

Supporting Information

Thiophene-Sulfur Doping in Nitrogen-Rich Porous Carbon Enabling High-ICE/Rate Anode Material for Potassium-Ion Storage

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Experiment Section

Preparation of NC and Sx-NC: In a typical synthesis, 10 g commercially available tetrasodium ethylenediaminetetraacetate (EDTA4Na) is first pyrolysed at a low temperature of 500 °C to obtain the complex of precarbonized nitrogen-rich carbon and Na₂CO₃ (Pre-NC@Na₂CO₃). Pre-NC is obtained by washing with deionised water and hydrochloric acid to remove Na₂CO₃ and drying at 80 °C for 12 h. Then, the Pre-NC and the sulfur powder in a mass ratio of 1:x are well ground, followed by further carbonization-sulfurization at a higher temperature of 700 °C for 2 h under an Ar atmosphere (heating rate = 5 °C min⁻¹) to obtain Sx-NC (x=0.5, 1 and 2; x represents the mass ratio of sulfur powder and Pre-NC). For comparison, Pre-NC is carbonized under the same conditions with the absence of sulfur powder to obtain NC.

Preparation of HPC: Firstly, 10 g EDTA4Na is directly carbonized at 700 °C for 1 h under Ar atmosphere. After removing the sodium salt in the carbonized product with 1.0 M HCl and deionized water, the filter cake was dried at 80 °C for 12 h. Then, the obtained filter cake and KOH in a mass ratio of 1:6 are added to 50 ml deionized water and stirred at room temperature for 3 h. After complete evaporation of the solvent by heating, the collected mixture is activated at 800 °C for 1 h under the protection of Ar atmosphere. Finally, the corresponding activation product are washed and dried to obtain hierarchical porous carbon (HPC).

Preparation of SHCS: SHCS is prepared by the previously reported literature with slight modifications.¹ Typically, 17.3 mL of TEOS is added to the dispersion solution containing 350 mL of ethanol, 50 mL of deionized water, and 15 mL of ammonium

hydroxide under vigorous stirring. After stirring at room temperature for 15 min, 2.0 g of resorcinol and 2.8 mL of formaldehyde are sequentially added to the above solution and stirred again for 24 h at room temperature. Subsequently, the obtained precipitated prepolymer is transferred into a Teflon-lined autoclave to continue the reaction for 24 h at 100 °C. After washing and drying at 80 °C for 12 h, the brown-yellow precipitate RF@SiO₂ is obtained. RF@SiO₂ is first pyrolysed at a low temperature of 500 °C. After removing SiO₂ with 10 wt % HF, the pre-carbonized porous hollow carbon spheres (Pre-HCS) are obtained. Then, Pre-HCS and sulfur powder in a mass ratio of 1:1 are well ground, followed by further carbonization-sulfurization at a higher temperature of 700 °C for 2 h under an Ar atmosphere (heating rate = 5 °C min⁻¹) to obtain thiophene-sulfur-doped porous hollow carbon spheres (SHCS). For comparison, Pre-NC is carbonized under the same conditions with the absence of sulfur powder to obtain HCS.

Materials characterization: The morphologies of the samples were observed by a Hitachi S-4800 field-emission SEM. HRTEM and EDS mapping were performed on a JEOL-2100 TEM to evaluate microstructure and elemental distribution in samples. XRD (Rigaku Ultima IV) tests were conducted to determine the phase composition. Raman spectrometer (HORIBA XploRA PLUS) with a 532 nm wavelength incident laser was applied to acquire (in-situ) Raman spectra. Organic elemental analysis were performed on a Thermo FLASH2000. The N₂ adsorption-desorption tests were undertaken on a Micromeritics ASAP 2020 to analyse the porosity of the samples. (In-situ) XPS (ESCALAB 250) tests were carried out to determine elemental content

and atomic configuration.

