



# Three-dimensional aluminum foam/carbon nanotube scaffolds as long- and short-range electron pathways with improved sulfur loading for high energy density lithium–sulfur batteries



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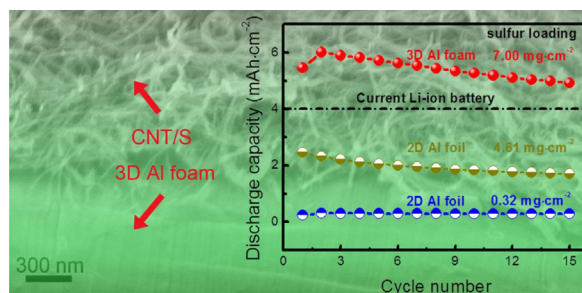
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## HIGHLIGHTS

- 3D Al foam/carbon nanotube scaffolds were applied as the current collectors.
- Short- and long-range electron pathways were efficiently constructed in a Li–S cell.
- A high discharge capacity of  $6.02 \text{ mAh cm}^{-2}$  ( $860 \text{ mAh g}^{-1}$ ) can be achieved on the cathode with sulfur loading of  $7.0 \text{ mg cm}^{-2}$ .

## GRAPHICAL ABSTRACT



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## ABSTRACT

Conductive carbon scaffolds are efficient and effective to build advanced carbon/sulfur composite cathodes for lithium–sulfur (Li–S) batteries. However, the areal sulfur loading is commonly less than  $4.0 \text{ mg cm}^{-2}$ , which limits the energy density and practical application of Li–S cells. In this contribution, three-dimensional (3D) aluminum foam/carbon nanotube (CNT) scaffolds were applied as the current collectors to build long- and short-range electron pathways and provided enough space for high sulfur loading. The sulfur loading amount on the 3D current collectors ranged from  $7.0$  to  $12.5 \text{ mg cm}^{-2}$ . A high initial discharge capacity of  $6.02 \text{ mAh cm}^{-2}$  ( $860 \text{ mAh g}^{-1}$ ) was achieved on an electrode with an improved sulfur loading of  $7.0 \text{ mg cm}^{-2}$ . Therefore, the combination of 3D long-range current collectors and short-range CNT conductive scaffold provides an efficient and effective route to make full use of sulfur with a very high sulfur loading amount in a Li–S cell.

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## 1. Introduction

With the rapid development of the portable electronic devices and laptops, the battery performance becomes a bottleneck. Up till now, tremendous efforts from scientific and engineering communities have been devoted in improving the energy density both in weight and volume of lithium-ion (Li-ion) batteries based on

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intercalation mechanism, which are nearly approaching their theoretical limits but still could not meet the requirements of personal electronics [1]. More importantly, the latest environmentally friendly electric vehicles (EVs) are in urgent need of advanced energy storage systems with high energy and power density, which can render EVs to be competitive to the vehicles with fossil fuel. Lithium–sulfur (Li–S) battery is one of the potential electrochemical systems with the capacity of 1675 mAh g<sup>-1</sup> (based on cathode sulfur) and energy density of 2600 Wh kg<sup>-1</sup> (based on Li–S redox couple), which is nearly five times more than the traditional Li-ion batteries [2–5]. Moreover, the elemental sulfur, as a common industrial by-product, also exhibits advantages of low cost, environmental friendliness, and natural abundance [6].

Apart from its advantages in theoretical calculation, Li–S battery suffers from several practical obstacles. Firstly, the insulative nature of sulfur (an ultra-low electron conductivity of  $5 \times 10^{-30}$  S cm<sup>-1</sup> at room temperature) results in a poor electrochemical kinetics and low utilization, which has been well addressed by the addition of the conductive scaffolds (e.g. ordered mesoporous carbon [7–10], carbon nanotubes (CNTs) [11–14], graphene [15,16], CNT/graphene hybrids [17], carbon hollow spheres [18], carbide-derived carbon [19], hierarchically porous carbon [20,21], polyacrylonitrile [22], etc.). However, the large amount addition of conductive materials hinders the full demonstration of the high energy density of Li–S cells. Secondly, during the discharge processes, higher-order polysulfides generate, then dissolve into the bulk electrolyte, and shuttle between anode and cathode, which severely degrades the discharge capacity and long-term stability of Li–S batteries. Several strategies (such as trapping the sulfur in the cathode [9,10,14,23–26], an ion selective membrane [27], as well as lithium nitrate (LiNO<sub>3</sub>) addition [28]) have been proposed to shield the polysulfide shuttle. Finally, the sulfur loading (the amount of sulfur in the whole electrode) significantly affects the gross capacity of the electrode and the energy density of the total cell, which, however, is usually ignored in previous reports. The areal loading density and the capacity of the reported electrode are, respectively, much lower than 4.0 mg cm<sup>-2</sup> and 4.0 mAh cm<sup>-2</sup>, which is desired for the industrial society towards practical Li–S cells with compatible energy density to current Li-ion batteries [29]. Conventional two-dimensional (2D) aluminum (Al) foils as current collectors can only support sparsely limited active weight. Thus, it is highly expected to explore effective strategy for efficiently loading sulfur phase in the cathode with high capacity, good utilization, robust framework, as well as excellent cycling performance.

