



# Nitrogen-doped porous carbon nanofiber webs/sulfur composites as cathode materials for lithium-sulfur batteries



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## ABSTRACT

Nitrogen-doped porous carbon nanofiber webs-sulfur composites (N-CNFWs/S) were synthesized for the first time with sulfur (S) encapsulated into nitrogen-doped porous carbon nanofiber webs (N-CNFWs) via a modified oxidative template route, carbonization-activation and thermal treatment. The composites were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), X-ray powder diffraction (XRD), and thermogravimetry (TG) measurements. The results show that sulfur is well dispersed and immobilized homogeneously in the micropores of nitrogen-doped porous carbon nanofiber webs (N-CNFWs) with high electrical conductivity, surface area and large pore volume. The electrochemical tests show that the N-CNFWs/S composites with 60 wt. % of S have a high initial discharge capacity of 1564 mA h g<sup>-1</sup>, a good cycling stability at the current density of 175 mA g<sup>-1</sup>, and excellent rate capability (reversible discharging capacity of above 400 mA h g<sup>-1</sup> at 1600 mA g<sup>-1</sup>).

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## 1. Introduction

To address rapidly decreasing energy supplies and global environment problems, extending the applications of Li-ion batteries with high energy-density to electric vehicles or efficient storage media for renewable energy sources is an urgent task. The electrode material is a crucial component that influences the electrochemical performance of Li-ion batteries. Consequently, more and more attention has been focused on exploring new electrode materials.

Elemental sulfur is a promising cathode material with the highest theoretical specific capacity of all known cathode materials for rechargeable lithium batteries (with the exception of oxygen cathodes). Elemental sulfur is inexpensive, abundant, nontoxic and environmentally friendly. Therefore, sulfur is very attractive as a cathode material for high-specific-energy, rechargeable lithium batteries. Furthermore, because of its low operating voltage of ~2.1 V, in contrast to 3.5–4.0 V of the transition-metal oxide cathode materials, this material is much safer. In recent years, lithium-sulfur batteries, which use sulfur as a cathode and Li as an anode, have received increasing interest because of their high theoretical

specific capacity of 1675 mA h g<sup>-1</sup> and high theoretical specific energy of 2600 W h kg<sup>-1</sup> [1–4].

However, several issues associated with the sulfur cathodes severely limit the practical use of sulfur in an electrode. For example, both the high resistivity of sulfur and the high solubility of lithium polysulfides, which are intermediates in the electrochemical reduction process of the organic electrolyte [5–7], result in a drastic reduction in the specific capacity and a fast decline in capacity [8,9]. In this work, various polymer [10–12] and carbon materials with good conductivity and large surface areas are introduced into sulfur composite cathodes to overcome these shortcomings.

In this paper, N-CNFWs/S composites for lithium-sulfur batteries have been prepared for the first time using a modified oxidative template route with nitrogen-doped porous carbon nanofiber webs (N-CNFWs) as a precursor and KOH as an activating agent [13,14]. Due to the unique porous nanostructure and the presence of heteroatoms, the N-CNFWs can both enhance the reactivity and electric conductivity [15–18] and shorten the transport length for the Li ion. In our work, elemental sulfur was encapsulated in the micropores of N-CNFWs using thermal treatment. The unique and rich channel structure of N-CNFWs can offer enough space to accommodate the volume expansion that occurs during the discharge process, confine the electrochemical reaction products of the sulfur cathode inside the micropores of the N-CNFWs, and correspondingly, show excellent electrochemical properties [19].

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## 2. Experimental

### 2.1. Preparation of nitrogen-doped porous CNFWs (N-CNFWs), S/N-CNFWs and S/CNF

PPy precursor was obtained using a modified oxidative template assembly method [20,21]. First, 0.02 M cetrimonium bromide (CTAB) was put in an ice bath and dissolved completely in 120 mL of 1 M HCl solution. After stirring for a few minutes, 0.06 M ammonium persulfate (APS) was added. After magnetic stirring for 30 min, the reaction mixture was cooled to 0–5 °C, and pyrrole (8.3 mL) monomer was added into the as-formed CTAB/APS complex template solution. The reaction continued for 24 h with stirring in an ice bath. The resulting solution was filtered and washed with 1 M aqueous HCl and deionized water until the filtrate was colorless and neutral. The product was collected and dried for 12 h at 80 °C in a vacuum oven.

The PPy precursor was heated to 650 °C (3 °C min<sup>-1</sup>, 1 h) under N<sub>2</sub> atmosphere to produce the N-CNFWs. The resulting N-CNFWs and KOH (at a 1:3 mass ratio) were stirred in a 30 mL aqueous solution for 1 h at room temperature and then dried at 100 °C. The resulting material was carbonized at 700 °C for 2 h under N<sub>2</sub> atmosphere. The prepared N-porous CNFWs (0.04 g) via the activation of potassium hydroxide were mixed with 0.06 g of sublimed sulfur in a quartz mortar for 1 h and then sealed in a PTFE container under N<sub>2</sub> atmosphere. The PTFE container was then thermally treated at 155 °C for 60 h to ensure that the melting sulfur could diffuse into the micropores. For comparison, a similar porous carbon nanofiber was prepared by mixing KOH and CNF (provided by Showa Giken Industrial Co., Ltd, Japan) at a 1:6 mass ratio with the above-mentioned same activation process. Subsequently, the S/porous CNF and S/CNF composites were prepared respectively by mixing sublimed S and CNF with the same sulfur-carbon ratio. These three types of sulfur composites, namely S/N-CNFWs, S/porous CNF and S/CNF, were tested to investigate the effect of different carbon-based materials as sulfur-fixed matrix on the electrochemical performance of the sulfur cathode.

