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# Preparation of mesohollow and microporous carbon nanofiber and its application in cathode material for lithium–sulfur batteries



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Yuanhe Wu, Mingxia Gao\*, Xiang Li, Yongfeng Liu, Hongge Pan\*

State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province & Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

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## ABSTRACT

Mesohollow and microporous carbon nanofibers (MhMpCFs) were prepared by a coaxial electrospinning with polyacrylonitrile (PAN) and polymethylmethacrylate (PMMA) as outer and inner spinning solutions followed by a carbonization. The carbon fibers were thermal treated with sublimed sulfur to form S/MhMpCFs composite, which was used as cathode material for lithium–sulfur batteries. Electrochemical study shows that the S/MhMpCFs cathode material provides a maximum capacity of 815 mA h/g after several cycles of activation, and the capacity retains 715 mA h/g after 70 cycles, corresponding to a retention of 88%. The electrochemical property of the S/MhMpCFs composite is much superior than the S-incorporated solid carbon fibers prepared from electrospinning of single PAN. The mechanism of the enhanced electrochemical property of the S/MhMpCFs composite is discussed.

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## 1. Introduction

With the development of high-performance portable electric devices, electric vehicles and battery energy-storage systems, secondary batteries with high-energy density and high-power density are considerably important. In terms of specific energy, lithiumsulfur (Li-S) batteries are promising. Li-S batteries provide a theoretical specific energy of 2567 W h/kg, which is much higher than 387 W h/kg of today's commercial LiCoO<sub>2</sub>/C lithium-ion batteries (LIBs) [1]. As the cathode material of Li–S batteries, sulfur has a theoretical specific capacity of 1675 mA h/g and an energy density of 2600 W h/kg, assuming that sulfur is fully reduced to Li<sub>2</sub>S [2,3]. Furthermore, sulfur has other advantages, such as low cost, natural abundance, and environmental friendliness [4]. Therefore, Li-S batteries show great potential for the next generation secondary lithium batteries and have been drawn much attention in recent years. However, Li-S batteries also suffer from several problems [5–8]. First, sulfur is electrically and ionically insulating, leading to poor electrochemical accessibility and low utilization of sulfur in the electrode, so it cannot serve as cathode solely. Second, the reduction products of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> are insulating. They precipitate on the electrode surface and thus increase consequentially the internal resistance of the battery. Third, the high solubility of

http://dx.doi.org/10.1016/j.jallcom.2014.04.073 0925-8388/© 2014 Elsevier B.V. All rights reserved. the intermediate products of lithium polysulfides  $(\text{Li}_2S_n, 4 \le n < 8)$  in the organic electrolyte lowers the utilization of sulfur and hence results in poor cycle performance of the batteries.

The main approaches to overcome the insulation of S focus on introducing electrical conductive polymers, such as polyaniline [9,10], polypyrrole [11,12] and polythiophene [13], carbonaceous materials, such as carbon nanotubes [14-16], porous carbon [17–19], carbon spheres [20] and grapheme [21], and the combination of electrical conductive polymers and carbonaceous materials [22–24]. In addition to promote the electrical conductivity of the S cathode, many of the above approaches also provide simultaneously a secondary action in improving the adsorption or store of sulfur by using porous electrical conductive matrices [17–19] to alleviate the dissolution of the intermediate polysulfides during cycling. Pore-structured electrical conductive matrices are appropriate in improving both the rate and capacity retention performances of the sulfur electrodes [25–27]. Previous investigations suggested that the ideal porous structure of a matrix for sulfur loading should be a hierarchical one consisting of properly distributed meso- and micro-pores [27-29]. Micropores act as the host of the impregnated sulfur and prevent the dissolution of polysulfides while the mesopores construct paths for electrolyte and make it easy for the sulfur to enter the deep pores. Furthermore, high specific surface area of the electrical conductive matrices is also important in increasing the utilization of S cathode, as it offers more sites for the deposition of the insulating lithiation products of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> [30]. In addition, mesoporous metal-organic frameworks



<sup>\*</sup> Corresponding authors. Tel./fax: +86 571 87952615. *E-mail addresses:* gaomx@zju.edu.cn (M. Gao), hgpan@zju.edu.cn (H. Pan).

have also been investigated as host materials for S cathodes and showed favorable electrochemical properties [31,32].

