Supporting Information

High Performance Potassium-Sulfur Batteries and Its Reaction Mechanism

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Experimental Section

Preparation of PCNF mat

The free-standing PCNF mat was prepared using an versatile electrospinning process, followed by a carbonization treatment. Typically, polyacrylonitrile (PAN, MW = 150,000 g mol\(^{-1}\), J&K, 1.0 g) was dissolved in N,N-dimethylformamide (DMF, > 99.5%, Titan, 10 mL) followed by magnetic stirring at 80 °C overnight to form an viscous and homogeneous solution. The obtained solution was loaded into a 5 mL plastic syringe with a 21-gauge blunt tip needle. Electrospinning process was then carried out by applying an voltage of 15 kV on the needle with a flow rate of 0.8 mL h\(^{-1}\). The polymer fiber mat was collected using a grounded roller with a distance of 14 cm to the syringe needle. The collected PAN mat was firstly stabilized at 280 °C for 3 hours in air with a heating rate of 2 °C min\(^{-1}\) followed by carbonization at a high temperature of 800 °C for 2 hours with a heating rate of 5 °C min\(^{-1}\) under nitrogen atmosphere, donated as PCNF-800. Finally, the resultant carbon fiber mat was treated at 350 °C in air for 2 hours, and the PCNF mat was obtained.

Preparation of PCNF/S composite

The mixture of bulk sulfur (cyclo-S\(_8\)) (99.5%, Alfa Aesar) and the PCNF mat in a mass ratio (3:1) was sealed into glass tube under vacuum and heated at 500 °C for 5 hours with a heating ramp of 5 °C min\(^{-1}\). The resulting product was then heated at 200 °C for 4 hours in argon atmosphere with a heating rate of 2 °C min\(^{-1}\) to remove the superficial sulfur and finally free-standing microporous carbon nanofiber/small-molecule sulfur (PCNF/S) composite was obtained with a sulfur loading of 0.5-1.0 mg cm\(^{-2}\).

Materials and structural characterizations

Morphological characterizations of the PCNF and PCNF/S composite mats were carried out on field-emission scanning electron microscopy (FESEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL, JEM-2100F). Both SEM and TEM energy dispersive X-ray spectroscopy (EDS) were performed on Oxford energy spectrometer. X-ray diffraction (XRD)
patterns were collected on Rigaku Ultima IV with Cu Kα radiation source (V = 40 kV, I = 40 mA and λ = 1.5418 Å). Raman spectra were collected using a laser wavelength of 532 nm on a Renishaw InVIA Reflex Raman microspectrometer. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with mono Al Kα radiation at room temperature. The microporous structure of the PCNF and PCNF/S composite mats was analyzed using CO₂ adsorption-desorption on a ASAP 2420-4 volumetric adsorption analyzer (Micromeritics). The pore size distribution was calculated using nonlocalized DFT method, and the pore volume was obtained using Horvath-Kawazoe method. The thermal stability of bulk cyclo-S₈ and the PCNF/S composite was investigated using a thermo-gravimetric analysis (TGA, TA, Q50) in nitrogen with a heating rate of 10 °C min⁻¹. Element analysis was applied on Elementar, Vario Micro Cube. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded using KBr pellets on a Bruker Alpha spectrometer. The UV-vis samples were prepared by collecting the electrolytes from the disassembled batteries and the data were conducted on Jindao UV-3600 plus.

**Electrochemical characterization**

The free-standing PCNF/S composites were directly used as working electrodes (~7 mm×7 mm) with the weight of 1-2 mg to assemble CR2032-type coin cells in an argon-filled glove box (H₂O, O₂ < 0.1 ppm). Potassium metal (K, 99.5%, Sigma-Aldrich) was used as counter and reference electrode and Celgard®2400 (Celgard, LLC Corp.) as separator. The K metal anode used in this work is ~6 mm*6 mm in size, ~300-500 μm in thickness with a mass of ~12 mg. 50 μL 1.0 M potassium bis(fluorosulfonyl)imid (KFSI)-dimethoxyethane (DME) and 0.8 M potassium hexafluorophosphate (KPF₆) in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) were used as electrolytes.

The galvanostatic charge/discharge performance of the half-cells was tested on a LAND CT-2001A (Wuhan) instrument in an voltage range of 0.5-3.0 V (vs. K⁺/K) at ambient temperature. Cyclic voltammetry (CV) curves were carried out on CHI660E electrochemical test station at a
scan rate of 0.02 mV s\(^{-1}\) in the range 0.5-3.0 V. A Solartron electrochemical workstation (1400+1470) was employed for electrochemical impedance spectrometry (EIS) test in the frequency range of 0.01 Hz to 1 MHz with an ac amplitude of 5 mV.

