In situ assembly of MnO₂ nanosheets on sulfur-embedded multichannel carbon nanofiber composites as cathodes for lithium-sulfur batteries

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ABSTRACT Rechargeable lithium-sulfur batteries have been regarded as the promising next generation energy storage system due to their overwhelming advantages in energy density. However, their practical implementations are hindered by severe capacity fading and low sulfur utilization, which are caused by polysulfide shuttling and the insulating nature of sulfur. Herein, sulfur-embedded porous multichannel carbon nanofibers coated with MnO₂ nanosheets (CNFs@S/MnO₂) are rationally designed and fabricated as cathode for lithium-sulfur battery. The high conductivity of porous multichannel carbon nanofibers facilitates the kinetics of electron and ion transport in the electrodes, and the porous structure encapsulates and sequesters sulfur in its interior void space to physically retard the dissolution of high-order polysulfides. Moreover, the MnO₂ shell exhibits a combination of physical and chemical adsorption for high-order polysulfides, which could sequester polysulfides leaked from the carbon matrix after long-time charge/discharge cycles, resulting in enhanced cyclic stability. As a result, the electrode delivers a specific capacity of 1286 mA h g⁻¹ at 0.1 C and 728 mA h g⁻¹ at 3 C. And the capacity could remain 774 mA h g⁻¹ after 600 cycles at 1 C.

Keywords: lithium-sulfur battery, carbon nanofibers, MnO₂

INTRODUCTION

Rechargeable lithium-sulfur (Li-S) batteries have been regarded as the promising next generation energy storage system due to their overwhelming advantages in energy density. However, their practical implementations are hindered by severe capacity fading and low sulfur utilization, caused by lithium polysulfides (LiPSs) shuttling and the insulating nature of sulfur. Various methods have been explored to address these issues. One of the main

strategies is to confine the sulfur in a porous conductive framework, resulting in enhanced reactive kinetics and mitigated mobility of the polysulfides. Various allotropes of carbon, including mesoporous/microporous carbons, carbon nanotubes (CNTs), hollow/porous carbon nanofibers (CNFs), hollow/porous carbon spheres [1,2], graphene/graphene oxides (GOs) [3,4], achieve the improved performances. Among the aforementioned carbonaceous matrices, one-dimensional (1D) CNFs have attracted extensive attention due to their unique properties of high aspect ratio and good electrical conductivity, tunable porosities, facile fabrication process and easily scalable production. Ji *et al.* [5] fabricated porous CNF@S composite electrodes *via* electrospinning for Li-S batteries, which delivered a high discharge capacity of 1400 mA h g⁻¹ at 0.05 C. Li and his colleagues [6] designed a pie-structured CNF filled with sulfur as “filling” and amino-functionalized graphene layers as “crust”. The free-standing electrode presented a high specific capacity of 1314 mA h g⁻¹ at 0.1 C with good cycling stability. Nevertheless, nonpolar carbon matrix cannot adsorb LiPSs due to its weak physical interaction with polar LiPSs. Furthermore, the adsorption energies become especially weak when LiPSs evolve to middle-lithiated stages (around Li₂S₄) [7]. In addition, the porous structure offers channels for LiPSs diffusion and shuttling, resulting in further active material loss and capacity fading over long-term cycling. To alleviate the loss of polysulfides, the introduction of polar sites onto carbon planes has been proposed [8,9]. Meanwhile, inorganic metal-dioxides and metal-disulfides including MnO₂ [10], TiO₂ [11], Al₂O₃ [12], SiO₂ [13], NiFe₂O₄ [14], Ba_{0.5}Sr_{0.5}-Co_{0.8}Fe_{0.2}O_{3-δ} [15], TiS₂ [16] and VS₂ [17] have been also applied as hosts for sulfur due to their much stronger

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chemical interactions with LiPSs, which are effective to inhibit LiPS diffusion and thus achieve improved cycling stability [18]. However, the sulfur utilization and rate performance are far from satisfactory due to the intrinsic low conductivity and slow kinetics of these inorganic hosts.

In order to surpass the limitations of single polar materials and nonpolar conductive carbon matrices, rationally designed structures and selected optimizing combination of different materials are expected to exhibit synergic properties and boost the full potential performance through a reinforcement or modification of each individual component. Enlightened by these ideas, researchers have developed various nanostructured composites with enhanced performance based on sulfur, metal oxides and conductive matrices.

