



# Nitrogen-doped carbon fiber foam enabled sulfur vapor deposited cathode for high performance lithium sulfur batteries



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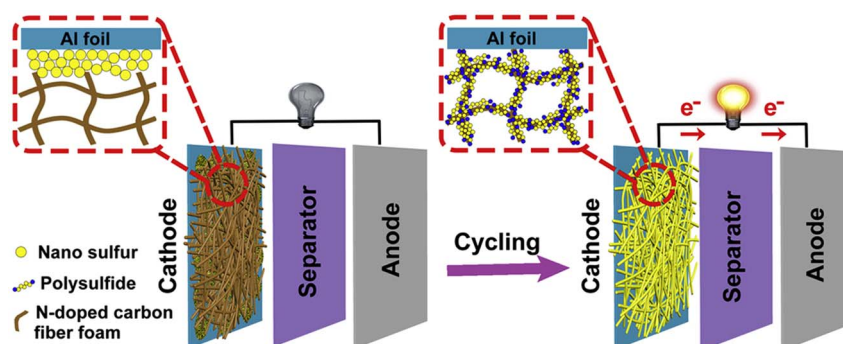
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## HIGHLIGHTS

- Binder-free sulfur cathode was fabricated via sulfur vapor deposition method.
- Nitrogen-doped carbon fiber foam provided adsorption sites for the polysulfide.
- A transfer and redistribution strategy was proposed for polysulfide immobilization.
- The work provided a practical way to fabricate sulfur cathode with gaseous sulfur.

## GRAPHICAL ABSTRACT

A sulfur transfer and redistribution strategy was proposed to enhance electrochemical performances of sulfur vapor deposited cathode for Li-S batteries.



## ARTICLE INFO

### Keywords:

Sulfur vapor deposition  
Nitrogen doping  
Carbon fiber foam  
Polysulfide trapping  
Lithium sulfur battery

## ABSTRACT

Lithium sulfur batteries are one of the most promising candidates for the next generation batteries due to its high energy storage density. However, the complicated fabricate method of the sulfur cathode limits its practical application. Recently, the fabrication of sulfur cathode via sulfur vapor deposition is becoming increasingly popular for the reason of simple process and easy industrialization. However, how to solve the severe shuttle effect of polysulfide during cycling remains a challenge in this kind of cathode. Herein, in order to decrease the immigration of polysulfide in the sulfur vapor deposition fabricated cathode, nitrogen-doped carbon fiber foam is designed by the carbonization of polyaniline treated cotton. The nitrogen species in nitrogen-doped carbon fiber foam act as the active sites for the capture of polysulfides, and the shuttle effect is suppressed effectively during cycling. With a high sulfur areal mass loading of  $3 \text{ mg cm}^{-2}$ , the prepared cathode exhibits a specific capacity of  $443.7 \text{ mAh g}^{-1}$  and capacity retention over 97% after 500 cycles at 2C.

## 1. Introduction

As one of the most promising candidate for next-generation batteries, lithium sulfur (Li-S) batteries have been extensively investigated because of their low cost and high theoretical energy density ( $2600 \text{ Wh kg}^{-1}$ ) [1–5]. Sulfur has a high theoretical specific capacity of

$1675 \text{ mAh g}^{-1}$ , which is 3 to 5 times higher than that of commercial lithium-ion batteries [6–8]. Furthermore, sulfur is a by-product in the petroleum industry and has the characteristics of low cost, weakly toxicity and abundant. However, the practical application of Li-S batteries is limited by the poor electrical conductivity of sulfur and the severe shuttle effect of intermediate polysulfide [8–12]. Considerable

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<https://doi.org/10.1016/j.cej.2018.02.057>

Received 18 December 2017; Received in revised form 3 February 2018; Accepted 12 February 2018

Available online 13 February 2018

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efforts such as functional separators [13–15], inorganic hosts [16–19], functional polymers [20,21] and novel carbon materials [22–24] have been introduced to increase the contact of sulfur with electron conductive materials and enhance the cycling stabilities of Li–S batteries.