In order to rule out the influence of element sulfur in the salt of KFSI, 0.8 M KPF\(_6\) in EC/DEC (1:1) was applied for SEM, TEM, ex-situ XPS and sulfur K-edge XANES measurements. In addition, all the batteries were potassiated and depotassiated to desired voltages and then kept for 6 hours. The potassiated/depotassiated PCNF/S composite electrodes were retrieved and rinsed with DEC solvent several times to remove residual electrolyte before analysis.

For the ex-situ XPS depth-profile test, the PCNF/S composite electrodes were potassiated and depotassiated to desired voltages at 20 mA g\(^{-1}\). The washed electrodes were sealed in a tightly-closed XPS sample holder in an argon-filled glove box and then transferred into the XPS test chamber without exposure to air. The profiles were obtained after a 20 s etching process with a rate of 0.32 nm s\(^{-1}\).

**TOF-SIMS measurement**

The time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis was conducted on a TOF-SIMS 5 spectrometer (ION-TOF GmbH, 2015). The spectrometer was run at an operating pressure below 1 \times 10^{-9} mbar. Bi\(^{3+}\) primary ion clusters at 60 keV were employed on a 200 \times 200 \(\mu\)m\(^2\) area. Sputtering process was done using a 10 keV Ar\(^+\) beam with an etching rate of 0.214 nm s\(^{-1}\) and SiO\(_2\) as reference. Data acquisition and post-processing analyses were performed using Software Surface Lab. Both positive and negative ion profiles were recorded and analyzed. The intensity reported used a logarithmic scale in order to magnify the low-intensity signals.

**Sulfur K-edge XANES spectroscopy analysis**

The sulfur K-edge X-ray absorption near-edge structure (sulfur K-edge XANES) data of the PCNF/S composite electrodes at different potassiated/depotassiated states were collected in partial fluorescence yield mode at beamline 4B7A of Beijing Synchrotron Radiation Facility.
(BSRF). The incoming X-ray beam was monochromatized by a fixed-exit Si (111) double-crystal monochromator. Monochromator energy was calibrated against the peak of the white line of K$_2$SO$_4$ at 2.4824 keV. Furthermore, to establish a relationship between the edge energy and oxidation state, bulk sulfur (cyclo-S$_8$) and phenyl disulfide were applied as reference materials. For sample preparation, the reference materials and PCNF/S composite electrodes were neatly pressed onto conductive double sided carbon adhesive tape in an argon-filled glove box to avoid the side reactions with oxygen and humidity. All of the raw XANES spectra were processed using Athena software package.

**The calculation of energy density**

The energy density value $E$ (Wh/kg) calculation process was showed as follows:

$$E = C_{d\text{-total}} \times V_d$$

Where $C_{d\text{-total}}$ represents the discharge capacity based on the total weight including active material, binder and conductive agents, $V_d$ represents the average discharge voltage.

$$C_{d\text{-total}} = (C_d \times m_{\text{active}})/(m_{\text{total}} + m_{\text{collector}})$$

Where $C_d$ represents the discharge capacity obtained from the literature, $m_{\text{active}}$ represents the weight of active electrode material, $m_{\text{total}}$ represents the total weight of the electrode including active electrode material, binder and conductive agents, and $m_{\text{collector}}$ represents the mass of the current collectors.

$$m_{\text{active}} = L_{\text{active}} \times A_{\text{electrode}}$$

$$m_{\text{total}} = m_{\text{active}}/w$$

$$m_{\text{collector}} = L_{\text{collector}} \times A_{\text{electrode}}$$

Where $L_{\text{active}}$ represents the area loading of the active materials, $A_{\text{electrode}}$ represents the area of the electrode, and $w$ represents the mass percentage of active material in the electrode. (The $L_{\text{active}}$, $L_{\text{collector}}$, and $A_{\text{electrode}}$ were set to be 1 mg cm$^{-2}$, 5 mg cm$^{-2}$ and 1 cm$^2$, respectively, when the values were not provided in the literature.)
**Figure S1.** (a,c) SEM images and (b,d) diameter distribution of the (a,b) PCNF mat and (c,d) PCNF/S composite.

**Figure S2.** (a) Light-field image and EDS element mapping images of (b) C, (c) N and (d) O of the PCNF/S composite.
Figure S3. TGA curves of PCNF/S and PCNF-800/S composites.