For example, Zhang *et al.* [19] used a polypyrrole (PPy)-MnO₂ coaxial nanotubes to encapsulate sulfur as high performance Li-S battery cathode. Compared with pure PPy encapsulated sulfur cathode, the S/PPy-MnO₂ exhibited much enhanced cyclic stability, coulombic efficiency and rate performance. Huang *et al.* [20] reported a graphene/RuO₂/S composite applied for Li-S battery cathode, in which the synergistic effect of RuO₂ and graphene made large improvements in reversibility and rate capability of the composite electrode. Li and co-workers [21] reported MnO₂/GO/CNTs-S composites showed excellent comprehensive performance. However, these synthetic strategies are complicated and cost ineffective, which also hinder their practical application.

Herein, we designed and fabricated 1D nanofiber composites, namely MnO₂ nanosheets coated 1D sulfur-embedded porous multichannel CNFs (CNF@S/MnO₂) as cathodes for Li-S battery *via* a facile single-nozzle co-electrospinning technique and *in-situ* growth of MnO₂ nanosheets on the surface of the carbon/sulfur nanofibers. This design has several obvious advantages: the 1D structure combined with the high conductive carbon matrix facilitates the kinetics of electron and ion transport in the electrodes; the multichannel porous carbon encapsulates and sequesters sulfur in its interior void space and meso/micro-porous walls, which could physically retard the high-order LiPSs dissolved into the electrolyte; the *in-situ* assembled MnO₂ shell exhibits a combination of physical and chemical adsorption for high-order LiPSs, which could sequester LiPSs leaked from the carbon matrix after long-time charge/discharge cycles, resulting in enhanced cyclic stability. Benefiting from these advantages, the prepared CNF@S/MnO₂ composites with unique characteristics are expected to

show excellent electrochemical performance. An optimal percentage of MnO₂, carbon and sulfur in the composite is found to be 21.6%, 13.3% and 63.5%, respectively, which balances the adsorption ability and the conductivity.

EXPERIMENTAL SECTION

Fabrication of CNF@S/MnO₂

Fabrication of porous multichannel CNFs

Polyacrylonitrile (1 g, PAN, $M_w=150,000$, Sigma-Aldrich) and polystyrene (0.5 g, PS, $M_w\sim 280,000$, Aldrich) were dissolved in 10 mL dimethylformamide (DMF, International laboratory USA) at 60°C with vigorous stirring for 1 h, respectively. Then the PS solution was transferred into the PAN solution and stirred overnight at room temperature to form the precursor solution. The precursor solution was electrospun *via* single-nozzle (20 G) with applied voltage of 17 kV, feed rate of 1.5 mL h⁻¹ and tip-to-collector distance of 20 cm. The obtained nanofibers were dried at 60°C for 3 h, stabilized at 220°C for 1.5 h under air atmosphere and calcinated at 800°C for 3 h with a heating rate of 3°C min⁻¹ under argon. Afterwards, a mixture of the obtained multichannel CNF and KOH (*w/w*, 1:5) was heated at 750°C for 1.5 h under Ar. Subsequently, the product was washed by centrifugation with deionized water (DIW) for several times until the centrifuged solution was neutral. Finally, the sample was dried at 60°C for 3 h, and the porous multichannel CNF was obtained.

Fabrication of CNF@S

A mixture of sulfur (Sigma-Aldrich) and the obtained porous multichannel CNF (4:1, *w/w*) was heated at 160°C for 12 h in a sealed vessel under Ar to obtain the CNF@S composite.

In-situ assembly of MnO₂

Typically, 0.12 g of CNF@S composite was dispersed in 40 mL DIW, and then the KMnO₄ solution (0.08 g KMnO₄ in 20 mL DIW) was added into CNF@S suspension slowly with vigorous stirring. After 12 h of stirring at room temperature, the suspension was centrifuged and re-dispersed in water for several times, and dried at 60°C for 3 h. Finally, the CNF@S/MnO₂ composite was obtained.