Electrospinning is an effective method to prepare conductive carbon nanofibers, which have also been investigated in anode materials [33–38] and cathode materials [39] for LIBs, Li–S batteries [40]. Polyacrylonitrile (PAN) electrospinning fibers can be readily carbonized to form carbon nanofibers [37,41]. Compared with particle materials, one-dimensional carbon nanofiber material possesses commonly higher electrical conductivity. In addition, carbon nanofibers have fine mechanical strength, which is also supposed to have good resistance for the volume change of the combined active materials during lithium insertion and extraction. Polymethylmethacrylate (PMMA) can produce volatile degradation products and creating micropores in the carbonization process of PAN while it is incorporated with PAN [40].

In the present study, PAN and PMMA were used as outer and inner spinning solutions to prepare mesohollow and microporous carbon nanofibers via a coaxial electrospinning method followed by a carbonization. It was found that PMMA was eliminated during the carbonization process of PAN and created mesohollows and micropores in the carbon fibers. With further introducing S by thermal treatment, the composite of S/mesohollow and microporous carbon nanofibers (S/MhMpCFs) shows superior electrochemical property as cathode material for Li–S batteries, which is much better than that of the composite of S-incorporated solid carbon nanofibers prepared from electrospinning of single PAN. The synthesis method of the MhMpCFs is facile, which is considered helpful in providing new hierarchically porous carbon matrix for highperformance S cathode for Li–S batteries.

#### 2. Experimental

PAN (Sigma–Aldrich) and PMMA (Aladdin) were respectively dissolved in N, N-dimethylformamide (DMF, Aldrich) by stirring at 80 °C for 24 h in concentrations of 8 and 16 wt.%, which were used as the outer and inner solutions for coaxial electrospinning. The outer and inner diameters of the nozzle were 1.2 and 0.4 mm, respectively. The work distance was 15 cm, and the work voltage was 16.8 kV. The feed rates of the outer and inner solutions were 1.0 and 0.5 mL/h, respectively. The obtained fibrous webs were collected by a Ni foil and were removed every 10 h.

The fibrous webs were stabilized by a thermal treatment in an air atmosphere oven at 250 °C for 1 h with a heating rate of 5 °C/min in order to convert PAN from thermo plastic to non-plastic compound, which is critical to obtain dimensional stability and, hence, a fibrous morphology [20]. The stabilized fibrous webs were subsequently carbonized at 900 °C for 1 h with a heating of 5 °C/min in a nitrogen atmosphere furnace, forming MhMpCFs with the elimination of PMMA. A guartz crucible was used as the holder for the stabilization and carbonization. The carbonized fibrous webs were ground by mortar and pestle. Therefore, the fibrous webs were broken, forming carbon fibers with open terminals, which are readily for immersion of S. Sublimed S (Aladdin, 99%) was incorporated to the carbon nanofibers by heating the mixture of S and the carbon fibers at 155 °C for 24 h in a sealed container, which was assembled in an Ar-filled glove box (Labstar, Braun, Germany). The obtained S/carbon fiber composite was taken out after the container was cooled to room temperature. A S to carbon fiber weight ratio of 3:2 was used. Schematic illustration of the synthesis processes of the S/MhMpCFs composite is shown in Scheme 1.

The morphologies of the as-spun webs, ground carbonized fibers and S/carbon fiber composite were observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The crystal structure of the samples was analyzed by X-ray diffraction (XRD, X'Pert PRO, PANalytical, Nederland). The pore volume, pore size distribution and specific surface area of the carbon fibers and the S/carbon fiber composites were analyzed by a N<sub>2</sub> sorption analyzer (NOVA 1000e, USA) at 77 K combining the Brunauer Emmett Teller (BET) method. Raman measurement of the carbon fibers was performed on a confocal Mirco-Raman spectrometer (inVia-Reflex, Renishaw plc) with a 514 nm wavelength incident laser light. The S loaded in the S/carbon fiber composite was characterized by thermogravimetric measurement (TG, NETZSCH QMS 403C, Germany).

Electrochemical testing of the S/MhMpCFs composite was carried out by using coin cells of CR2025 type with Li foil as anode and counter electrode. The cathode was prepared by coating the slurry of the S/MhMpCFs composite, acetylene black (AB) conductive additive and polyvinylidene fluoride (PVDF) binder in a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP) on an aluminum foil and followed by a heating at 60 °C in vacuum for 24 h. The loading of the active material of 5/ MhMpCFs composite in the electrode was ca. 1.8 mg/cm<sup>2</sup>. Cells were assembled