Electrochemical characterization: The working electrodes were prepared by scraping the homogeneous slurry of active material, Super P and sodium alginate in deionized water with a mass ratio (7:2:1 for NC and Sx-NC, 8:1:1 for HPC) onto the current collector. After drying under vacuum at 120 °C for 12 h, the electrodes were cut into 12 mm diameter circles and set aside for use. The loading of the anodes is about 0.8 mg, and the loading of the cathodes is adjusted to approximately 0.65 mg~1.4 mg according to the different mass ratios of the cathode and anode. All coin cells were assembled in a glove box filled with Ar gas (both H₂O and O₂ levels are less than 0.1 ppm). For half-cell tests, K foil is employed as the counter electrode, and glass fiber (Whatman, GF/D) and 1 M KFSI (EC/DEC=1:1 in volume) are selected as the separator and electrolyte, respectively. The PIHCs were assembled using a S1-NC anode and a HPC cathode at various mass ratios (the electrolyte and separator are the same with the half-cell). The LAND CT2001A battery test system (Wuhan LAND) is employed to finish GCD tests. The CV and EIS tests were conducted on a CHI 760E workstation (Shanghai Chenhua). The GITT was tested using a pulse current of 0.1 A g⁻¹ for 900 s accompanied by a rest interval of 2 h. The energy and power densities of PIHCs are calculated by numerically integrating the galvanostatic discharge profiles using equations (1) and (2)

$$E = \int_{t_1}^{t_2} UI/mdt \quad (1)$$

$$P = \frac{E}{t} \times 3600 \quad (2)$$

where m refers to the total mass (kg) of active materials. I and U represent the discharge current (A) and operating voltage (V), respectively. t (s) is t_1 (start time of the discharge) - t_2 (end time of the discharge).

Density Functional Theory (DFT) Calculation Details: All the theoretical investigations were carried out using density functional theory with G.09 and quantum espresso simulation package. The generalized gradient approximation (GGA) with the function of Perdew-Becke- Ernzerh of (PBE) was employed to describe the electron interaction energy of exchange-correlation. The projector augmented wave was applied to describe the electron-ion interaction and the plane-wave energy cutoff was set to 400 eV. All structures were optimized with a convergence criterion of 1×10^{-5} eV for the energy and 0.01 eV/Å for the forces. Using a Monkhorst-Pack grid of $2 \times 2 \times 1$, $3 \times 3 \times 1$ Brillouin zone sampling was used. The K^+ adsorption energy (ΔE_a) is defined as the following Equation:

$$\Delta E_a = [E_2 - (E_1 + \mu_K)]$$

where E_1 and E_2 are the total energies of the system before and after potassium adsorption, respectively, and μ_K is the chemical potential of potassium bulk. A positive ΔE indicates an endothermic and unstable reaction while a negative ΔE suggests an exothermic and stable reaction.

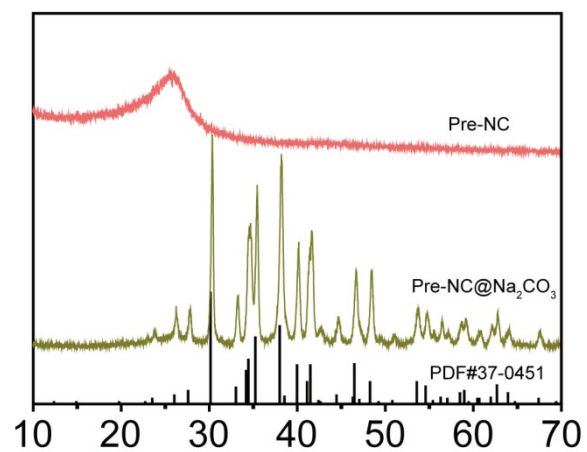


Figure S1. XRD of Pre-NC@ Na_2CO_3 and Pre-NC.

