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Large-scale synthesis of ordered mesoporous carbon fiber and its application as cathode material for lithium–sulfur batteries

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ABSTRACT

A novel type of one-dimensional ordered mesoporous carbon fiber has been prepared via the electrospinning technique by using resol as the carbon source and triblock copolymer Pluronic F127 as the template. Sulfur is then encapsulated in this ordered mesoporous carbon fibers by a simple thermal treatment. The interwoven fibrous nanostructure has favorably mechanical stability and can provide an effective conductive network for sulfur and polysulfides during cycling. The ordered mesopores can also restrain the diffusion of long-chain polysulfides. The resulting ordered mesoporous carbon fiber sulfur (OMCF-S) composite with 63% S exhibits high reversible capacity, good capacity retention and enhanced rate capacity when used as cathode in rechargeable lithium–sulfur batteries. The resulting OMCF-S electrode maintains a stable discharge capacity of 690 mAh/g at 0.3 C, even after 300 cycles.

1. Introduction

Due to its ultra-high energy density (theoretically 2567 Wh kg^{-1}) and high theoretical specific capacity (1675 mAh/g), the rechargeable lithium–sulfur (Li–S) battery has attracted enormous attention in the last several years [1–3]. Sulfur cathodes face several major challenges, however, which limit their practical applications, including the low conductivity of sulfur and lithium sulfide [4,5], as well as the large volume changes in the sulfur particles during charge and discharge processes. A more significant challenge that needs to be overcome is the high solubility of high-order polysulfide intermediates in organic electrolytes. The dissolved high-order polysulfides can diffuse from the cathode and react with the lithium anode either to generate insoluble lower-order polysulfides in the form of Li_2S or Li_2S_2, leading to the precipitation of these species on the surface during cyclic processes, or form soluble low-order polysulfides, which is then transported back to the cathode side, resulting in a shuttle reaction [6,7]. The shuttle reaction and deposition of Li_2S or Li_2S_2 on the Li anode lead to the low utilization of sulfur, low coulombic efficiency of the sulfur cathode, and fast capacity fading [8,9].

There are two basic strategies to address this problem. The major stream of Li–S research has focused on the design "inside" the cathode, confining sulfur within various kinds

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of porous matrixes, such as porous carbon [10–16] or graphene [17–19], or applying surface coatings of conductive polymer [20–21] or metal oxides such as TiO_2 [22] or Al_2O_3 [23] to act as a physical barrier to prevent the soluble polysulfides from dissolving in the organic electrolyte. An alternative route has concentrated on the "outside" of the cathode, such as by modification of the electrolyte [24–26] and novel cell configurations [27–29].

Herein, we report a simple electrospinning deposition method (ESD), which can mass-produce ordered mesoporous carbon fiber (OMCF). Currently, the majority of carbon materials used for confining sulfur so far are difficult to be applied in practical applications due to their complicated preparation processing and high cost. The ESD method is considered a promising method to mass-produce one-dimensional (1D) carbon materials with the advantages of simplicity, efficiency, low cost, and high yield. We have employed 1D OMCF as an improved confinement matrix for high-level sulfur impregnation. The ordered mesoporous fibrous structure builds a framework of well-connected empty sites, which could encapsulate a large amount of sulfur. Furthermore, the OMCF framework could facilitate the transport of electrons and ions and the electrolyte diffusion, and retain the polysulfides, enhancing the reversibility of electrode, which is hardly achieved by random porous structures.