### 2.2. Morphological characterization and electrochemical measurements

The as-prepared composites were characterized by powder XRD patterns (Bruker D8 Advance, Cu K $\alpha$  radiation,  $\lambda$  = 1.5406 Å). The morphologies and microstructure of the composites were investigated using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2100F). Nitrogen adsorption isotherms were measured at 77 K on a Quantachrome Autosorb-1-MP (Quantachrome, USA). Thermogravimetric (TG) analysis was conducted on a Mettler Toledo TGA-SDTA851 analyzer (Mettler Toledo, Switzerland) from 35 °C to 500 °C under nitrogen with a heating rate of 10 °C min<sup>-1</sup>.

The S/N-CNFWs, S/porous CNF and S/CNF electrodes were prepared from a mixture of 70 wt. % of composites, 15 wt. % of super p and 15 wt. % of PVDF binder in NMP (N-methyl-2-pyrrolidone), which served as the dispersant. The slurries were uniformly cast onto carbon-coated aluminum foil substrate using a doctor blade. After the NMP was evaporated, the cathode was subsequently pressed into disks with a diameter of 12 mm and then dried under vacuum at 60 °C for 18 h. The test cell was assembled in an argon-filled glove box (Mikarouna, Superstar 1220/750/900) with a Li counter electrode and a Celgard 2300 sheet as separator. The electrolyte employed was 1 M LiTFSI in a mixture of 1, 3 - dioxolane (DOL)/1, 2 - dimethoxyethane (DME) (1:1 by volume) solution. The charge-discharge measurements were carried out at certain current density with a voltage range of 1.0–3.0 V vs. Li/Li<sup>+</sup> using a Land Cycler (CT2001A, Wuhan Jinnuo Electronic Co. Ltd.). The

specific capacity values in this work were calculated on the basis of sulfur mass.

## 3. Results and discussion

### 3.1. Morphology and structure of S/N-CNFWs composites

FESEM and TEM were used to investigate the morphologies of N-CNFWs. As shown in Fig. 1a, the as-obtained N-CNFWs demonstrate homogeneously structured cross-linked nanofibers with diameters in the range of 60–90 nm. These materials are composed of porous carbon nanofibers with a unique, interconnected 3D framework, which can not only shorten the transport length for Li ions but also offer a large electrode/electrolyte interface for the charge-transfer reaction. Furthermore, N-CNFWs can offer a stable 3D framework for the sulfur cathode, which improves the integrity of the electrode during the charge and discharge process. Another recent approach to improve the electrochemical performance of these carbon-based materials is to modify the surface functional groups with heteroatoms such as nitrogen. The presence of heteroatoms at the carbon surface can reportedly enhance the reactivity, electrical conductivity, and the Li-ion storage capacity [15]. A porous structure with a large concentration of small micropores can be observed in the TEM image in Fig. 1b, which can be further confirmed using the Brunauer–Emmett–Teller (BET) measurement. The distribution of C and N in N-CNFWs was investigated with elemental analysis mapping at low magnification as shown in Fig. 1 (c, d, e, f), the two elements are uniformly distributed in N-CNFWs. From the image at low magnification, we could conclude that the N was dispersed uniformly in the entire range without aggregation. Additionally, element mapping can only show the element distribution horizontally along the N-CNFWs; the vertical distribution in the material is still unknown. By taking advantage of the different detecting depth of EDX and XPS, we could study this problem. EDX has a detection depth of a few micrometers. In our work, the EDX result reveals that the N content in N-CNFWs is approximately 14.03 wt. %, as shown in Fig. 1g, which indicates that a high concentration of N heteroatoms has been successfully introduced into our carbon-based material. The XPS study clearly shows the presence of nitrogen in the N-CNFWs samples, and the corresponding result is listed in Fig. 1h. After the sulfur impregnation, both the FESEM image in Fig. 2a and the TEM image in Fig. 2b of the N-CNFW/S composites show similar morphology and structure to the pristine N-CNFWs material. There is no obvious surface deposition and aggregation of sulfur inside or outside the nanofiber web structure. The encapsulation of sulfur in the N-CNFWs was further studied with element mapping at high magnification. Sulfur was uniformly dispersed into the micropores of N-CNFWs, as observed in the C and S element maps shown in Fig. 2 (c, d). The pore size distribution of the N-CNFWs is shown in Fig. 3b and indicates the characteristic microporous structure of N-CNFWs. The large specific surface area of 2808 m<sup>2</sup> g<sup>-1</sup> and the V<sub>t</sub> of 2.137 cm<sup>3</sup> g<sup>-1</sup> for the N-CNFWs (calculated according to Fig. 3a) indicate an excellent opportunity for sulfur entrance, moreover, large specific surface area of 2798 m<sup>2</sup> g<sup>-1</sup> and V<sub>t</sub> of 2.148 cm<sup>3</sup> g<sup>-1</sup> of the porous CNFWs for comparison are also observed and calculated from the Fig. 3, which has a similar pore structure with N-CNFWs. The dispersion of sulfur in micropores of N-CNFWs can be also explained by X-ray diffraction. The XRD pattern of the N-CNFWs, sublimed sulfur and N-CNFWs/S composites are shown in Fig. 4. The N-CNFWs show wide-angle XRD patterns with two characteristic diffraction peaks located at approximately 25° and 43°, corresponding to the (002) and (100) planes of graphite. The broad and low-intensity peaks suggest that the as-synthesized N-CNFWs have a low degree of graphitization, which indicates the amorphous characteristic of N-CNFWs. Sublimed sulfur exhibits several sharp

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