in the glove box (Labstar) with a porous polyethylene sheet (Celgard 2400, Celgard) as separator, and a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 by volume) with 2 wt% LiNO<sub>3</sub> addition as electrolyte. The electrochemical properties of the S/MhMpCFs composite cathode was tested by galvanostatic discharge (delithiation) and charge (lithiation) in a potential range of 1.5–3.0 V (vs. Li<sup>+</sup>/Li) at a current density of 0.1 C (1 C = 1675 mA/g). Cyclic voltammetry (CV) measurement was conducted in a potential range of 1.5–3.0 V (vs. Li<sup>+</sup>/Li) at a scanning rate of 0.1 mV/s for first 3 cycles by using an electrochemical workstation (MATAT, Arbin Instrument, USA). Electrochemical impedance spectrum (EIS) measurements were performed using a frequency response analyzer (Solartron) in a frequency range of 100 kHz to 0.01 Hz and a potentiostatic signal amplitude of 5 mV. Prior to the EIS measurement, the cell was activated by three cycles at 0.1 C between 1.5–3.0 V vs. Li<sup>+</sup>/Li. All of the electrochemical tests were performed at 25  $\pm$  1 °C.

For comparison, uniaxial electrospinning by using only the PAN solution was used to prepare solid carbon nanofibers, which were further incorporated with S in a same weight ratio as the porous ones as cathode material for Li–S batteries. Parallel analyses on the structure and electrochemical properties of the S/solid carbon nanofibers (S/SCFs) were also performed.

#### 3. Results and discussion

## 3.1. Structural characterization

Fig. 1 shows the SEM micrographs of the as-spun webs of PAN/ PMMA. It is seen that continuous fibrous webs with smooth surface and almost even diameters of 0.8-1 µm form by electrospinning. The morphology of the carbonized webs (at 900 °C for 1 h) after grinding is shown in Fig. 2a. It shows that hollow fibers with outer-diameter in the range of 200-300 nm form. The length of the fibers is in an order of several micrometers, which is not even, due to the uncontrollable grinding. Comparison of Figs. 1 and 2a show that the diameters of the fibers are much smaller that of the organic webs, indicating that the fibers were condensed after carbonization. The PMMA in the core of the as-spun webs was decomposed to gaseous products and eliminated during the carbonization process, leaving the hollow cores in the fibers. The diameter of the hollows is not even. It is in the range of 30-60 nm as seen from Fig. 2a. Fig. 2b shows the morphology of the as-ground fibers prepared from carbonizing single PAN spinning. The fibers show solid structure with no hollow observed as expected. The diameter of the fibers is in the range of 300-400 nm, slightly larger than that of the hollow ones, which is supposed due to the less shrinkage during carbonization without the addition of PMMA.

Micropores cannot be observed under SEM for either type of the carbon fibers. However, N<sub>2</sub> adsorption isotherm measurement and the obtained pore size distribution of the two types carbonized fibers, which are shown in Fig. 3a and b, respectively, demonstrate that that there are numerous micropores in diameters around 6-8 nm in the hollow fibers, whereas there are limited micropores in the solid fibers. It was reported that PMMA decomposed without carbon residue during the carbonization of PAN [41]. It is supposed that the small molecule gaseous products from the decomposition of PMMA penetrate through the fiber wall, leaving the extra micropores in the hollow carbon fibers. The pore volume of the hollow fibers is detected to be  $0.18 \text{ cm}^3/\text{g}$ , and that of the solid fibers is only  $0.09 \text{ cm}^3/\text{g}$ . As the diameters of the hollows are in the range of 30-60 nm (Fig. 2a), which are much larger than the detected micropore sizes of 6-8 nm (Fig. 3b), it is noted that the volume of the hollows is not involved in the detected pore volume for the hollow fibers. The specific surface area of the hollow fibers calculated by the BET method is 443  $m^2/g$ , whereas that of the solid ones is only 215  $m^2/g$ .

XRD analysis of the carbonized hollow and solid fibers shows that there is only a hump at diffraction angle  $2\theta$  around  $23^{\circ}$  in their patterns, corresponding to the general disordered stacking carbon. The hollow and solid fibers show no intrinsic difference in their XRD patterns. The pattern of the porous fibers is representatively



Scheme 1. Schematic illustration of the synthesis processes of the S/MhMpCFs composite: (a) electrostatic spinning process; (b) as-spun fiber of PAN/PAMMA; (c) carbonized mesohollow and microporous nanofiber; (d) S incorporated hierarchically porous carbon nanofiber composite.

shown in Fig. 4. Further Raman spectra measurement of the carbonized fibers showed that there were typical D band around 1360 cm<sup>-1</sup> for disordered carbon and G band around 1590 cm<sup>-1</sup> for graphene (the spectra were omitted here), confirming the formation of carbon fibers.

