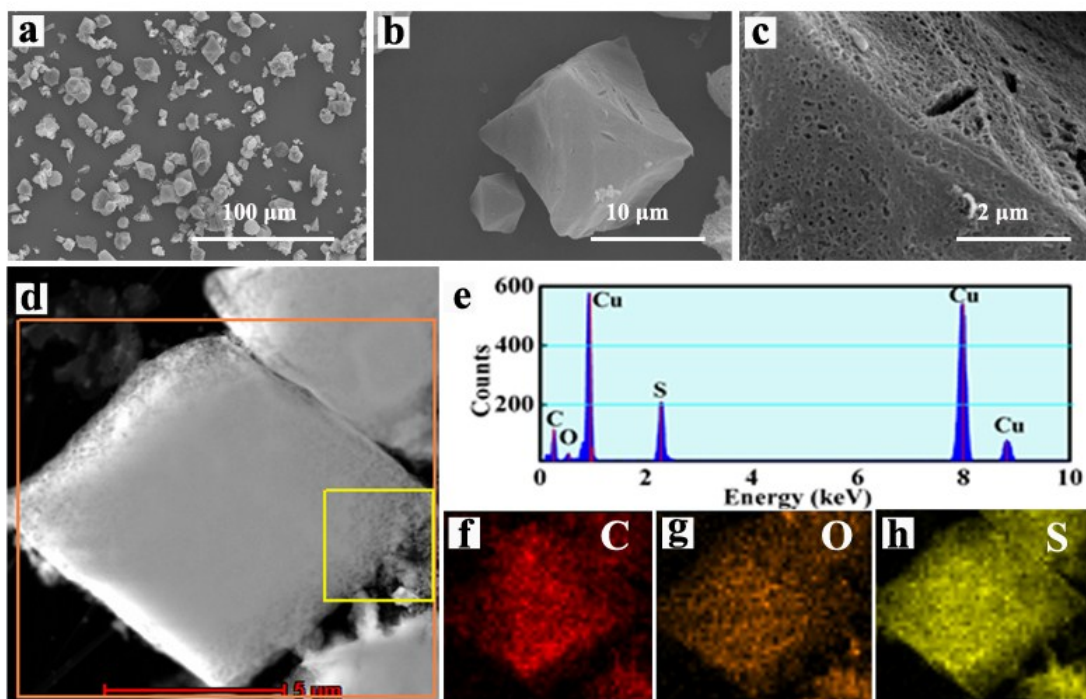


Fig. S7. (a) ~ (c) SEM images of HKC at different magnifications. (d) STEM images and (e) relevant EDX of S/HKC. Elemental mapping of (f) carbon, (g) oxygen and (h) sulfur.

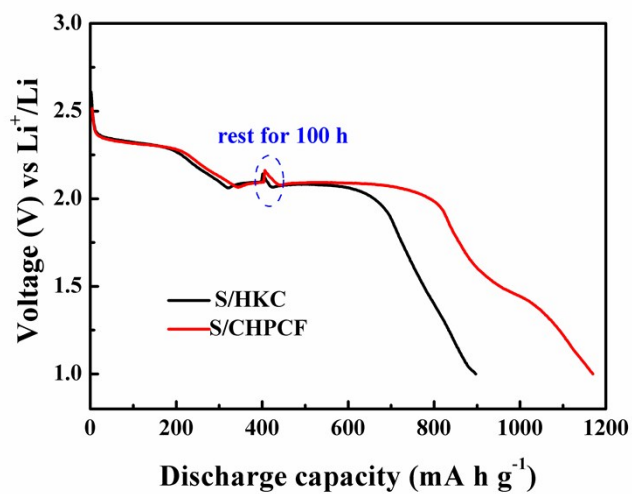


Fig. S8. Self discharge investigation of cells assembled with S/HKC and S/CHPCF electrodes.