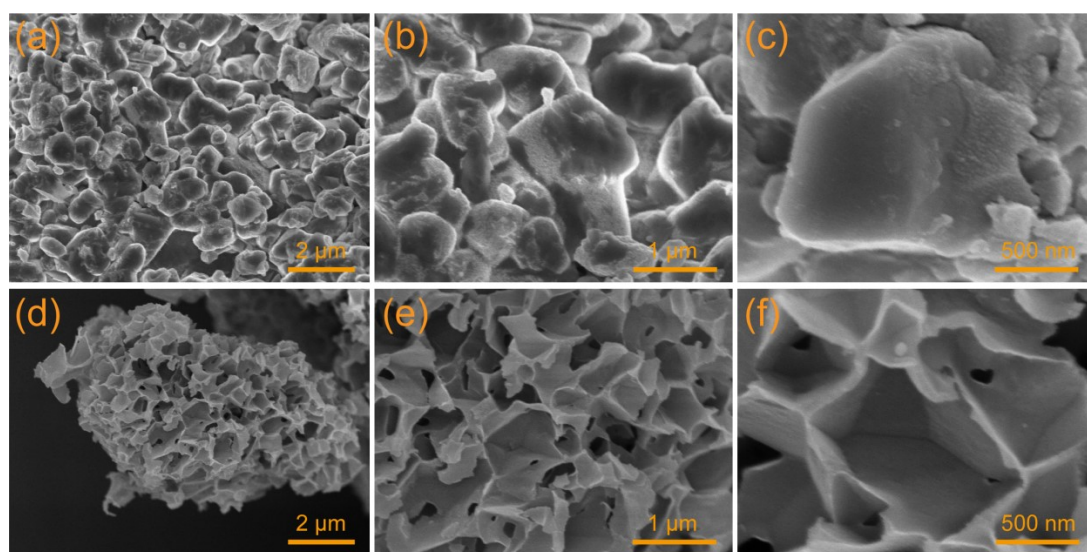


Figure S2. SEM images of (a-c) Pre-NC@ Na_2CO_3 and (d-f) Pre-NC.

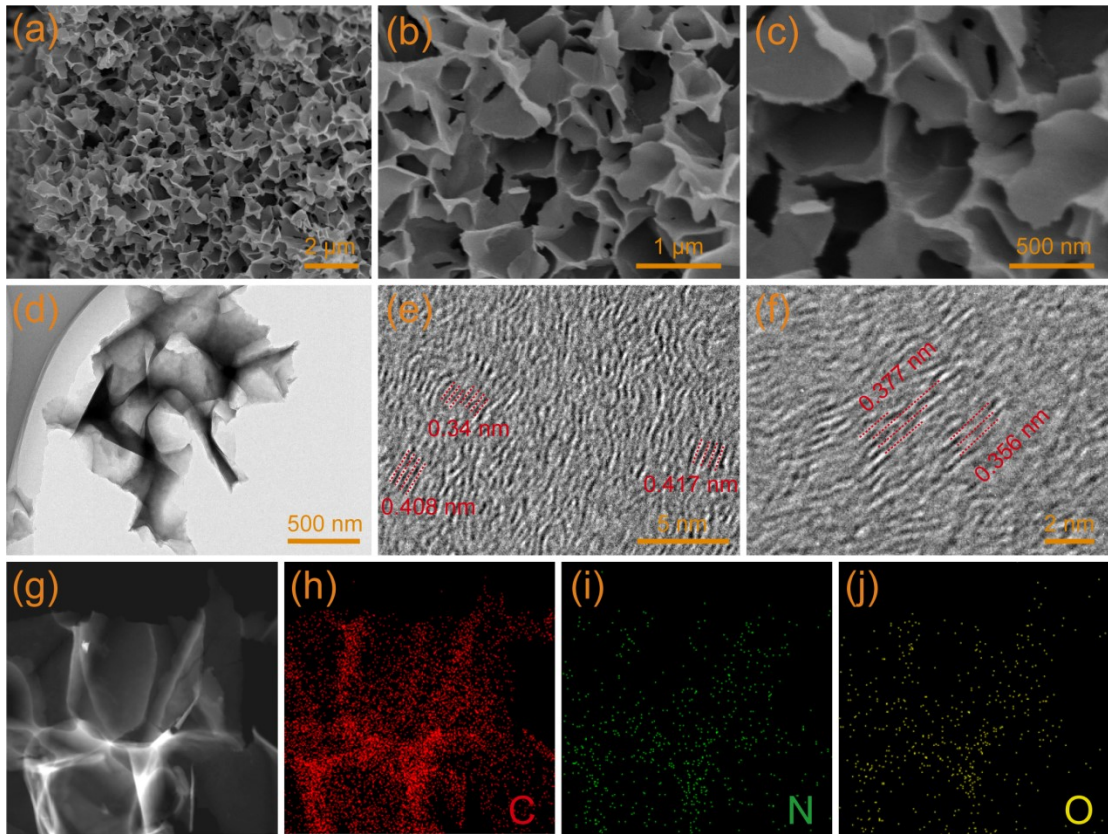


Figure S3. (a-c) SEM images, (d) TEM image, (e, f) HRTEM images, (g) HAADF-STEM image, (h-j) EDS elemental mapping images of NC.