The SEM morphologies of the hollow and solid fibers incorporated with S are shown in Fig. 2c and d, respectively. As seen from Fig. 2c, considerable hollow carbon fibers were almost fully filled with S after the thermal treatment. Nevertheless, hollows still exist in many fibers. However, the diameters of the residual hollows are evidently reduced compared with the original ones. The inset in Fig. 2c is a magnified image of the rectangular area, showing clearly the dense S-incorporated fibers and the residual hollow in some other fibers. Due to the high capillary force of the molten S in the mesohollows, considerable amount of S fills in the hollows. In addition, some of the S-incorporated fibers shows undulating surface, which are much clearly seen in the inset in Fig. 2c. Such imbricate coating is suggested to be the S coating. Meanwhile, considerable fibers show relatively smooth surface. However, the relatively smooth surface does not mean there is no S coating. It is also probably that the coating is much even. Moreover, congregated S in between the carbon fibers, as marked by the solid arrows in Fig. 2c, is also found in the S/MhMpCFs composite. There is residual S incorporated outside the carbon fibers, which means that S is sufficient for the hollows and pores. Hollows could not be fully filled with S in the case that the loaded S was sufficient was also found in a S/tubular polypyrrole system [42]. For the solid carbon fibers permeated with S (S/SCFs), SEM observation shows that there is more amount of congregated S in between the carbon fibers. As seen in Fig. 2d, some of the carbon fibers are bundled together by the congregated S.

The specific surface area of the S/MhMpCFs composite calculated by the BET method is only  $6.0 \text{ m}^2/\text{g}$ , which is decreased by nearly two orders compared with the pristine hollow and porous fibers (443 m<sup>2</sup>/g). The calculated residual pore volume of the S/ MhMpCFs composite is only  $0.02 \text{ cm}^3/\text{g}$ , which is also evidently lower than that of  $0.18 \text{ cm}^3/\text{g}$  for the pristine hollow fibers. The results demonstrate that most of the micropores are filled with S. The capillary force of the molten S in the micropores is extremely high. The specific surface area of the S/SCFs composite is  $1.1 \text{ m}^2/\text{g}$ , which is also greatly reduced compared with that of the pristine solid fibers ( $215 \text{ m}^2/\text{g}$ ). However, the value is much smaller than that of the S/MhMpCFs composite, as there are still residual hollows in the S-incorporated hollow carbon fibers. In addition, the residual pore volume in the S/SCFs composite can almost be ignored (Fig. 3a). Both the decreased specific surface area and the residual pore volume of the S/SCFs composite indicate that S also fills mostly in the micropores of the solid carbon fibers. However, as the limited total volume of the micropores, considerable amount of S incorporated in between the carbon fibers and bundled the carbon fibers, which also led to the low specific surface area of the composite.

Fig. 5 is the TG curves of the S/MhMpCFs and S/SCFs composites as well as the individual S. As seen from Fig. 5, the content of S incorporated in either the S/MhMpCFs composite or S/SCFs composite is almost 60 wt.%, which is identical to the amount set in their original mixtures. However, further seen from Fig. 5, though the visible weight loss of the individual S and the S in the composites takes place at an almost same temperature of ca. 200 °C, the sublimation process of the S in the S/MhMpCFs composite is very different from either of the individual S or the S in the S/SCFs composite. The sublimation temperature of the S in the S/SCFs composite is only slightly higher than that of the individual S, and the sublimation completes at 328 °C, which is almost the same as that of the individual S. However, the S in the S/ MhMpCFs composite shows a much lower sublimation rate, and the sublimation completes at a much higher temperature of 469 °C. The much difficulty of the sublimation of the S in the S/ MhMpCFs composite is due to the strong adsorption force between the S confined in the mesohollows/micropores and the carbon matrix.

Based on the density of sulfur (2.07 g/cm<sup>3</sup>) and the pore volume of the hollow fibers  $(0.18 \text{ cm}^3/\text{g})$ , it can be estimated that there is ca. 25 wt.% of the incorporated S able to immerse in the micropores of the hollow carbon fibers. Partial sulfur is filled in the hollow cores and the other is coated on the fiber surface and exists as conglomerations in between the carbon fibers. Further seen from Fig. 5, the TG curves of the whole sublimation processes of the S/MhMpCFs composite and the individual S are almost fully separate. There is no evidently overlapped part, even at the beginning of the sublimation. This phenomenon suggests that the S coated on the outer surface of the hollow fibers also shows lower sublimation rate than the individual S. The strong absorption derived from the porous structure is also effective for the surface coated S. For the solid carbon fibers, as the much less pore volume and there is no hollow in the fibers, the incorporated S exists mostly as conglomerations in between the carbon fibers (Fig. 2d) and is coated on the surface of the fibers in addition to the limited trapping in the micropores. That is also the reason for the similar sublimation characteristics with the individual S. The slightly



Fig. 1. SEM image of the as-spun webs of PAN/PMMA.

higher onset sublimation temperature of the S/SCFs composite than that of the individual S as shown in Fig. 5 is attributed to the few amount of S trapped in the micropores of the solid carbon fibers. In addition, the TG curves of the S/MhMpCFs and S/SCFs composites are almost fully separate without visible overlap, which also indicates that the congregated S in between the carbon fibers in the former is much less that in the latter.