Structural characterization

The scanning electron microscopy (SEM) images of the

obtained samples were obtained by using a JEOL 6490 instrument, and the transmission electron microscopy (TEM) images were conducted on a JEOL JEM-2010F instrument. The X-ray diffraction (XRD) patterns were collected by using a Rigaku SmartLab diffractometer with Cu K α radiation. Raman spectra were carried out on LabRAM HR 800 spectrometer with a laser wavelength of 514.5 nm. Thermogravimetric analysis (TGA) was conducted by using a Mettler Toledo TGA/DSC3+ instrument under N₂ and air atmosphere at a ramp rate of 10°C min⁻¹, for confirmation of the content of sulfur and MnO₂, respectively.

Cell assembly and electrochemical measurements

Cell assembly

The electrochemical measurements were carried out at room temperature by using 2032 coin-type batteries. The mixture of the obtained material, Ketjen black, and polyvinylidene fluoride (PVDF) at a weight ratio of 8:1:1, was ground with *N*-methyl-2-pyrrolidone (NMP) to form slurry, which was then coated on an aluminum (Al) foil and dried at 60°C for 12 h. The dried film was punched into a disk with a diameter of 14 mm, and then the working electrode was obtained. The sulfur mass loading in the working electrode was about 1.0–1.2 g cm⁻². A metal Li foil disk with a diameter of 16 mm was applied as the counter and reference electrode. The electrolyte was 1 mol L⁻¹ lithium-bis(trifluoromethanesulfonyl)-imide (LiTFSI) with 1% LiNO₃ in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v/v). The amount of electrolyte added for each cell was based on the electrolyte/sulfur ratio of 15 mL g⁻¹. Celgard 2400 film was applied as the separator. The cell was assembled in an Ar-filled glovebox.

Electrochemical measurements

Galvanostatic charge-discharge cycles were performed on a LAND CT2001A battery test system in the potential range of 1.7 to 2.8 V (vs. Li/Li⁺) at different rates from 0.1 to 3 C (1 C = 1672 mA h g⁻¹). The cyclic voltammetry (CV) measurements were carried out on a CHI 660E electrochemical workstation at a scan rate of 0.1 mV s⁻¹ (within 1.7–2.8 V). The electrochemical impedance spectroscopy (EIS) was recorded by using a constant voltage mode with amplitude of 5.0 mV in the frequency range from 100 kHz to 0.01 Hz.

Visible adsorption observation

CNF/MnO₂ was prepared in the same way of CNF@S/

MnO₂ by using CNF. Li₂S₄ solution was prepared by adding 4 mmol (184 mg) of Li₂S and 12 mmol (384 mg) of sulfur in 100 mL DME with vigorous stirring for about 2 h. Then, 0.4 mol L⁻¹ Li₂S₄ solution was diluted into 0.04 mol L⁻¹ by using DME. After that, 8 mg of CNF or CNF/MnO₂ was added into 5 mL of 0.04 mol L⁻¹ Li₂S₄ solution with stirring for 5 min, and then the mixture was statically sustained for 2 h to observe color variation. 5 mL of blank Li₂S₄ solution (0.04 mol L⁻¹) was employed as a contrast.

RESULTS AND DISCUSSION

Formation mechanism of CNF@S/MnO₂

The overall synthesis procedure of CNF@S/MnO₂ is schematically illustrated in Fig. 1. Single-nozzle electrospinning was employed to fabricate the nanofibers. The immiscible polymers (PAN and PS) in DMF formed an emulsion, in which the discontinuous PS droplets were dispersed into the continuous PAN solution. This was verified by the light scattering/refraction (Fig. S1a). The optical microscopy (Fig. S1b) of the blended polymer solution of PAN and PS further confirmed the uniform dispersion of PS droplets in the PAN solution. During the electrospinning process, the PS was stretched into parallel wire within PAN sheath by the electrostatic force (Fig. S1c). Then the obtained PAN/PS nanofibers were stabilized at 220°C in air and calcinated at 800°C under Ar. During the calcination process, the PS completely decomposed into gaseous molecule; whereas the sheath PAN was carbonized to generate multichannel CNFs [6,22,23]. Afterwards, during the KOH activation process,

Figure 1 Schematic illustration of the synthetic process of CNF@S/MnO₂.

the KOH decomposed into K_2O and H_2O under the heating condition under Ar, and then the carbon was consumed by the reaction between carbon and $H_2O/CO_2/K_2O/K_2CO_3$, resulting in micro/mesoporous structures in the multichannel CNFs. The reaction details are shown in Equations (1–7) [24].