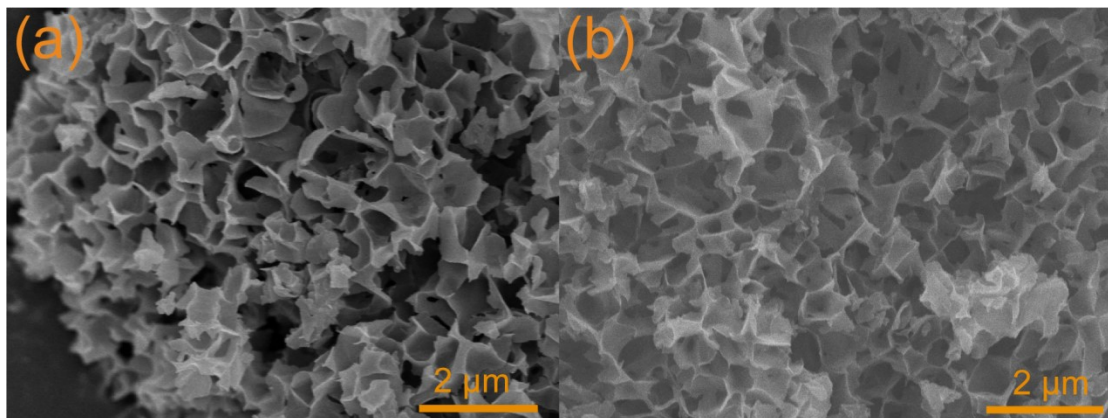


Figure S4. SEM image of (a) S0.5-NC and (b) S2-NC.