XRD patterns of the S/MhMpCFs and S/SCFs composites are also shown in Fig. 4. For comparison, the pattern of the pristine S is also shown. All the diffraction peaks in the composites correspond to orthorhombic S (JCPDS#08-0247). There is only S, no other impurity, detected. It was reported that the S confined in micropores in nanosize showed no evident diffraction peaks due to their amorphous or nanocrystalline feature [29,43]. The presence of the diffraction peaks of crystalline S in the S/MhMpCFs composite is attributed to the S filled in the hollow cores and the S incorporated outside the carbon fibers, including both coated on the surface of the fibers and congregated in between the fibers. In addition, it is certain that the S in the S/SCFs composite shows crystal structure as it exists mostly on the outer surface of the carbon fibers and as conglomerations in between the carbon fibers. The main crystalline facet indexes of S are marked in the patterns of the composites and pristine S. The lattice parameters and cell volume of the S in both composites and the pristine S were calculated from the XRD data and are listed in Table 1. It is seen that the values of the S in the two composite are very close, whereas they are slightly lower than those of the pristine S. It seems that with the incorporation with the carbon fibers, the lattice parameter of the S is slightly reduced.

#### 3.2. Electrochemical properties

Fig. 6 shows the cycle performance of the S/MhMpCFs as well as the S/SCFs composite cathodes. As seen from Fig. 6, the first discharge capacity of the S/MhMpCFs composite is only 640 mA h/g, which is much lower than 940 mA h/g of the S/SCFs composite. However, the capacity of the S/MhMpCFs composite increases continuously in the subsequent cycles up to 6 cycles, reaching a maximum value of 815 mA h/g. Thereafter, the S/MhMpCFs composite shows considerable stable cycling stability, and the capacity remains 715 mA h/g after 70 cycles, corresponding to a capacity retention of 88% with respect to the maximum capacity. Meanwhile, the S/SCFs composite shows continuous drop in the capacity with cycling, and the capacity drops to 730 mA h/g at the 6th cycle. The capacity is only 428 mA h/g after 70 cycles, corresponding to a capacity retention of only 47%. Activation in initial several cycles was also found in S/acetylene black cathodes with and without CNF (carbon nanofiber) addition using PEO (polyethylene oxide) as binder [44]. Activation up to 20 cycles was also reported in a S-polypyrrole/graphene multi-composite cathode [23]. Activation was considered due to the slow penetration and transportation of solvated electrolyte and lithium ions in the electrodes. In the present study, the incomplete utilization of sulfur in the S/MhMpCFs composite cathode in the initial several cycles is also due to that the electrolyte cannot fully penetrate into the micropores and mesohollows, and contact sulfur effectively. However, the condition was solved after several cycles.

The superior cycling performance of the S/MhMpCFs composite is attributed to the low dissolution of the soluble intermediates of polysulfides generated from the S encapsulated in the micropores and meshollows in the electrolyte. The mobility of the electrolyte in the mesohollows and the micropores is low, therefore, the dissolved polysulfides are readily to reach a high concentration in the electrolyte, which reduce the dissolution rate and lead to a high utilization of the active materials. Moreover, the residual hollows provide more channels for the transportations of electrolyte and lithium ions, which also favor the utilization of the sulfur either incorporated in the hollows or trapped in the micropores. Whereas for the S/SCFs composite, the loaded S exists mostly on the surface of the fibers and congregates in between the fibers, which exposes in the electrolyte without defense. The dissolution of the soluble intermediate polysulfides during cycling is severe, resulting severe mass loss of the active materials. A capacity retention of 92% for 20 cycles at 0.1 C was reported for carbon nanofibers with single microporous structure prepared from carbonization of PAN and incorporated with 42 wt.% S [40]. The present S/MhMpCFs composite with 60 wt.% S provides a capacity retention of 88% for 70 cycles at 0.1 C. The average retention for per cycle is higher than that reported in the literature. The capacity and capacity retention of the present S/MhMpCFs composite are also higher than those of the composite of non-porous tubular polypyrrole (T-PPy) fibers incorporated with 30 wt.% S [42]. It demonstrates that the combination of mesohollows and micropores in the carbon fibers is much effective in improving the electrochemical performance of the S cathode compared with either single microporous structure or single hollow structure.

