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A hierarchical carbon fiber/sulfur composite as cathode material for Li–S batteries

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ABSTRACT

A novel hierarchical structure carbon/sulfur composite is presented based on carbon fiber matrices, which are synthesized by electrospinning. The fibers are constituted with hollow graphitized carbon spheres formed using catalytic Ni nano-particles as hard templates. Sulfur is loaded to the carbon substrates via thermal vaporization. The structure and composition of the hierarchical carbon fiber/S composite are characterized with X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, and nitrogen adsorption isotherms. The electrochemical performance is evaluated by cyclic voltammetry and galvanostatic charge–discharge. The results exhibit an initial discharge capacity of 845 mA h g^{-1} at 0.25 C (420 mA g^{-1}), with a retention of 77% after 100 cycles. A discharge capacity of 533 mA h g^{-1} is still attainable when the rate is up to 1.0 C. The good cycling performance and rate capability are contributed to the uniform dispersion of sulfur, the conductive network of carbon fibers and hollow graphitized carbon spheres.

1. Introduction

Since 2000 lithium–sulfur batteries have attracted much attention because sulfur cathode has almost the highest theoretical capacity (1672 mA h g^{-1}) and theoretical energy density (2600 Wh kg^{-1}) [1,2]. In addition, element sulfur possesses the characteristics of high natural abundance, low cost and environmental friendliness. These advantages make Li–S battery be considered as one of the most promising technologies to meet the increasing demands for the batteries with higher energy density in large-scale applications such as portable equipments, electric vehicles, and stationary storage [3,4].

Indeed, sulfur-contained batteries were already reported by Danuta and Juliusz in 1962 [5]. However, no significant progress was achieved before 2000s due to such drawbacks: the rapid capacity decay, the dissolution of intermediates (Li_2S_x, $3 \leqslant x \leqslant 8$) [1,6], the insulating property of pure sulfur (5×10^{-30} S cm^{-1}), and the dendrite growth caused with metallic lithium anode. Entering the 21st century, along with the huge success in Li-ion batteries and the prosperity of carbon nano materials, the interests in Li–S batteries are growing increasingly, especially, with the work reported by Nazar et al.'s [7] in 2009.

To greatly improve the electrochemical performance of sulfur cathodes, various strategies have been developed, including the combination of sulfur with carbon skeletons, conductive polymer [8–11] and metal oxides [12] etc. As commonly-used materials for modifying the cathodes, carbonaceous materials vary from 0-dimension (0-D) to 3-D [13–16].

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Hard template approach has been widely used to effectively generate pores in carbon composites [17], for example, Zhang et al. [18] and Peng et al. [19] reported that carbon shells were delicately obtained using SnO_2 spheres and NiO nanoparticles as hard templates, exhibiting good electrochemical performances in Li–S batteries. Carbon fibers (CFs) as supporters to sulfur have also aroused much interest because of their good electrical conductivity, large surface area, and superior mechanical property [20–23]. Electrospinning technique is often used to fabricate continuous CFs for it is facile and low-cost. A porous polyacrylonitrile (PAN)-based CF/S composite was reported [24] using poly (methyl methacrylate) as sacrificial template, showing a high discharge capacity within 30 cycles. However, PAN is usually pyrolized as a kind of hard carbon which cannot be well graphitized at the temperature below 2000 °C [25]. It impedes the further development with a comparatively low electrical conductivity and low module [26–28]. Much effort has been made to improve the carbon structure [29,30], such as the introduction of transition metal salts (Mn, Co, Ni) into electrospinning solution to catalyze the graphitization of CFs at lower temperature [31–33]. Ji et al. [34,35] and Chen et al. [36] reported that the in-situ formation of graphitic carbon shells in CFs modified the rate performance of the anode. In addition, the construction of novel electrode configuration [37–40] is concerned to modify the cathode performance as well with a higher areal loading of sulfur.