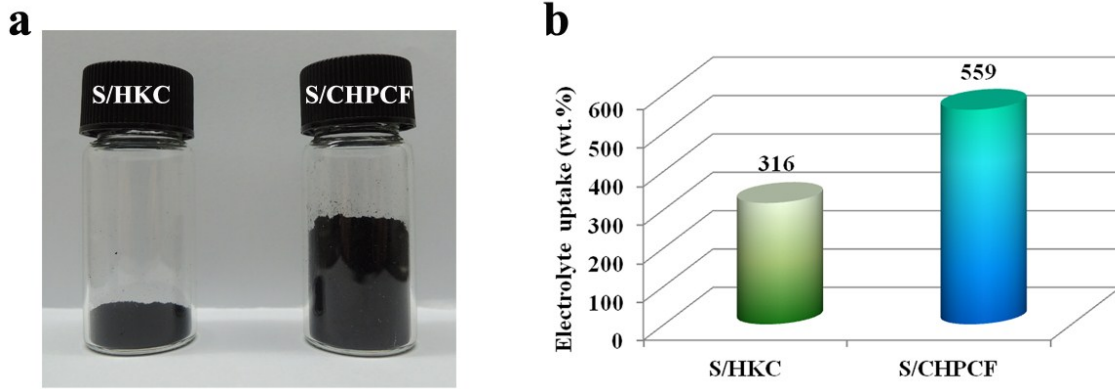


Fig. S9. (a) The optical images of HKC and CHPCF with same weight of 0.1 g. (b) Electrolyte uptake of S/HKC and S/CHPCF electrodes.

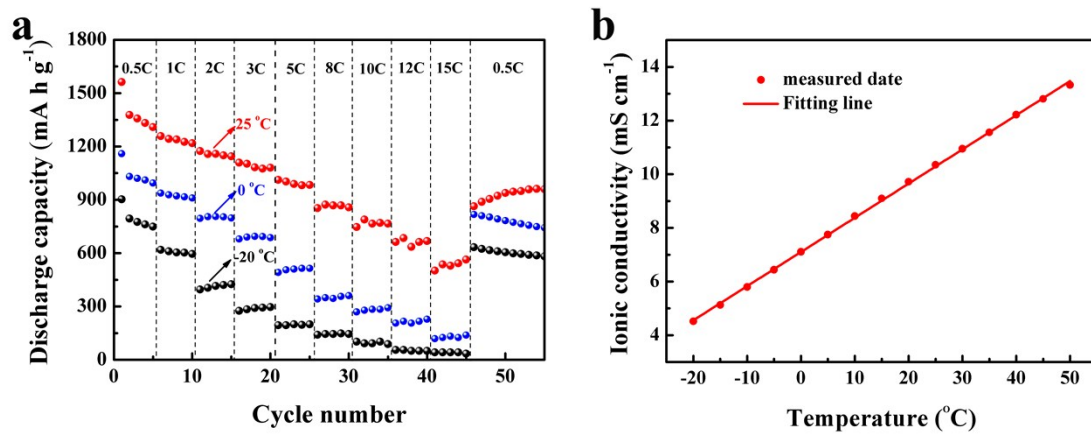


Fig. S10. (a) C-rate performance of S/CHPCF electrode at different temperatures of 25 °C, 0 °C and -20 °C. (b) The relationship between ionic conductivity and temperature.

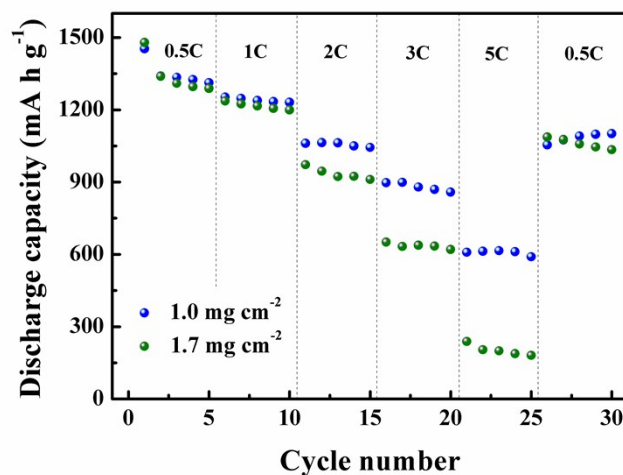


Fig. S11. (a) C-rate performance of S/CHPCF electrode at C-rates varied from 0.5C to 5C with high loadings of 1.0 mg cm⁻² and 1.7 mg cm⁻².

References

1. S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science* 1999, **283**, 1148-1150.
2. N. Yan, X. Yang, W. Zhou, H. Zhang, X. Li and H. Zhang, *RSC Advances*, 2015, **5**, 26273-26280.
3. Z. Lyu, D. Xu, L. Yang, R. Che, R. Feng, J. Zhao, Y. Li, Q. Wu, X. Wang and Z. Hu, *Nano Energy*, 2015, **12**, 657-665.