Fig. 7a and b depicts the discharge/charge profiles of selected cycles of the S/MhMpCFs and S/SCFs composites, respectively. As a general look from Fig. 7a and b, there are two plateaus in the discharge curves for both composites, indicating a two-step reaction. Generally, the first discharge plateau in the comparatively higher potential range corresponds to the conversion of S (in the first cycle) or high-order polysulfides (e.g.  $Li_2S_8$ , in the subsequent cycles) to low-order polysulfides ( $Li_2S_n$ ,  $4 \le n < 8$ ). The second discharge plateau in the comparatively lower potential range corresponds to the low-order polysulfides to lithium sulfides ( $Li_2S_2$ ) [41,43,45].

As seen from Fig. 7a, the two plateaus in the first discharge process of the S/MhMpCFs composite are all considerably lower than those in the subsequent cycles up to 70 cycles, which is attributed to the large polarization caused by the insufficient penetration of electrolyte in the composite in the first cycle. Both plateaus rise to higher potential ranges in the second discharge, indicating an improved lithium reaction kinetics, due to the improved penetration of electrolyte in the composite and also probably the change in structure of the active materials, such as from S<sub>8</sub> to high-order polysulfides (e.g.  $Li_2S_8$ ) [43]. Further seen from Fig. 7a, the discharge capacities generated from the first plateau (in the comparatively higher potential range) increases from ca. 230 mA h/g at the first cycle to the maximum value of ca. 270 mA h/g at the 6th cycle due to the activation. Thereafter, the capacity decreases with



Fig. 2. SEM images of the carbonized fibers from PAN/PMMA (a), carbonized fibers from single PAN (b), S/MhMpCFs (c) and S/SCFs (d) composites.



Fig. 3. N2 adsorption isotherms (a) and pore size distribution (b) of the hollow and solid carbonized fibers and their composites with S.



**Fig. 4.** XRD patterns of the hollow carbon fibers, the S/MhMpCFs and S/SCFs composites as well as pristine S.

cycling and to a value of ca. 220 mA h/g at the 70th cycle. Whereas for the S/SCFs composite, the capacity generated from the first discharge plateau decreases in a large extent from ca. 300 to 150 mA h/g from the first cycle to the 70th cycle. This result indicates that the reversibility of the conversion reaction of S<sub>8</sub>/highorder polysulfides to low-order  $\text{Li}_2S_n$  (4  $\leq n < 8$ ) of the S/MhMpCFs composite is much higher than that of the S/SCFs composite, confirming a less loss of the active material during cycling for the former. In addition, the length of the second plateau (in the comparatively lower potential range) of the S/MhMpCFs composite also extends to a maximum value, and the plateau seems to be the flattest at the 6th cycle. It is noted that each plateau generates the maximum capacity at the 6th cycles, and results in totally the maximum capacity of the composite. Thereafter, either the length or the plateau potentials decrease continuously with the cycling, corresponding to a decreasing capacity and an increasing polarization. Moreover, the discharge plateau in the low potential range is



Fig. 5. TG curves of the S/MhMpCFs and S/SCFs composites as well as individual S.

 Table 1

 Lattice parameter and cell volume of the S in the composites and pristine S.

Samples	Lattice parameters (Å)			Cell volume (Å <sup>3</sup> )
	а	b	с	
S/MpMhCFs	10.46	12.86	24.47	3291.40
S/SCFS Pristine S	10.47	12.87	24.53 24.65	3306.13 3352.74



Fig. 6. Cycling performance of the S/MhMpCFs and S/SCFs composites.

always much longer than the one in the high potential range. The conversion reaction from the low-order polysulfides to lithium sulfides represents the major discharge capacity of composite, as the common Li–S batteries.

The charge process is associated with the reversible conversion of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> to low-order polysulfides and then to high-order polysulfides. The two-step conversion feature is not evident in the initial several cycles for the S/MhMpCFs composite. The high overlap of the plateaus for the different conversion reactions is probably due to the high overvoltage for the conversion of Li<sub>2</sub>S/ Li<sub>2</sub>S<sub>2</sub> to Li polysulfides [46]. However, two-plateau feature becomes visible after initial several cycles and tends to be much evident with the further cycling. In addition, lithium extraction from the active material on the outer surface of the fibers is much easier than from that confined in the micropores and mesohollows of the fibers. With the preferred dissolution of the polysulfides incorporated on the outer surface of the fibers, the amount of the active material incorporated on the surface of the fibers reduced. The much visibly raised plateau in the comparatively higher potential range as seen in Fig. 7a, which corresponds to the conversion reaction of low-order polysulfides to high-order polysulfides, is associated with the much difficulty for the extraction of lithium from the polysulfides confined in the micropores and mesohollows, i.e., associated with an increased polarization. Whereas the plateau corresponding to the conversion reaction of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> to low-order polysulfides shows only very limited rise in the potential during cycling, corresponding to a less deterioration in polarization. In addition, the conversion of the loworder polysulfides to high-order polysulfides generates the major charge capacity as seen also from Fig. 7a.