The general principle of preparing the sulfur cathode composite for Li–S batteries is dispersing sulfur in functional host materials uniformly. Mechanical mixing, melt diffusion and solution method is commonly used to prepare the sulfur cathode materials [25–27]. Although the sulfur cathode with high electrochemical performances can be fabricated by these methods, there are also limitations. Mechanical mixing such as ball milling can ground the sulfur/host materials into nano-scaled particles easily, but the micro/nano structures of the host materials can also be destroyed in the meantime [28]. Sulfur can diffuse into the nano-pores of the host materials by melt diffusion and solution method, but the precipitated sulfur on the surface of the host materials will block the transfer path of electron [29]. In addition, these methods have the shortcomings of time consuming and complication which is unsuitable for large-scale production [30]. Furthermore, solvent pollution such as waste acid, CS<sub>2</sub> and N-Methyl pyrrolidone (NMP) generated in the fabrication process has to be concerned. Therefore, a technically and economical feasible strategy for fabricating the cathode materials for Li–S batteries is needed.

The direct application of gaseous sulfur to prepare binder-free sulfur cathode via vapor deposition is more practical for industrial production than traditional methods because sulfur vapor can be directly obtained from the Claus process in the oil refinery factories [31–33]. The main strategy of fabricating sulfur cathode with sulfur vapor is the deposition of sulfur onto conductive materials. Nano-carbons including carbon fiber web [34], 3D carbon nanotube foam [35], carbon scaffold [30], carbon nanotube array [36] and hybrid carbon films [37] have been used as deposition substrate for sulfur vapor to fabricate binder free cathode. With a 3D interconnected conductive carbon network and uniform sulfur coating, this strategy not only improves the electrical contact between active materials and conductive materials but also provides porous structures for electrolyte infiltration [38–40]. However, unlike partly encapsulated or fully encapsulated sulfur in traditional sulfur cathodes, the sulfur in sulfur vapor deposition (SVD) based cathode is completely non-encapsulated, and sulfur species tend to dissolve into their surrounding electrolyte to cause fast capacity loss during cycling [34,41].

In this study, a transfer and redistribution strategy was proposed to prevent polysulfide immigration in SVD based cathodes by introducing nitrogen-doped carbon fiber foam (Fig. 1a). First, nano-sized sulfur was fabricated via SVD method on the aluminum current collector (Fig. 1b). The nano-sized sulfur and highly porous structure of the SVD sulfur are beneficial for infiltration of electrolyte and rapid transport of Li<sup>+</sup>. Second, nitrogen-doped carbon fiber foam (NCFF) was employed as a polysulfide redistribution host since it has properties of fast electron transport and high adsorption ability for polysulfide in Li–S batteries. In view of low cost and sustainable progress, NCFF was derived from the natural abundant cotton fiber. NCFF can immobilize the sulfur species with its porous structure and N-heteroatoms during charge/discharge cycling process. As a result, sulfur on the current collector can be transferred and redistributed onto NCFF during charge/discharge cycles (Fig. 1c). The sulfur/carbon composites with homogenous distributed sulfur after several cycles can undergo high-rate and long-term charge/discharge cycles. Owing to the synergistic effect of nano-structured sulfur and polar conductive carbon foam, the cathode displayed excellent electrochemical performances.

## 2. Experimental section

### 2.1. Preparation of the NCFF

NCFF was prepared by polyaniline (PAN) treatment and carbonization of cotton fiber. First, 300  $\mu\text{L}$  of ammonium persulfate solution

(APS, 66.7 mg ml<sup>-1</sup> in water) was added dropwise to the cotton disk. After complete wetting, 300  $\mu\text{L}$  of aniline solution (16.7 vol% in ethanol) was added, and the reaction was left overnight at room temperature for full polymerization. The dark brown cotton disks were thoroughly washed with deionized water and ethanol to remove the unreacted monomers and initiators. After washing, the samples were dried at 80 °C in an oven for 5 h. Second, the PAN treated cotton disks were carbonized at 800 °C for 2 h with a heating rate of 5 °C min<sup>-1</sup> in a tube furnace under Ar atmosphere. Thus, NCFF disks with areal mass of  $\sim 3 \text{ mg cm}^{-2}$  and thickness of  $\sim 2.5 \text{ mm}$  were obtained (Figs. S1 and S2).