The sulfur was loaded in the porous multichannel CNFs by using a molten diffusion method. The α - S_8 firstly formed β - S_8 at 94.4°C, and then the monoclinic crystal β - S_8 started to melt when the temperature went up to 119.6°C. When the temperature further rose to 159.4°C, the ring structure of β - S_8 started to open and form linear polysulfane with diradical chain ends, which delivered a lowest viscosity of liquid sulfur [4,25,26]. The molten sulfur with the lowest viscosity flowed into the channels and pores by capillary forces, resulting in intimate contact with the conductive porous multichannel CNFs.

Finally, the MnO_2 nanosheets *in-situ* assembled on the porous multichannel CNFs through redox reaction between $KMnO_4$ and carbon/sulfur under room temperature, as described in Equations (8 and 9) [27,28]. To optimize the structure and component in the CNF@S/ MnO_2 composite, we altered the addition amounts of $KMnO_4$ precursor from 0.04, 0.08 to 0.12 g under the same conditions described in the experimental section,

and obtained three different kinds of CNF@S/ MnO_2 composites designated as CNF@S/ MnO_2 -1, CNF@S/ MnO_2 -2, CNF@S/ MnO_2 -3, respectively.

Characterizations of the CNF@S/ MnO_2

The TGA was carried out to calculate the content of each component in CNF@S/ MnO_2 -1, CNF@S/ MnO_2 -2 and CNF@S/ MnO_2 -3. As shown in Fig. 2a, the TGA curve of CNF@S composite performed under N_2 flow delivers a significant mass loss of about 79.5% between 100 and 600°C, corresponding to the evaporation of sulfur, and the mass remained responds to the carbon content of about 18% with the weight loss below 100°C attributed to water evaporation. Noticeably, there is a two-stage thermal degradation in the TGA curve of CNF@S composite, which should be ascribed to the distinguished strength of sulfur adsorption to different porous/channel structures. According to the TGA results, the contents of sulfur, carbon and MnO_2 of CNF@S/ MnO_2 -2 can be determined to be 63.5%, 13.3%, 21.6%, respectively. The mass of sulfur and carbon both suffer partial loss after *in situ* assembly of MnO_2 . The contents of sulfur, carbon and MnO_2 in CNF@S/ MnO_2 -1, CNF@S/ MnO_2 -2 and CNF@S/ MnO_2 -3 were calculated based on the TGA results (Fig. S2). As shown in Fig. 2b, as the amount of $KMnO_4$ increased, the sulfur and carbon content decreased from 70% and 15% to 57.6% and 10.2%, respectively while the MnO_2 content increased from 12% to 29.2%.

As shown in Fig. 3a, the pure porous multichannel

Figure 2 (a) TGA curves of CNF@S performed under N_2 , and CNF@S/ MnO_2 -2 performed under N_2 and air, respectively. (b) The content of S, C and MnO_2 in CNF@S, CNF@S/ MnO_2 -1, CNF@S/ MnO_2 -2 and CNF@S/ MnO_2 -3, respectively.

Figure 3 SEM images of porous multichannel CNFs (a, b) and CNF@S/MnO₂-2 (c, d).

CNFs deliver a long continuous nanofiber morphology and relatively uniform diameters ranging from 300 to 500 nm. Obvious hollow channels can be seen from the cross section of CNF shown in the high-magnification SEM image (Fig. 3b), which was generated by the complete decomposition of elongated PS phase and the simultaneous carbonization of the PAN phase. The rugged surface of CNF is regarded as the combinative results of carbon densification and the abrupt small molecular gas evolution of the decomposition of both polymers [29]. As displayed in Fig. 3c, the typical CNF@S/MnO₂-2 nanofibers with granular surface are in sharp contrast to the rugged surface of CNFs, indicating uniformly covering of MnO₂ layers. The high-magnification SEM image of the typical CNF@S/MnO₂-2 (Fig. 3d) further confirms the uniform assembly of MnO₂ nanosheets on CNF@S.