For the S/SCFs composite, as seen from Fig. 7b, there are two plateaus with limited flat range in the first discharge. The discharge plateau corresponding to the conversion reaction of S<sub>8</sub>/high-order polysulfides to low-order Li<sub>2</sub>S<sub>n</sub> ( $4 \le n < 8$ ) rises in a very early stage of the reaction upon cycling, i.e., rise occurs only in a very high potential range, thereafter the plateau drops and to larger extent with cycling, indicating an increasing polarization. Whereas, the plateau corresponding to the conversion reaction of low-order polysulfides to Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> shows evidently raised flat feature in the subsequent cycles, and the plateau potential is almost not changed with cycling, indicating a facile lithium insertion. However, the length of the plateau is evidently shortened with cycling, indicating a rapid loss of the active material and thus a rapid decrease in capacity. For the charge process, there is only one flat plateau observed, and the plateaus are highly overlapped, indicating that the lithium extraction takes place in an almost same potential upon cycling.



Fig. 7. Voltage profiles of selected cycles of the S/MhMpCFs (a) and S/SCFs (b) composites.

The polysulfides in the S/MhMpCF composite suffer from less dissolution in the electrolyte due to the confinement, which improves the utilization of the active materials. In addition, the strong interaction between the active materials encapsulated in the micropores/mesohollows and the carbon matrix are all beneficial in improving the electron contact of the active materials, which are also favorable to the electrochemical property of the S/MhMpCFs composite. The residual hollows in the S-incorporated hollow fibers enhance the penetration of the electrolyte to the active materials incorporated in the inner wall of the fibers, favoring the mobility of lithium ions for the electrochemical reaction, and provide rooms for alleviating the volume change of the active materials during cycling. As a result, the S/MhMpCFs composite shows favorable capacity and cycling stability as cathode material for Li-S batteries. Further more, it is considered that there is also room for adjusting the micropore size and pore volume of the porous carbon fibers by adjusting the fraction of PAN and PMMA used for the electrospinning to improve the overall electrochemical property of S/MhMpCFs composite in the future study. Increasing the operating voltage of the S cathode is important for practical applications. Though the operating voltage for S cathode is intrinsically low, exploring approaches to achieve comparatively high operating voltage is still possible. Introducing high conductive matrix to improve the electrical contact of the S active materials is demonstrated effective in improving the discharge potential (vs. Li<sup>+</sup>/Li) [47,48]. Application of suitable electrolyte to reduce polarization is also important to achieve comparatively high discharge potential [49].

Fig. 8a and b shows the CV curves of the S/MhMpCFs and S/SCFs composites of the first three cycles at a scanning rate of 0.1 mV/s. Both composites show two cathodic peaks corresponding to the typical two-step conversion reactions [18,50]. The one centered around 2.3 V corresponds to the transformation of S<sub>8</sub> to  $Li_2S_n$  (4  $\leq n < 8$ ), and the other centered around 2.0 V corresponds the further reduction of  $\text{Li}_2S_n$  (4  $\leq n < 8$ ) to  $\text{Li}_2S/\text{Li}_2S_2$ . In addition, the cathodic peak positions of the S/MhMpCFs composite are slightly lower than those of the S/SCFs composite, as shown in Fig. 8, indicating slightly lower reaction kinetics for the former. There are two partially overlapped anodic peaks in the S/MhMpCFs composite. The main one is centered at ca. 2.42 V (vs. Li<sup>+</sup>/Li), and the minor one is centered at a slightly lower value of 2.39 V, which correspond to the conversions of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> to low-order polysulfides and the low-order polysulfides to highorder polysulfides, respectively. The partially overlapped anodic peak feature is also consistent with the phenomenon that the two charge plateaus show very close potentials in the charge curves, especially for the initial several cycles (Fig. 7a). However, it is noteworthy that the CV analysis is generally effective in characterizing the step-feature of the redox reactions of the electrode. Two overlapped anodic peaks for S cathode were also reported in previous literature [51]. Moreover, it seems that there is only one anodic peak centered at ca. 2.40 V in the anodic process of the S/SCFs composite, which is also well consistent with the one flat charge plateau in the charge curve (Fig. 7b). The slightly lower anodic peak potential of the S/SCFs composite than that of the S/MhMpCFs composite (2.39-2.40 V) is also well consistent with their charge plateaus. The one anodic peak feature is supposed due to the facile conversion of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> to high-order polysulfides, which consists of multistep oxidation reactions. One anodic peak feature is also commonly reported in other S cathodes [43,52]. In addition, there is no anodic peak centered at ca. 2.8 V (vs. Li<sup>+</sup>/Li) found in the present study for the formation of S<sub>8</sub> as reported in a S loaded hierarchically pore-structured carbon pillars cathode [29], indicating that there is likely no  $S_8$ formed in the present final lithium extraction product. In the second cathodic process, the cathodic process moves to higher potential ranges for both composites, especially for the peak located in the relatively higher potential, which is mainly attributed to the change of the active material from S<sub>8</sub> to high-order polysulfides. The phenomenon is also in good agreement with the raised discharge plateaus in the discharge curves.



