



# Nitrogen-doped micropores binder-free carbon-sulphur composites as the cathode for long-life lithium-sulphur batteries

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## ABSTRACT

Nitrogen-doped micropores-contained carbon nanofibres (NMCNFs) were prepared by carbonizing ZIF-8 grown in liquid-phase along with electrospinning. When NMCNFs act as sulphur host materials in lithium-sulphur batteries, NMCNFs can retard the shuttle effect and dissolution of polysulfides through the synergic action of effective physical confinement to micropores and nitrogen surface chemical absorption. NMCNFs show a capacity up to 636 mAh g<sup>-1</sup> after 500 cycles against Li anode.

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## 1. Introduction

Lithium-sulphur batteries with high theory capacity (1675 mAh g<sup>-1</sup>) have been a focus of research owing to element sulphur being cheap, abundant, environmental-friendly [1]. However, some serious questions are deeply restricting the application of lithium-sulphur batteries. Firstly, element sulphur has low conductivity ( $5.0 \times 10^{-30}$  S·cm<sup>-1</sup>) and its discharge products (Li<sub>2</sub>S, Li<sub>2</sub>S<sub>2</sub>) are insulated too; secondly, the reaction intermediates, lithium polysulfides (LiS<sub>n</sub>), are highly soluble in organic electrolytes and are easily reduced on the lithium-anode surface; Thirdly, the sulphur expansion/contraction (~80%) in charge-discharge process against lithium results in the disconnection of electrode material with current collector [2,3], which will lead to fast capacity decay and unstable coulombic efficiency.

In recent years, lots of measures have been conducted to improve the conductivity of cathode, suppress the dissolution of polysulfide and volume change, such as using conductive host materials for sulphur [4] and heteroatoms absorption [5]. Carbon nanofibres (CNFs) are good sulphur hosts because of their excellent conductive network and binder-free merits. Polyacrylonitrile

(PAN)-based CNFs have high spinnability, high carbon yield, and high nitrogen-doped with nitrile groups [6]. However, the low specific surface area of PAN-based porous CNFs commonly cannot be employed as an effective sulphur host material because of lacking the sites for the absorption of sulphur/polysulfides. Thus, trying to obtain nitrogen-doped high specific surface area (SSA) nitrogen-doped flexible carbon nanofibres for sulphur host materials is highly desired.

In this paper, we prepared high SSA nitrogen-doped micropores flexible carbon nanofibres (NMCNFs) by electrospinning (ZnBr<sub>2</sub>/PAN nanofibres) and liquid phase growth (ZIF-8/ZnBr<sub>2</sub>/PAN nanofibres), followed by pyrolysis process. Furthermore, the NMCNFs/S composites were synthesized via vapour diffusion of commercial sulphur powder. Electrochemical performances of the NMCNFs/S samples were also investigated as promising electrodes for lithium-sulphur batteries.

## 2. Experimental

### 2.1. The synthesis of NMCNFs

The fabrication process for high SSA nitrogen-doped micropores flexible carbon nanofibres (NMCNFs) is illustrated schematically in Fig. 1. The ZnBr<sub>2</sub>/PAN composite nanofibres were synthesized by electrospinning. 2.2 g ZnBr<sub>2</sub> particles were dispersed in 4 ml N, N-dimethylformamide by sonication. Polyacrylonitrile was dissolved in 7 ml DMF solution with a vigorous stirring at room

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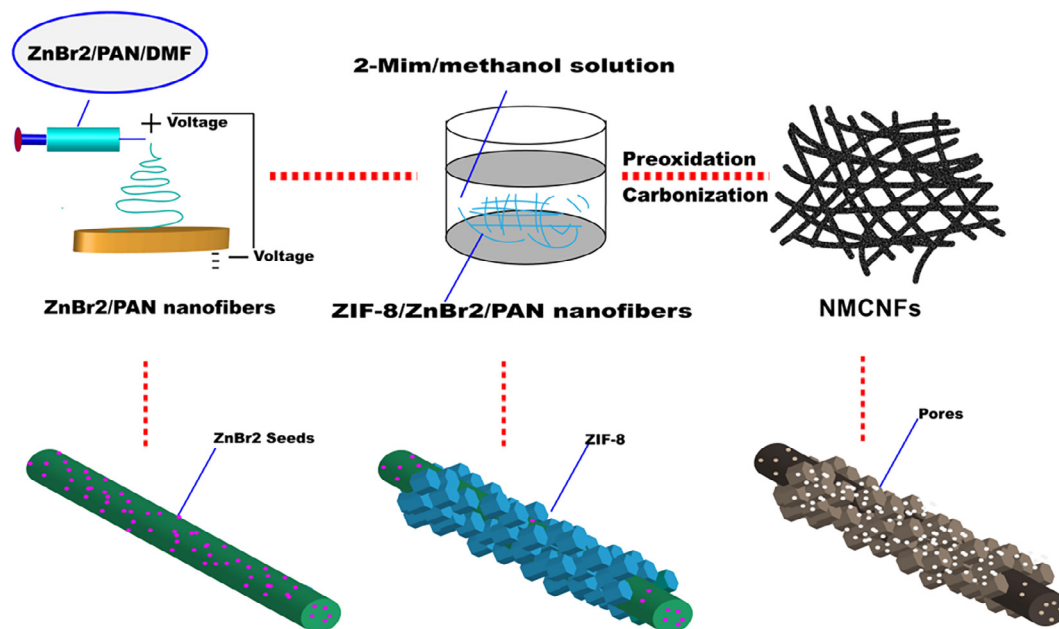


Fig. 1. Schematic illustration of the NMCNFs preparation process.