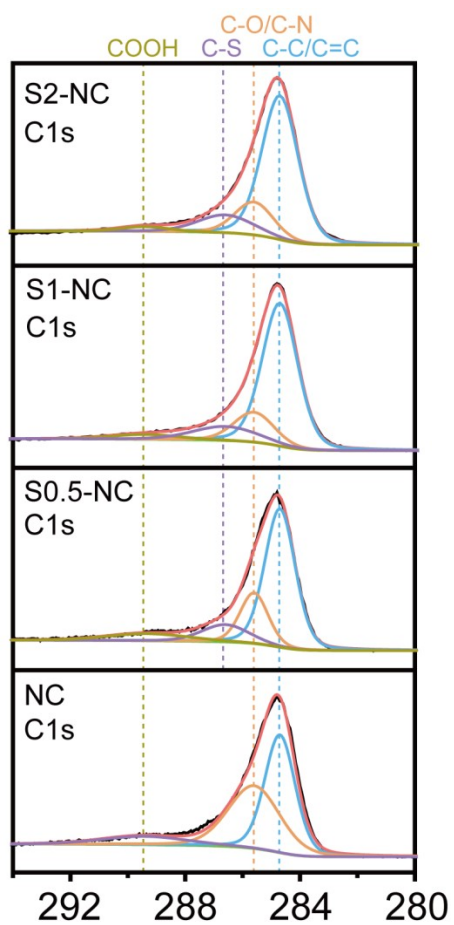


Figure S5. High-resolution XPS C 1s spectra of NC and S_x-NC

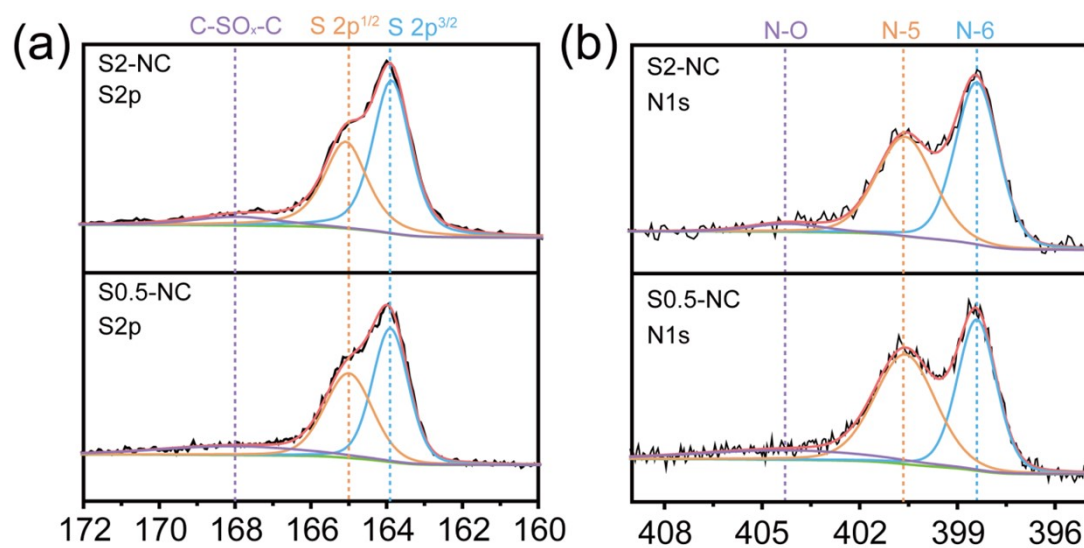


Figure S6. (a) High-resolution XPS S 2p spectra, (b) High-resolution XPS N 1s spectra of S0.5-NC and S2-NC.

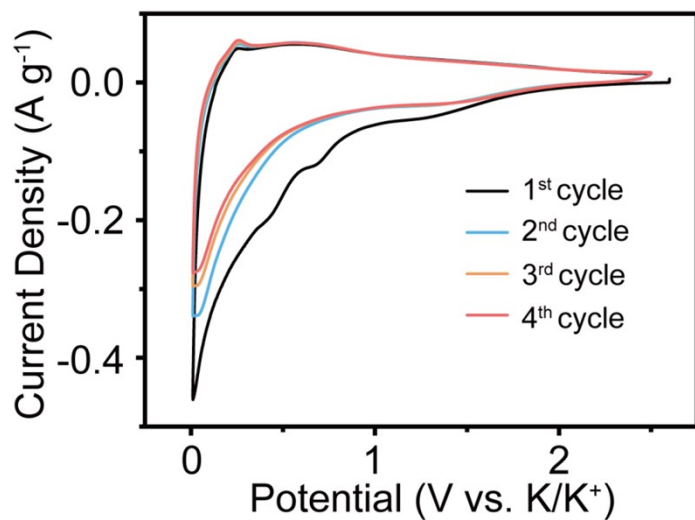


Figure S7. The initial four cyclic CV curves at 0.1 mV s^{-1} of NC.

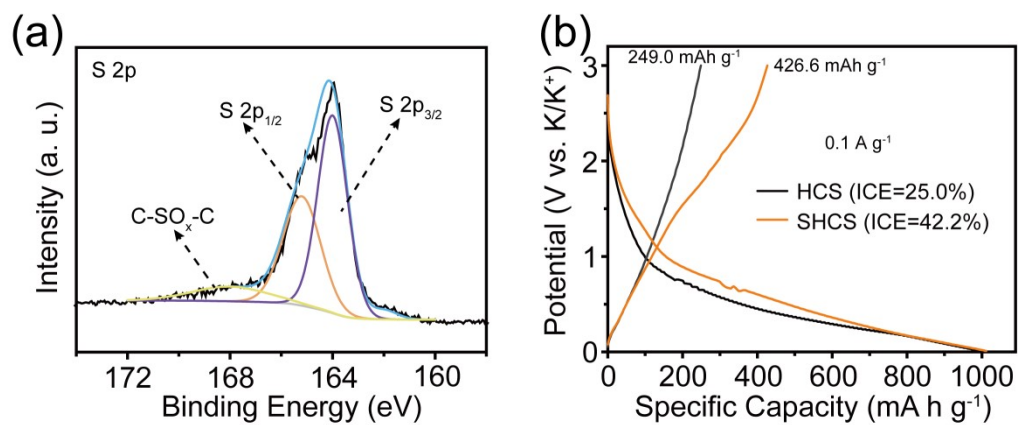


Figure S8. (a) High-resolution XPS S 2p spectra of SHCS, (b) the initial cyclic GCD curves at 0.1 A g^{-1} of HCS and SHCS.