The TEM image of CNF shown in Fig. 4a further confirms the continuous hollow channels are well generated along the axial direction. The mesoporous structure can be clearly observed in Fig. S3, produced by KOH activation. The TEM image of CNF@S/MnO₂-2 (Fig. 4c) reveals that the thin shell layer coated on the CNF@S consists of nanosheets, agreeing well with the SEM observation. A clear interface between CNF@S and the external shell of ~20 nm thickness can be observed in the high magnification TEM image of CNF@S/MnO₂-2 (Fig. 4e). In sharp contrast, the MnO₂ nanosheets of CNF@S/MnO₂-1 are not completely and uniformly covered on the CNF@S (Fig. 4b). However, the CNF@S in CNF@S/MnO₂-3 are totally covered by MnO₂ nanosheets,

Figure 4 TEM images of CNF (a), CNF@S/MnO₂-1 (b), CNF@S/MnO₂-2 (c) and CNF@S/MnO₂-3 (d); HRTEM image (e) and EDX elemental mapping of Mn, O, S and C (f) of CNF@S/MnO₂-2.

and the MnO₂ shell is too thick to observe the clear interface between MnO₂ and CNF@S (Fig. 4d). The high resolution TEM (HRTEM) image of CNF@S/MnO₂-2 (Fig. 4e) further reveals the detailed structure and distinguishes the δ-MnO₂ nanosheet shell from the CNF@S core. The characteristic lattice of 0.70 nm corresponding to the (001) plane of birnessite δ-MnO₂ phase, further confirms the existence of δ-MnO₂. The thickness of the MnO₂ nanosheet is measured to be 3–4 nm, corresponding to 5–6 layers of δ-MnO₂ stacked along the (001) direction. The thin MnO₂ nanosheets offer more projecting part of the surface, which benefits the distribution of surface field intensity, resulting in enhanced polysulfide adsorption capability [30]. The energy dispersive X-ray spectrum (EDX) was performed to uncover the element distribution of the CNF@S/MnO₂-2. The Mn, O, S and C are uniformly distributed along the nanofiber (Fig. 4f). Notably, the signals of Mn and O are overlaying while the distribution widths of S, C and Mn present an ascending order, further confirms the sulfur has been uniformly confined in the CNF host and completely surrounded by MnO₂ sheets. The sulfur distribution scope is slightly smaller than that of carbon, which is attributed to the reaction between the sulfur storage in near-surface of CNF and KMnO₄.

XRD was performed for the evaluation of crystal phase.

As shown in Fig. 5a, the pure CNF presents a broad peak located at about $2\theta = 22^\circ$ and a weak reflection centered at about $2\theta = 44^\circ$, corresponding to the (002) and (100) planes of typical graphitic carbon with limited degree of graphitization [31,32]. The sharp and strong reflection of sublimed sulfur indicates the crystalline state. After encapsulated in the porous multichannel CNF, the sharp diffraction peaks of sulfur were significantly weakened, indicating good dispersion of sulfur particles inside the porous multichannel CNF. Two weak reflections corresponding to (001) and (020) planes of birnessite δ -MnO₂ can be observed in the pattern of CNF@S/MnO₂-2. However, the characteristic peaks of MnO₂ are not very obvious due to the influence of strong sulfur signal. CNF@S/MnO₂ with a higher MnO₂ content was generated by using excess KMnO₄. The CNF@S was incapable of being completely consumed due to the diffusion-controlled characteristics. As shown in Fig. 5b, the XRD pattern of CNF@S/MnO₂ with higher MnO₂ content indicates the existence of birnessite δ -MnO₂ (JCPDS No. 80-1098) and sulfur.

The variation of structural characteristics of porous multichannel CNF, sulfur encapsulated CNF (CNF@S)

and MnO₂ covered sulfur encapsulated CNF (CNF@S/MnO₂-1,2,3) were illustrated by nitrogen adsorption/desorption measurements. As shown in Fig. 5c. The isotherm of CNF presents a typical type-IV (IUPAC 1985) behavior with a H3-type hysteresis loop at relative pressure P/P_0 from 0.45 to 1.0, indicating the existence of narrow channel and meso/macropores, which agrees well with the TEM results [33,34]. The CNF exhibits a high specific surface area of $1402 \text{ m}^2 \text{ g}^{-1}$ calculated based on the Brunauer-Emmett-Teller (BET) equation. After sulfur loading, the specific surface area of CNF@S decreases from 1402 to $20 \text{ m}^2 \text{ g}^{-1}$, indicating the sulfur almost completely penetrates into the porous structure of the CNF during the melt-diffusion process. As the MnO₂ content increases, the specific surface area of CNF@S/MnO₂-1, CNF@S/MnO₂-2 and CNF@S/MnO₂-3 increases from 88, 140 to $186 \text{ m}^2 \text{ g}^{-1}$, respectively. The increased specific surface area might come from the stacking of MnO₂ nanosheets. The pore size distribution of the obtained samples derived by density functional theory (DFT) method is presented in Fig. 5d. For CNF, the pore size peaks centered at ~ 2 and 3 nm are mainly generated by KOH activation and PAN pyrolysis. The peak centered