The one-dimensional (1D) CNTs exhibit ultrahigh conductivity ( $>10^3$  S m<sup>-1</sup>). The multi-walled CNTs produced by fluidized bed chemical vapor deposition possess a very low cost (less than \$100 kg<sup>-1</sup>) and robust mechanical properties that can withstand volume changes during long-cycle charge–discharge process [30,31]. This is especially beneficial for the construction of a robust conducting network as short-range electron pathways. Therefore, CNTs have been strongly recommended as conductive fillers with quite high sulfur loading capability in a Li–S cell [32]. The use of nanocarbon as short-range conductive networks is quite efficient and effective for the line-to-point contact, and the current applied on each CNT is mostly collected by the plate Al foil through point/line-to-plate contact in the above mentioned researches. In some cases, the short-range CNT conductors are detached from the Al foil due to the unexpected random expansion at the CNT/sulfur–Al foil interface. With the increasing of sulfur loading, the pathways of electron from the Al foil to the sulfur become longer, consequently, the diffusion of ions through the thick electrode is restrained, which hinder the full use of sulfur for Li ion storage. Thus, designing the whole configuration of current collectors for the efficient multi-range electron/ion transfer is highly considered.

In this contribution, a 3D Al foam instead of routine 2D Al foil was employed as the long-range conductive matrix. The combination of 3D Al foam with CNT frameworks not only exhibits long-/short-range scaffolds as electron pathways through hierarchical point-line-plate contact, but also offers vast void space to accommodate huge amount of active materials and interconnected channels with short diffusion pathways and low resistance. A high sulfur loading of 7.0 mg cm<sup>-2</sup> (based on the surface area of the electrode) was available with a discharge capacity of 6.02 mAh cm<sup>-2</sup> (860 mAh g<sup>-1</sup>) at a current density of 1.17 mA cm<sup>-2</sup> (167 mA g<sup>-1</sup>). This was much higher than the Li–S cell with routine Al foil current collectors.

## 2. Experimental

### 2.1. Fabrication of composite cathode

The CNTs were mass-produced on Fe based catalysts in a fluidized bed reactor [33]. The as-grown carbon products were purified by sodium hydroxide (12.0 mol L<sup>-1</sup>) aqueous solution at 160 °C for 4.0 h and hydrochloric acid (5.0 mol L<sup>-1</sup>) aqueous solution at 70 °C for 4.0 h, subsequently. The high purity CNT bundles were available after filtering, washing, and freeze–drying. Then the CNTs were mixed with sulfur powder in the anticipated mass ratio of 1:1 and ball-milled for 3.0 h to form CNT/sulfur composites.

### 2.2. Structure characterizations

The structure of the cathode was identified by an X-ray diffractor (XRD, D8-Advance, Bruker, Germany). A JSM 7401F scanning electron microscopy (SEM, JEOL Ltd., Tokyo, Japan) and a transmission electron microscopy (TEM, JEOL Ltd., Tokyo, Japan) were employed to detect the morphology of raw materials and composite electrodes. The sulfur content of CNT/sulfur composite was determined as 50% (Fig. S1) by thermal gravimetric analysis (TGA) using TGA/DC1 STAR<sup>c</sup> system in N<sub>2</sub> atmosphere at a temperature ramp rate of 10 °C min<sup>-1</sup>. The N<sub>2</sub> adsorption–desorption isotherms were collected by using a N<sub>2</sub> adsorption analyzer (Autosorb-IQ<sub>2</sub>-MP-C system) at 77 K. The sample was degassed at a low temperature of 50 °C until a manifold pressure of 2.0 mmHg was reached before N<sub>2</sub> sorption isotherm measurements to avoid the sulfur sublimation. The surface area was determined by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution plot was calculated by the nonlocal density functional theory.

### 2.3. Li storage performance of composite cathode

The composite CNT/sulfur cathode was fabricated with poly(vinylidene fluoride) (PVDF) binder in *N*-methyl-2-pyrrolidone (NMP) with a mass ratio of CNT:sulfur : PVDF = 42.5:42.5:15. A homogeneously mixed slurry was prepared by magnetic stirred for 24.0 h. The slurry was then coated onto a Al foam with a controllable sulfur loading amount ranging from 7.0 to 12.5 mg cm<sup>-2</sup>, which was punched into 13.0 mm disks. The Al foam fabricated by an artificial punched method was with a bulk density of 0.34 g cm<sup>-3</sup>, a porosity of 0.88, a bulk thickness of ca. 150 μm, and a surface area of 0.04 m<sup>2</sup> g<sup>-1</sup>. The obtained electrode was dried in a vacuum drying oven at 60 °C for 12.0 h. The electrodes were assembled in a two-electrode cell configuration using standard 2025 coin-type cells. Li metal foils with 1.0 mm thick was selected as counter electrodes. The mixed solution of DOL and DME (v/v = 1/1) dissolving 1.0 mol L<sup>-1</sup> lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) was employed as the electrolyte, and the Celgard 2400 polypropylene membranes as the separator. The assembling of cells was conducted in an Ar-filled glove box with oxygen and

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