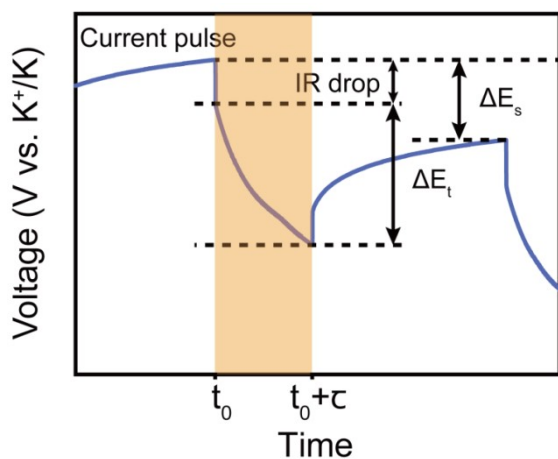


Figure S9. The calculation schematic of diffusion coefficient (D_k) using the GITT technique.

$$D_k = \frac{4}{\pi\tau} \left(\frac{m_b V_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad \left(t \ll \frac{L^2}{D} \right)$$

where τ is the pulse time (s), m_b is the mass of the active material, M_B is the molar mass of the active material (12 g mol^{-1}), V_M represents the molar volume of the active material, S is the geometric area of the electrode, ΔE_t and ΔE_s are defined as shown in the Figure S9.

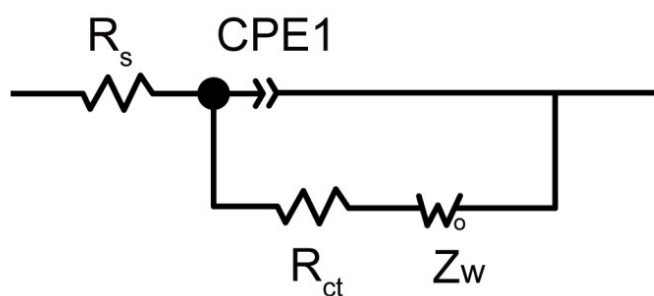


Figure S10. The equivalent circuit diagram.

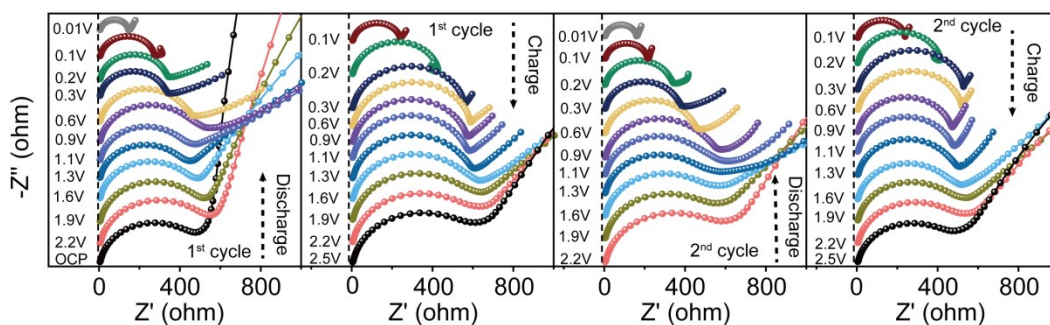


Figure S11. In situ EIS test during initial two cycles for NC.

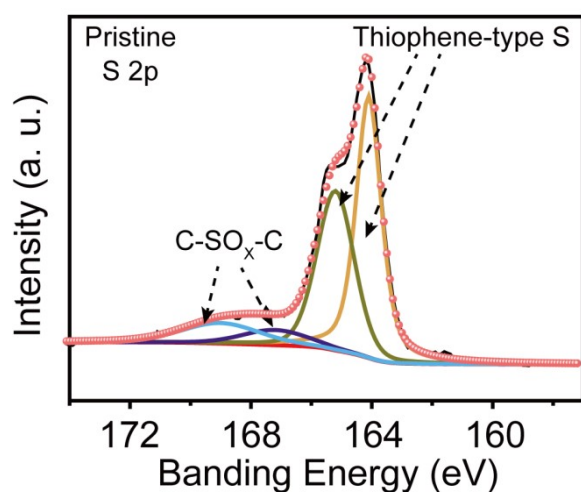


Figure S12. The XPS S2p spectra in the pristine state for S1-NC.

