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Synthesis of hierarchical porous honeycomb carbon for lithium-sulfur battery cathode with high rate capability and long cycling stability

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ABSTRACT

Sulfur has a high specific capacity of 1675 mAh g^{-1} as lithium battery cathode, but its rapid capacity fading due to polysulfides dissolution presents a significant challenge for practical applications. Here we report a novel hierarchical porous honeycomb carbon (HPHC) for lithium-sulfur battery cathode with effective trapping of polysulfides. The HPHC was prepared by a simple template process, and a sulfur-carbon composite based on HPHC was synthesized for lithium-sulfur batteries by a melt-diffusion method. It is found that the elemental sulfur was dispersed inside the three-dimensionally hierarchical pores of HPHC based on the analyses. Electrochemical tests reveal that the sulfur-HPHC composite shows high rate capability and long cycling stability as cathode materials. The sulfur-HPHC composite with sulfur content of 66.3 wt% displays an initial discharge capacity of 923 mAh g^{-1} and a reversible discharge capacity of 564 mAh g^{-1} after 100 cycles at 2 C charge-discharge rate. In particular, the sulfur-HPHC composite presents a long term cycling stability up to 300 cycles at 1.5 C. The results illustrate that the electrochemical reaction constrained inside the interconnected macro/meso/micropores of HPHC would be the dominant factor for the excellent high rate capability and long cycling stability of the sulfur cathode, and the three-dimensionally honeycomb carbon network would be a promising carbon matrix structure for lithium-sulfur battery cathode.

1. Introduction

High energy density rechargeable batteries have received great attention in recent years because of their potential applications, such as the power source for electric vehicles, energy storage devices and smart grids [1]. Among various types of rechargeable batteries, lithium-sulfur (Li-S) batteries hold great potential due to their high theoretical specific capacity of 1675 mAh g^{-1} and specific energy of 2600 Wh kg^{-1} [2]. Furthermore, sulfur as an active cathode material is non-toxic, naturally abundant, and environmentally benign. However, a commercially viable lithium-sulfur battery has not yet been realized because of the insulating nature of sulfur and the active mass shuttling loss [3–7].

In attempts to overcome the above problems, various strategies have been explored, including preparation of the sulfur-conductive polymer composite [8–10], and fabrication of the sulfur-carbon composite [3,11,12]. In particular, porous carbon materials have been proved to be effective and facile candidates to improve the sulfur utilization and restrain the solubility of polysulfides on account of their excellent conductivity, large surface area, abundant porous channels and strong adsorbent properties. Various structures of porous carbon materials have been applied, such as microporous carbon [13], mesoporous carbon [5], hollow carbon [14,15], porous carbon fibers [16,17].

However, after absorbing sulfur into the pores of the carbon matrix, the specific surface area (SSA) and pore volume of the sulfur-carbon composite was reduced markedly. Such a structure with carbon pores fully or partially filled with sulfur may induce kinetic inhibition to Li^+ diffusion within the matrix [13,16]. Recently, some reports suggested that the carbon matrix with/without hierarchical pore structure has significant effects on the kinetics of effective ion transport due to the enhanced permeation of electrolyte and better electrolyte accessibility [18,19]. Recent studies have also shown that the three-dimensional architecture can not only provide a continuous electron pathway to ensure good electrical contact, but also facilitate ion transport by

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shortening diffusion pathways [20,21]. Herein, we were motivated to prepare a three-dimensional (3D) hierarchical porous carbon with three-dimensionally nanoscaled architecture and hierarchical pore structure.

Therefore, in this study, we synthesis a novel three-dimensional (3D) hierarchical porous honeycomb carbon (HPHC) to encapsulate sulfur for lithium-sulfur batteries. The HPHC was prepared by a simple template process, the obtained HPHC possesses a unique three-dimensional hierarchical porous honeycomb structure with interconnected macro/meso/micropores, and has a hollow structure with large internal void space and thin porous wall (only about 3-4 nm). The sulfur-HPHC composite was prepared by a melt-diffusion method. The as-prepared sulfur-HPHC composite was found to have excellent high rate capability and long cycling stability.

