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# Cathode materials based on carbon nanotubes for high-energy-density lithium-sulfur batteries



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#### ABSTRACT

The rational integration of conductive nanocarbon scaffolds and insulative sulfur is an efficient method to build composite cathodes for high-energy-density lithium-sulfur batteries. The full demonstration of the high-energy-density electrodes is a key issue towards full utilization of sulfur in a lithium-sulfur cell. Herein, carbon nanotubes (CNTs) that possess robust mechanical properties, excellent electrical conductivities, and hierarchical porous structures were employed to fabricate carbon/sulfur composite cathode. A family of electrodes with areal sulfur loading densities ranging from 0.32 to 4.77 mg cm<sup>-2</sup> were fabricated to reveal the relationship between sulfur loading density and their electrochemical behavior. At a low sulfur loading amount of 0.32 mg  $\rm cm^{-2},$  a high sulfur utilization of 77% can be achieved for the initial discharge capacity of 1288 mAh  $g_S^{-1},$  while the specific capacity based on the whole electrode was quite low as 84 mAh  $g_{C/S+binder+Al}^{-1}$  at 0.2 C. Moderate increase in the areal sulfur loading to  $2.02 \text{ mg cm}^{-2}$  greatly improved the initial discharge capacity based on the whole electrode (280 mAh  $g_{C/S+binder+Al}^{-1}$ ) without the sacrifice of sulfur utilization. When sulfur loading amount further increased to  $3.77 \text{ mg cm}^{-2}$ , a high initial areal discharge capacity of 3.21 mAh  $\rm cm^{-2}$  (864 mAh  $\rm g_S^{-1})$  was achieved on the composite cathode.

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#### 1. Introduction

Exploring the energy storage systems for high energy and power density is highly required to meet the rapid development of renewable energy (such as wind, solar energy) harvest, as well as rising energy storage devices for electric vehicle, peaking power station, stand-by electric source, portable electronic (*e.g.* cell phone, laptop, camera), personal healthcare (*e.g.* pacemaker), etc. Among various energy storage systems, lithium–sulfur (Li–S) batteries with a theoretical capacity and energy density of  $1672 \text{ mAh g}^{-1}$  and  $2600 \text{ W h kg}^{-1}$ , respectively, have been considered as an important candidate [1–4]. For a Li–S cell, the overall redox couple, described by the reaction  $S_8 + 16\text{Li} \leftrightarrow 8\text{Li}_2\text{S}$ , lies at an average voltage of approximately 2.15 V with respect to Li<sup>+</sup>/ Li, a potential about 2/3 of that exhibited by routine lithium ion battery systems [4]. The sulfur electrode possesses valuable characteristics, such as low equivalent weight, high capacity, low cost (about \$150 per ton), and nontoxicity. Compared to conventional lithium-ion batteries, Li–S

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batteries offer the opportunity to provide a gravimetric energy density at least five times higher at a much lower cost.

Despite the considerable advantages of the Li-S battery, its practical realization is plagued with tremendous problems. The insulating nature of S and  $Li_2S_x$  (x = 1 or 2), the low utilization of active phase, and the fast capacity degradation are the main challenges [1-6]. Most of nanocarbon materials exhibit excellent mechanical properties, electrical, and thermal conductivities, which facilitate their applications as electrodes for electrochemical energy storage [1,7-9]. The incorporation of nanocarbon (e.g. the activated carbon [10], carbon nanotubes (CNTs) [11-13], graphene [14-17], meso/micro-porous carbon [18-21], carbide derived carbon [22], carbon nanospheres [23-25], and their hybrid [26-29]) into sulfur cathode gives rise to advanced electrodes with improved discharging capacity and cycling performance. Such concept has been strongly recommended by many research groups; however, the sulfur loading amount in the composite electrodes is usually less than  $1.5\,\mathrm{mg\,cm^{-2}},$  far below the value that could be practically applied [16,21,23,26,27,30]. Such a low sulfur loading amount is beneficial to demonstrate the potential of nanocarbon/sulfur cathode with high discharge capacity, but the energy density of the cell (with the consideration of mass contribution from the binder and current collector) is quite low due to limited sulfur loading. Building efficient nanocarbon/sulfur electrode with high areal capacity and acceptable cycling life for high-energy-density cells is the key issue towards full utilization of sulfur for superior Li-S batteries.