Figure 5 (a) XRD patterns of sublimed sulfur, CNF, CNF@S and CNF@S/MnO₂-2. (b) XRD pattern of CNF@S/MnO₂ with higher MnO₂ content. Nitrogen adsorption-desorption isotherms (c) and pore size distribution curves (d) of CNF, CNF@S, CNF@S/MnO₂-1, 2 and 3.

at ~ 30 nm corresponds to the inner multichannel structure in the CNF produced by PS decomposition, agreeing with the TEM and SEM results. The rich abundance of hierarchical porous structure and inner multichannel offers a large space for sulfur storage, resulting in a high loading of sulfur. The curve of pore size distribution of the CNF after sulfur loading exhibits no obvious peak, which further verifies that the porous structures are filled with sulfur. The pore size distribution of CNF@S/MnO₂ presents broad peaks ranging from about 3 nm to tens of nanometers. With the MnO₂ content increasing, the sample delivers wider pore size distribution and content, due to the MnO₂ nanosheets stacking.

To investigate the effects of the introduction of MnO₂ nanosheet shell, the CNF@S and CNF@S/MnO₂ composite were assembled into the 2032-coin Li-S battery with a metallic Li counter electrode, respectively. The cyclic performances of CNF@S, CNF@S/MnO₂-1, CNF@S/MnO₂-2 and CNF@S/MnO₂-3 measured at the rate of 1 C are shown in Fig. 6. The initial specific capacities of CNF@S, CNF@S/MnO₂-1, CNF@S/MnO₂-2 and CNF@S/MnO₂-3 were 976, 945, 933 and 919 mA h g⁻¹ calculated based on the mass of sulfur (Fig. 6a), and were 776, 661, 593 and 529 mA h g⁻¹ based on the mass of the composites (Fig. 6b). The residual specific capacities of these four electrodes remained at 560, 659, 774 and 744 mA h g⁻¹ after cycling over 600 cycles based on sulfur, corresponding to capacity retention of 57.37%, 69.73%, 82.95% and 80.95% of their initial capacities, with a fading rate of 0.071%, 0.050%, 0.028% and 0.032% per cycle, respectively. These values indicate that compared with simple physical confinement of polysulfides with porous carbon, the MnO₂ nanosheet shell can more effectively restrain the dissolution of polysulfides, resulting in higher content maintenance of active sulfur. With the MnO₂ content increasing, the fading rate of the four electrodes firstly decreases from 0.071% to 0.028%, then increases to 0.032%. It can be concluded that the CNF@S/MnO₂-2 with 63.5% sulfur, 13.3% carbon, 21.6% MnO₂ is the optimized choice in this work by providing high sulfur utilization and excellent cycling stability. The CNF@S/MnO₂-2 possesses both good conductivity and strong chemisorption of polysulfides, resulting in a synergic advantage. Fig. 6c further compares the initial and 600th cycle's charge-discharge profiles of these four samples. The voltage profiles of all samples deliver two typical sulfur electrode behaviors with two discharge plateaus, which respond to high-order polysulfides and low-order polysulfides reduction, respectively. An intriguing observation is that there are obvious differences in