**Fig. 9.** Electrochemical impedance spectra of the S/MhMpCFs and S/SCFs composites. The inset is the equivalent circuit. The solid symbols denote the experimental data, and the lines represent the fitting results from the calculation based on the equivalent circuit.



Fig. 8. CV curves of the S/MhMpCFs (a) and S/SCFs (b) composites of the first three cycles at a scanning rate of 0.1 mV/s.

Fig. 9 illustrates the electrochemical impedance analyses of the S/MhMpCFs and S/SCFs composites. The solid symbols denote the experimental data, and the lines represent the fitting results from the calculation based on the equivalent circuit inserted in Fig. 9. The experimental data show that the electrochemical impedance spectra of the two composites all consist of two depressed semicircles in the high and medium frequency ranges followed by a short line in the low frequency range. The intercept of the real axis at the high frequency is ascribed to the ohmic resistance resulting from electrolyte resistance and cell components [53,54], which is denoted as R<sub>s</sub>. The semicircle from high to medium frequency represents the resistance from the SEI film on the surface of the cathode [54], which is denoted as  $R_{\rm f}$ . The second semicircle at medium frequency relates to the charge transfer resistance [54],  $R_{ct}$ . The short line in the low frequency region is generally named as Warburg resistance, denoted as  $W_0$ , which is attributed to the diffusion resistance of lithium ions within the S cathode. CPE1 and CPE2 in the equivalent circuit represent the capacitive elements [53]. As seen from Fig. 9, the radiuses of the two semicircles of the S/MhMpCFs composite are all smaller than those of the S/SCFs composite. The calculated values of R<sub>f</sub> and R<sub>ct</sub> of the S/MhMpCFs composite are 9.6 and 8.1  $\Omega$ , respectively, which are significantly lower than 17.1 and 69.0  $\Omega$  of the S/SCFs composite. Especially for the charge transfer resistance, the value of the S/MhMpCFs composite is nearly one order smaller than that of the S/SCFs composite. The much smaller charge transfer resistance of the S/MhMpCFs composite indicates a much higher electronic conductivity and a much better reaction kinetics of the composite. The result further demonstrates that the mesohollow and microporous structure of the carbon fibers provides better electronic connection for the incorporated S than the solid structured carbon fibers.

## 4. Conclusions

Hierarchically porous carbon fibers in diameters of 200-300 nm with mesohollows of 30-60 nm and micropores of several nanometers have been successfully synthesized by coaxial electrospinning PAN and PMMA as the outer and inner spinning solutions, respectively, followed by a carbonization. PMMA decomposed in the carbonization process and induced the mesohollows and micropores. S fills fully in the micropores and fills mostly in the mesohollows via the thermal treatment, forming hierarchical structured-S/carbon fiber composite with 60 wt.% S. This sulfur/ porous carbon fiber composite shows a maximum capacity of 815 mA h/g at 0.1 C after several activation cycles as a cathode material for Li-S batteries, and a capacity retention of 88% is obtained after 70 cycles with respect to the maximum capacity. The cycling stability is much better than that of the sulfur/solid carbon fiber composite cathode, the solid fibers of which were prepared from individual PAN. The micropores, which encapsulate effectively the S active material and alleviate the dissolution of soluble polysulfides in the electrolyte, and the mesohollows, which allow a sufficient penetration of electrolyte for the mobility of lithium ions, play synergetic roles in improving the electrochemical property of the S/porous carbon fiber composite.

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