Untreated carbon fiber foam (CFF) with areal mass of  $\sim 2.8 \text{ mg cm}^{-2}$  and thickness of  $\sim 2.6 \text{ mm}$  was made by the same method except the PAN treatment (Fig. S4).

### 2.2. Vapor deposition of sulfur on aluminum foil

10.0 g sulfur powder was heated to 160 °C in a three necked flask bottle with vigorous stirring to generate sulfur vapor. Then, the sulfur vapor was blown to the surface of the aluminum foil disk (diameter: 16 mm) with the assistance of N<sub>2</sub> flux (flow rate: 2 L/min) (Fig. 1b). SVD sulfur with different mass loadings on the aluminum foil disk can be obtained by adjusting the blowing time of sulfur vapor. The aluminum foil disks with sulfur mass loading of 2 mg, 4 mg and 6 mg were combined with NCFF for the electrochemical test and marked as NCFF-2, NCFF-4 and NCFF-6, respectively (Fig. 1b). In particular, cathodes with the same sulfur mass loading that combined with SVD sulfur and CFF were marked as CFF-2, CFF-4 and CFF-6, respectively. The percentages of sulfur to carbon foam/sulfur combination in NCFF-2/CFF-2, NCFF-4/CFF-4 and NCFF-6/CFF-6 are approximately 16.7%, 33.3% and 50%, respectively. The areal sulfur loadings of NCFF-2, NCFF-4 and NCFF-6 are approximately 1 mg cm<sup>-2</sup>, 2 mg cm<sup>-2</sup> and 3 mg cm<sup>-2</sup>, respectively.

### 2.3. Preparation of polysulfide solution

Li<sub>2</sub>S<sub>4</sub> solution with a concentration of 5 mmol L<sup>-1</sup> was prepared by dissolving Li<sub>2</sub>S and sulfur with a molar ratio of 1:3 in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) by 1:1 in volume. CFF and NCFF with the weight of  $\sim 20 \text{ mg}$  were immersed into 3 mL Li<sub>2</sub>S<sub>4</sub> solution for 24 h for the adsorption test.

### 2.4. Characterization of the materials

The surface morphology and structure of the samples were performed by a field emission scanning electron microscopy (FESEM, SU8220, Hitachi, Japan) equipped with an energy dispersive X-ray spectroscopy spectra (EDX, X-Max, Horiba, Japan). Thermal gravity analysis (TGA) was performed with a Series Q500 instrument (TA Instrument, USA) from room temperature to 800 °C under N<sub>2</sub> flow. X-ray diffraction (XRD) patterns were recorded by SmartLab 9 Kw (Rigaku, Japan) at a scanning rate of 10 °min<sup>-1</sup> in the 2 $\theta$  range from 5° to 80°. Nitrogen adsorption-desorption isotherms were measured at 77 K with a Quantachrome Autosorb iQ (ASiQ, USA) micropore analyzer. NCFF and CFF were degassed at 300 °C under vacuum for 10 h, SVD sulfur was degassed at 60 °C under vacuum for 12 h. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. Pore size distributions were derived from desorption branch of the isotherm with the Barrett-Joyner-Halenda (BJH) method. The total pore volume was calculated from the amount of adsorbed at a relative pressure of 0.99. The Raman spectra of the samples were recorded by DXR Smart Raman (Thermo Fisher, USA) excited with a 532 nm laser. X-ray photoelectron spectra were obtained by an X-ray photoelectron spectrometer (XPS, ESCALAB™ 250Xi, ThermoFisher, USA).

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