the voltage hysteresis and length of charge/discharge voltage plateau among the samples, which are related to the redox reaction kinetics and the reversibility of system. The voltage length became shorter as the MnO₂ loading decreased. The polarization potential between the charge and discharge profiles of both 1st and 600th were enlarged with the MnO₂ content increased, and the coulombic efficiency of the initial cycle of the four samples showed an increasing order: CNF@S < CNF@S/MnO₂-1 < CNF@S/MnO₂-2 < CNF@S/MnO₂-3. The initial capacity of four samples delivers a decreasing order: CNF@S > CNF@S/MnO₂-1 > CNF@S/MnO₂-2 > CNF@S/MnO₂-3. After 600 cycles, the coulombic efficiency of each sample is almost 100%. And the discharge plateau shows an obvious decline after 600 cycles. Several reasons could be responsible for this: 1) the MnO₂ content is negatively correlative to the electrical conductivity, but the carbon content shows a positive effect, resulting in higher sulfur utilization and less polarization; 2) the MnO₂ nanosheets coated on the CNF@S surface offer physical entrapment and strong chemical bonding to high-order polysulfides, resulting in efficient prevention of the shuttling effects during the charge-discharge process, which benefits the enhanced coulombic efficiency; 3) the increasing resistance causes enhanced polarization during cycles.

To further investigate the electrochemical performances of the electrodes, the EIS measurements of newly assembled batteries after 12 h at open circuit voltage and tested batteries after 600 discharged/charged cycles were carried out, respectively. Fig. 6d and e show their Nyquist plots. All the Nyquist plots consist of one semicircle at high frequency and one inclined line at low frequency. The semicircular profile at high frequency is attributed to the charge transfer resistance (R_{ct}), originating from the electrochemical reaction at the interface between the electrode and electrolyte. The inclined line represents Warburg impedance, which is associated with semi-infinite diffusion [35]. The corresponding Nyquist profiles were fitted by a widely used equivalent circuit (Fig. S4). The R_{ct} of CNF@S, CNF@S/MnO₂-1, CNF@S/MnO₂-2 and CNF@S/MnO₂-3 for the fresh one is ~ 54.4 , 80, 107.9 to 120.5 Ω , respectively. The increase of R_{ct} for the CNF@S/MnO₂-based electrodes is due to the outside insulating MnO₂ coating when compared with the CNF@S electrode. After 600 cycles, the value of the R_{ct} increases to 128.2, 156.3, 178.8 and 237 Ω , with the increase rate of 136%, 95%, 66% and 97%, respectively. The increase of the R_{ct} might be attributed to the formation of the insulating Li₂S/Li₂S₂ passivation layer on the Li metal surface produced by the reaction between high-order

Figure 6 Cyclic capacities based on sulfur (a) and composite (b); (c) discharge/charge profiles of CNF@S, CNF@S/MnO₂-1, CNF@S/MnO₂-2 and CNF@S/MnO₂-3 for 600 cycles at 1 C; Nyquist plots of CNF@S, CNF@S/MnO₂-1, CNF@S/MnO₂-2 and CNF@S/MnO₂-3 batteries for fresh (d) and 600th cycle (e); (f) advantages of CNF@S/MnO₂ over CNF@S.

polysulfides and the lithium anode, and the aggregation of solid sulfur species on the outer surface of active materials [36]. The polar MnO₂ is beneficial to the interfacial contacts between the soluble sulfur species and the CNF matrix, promoting the uniform deposition of Li₂S/Li₂S₂ and further avoiding the formation of dead active material (Fig. 6f). Among the four samples, CNF@S/MnO₂-2 delivers the lowest R_{ct} increment between the fresh battery and the 600th cycled one. This phenomenon can be

attributed to the fact that when the MnO₂ content is high, the conductivity is not excellent enough to improve the electrochemical performance. Meanwhile, when the MnO₂ content is low, the heterostructure cannot provide enough anchoring capability. The EIS results agree well with the cycling performance.

The rate performance of CNF@S/MnO₂-2 was carried out by increasing the current rate from 0.1 to 3 C every twenty cycles, and then recovering back to 0.1 C. As

Figure 7 (a) Rate performance of CNF@S/MnO₂-2; (b) CV curves of CNF@S/MnO₂-2 at a scan rate of 0.1 mV s⁻¹.

shown in Fig. 7a, the reversible specific capacity is 1286, 1086, 974, 846, 786 and 728 mA h g⁻¹ at 0.1, 0.2, 0.5, 1, 2 and 3 C, respectively. The coulombic efficiencies are almost 100% except for the first two cycles, indicating the shuttle effect owing to polysulfide dissolution can be effectively restrained by the MnO₂ shell. When the current rate suddenly switches back to 0.1 C after undergoing high rates up to 3 C, the CNF@S/MnO₂-2 delivers a reversible capacity of 1040 mA h g⁻¹ (93% of the original capacity), verifying the excellent stability and reliability of CNF@S/MnO₂-2 electrode. The rate performance of CNF@S/MnO₂-2 electrode is much superior to that of previous reported examples having similar “S₈-in-carbon matrix” configurations [37,38].