Figure S4. The second sputtering process under negative ion sputtering of the PCNF/S composite.
**Figure S5.** Positive ion mass spectra of TOF-SIMS analysis of the PCNF/S composite: (a) $S_1^+$, (b) $S_2^+$, (c) $S_3^+$ and (d) $S_4^+$. The black curves are on the pristine surface, the pinks are the curves after the first sputtering and the light blues are those after second sputtering process, respectively.

**Figure S6.** Negative ion mass spectra of TOF-SIMS analysis of the PCNF/S composite: (a) $S_1^-$, (b) $S_2^-$, (c) $S_3^-$ and (d) $S_4^-$. The black curves are on the pristine surface, the pinks are the curves
after the first sputtering and the light blues are those after second sputtering process, respectively.

**Figure S7.** Chemical property characterization of the PCNF/S composite: (a) XPS survey and high-resolution XPS spectra of (b) C 1s, (c) N 1s and (d) O 1s, respectively.

**Figure S8.** Chemical property characterization of the PCNF/S composite: (a) FTIR spectra of bulk sulfur and the PCNF/S composite and (b) summary of FTIR peaks and assignments.
Figure S9. Electrochemical performance of the PCNF electrodes with the electrolyte of 1.0 M KFSI in DME: (a) CV curves at a scan rate of 0.05 mV s\(^{-1}\), (b) galvanostatic charge/discharge profiles at 20 mA g\(^{-1}\).

Figure S10. Electrochemical performance of the PCNF/S composite electrodes in the voltage window of 0.5-3.0 V with the electrolyte of 0.8 M KPF\(_6\) in EC/DEC: (a) galvanostatic charge/discharge profiles in the first five cycles at 20 mA g\(^{-1}\) and (b) cycling stability at 50 mA g\(^{-1}\).
Figure S11. Optical photographs of PCNF/S composite electrodes after disassembling the batteries at different potassiation states in the electrolyte of 0.8 M KPF$_6$ in EC/DEC.

Figure S12. UV-vis spectra of electrolytes collected from the disassembled batteries at different discharge states in the electrolyte of 0.8 M KPF$_6$ in EC/DEC.
**Figure S13.** Rate capability of the PCNF/S composite electrode of (a) voltage profiles of Figure 3c, (b) rate performance based on the whole electrode weight.

**Figure S14.** Comparison of energy density of the PCNF/S composite electrode with those of representative reported cathode materials for KIBs in literature.[81-S7] (Values are taken or estimated from the references and the capacity was calculated based on the whole weight of the electrode, including active materials, conductive agents, binders and current collectors.)

**Figure S15.** Voltage profiles in selected galvanostatic charge/discharge cycles of the PCNF/S composite electrode of (a) at 20 mA g⁻¹ of Figure 3e and (b) at 200 mA g⁻¹ of Figure 3f.
Figure S16. (a) Cycling stability at 20 mA g\textsuperscript{-1} and (d) long-life cycling performance at 200 mA g\textsuperscript{-1} of PCNF/S composite electrode based on the total mass of the composite electrode.

Figure S17. \textit{In-situ} electrochemical impedance spectra evolution of the PCNF/S composite electrode at fresh state and fully depotassiated states with cycling.
Figure S18. Cross-sectional SEM images of PCNF/S composite electrodes at (a) pristine state and (b) after cycling.

Figure S19. SEM images of the PCNF/S composite electrode at different states: (a) pristine, (b) potassiated to 0.5 V and (c) depotassiated to 3.0 V at the current density of 20 mA g⁻¹, and (d-f) the corresponding diameter distributions.
Figure S20. (a) HAADF-STEM image and (b) EDS line-scanning analysis of the PCNF/S composite electrode along with the marked line of blue arrow during the *in-situ* TEM experiment.

Figure S21. Morphology and structural characterization of the tested PCNF/S composite electrode after 200 cycles at 20 mA g\(^{-1}\) with the electrolyte of 0.8 M KPF\(_6\) in EC/DEC: (a) TEM, b) light-field and (c-h) EDS element mapping images of C, O, N, F, K and P, respectively.
Figure S22. Morphology and structural characterization of the tested PCNF/S composite electrode after 200 cycles at 20 mA g\(^{-1}\) with the electrolyte of 1.0 M KFSI in DME: (a) SEM, (b) TEM, (c) HRTEM and (d) light-field and (e-j) EDS elemental mapping images of C, N, O, S, F and K, respectively.