2. Experimental section

2.1. Synthesis of OMCF

The OMCF was synthesized through the electrospinning technique. In a typical synthetic process, 2 g F127 was put in 8 g of ethanol with 1.2 g 0.2 M HCl and stirred for 1 h at 40 °C to yield a transparent solution. Next, 6 g of 20 wt% resol ethanolic solution and 1.8 g tetraethyl orthosilicate (TEOS) were added in that order. The resol precursor ($M_w < 500$) was synthesized on the basis of previous report [30]. After being stirred for 5 h, 3 g 25% polyvinyl butyral (PVB) solution in ethanol was added to the mixture. Finally, a homogeneous solution was obtained after 4 h strong mechanical stirring. Triblock copolymer Pluronic F127 and resol are regarded as template and carbon source, respectively. The role of PVB is to improve the "spinnability" of the solution, while the TEOS acts as a skeleton in the formation process for the mesoporous structure, which can be removed in the next step. The experimental procedure and the formation of ideal mesoporous structure of OMCF are shown in Fig. 1. During electrospinning process, the solution was loaded into a syringe with a metallic needle (inner diameter 0.5 mm) and a flow rate of 0.8 mL h^{-1} under the voltage of 14.5 kV. The distance from needle tip to stainless steel mesh collector was 12 cm. Then, the collected primary film was dried at room temperature for 24 h. The as-prepared products were heat-treated at 700 °C for 2 h under flowing nitrogen gas. Afterwards, the resultant ordered mesoporous carbon–silica fiber was put into 2 mol/L boiling NaOH solution for 2 h to remove the silica to obtain OMCF. In our study, 0.2 g OMCF can be obtained per hour under our preparation condition, and the production can be easily scale-up. The control sample ordered mesoporous carbon powder (OMCP) was synthesized through the same process as the OMCF, but without electrospinning technique.

2.2. Fabrication of ordered mesoporous carbon fiber sulfur (OMCF-S) composite

The as-prepared OMCF and OMCP were mixed with sulfur in a weight ratio of 25:75 and heated to 160 °C in a sealed stainless steel autoclave for 24 h to facilitate sulfur diffusion into the carbon host to obtain the OMCF-S and ordered mesoporous carbon powder sulfur (OMCP-S) composite, respectively. Then, the OMCF-S and OMCP-S composite was heated at 200 °C and kept for 10 min under flowing argon gas (50 cm^3 s^{-1}) to vaporize the sulfur deposited on the outside surface of the composite.

2.3. Characterization

The crystal structures of the samples were carried out by powder X-ray diffraction (XRD, MMA GBC, Australia) and by Raman spectroscopy on an instrument (JOBIN YVON HR800) equipped with a 632.8 nm diode laser. Thermogravimetric analysis (TGA) was performed to measure the sulfur content with a METTLER TOLEDO TGA/DSC instrument with a heating rate of 10 °C min^{-1} from room temperature to 500 °C under a

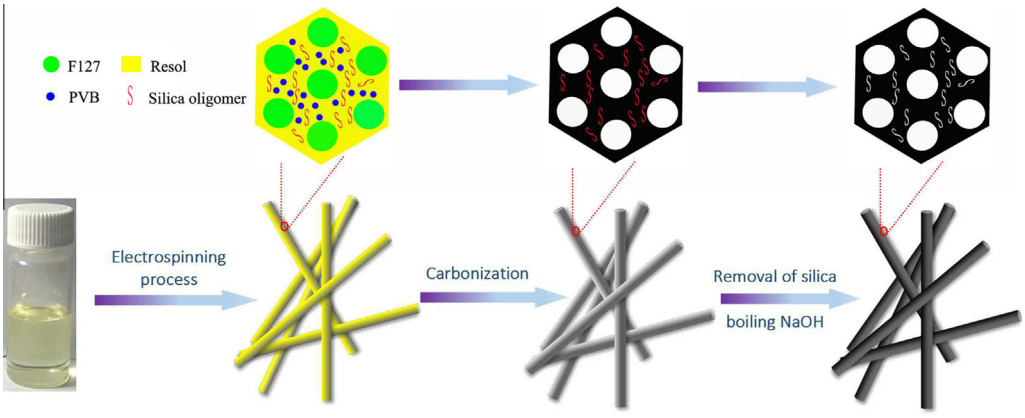

Fig. 1 – A schematic illustration of the experimental procedure and the formation of ideal mesoporous structure of OMCF. (A color version of this figure can be viewed online.)

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