



A simple synthesis of hollow carbon nanofiber-sulfur composite via mixed-solvent process for lithium–sulfur batteries



Qiang Li^a, Zhian Zhang^{a,b,*}, Kai Zhang^a, Jing Fang^a, Yanqing Lai^{a,b}, Jie Li^{a,b}

^aSchool of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, China

^bEngineering Research Center of High Performance Battery Materials and Devices, Research Institute of Central South University in Shenzhen, Shenzhen 518057, China

HIGHLIGHTS

- HCNF-S composite prepared via a mixed-solvent process was applied for lithium–sulfur batteries.
- The prepared HCNF-S composite showed a highly conductive network-like structure.
- The HCNF-S composite showed perfect cycling stability and rate capability.
- The hollow fibrous HCNFs would be a promising carbon matrix for Li–S batteries.

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ABSTRACT

A hollow carbon nanofiber supported sulfur (HCNF-S) composite cathode material is prepared by a mixed-solvent (DMF/CS₂) process in an organic solution for lithium–sulfur batteries. Scanning electron microscope (SEM) and transmission electron microscope (TEM) observations show the hollow structures of the HCNF and the homogeneous distribution of sulfur in the composite. The performance of the HCNF-S cathode is evaluated in lithium-sulfur batteries using cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy. It is found that the HCNF-S cathode shows perfect cycling stability. The results exhibit an initial discharge capacity of 1090 mAh g⁻¹ and retains 600 mAh g⁻¹ after 100 discharge/charge cycles at a high rate of 1 C. The excellent electrochemical properties benefit from the hollow and highly conductive network-like structure of HCNFs, which contribute to disperse sulfur and absorb polysulfides, and suppress the formation of residual Li₂S layer.

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1. Introduction

The lithium–sulfur (Li–S) system, based on the electrochemical reaction $16\text{Li} + \text{S}_8 \leftrightarrow 8\text{Li}_2\text{S}$, is one of the most promising candidates for high energy density applications especially in electric vehicles (EVs) and hybrid electric vehicles (HEVs), due to its low cost, environment friendliness, availability of resource materials, large theoretical specific capacity and energy of 1675 mAh g⁻¹ and 2500 Wh kg⁻¹, respectively [1–4]. Despite these significant advantages, the application of Li–S batteries still suffers from several serious challenges such as the low electrochemical utilization of sulfur, poor cycling stability, and poor rate capability [5–9]. These

problems could be attributed to the poor electrical conductivity of sulfur and its reduced products and the dissolution and shuttling effect of the intermediate products lithium polysulfides (Li₂S_n, 4 ≤ n ≤ 8) in organic liquid electrolytes during cycling [10–12].

To overcome these problems, many attempts have been made, which focus on enhancing the electrical conductivity of the cathode and suppressing the loss of soluble polysulfide intermediates during cycling [13,14]. Various conductive porous carbons [15–20], conducting polymers [21,22] and graphenes [23,24] have been used as host materials for sulfur cathode in recent years to improve the electrochemical performance of Li–S batteries. These carbon-sulfur and polymer-sulfur composites improve electrical conductivity and trap some of the soluble polysulfides during cycling. Among these efforts, conductive matrixes with hollow structures, such as hollow carbon spheres [25,26], polyaniline nanotubes [27] and carbon nanotubes [19,28] are very attractive materials, because the hollow structure might have several advantages including high surface

* Corresponding author. School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, China. Tel./fax: +86 731 88830649.

E-mail address: zza75@163.com (Z. Zhang).

area for efficient sulfur uptake and polysulfides containment, sufficient space to withstand volumetric expansion and short transport length for lithium ions.

The hollow carbon nanofibers (HCNFs) are an attractive carbon material for the sulfur electrode, because linear carbon materials can provide an effective conduction path of lithium ions and an ideal network-like structure that forms a stable structure for trapping polysulfides during the charge-discharge process [19,29]. In recent years, the reports about HCNFs acting as host materials of elemental sulfur are relatively rare. Cui et al. [30] has reported a hollow carbon nanofiber-encapsulated sulfur cathode for effective trapping of polysulfides and demonstrate experimentally high specific capacity and excellent electrochemical cycling of the cells. In their research, hollow carbon nanofiber arrays were fabricated using anodic aluminum oxide (AAO) templates through thermal carbonization of polystyrene. To prepare hollow carbon nanofiber-sulfur composite, 15 mg of carbon-coated AAO template was loaded into a small glass vial and 300 μl of 1% sulfur solution in toluene was dropped onto the template. After drying, the mixture was heated up to 155 $^{\circ}\text{C}$ and kept for 12 h to facilitate sulfur diffusion into the hollow nanofibers. The high aspect ratio of hollow carbon nanofibers reduces the random diffusion of polysulfides in the organic electrolyte, while the thin carbon wall allows fast transport of lithium ions. In addition, Cairns et al. [31] has also reported a sulfur-coated carbon nanofiber composite cathode material prepared by a chemical deposition method based the reaction between sodium polysulfide and formic acid. The composite material exhibits good electrochemical properties in rechargeable lithium-sulfur cells due to the chain-like electron transport network of carbon nanofibers.

