Experimental

Materials

3,3’,4,4’-biphenyl tetracarboxylic dianhydride (BPDA, >99.5%, Changzhou Sun Chem Chemical Co., Ltd.), p-phenylenediamine (PPD, >99%, Wuxi Changan Fine Chemical Factory), N,N-dimethylformamide (DMF) (Xilong Chemical Co., Ltd), potassium permanganate (KMnO₄, Sigma-Aldrich), lithium sulfide (Li₂S, 99.9%, Sigma-Aldrich) and sulfur (S, 99.5%, Aladdin Co. Ltd.) were used as received.

Preparation of MnO₂/N-rich CNF

BPDA and PPD (with a molar ratio of 1.05:1) were added to DMF in sequence to get a 13 wt% electrospinning solution. The blended solution was stirred at 0 °C for 12 hours. Electrospinning parameters were set as follows: applied voltage of 20-25 kV, tip-to-collector distance of 25 cm and flow rate of 0.8 ml h⁻¹. As-spun fibers were heated in a horizontal tubular furnace. Temperature of the furnace was first increased from room temperature to 250 °C at the rate of 5 °C min⁻¹ and maintained for 0.5 hour in air flow. Then the temperature was increased to 370 °C at the rate of 1 °C min⁻¹ and maintained for 0.5 hour. Then the temperature was increased to 400 °C at the rate of 1 °C min⁻¹ and maintained for 0.5 hour for imidization. Then the temperature of the furnace was increased to 900 °C at the rate of 5 °C min⁻¹ and maintained for 1 hour under N₂ atmosphere for carbonization.

The MnO₂/CNF composites were synthesized by a one-step facile redox method. In brief, 40 mg as-prepared CNF after a plasma treatment was soaked in 400 ml deionized (DI) water. Then 10 mg KMnO₄ was added and stirred until completely dissolved. After heating in a thermostatic oven at 80°C for 24 h, the composites were washed with DI water and air-dried.

Characterizations

The morphology of MnO₂/CNF was observed by SU-8010 scanning electron microscope (SEM). Transmission electron microscopy (TEM) was performed on a JEM-2100F TEM/STEM operating at 200 keV. X-ray diffraction (XRD) analysis was performed using D/MAX-RM 2000 at a scanning rate of 5° min⁻¹ in a range of diffraction angle 2θ from 10° to 80°. Raman spectra were performed by HORIBA LabRAM HR Evolution with an excitation laser beam with wavelength of 532 nm. X-ray photoelectron
spectroscopy (XPS) measurement was investigated using a thermo ESCALAB 250 spectrometer. And XPS data was analyzed with Thermo Avantage software. The binding energy values were calibrated to the C 1s peak at 284.8 eV. The specific surface area and pore-size distribution of the composites were conducted by an automatic adsorption system (Bellsorp-mini) from adsorption isotherms of N\textsubscript{2} at 77 K with the Brunauer-Emmett-Teller method and density functional theory model. The content of MnO\textsubscript{2} in the interlayer was obtained by Thermogravimetric analysis (TGA, Mettler TGA Q5000) at the rate of 5 °C min\textsuperscript{-1} from 25 °C to 800 °C under air flow.

Cell assembly and electrochemical measurements

Sulfur, super P and PVDF were dispersed homogeneously in NMP to form a slurry (S: super P: PVDF=6:3:1 in weight). The slurry was then cast onto Al foil to get a thin slice in a diameter of 12 mm. The sulfur loading of cathode was about 1.65 mg cm\textsuperscript{-2}. All cells were assembled in a glove box with Ar atmosphere. CR2032-type coin cells were applied to perform the electrochemical experiments with lithium metal as the anode. Celgard 2400 membrane was utilized as the separator. The as-prepared MnO\textsubscript{2}/CNF was cut into wafers in a diameter of 16 mm as the interlayer between separator and cathode. DOL and DME by 1:1 in volume with 1M LiTFSI (lithium bistrifluoromethanesulfonylimide) and 0.1 M LiNO\textsubscript{3} were used as the electrolyte.

Galvanostatical charge-discharge measurements of batteries were carried out in voltage range from 1.7 to 2.8 V (vs. Li/Li\textsuperscript{+}) by the Neware battery tester. A Chenhua electrochemical workstation CHI608E was employed to characterize the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and voltammetric curves. CV tests were performed at a scan rate of 0.3 mV s\textsuperscript{-1} in a voltage range of 1.5-3.0 V. EIS measurements were carried out at open-circuit potential in the frequency range between 100 kHz and 10 mHz with a perturbation amplitude of 5 mV. Stainless steel sheets were directly applied on both sides of CNF or MnO\textsubscript{2}/CNF membrane in cells to test voltammetric curves at a scan rate of 2 mV s\textsuperscript{-1} in a voltage range of 0-2.0 V.

Li\textsubscript{2}S and S (in a 1:5 molar ratio) were added to a mixture of 1,2-dimethoxyethane (DME, 99.5%, Aladdin Co. Ltd., China) and 1,3-dioxolane (DOL, 99.8%, Aladdin Co. Ltd., China) (v/v, 1:1) with magnetic stirring in a glove box to synthesize a Li\textsubscript{2}S\textsubscript{x} solution (0.3M) for testing the diffusion process of polysulfides.
Fig. S1 The SEM images of the MnO₂/CNF after soaking in KMnO₄ for different reaction time

Fig. S2 Elements mapping of MnO₂/CNF
Fig. S3 Axial and radial resistance tests of CNF and MnO$_2$/CNF membrane

Fig. S4 Voltammetric curves of cells with CNF and MnO$_2$/CNF interlayer, without cathode and anode

Fig. S5 Cycle performance of cells with MnO$_2$/CNF utilized as interlayer and cathode scaffold at 01C
Table S1. Potential gaps between corresponding reduction peaks and oxidation peaks in the CV curves in scan rate of 0.3 mV s\(^{-1}\) of different cells

<table>
<thead>
<tr>
<th></th>
<th>Without interlayer</th>
<th>CNF interlayer</th>
<th>MnO(_2)/CNF interlayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>The 1(^{st}) platform</td>
<td>430 mV</td>
<td>380 mV</td>
<td>330 mV</td>
</tr>
<tr>
<td>The 2(^{nd}) platform</td>
<td>600 mV</td>
<td>490 mV</td>
<td>480 mV</td>
</tr>
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Table S2. The area ratio of Mn of different peaks of the MnO\(_2\)/CNF interlayer with and without Li\(_2\)S\(_6\) solution

<table>
<thead>
<tr>
<th></th>
<th>Mn(II)</th>
<th>Mn(III)</th>
<th>Mn(IV)</th>
<th>Mn(II)*</th>
<th>Mn(III)*</th>
<th>Mn(IV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before soaking</td>
<td>18.3%</td>
<td>32.5%</td>
<td>29.8%</td>
<td>11.7%</td>
<td>4.4%</td>
<td>3.3%</td>
</tr>
<tr>
<td>After soaking</td>
<td>29.6%</td>
<td>31.4%</td>
<td>21.6%</td>
<td>10.6%</td>
<td>3.3%</td>
<td>3.5%</td>
</tr>
</tbody>
</table>

* means different multiples