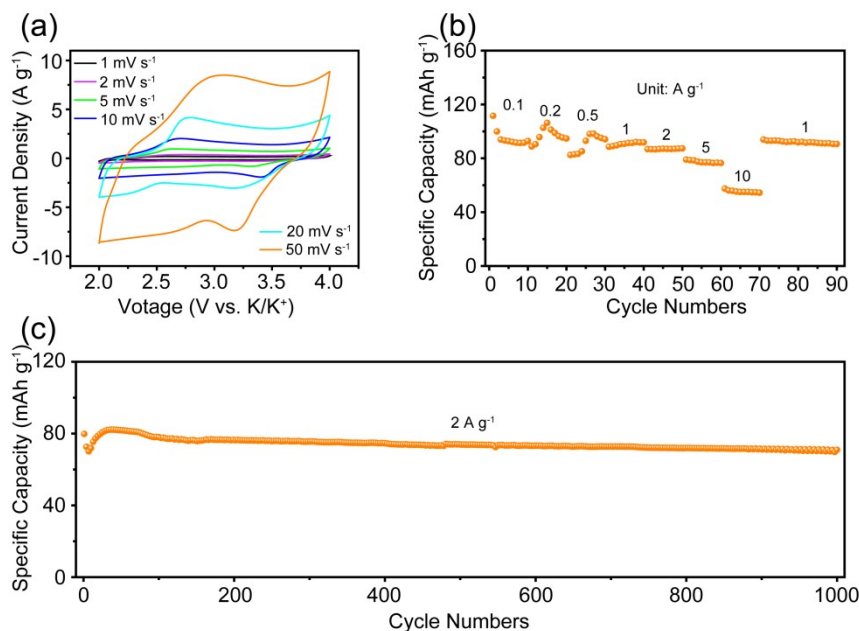


Figure S13. Electrochemical performance of HPC cathode. (a) CV curves at different scan rate;

(b) rate capability; (c) cycling stability at 2 A g⁻¹.

Table S1. Pore structure parameters of NC and Sx-NC.

Sample	^a S _{BET}	^b V _{<2 nm}	^c V _{2-50 nm}	^d V _{>50 nm}	^e V _{total}
	(m ² g ⁻¹)	(cm ³ g ⁻¹)			
NC	209	0.038	0.013	0.027	0.078
S0.5-NC	209.4	0.089	0.022	0.030	0.141
S1-NC	243.4	0.077	0.094	0.014	0.187
S2-NC	354.5	0.139	0.031	0.064	0.234

a: The BET specific surface area; b: Pore volume of d<2 nm calculated by DFT; c: Pore volume of 2<d<50 nm calculated by DFT; d: Pore volume of d>50 nm calculated by DFT; e: The total DFT pore volume.

Table S2. Surface element composition evaluated from XPS of NC and Sx-NC.

Sample	C	O	N	S	N-O	N-Q	N-5	N-6	thiophene-type sulfur	C-SO _x -C
	(at.%)									
NC	86.64	5.71	7.65	-	1.06	0.90	2.79	2.89	-	-
S0.5-NC	83.02	5.01	8.03	3.95	0.95	-	3.76	3.31	3.44	0.52
S1-NC	81.04	4.54	9.55	4.86	0.43	-	4.65	4.47	4.26	0.60
S2-NC	79.55	6.11	8.59	5.75	0.38	-	3.66	4.55	5.34	0.41

Table S3. Elemental content evaluated from organic elemental analysis of Sx-NC.

Sample	C	H	N	S	O*
	(at.%)				
S0.5-NC	66.19	16.11	8.06	3.10	6.54
S1-NC	66.23	13.84	8.24	4.51	7.17
S2-NC	63.96	15.00	8.38	5.51	7.15

* difference method.

Table S4. The variation in the relative content of thiophene-type S and $-K_2S_x$ for S1-NC in first cycle.

State	Thiophene-type sulfur	$-K_2S_x$
	(at. %)	
Pristine	84	0
Discharge-0.01V	39.5	48.4
Charge-2.5V	80	7.6

1 C. Qiu, M. Li, D. Qiu, C. Yue, L. Xian, S. Liu, F. Wang and R. Yang, ACS Applied Materials & Interfaces, 2021, 13, 49942-49951.