Figure S23. XRD patterns at pristine, potassiated to 0.5 V and depotassiated to 3.0 V states of the PCNF/S composite electrodes at the current density of 20 mA g\(^{-1}\) with 1.0 M KFSI in DME.
Figure S24. Sulfur K-edge XANES spectra of selected different potassiation states during the first potassiation process of the PCNF/S composite electrode in the electrolyte of 0.8 M KPF$_6$ in EC/DEC.

Figure S25. High-resolution XPS spectra of S 2p at different potassiated states during the first potassiation process of the PCNF/S composite electrode in the electrolyte of 0.8 M KPF$_6$ in EC/DEC.
Figure S26. Structural and morphology characterization of the K metal anode after cycling: (a) SEM and (b-d) EDS elemental mapping images of the K metal anodes after 200 cycles at the current density of 20 mA g\(^{-1}\) in the electrolyte of 0.8 M KPF\(_6\) in EC/DEC. The insets show the optical photograph and the EDS energy spectrum of the K metal anode.
Table S1. Electrochemical performance comparison of sulfur cathodes in KIBs.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sulfur content (wt%)</th>
<th>Voltage window (V)</th>
<th>Electrolyte amount (µL)</th>
<th>Sulfur loading (mg cm(^{-2}))</th>
<th>Cycling (mAh g(^{-1})) @cycle life</th>
<th>Capacity retention (%)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>PCNF/S</td>
<td>25</td>
<td>0.5-3.0</td>
<td>50</td>
<td>0.5-1</td>
<td>1002.4@2000 at 200 mA g(^{-1})</td>
<td>88</td>
<td>This work</td>
</tr>
<tr>
<td>PANI@CMK-3/sulfur</td>
<td>39.2</td>
<td>1.2-2.4</td>
<td>---</td>
<td>---</td>
<td>329.3@50 at 50 mA g(^{-1})</td>
<td>63</td>
<td>S8</td>
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<tr>
<td>70S/30CNT</td>
<td>70</td>
<td>1.2-3.0</td>
<td>80</td>
<td>0.478</td>
<td>184@5 at 50 mA g(^{-1})</td>
<td>26</td>
<td>S9</td>
</tr>
<tr>
<td>K(_2)S(_x) catholyte/3D-FCN</td>
<td>30</td>
<td>1.2-2.4</td>
<td>50</td>
<td>0.56</td>
<td>376@20 at 55.8 mA g(^{-1})</td>
<td>94</td>
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<tr>
<td>SPANs</td>
<td>38</td>
<td>0.8-2.9</td>
<td>---</td>
<td>0.38</td>
<td>387@100 at 125 mA g(^{-1})</td>
<td>54</td>
<td>S11</td>
</tr>
<tr>
<td>S/CNF</td>
<td>---</td>
<td>1.0-2.8</td>
<td>20</td>
<td>1</td>
<td>600@50 at 114.4 mA g(^{-1})</td>
<td>53</td>
<td>S12</td>
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<tr>
<td>CMK-3/S</td>
<td>76</td>
<td>1.2-3.0</td>
<td>---</td>
<td>1.8-2.0</td>
<td>220@10 at 10 mA g(^{-1})</td>
<td>36</td>
<td>S13</td>
</tr>
<tr>
<td>SPAN (PAA binder)</td>
<td>45.5</td>
<td>0.3-3.0</td>
<td>---</td>
<td>---</td>
<td>450@300 at 837 mA g(^{-1})</td>
<td>49</td>
<td>S14</td>
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<tr>
<td>CCS (SPAN)</td>
<td>39.25</td>
<td>0.8-3.0</td>
<td>120</td>
<td>0.39-0.59</td>
<td>672@300 at 150 mA g(^{-1})</td>
<td>86</td>
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<td>Microporous C/S</td>
<td>18.6</td>
<td>0.5-3.0</td>
<td>---</td>
<td>0.5-1.0</td>
<td>869.9@150 at 20 mA g(^{-1})</td>
<td>73</td>
<td>S16</td>
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<tr>
<td>SPAN</td>
<td>39.52</td>
<td>0.5-3.0</td>
<td>---</td>
<td>---</td>
<td>490@100 at 35 mA g(^{-1})</td>
<td>95</td>
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<td>I-S@pPAN</td>
<td>42</td>
<td>0.8-2.9</td>
<td>246</td>
<td>0.42</td>
<td>388@180 at 1675 mA g(^{-1})</td>
<td>54</td>
<td>S18</td>
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</table>

*Capacities are calculated based on the mass of sulfur.

Video S1. In-situ TEM experiment video during potassiation/depotassiation processes.
Reference