Herein, a hierarchical structure carbon fiber/sulfur (HCF/S) composite was prepared using electrospinning process during which nickel acetate was employed to catalyze the graphitization of carbon at lower temperature. The carbon fiber network was consisted of hollow graphitized carbon spheres. Sulfur was encapsulated into the cage-like spheres to mitigate the dissolution of polysulfides into the electrolyte. The hierarchical structure may conduce to high electrical conductivity, and offer the buffer against the volume change during charge and discharge. The architecture of the composite was examined with various characterizations and its electrochemical performance was investigated in detail.

2. Experimental

2.1. Materials preparation

Polyacrylonitrile (molecular weight = 150,000) was purchased from J&K. All other reagents were purchased from Aladdin unless described otherwise and were used without further purification.

Typically, 1 g PAN and 1.5 g $Ni(Ac)_2{\cdot}H_2O$ were dissolved in 20 g N,N-dimethylformamide and stirred at room temperature for 12 h. Then the homogenous solution was loaded into a 5 mL syringe with a 19-gauge blunt tip needle for electrospinning at 15 kV (SS-2535). The as-collected electrospun film was denoted as PAN/Ni precursor fibers. It was first stabilized at 250 °C for 2 h, then carbonized at 1300 °C in an argon atmosphere (heating rate was 5 °C min^{-1}) for 2 h. The obtained black product was denoted as HCF/Ni. It was washed using nitric acid reflux for 4 h. The sample was filtered, rinsed with distilled water, and dried at 60 °C for 12 h. The final product was denoted as HCFs. To prepare HCF/S, sublimed sulfur

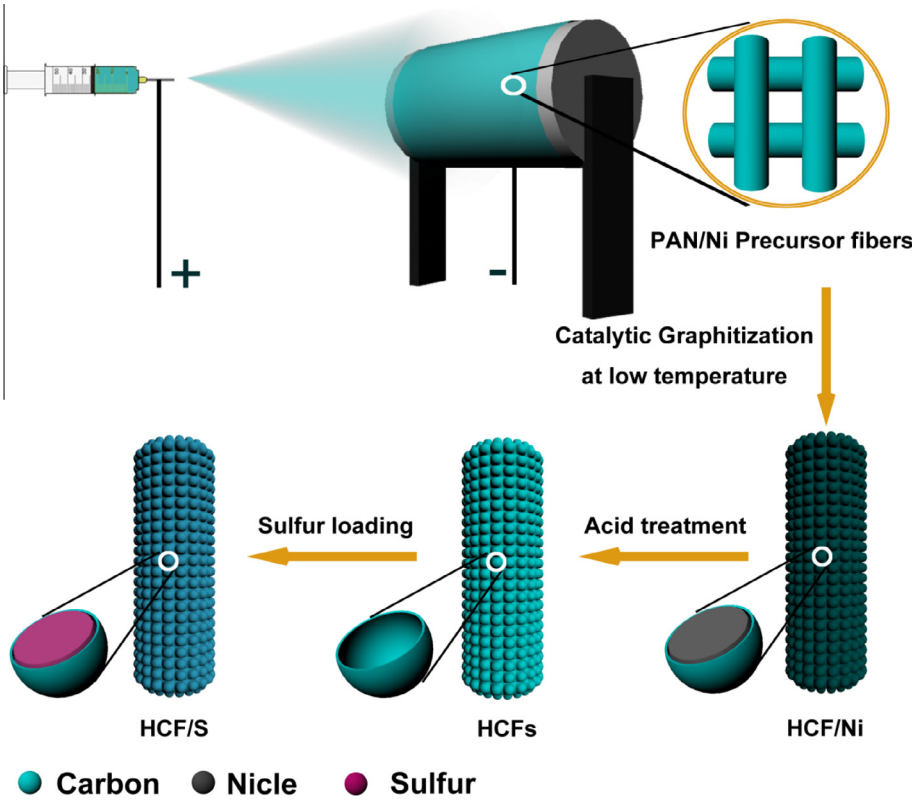

Fig. 1 – Schematic illustration of the synthetic route of HCF/S composite. (A color version of this figure can be viewed online.)