2. Experimental

2.1. Materials Synthesis.

The hierarchical porous honeycomb carbon (HPHC) was prepared using glucose and colloidal silica spheres as the carbon precursor and removable templates, respectively. First, the colloidal silica spheres with a diameter of 130 nm were prepared by Stŏber method as reported previously [22]. Second, 0.8 g glucose was dissolved in the above colloidal silica spheres (100 ml) to form a homogeneous solution under stirring, the solution was then transferred into a flask and kept in a water bath at 90 °C under vigorous stirring until the solvent was completely evaporated. Third, the dried solid samples were subjected to carbonization by heating at 900 °C for 3 h under argon gas flow in a tube furnace. Finally, the silica spheres were removed by etching the products in 10 wt% HF to generate HPHC.

The sulfur-HPHC composite was prepared via a simple melt-diffusion method [5,23]. Sublimed sulfur (AR, Aladdin, China) and the as-prepared HPHC with a weight ratio of 7:3 were mixed together and placed in a sealed vessel, and the mixture was heated to 155 °C for 12 h under an argon atmosphere with the heating rate of 5 °C min^{-1}, then the sulfur-HPHC composite was obtained. As a comparison, sulfur-CMK-3 composite was prepared via the same method. CMK-3 is a well-known mesoporous carbon and widely used as a carbon matrix for sulfur electrode in lithium-sulfur batteries [5]. Mesoporous carbon material CMK-3 was purchased from Fudan University, China.

2.2. Materials Characterization.

Field emission scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, Tecnai G2 20ST) were applied to characterize the materials. X-ray

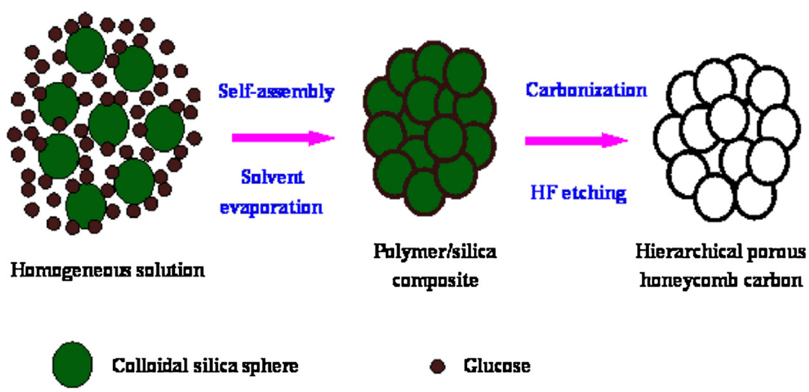

Fig. 1. Schematic illustration of the synthesis procedure of the HPHC.

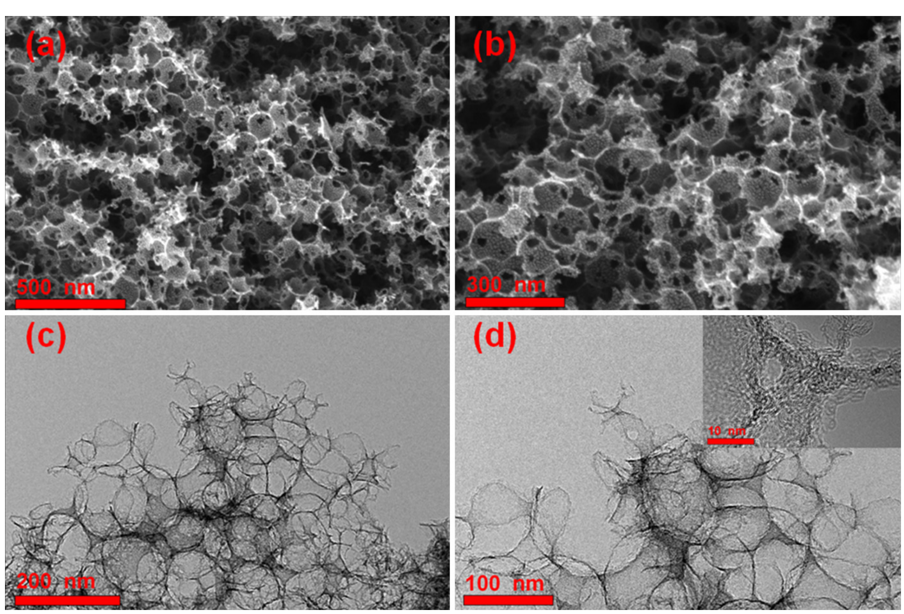

Fig. 2. SEM images of the HPHC (a and b), TEM images of the HPHC (c and d), and HRTEM (inset) image of the HPHC (d).