However, these kinds of intertwined linear nanostructured carbon materials such as CNTs and CNFs are difficult to be dispersed. Ultrasonication in solvents is usually a primary step for producing homogeneous and relatively aggregate-free dispersions. The dispersant used needs to overcome the strong van der Waals

force between CNTs to resist their agglomeration [32]. Ham et al. [33] has proved N,N-dimethylformamide (DMF) to be better than ethanol, water, acetone and methanol for making CNTs dispersions, which is also confirmed by Inam et al. [34].

In this work, we report a well-dispersed hollow carbon nanofiber-sulfur (HCNF-S) composite material prepared by a simple method via a mixed-solvent (DMF/ CS_2) process for rechargeable Li-S batteries. In this method, N,N-Dimethylformamide (DMF) acts as a dispersant for HCNFs and carbon disulfide (CS_2) dissolves elemental sulfur. The prepared HCNF-S composite material shows good dispersity and an ideal network-like structure, which forms a stable structure for trapping polysulfides during the charge-discharge process. Electrochemical results exhibit an initial discharge capacity of 1090 mAh g^{-1} and retains 600 mAh g^{-1} after 100 cycles at a high rate of 1 C. The excellent electrochemical properties benefit from the hollow and highly conductive network-like structure of HCNFs with abundant pores, which contribute to disperse sulfur and absorb polysulfides, and suppress the formation of residual Li_2S layer.

2. Experimental

2.1. Materials preparation

First, in order to compare the dispersion effects of HCNFs in deionized water and DMF, we designed and conducted a sedimentation experiment. Firstly, 50 mg HCNFs was added into a vial filled with 20 ml deionized water and DMF, respectively. Then, the two vials were hand-mixed for 30 s and high power bath ultrasonicated for 2 h at 20 $^{\circ}\text{C}$. Finally, the dispersions were placed statically to observe its re-aggregation behavior. Fig. 1(a) shows the colloidal dispersion for HCNFs/water and HCNFs/DMF after ultrasonication at different time intervals. As seen in Fig. 1(a), the HCNFs/DMF dispersion was more stable, showing no signs of

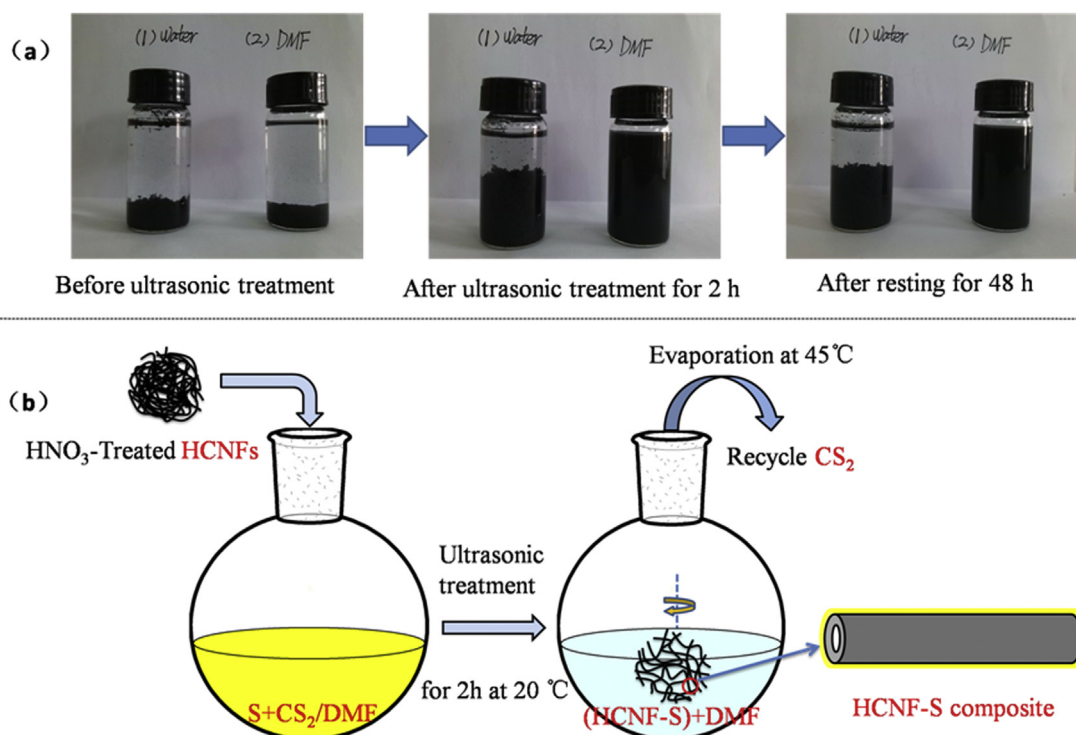


Fig. 1. (a) Images of HCNFs dispersion experiment. (b) Schematic of synthesis process for HCNF-S composite.

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