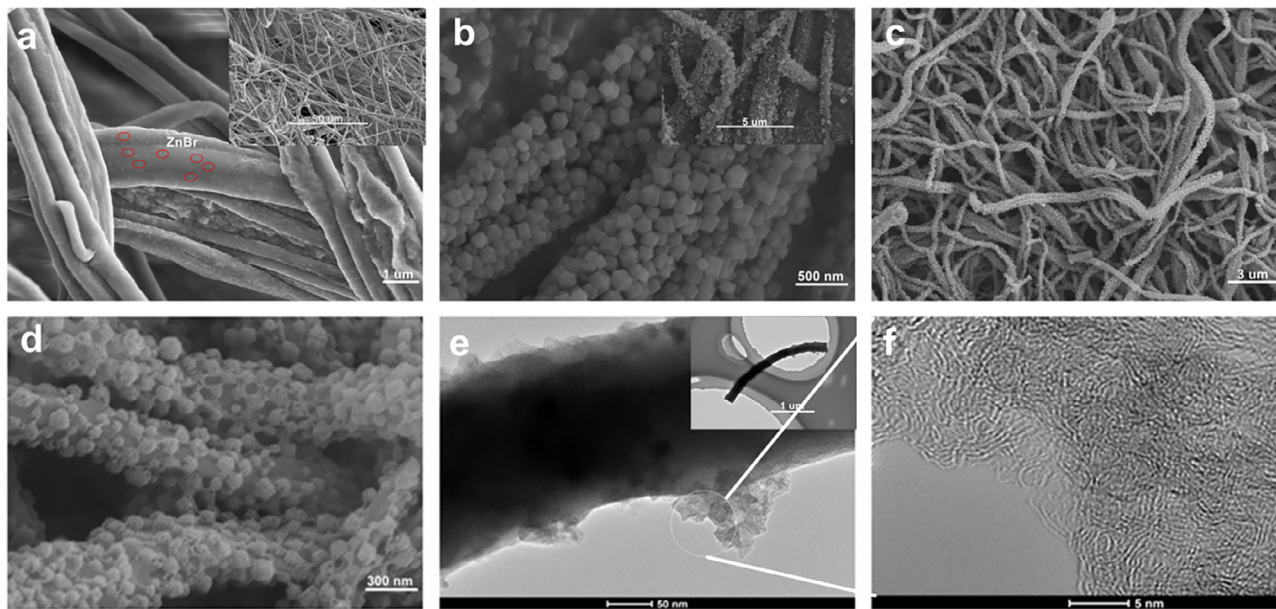


Fig. 2. SEM image of (a)  $\text{ZnBr}_2/\text{PAN}$  nanofibres, (b)  $\text{ZIF-8}/\text{ZnBr}_2/\text{PAN}$  nanofibres, (c-d) NMCNFs, (e-f) TEM image of NMCNFs.

temperature. Then, these two solutions were mixed and stirred for 24 h at room temperature. 2.3 g sheet-type  $\text{ZnBr}_2/\text{PAN}$  nanofibres were dipped into a mixed solution of 2-methylimidazole (13 g) and methanol (400 ml) for 3 days. The obtained  $\text{ZIF-8}/\text{ZnBr}_2/\text{PAN}$  nanofibres were washed twice by methanol. Afterwards,  $\text{ZIF-8}/\text{ZnBr}_2/\text{PAN}$  nanofibres were left in air at  $220^\circ\text{C}$  for 180 min and subsequently carbonized under Ar flow at  $900^\circ\text{C}$  for 2 h with a rate of  $5^\circ\text{C min}^{-1}$ .

### 2.2. The synthesis of NMCNFs/S composites.

The obtained high SSA NMCNFs were cut into electrodes ( $\phi = 15$  mm). Then, the NMCNFs/S cathodes were synthesized via vapour diffusion of commercial sulphur powder. Firstly, the NMCNFs sheet

and sulphur were sealed in a glass bottle and heated to  $200^\circ\text{C}$  at a heating rate of  $2^\circ\text{C/min}$  in an oven and maintained at  $200^\circ\text{C}$  for 4 h (sulphur and NMCNFs are separated). Then, the temperature was raised to  $250^\circ\text{C}$  and maintained 2 h.

### 2.3. The fabrication of electrode and electrochemical measurements

The obtained NMCNFs cathodes were used after being dried at  $60^\circ\text{C}$  for 12 h under vacuum. The loading amount of sulphur is about  $1.5\text{--}2.0\text{ mg/cm}^2$  in a cell and the amount of electrolyte is  $30\ \mu\text{L/mg S}$ . The charge-discharge tests were conducted on NEW-ARE instruments with voltage window of  $1.5\text{--}3.0\text{ V}$  versus  $\text{Li}^+/\text{Li}$ . Cyclic voltammetry (CV) experiment was performed on a CHI 660E electrochemical workstation at a scan rate of  $0.2\text{ mV/s}$  from

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