Fig. 7b presents the CV curves of CNF@S/MnO₂-2 for the first five cycles within the voltage range from 1.7 to 2.8 V at the scan rate of 0.1 mV s⁻¹. Two cathodic peaks and one anodic peak can be observed in all the CV curves. The cathodic peak at ~ 2.23 V is attributed to the reduction of S₈ to long chain lithium polysulfides (Li₂S_x, 4 ≤ x ≤ 8), which can dissolve in electrolyte and cause shuttling effects. The following cathodic peak at about 2.04 V is related to the further reduction of the high-order polysulfides to Li₂S₂ and Li₂S, thus producing Li₂S₂ and Li₂S precipitation on the cathode surface and forming an insulating layer [25]. The two expected anodic peaks overlap and form an anodic peak located at ~2.40 V. The anodic peak is attributed to the transformation of Li₂S and Li₂S₂ to Li₂S₈ and eventually to elemental sulfur. The overlap has been observed in many carbon/S composite cathodes reported previously, which might be attributed to the fast reaction kinetics of oxidation of polysulfides to sulfur [39,40]. The reduction peaks in the second cathodic scan shift to higher potential side relative to these in the first scan, which could be attributed to the electrode activation process [41]. The last fourth CV curves are almost overlapped, suggesting relatively high stability,

which benefits from the MnO₂ nanosheet shell offering chemical and physical adsorption of long chain polysulfides.

To further verify the strong adsorption ability of MnO₂ towards high-order polysulfides, the visible adsorption observation experiment was performed. 8 mg of CNF and CNF/MnO₂ were added into 5 mL of 0.04 mol L⁻¹ Li₂S₄ solution separately. As presented in Fig. S5, the color of the solution containing the CNF/MnO₂ composite changed from yellow to nearly colorless, indicating the MnO₂ nanosheets possess strong chemical adsorption towards polysulfides. The CNF solution's color became shallow compared with the blank Li₂S₄ solution, suggesting the CNF with large porous structure possesses adsorption ability to polysulfides. The above results confirm the CNF@S/MnO₂ composite has strong adsorption capability for high-order polysulfides, which is beneficial to enhancing the electrochemical performance.

CONCLUSIONS

In summary, we have designed and prepared nanosheet MnO₂ coated multiple-channel CNF filled with sulfur composites. The multiple-channel CNF is available by facile single-nozzle electrospinning, and the outer coated MnO₂ nanosheets are simply produced by *in situ* redox reaction between sulfur/carbon and KMnO₄ under ambient conditions. The novel structure with optimized ratio of MnO₂, carbon, sulfur (21.6%, 13.3% and 63.5%), which balances the long-chain polysulfides adsorption ability and the electronic conductivity, endows the electrode based on CNF@S/MnO₂-2 with high electrochemical performance.

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Supplementary information Supporting data are available in the online version of the paper.

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自组装二氧化锰纳米片包覆嵌硫多通道碳纳米纤维复合物在锂硫电池阴极中的应用

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摘要 由于可充电锂硫电池在能量密度方面具有显著的优势, 因此被认为是很有前途的下一代储能体系。然而, 多硫化物的穿梭和硫的绝缘特性, 导致了锂硫电池严重的容量衰减和低硫利用率, 阻碍了它们的实际应用。因此, 本研究合理设计制备了一种二氧化锰纳米片包覆嵌硫多通道碳纳米纤维复合物用于锂硫电池阴极。多孔多通道碳纳米纤维的高导电性促进了电极中电子和离子的传输动力学, 多孔结构将硫包裹并隔离在其内部空隙中, 在物理上延缓了高阶多硫化物的溶解。此外, 二氧化锰壳层对高阶多硫化物的物理限制和化学吸附相结合, 可以隔离长时间充放电循环后从碳基体中泄漏的多硫化物, 从而进一步提高电极的电化学性能。