In this contribution, a family of CNT/sulfur (CNT/S) electrodes with sulfur loadings ranging from 0.32 to 4.77 mg cm $^{-2}$ were fabricated to illustrate the relationship between electrode thickness and their electrochemical behavior. The reason we selected CNTs as the typical nanocarbon model is that CNTs are with extremely large aspect ratio, excellent mechanical properties, excellent electrical conductivities, hierarchical porous structures, and robust commercial production. High quality CNTs have been world widely produced in a fluidized bed reactor at a low cost [31,32]. The lithium ion storage performance of the CNT/S electrodes with different loading amounts is evaluated. This will shed light on the dependence of the electrode thickness on the electrochemical energy storage performance, which provides a reference to the rational evaluation of the nanocarbon-based electrodes in research laboratory and real design of nanocarbon-based Li-S batteries with high energy density.

#### 2. Experimental

#### 2.1. Fabrication of CNT/S cathodes

The sulfur powder was purchased from Alfa Aesar, and the CNTs were large scale produced in a fluidized bed reactor reported in our previous work [33]. The as-grown carbon products were chemically purified by sodium hydroxide aqueous solution ( $12.0 \text{ mol } \text{L}^{-1}$ ) at  $160 \,^{\circ}\text{C}$  for 4.0 h first. Subsequently, after routine filtering and washing, hydrochloric acid ( $5.0 \text{ mol } \text{L}^{-1}$ ) was used to remove the residual metal catalysts at 70 °C for 4.0 h. Finally, CNTs with high purity were available after further filtering, washing, and freeze-drying. 15.0 g of

the sulfur powder was then mixed with 15.0 g of the CNTs within a QM-3SP2 planetary ball mill which was ran with a rotation frequency of 10 Hz for 12.0 h. The ball mill contained four agate jars, and each had a diameter of 90 mm and a height of 100 mm, within which agate balls with a diameter of 5.0 mm were employed. Without heating treatment, the sulfur powder was successfully dispersed into the CNT scaffolds.

The electrode of CNT/S was fabricated by a routine doctor blade method. The poly vinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP) was added to the ball-milling tank with a mass ratio of CNT/S: PVDF = 9.0. Homogeneously mixed slurry was obtained by further ball-milling for 12.0 h. The as-obtained slurry was coated onto a 20- $\mu$ m-thick aluminum (Al) current collector by an automatic thick film coater (MSK-AFA-III), which can easily realize the modulation of the thickness and sulfur loading amount in the electrode. The CNT/S composite electrode was then available after having been dried at 60 °C for 12.0 h and punched into disks with a diameter of 13.0 mm.

## 2.2. Electrochemical performance of CNT/S electrode with different loading amounts

The electrodes with different loading amounts were assembled in a two-electrode cells configuration using standard 2025 coin-type cells in an argon-filled glove-box. The mixed solvent of dimethyl ether (DME) and 1,3-dioxolane (DOL) (volume ratio = 1:1) having  $1.0 \text{ mol } L^{-1}$  of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved was selected as the electrolyte, Li metal foil with a thickness of 1.0 mm was used as the anode, and the Celgard 2400 polypropylene membrane was employed as the separator. Both the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on Solartron 1470E electrochemical workstation. CV measurement was performed at a scan rate of  $0.1 \text{ mV s}^{-1}$ . EIS measurement was conducted within the frequency range of  $10^{-2}$  to  $10^5$  Hz. The cyclic performance was tested by a Neware multi-channel battery cycler with a voltage window of 1.0-3.0 V.

#### 2.3. Structure characterizations

The structure of the electrodes was identified by an X-ray powder diffractometer (XRD, D8-Advance, Bruker, Germany). The morphology of CNT/S based electrodes was characterized by a high-resolution transmission electron microscopy (TEM, JEM 2010, JEOL Ltd., Tokyo, Japan) and a field-emission high resolution scanning electron microscopy (SEM, JSM 7401F, JEOL Ltd., Tokyo, Japan). The Raman spectra of the CNT and CNT/S cathode were recorded using a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer with He-Ne laser excitation at 633 nm. The sulfur ratio in the CNT/S composites was determined by thermogravimetric analysis (TGA) using TGA/ DSC1 STAR<sup>e</sup> system in  $N_2$  atmosphere with a temperature ramp rate of 20 °C min<sup>-1</sup>. An N<sub>2</sub> adsorption analyzer (Autosorb-IQ2-MP-C system) was employed to collect the N2 sorption isotherms of the CNT/S composites at -196 °C. Before N<sub>2</sub> sorption isotherm measurement, the sample was degassed at a low temperature of 50 °C until a manifold pressure of

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2.0 mmHg was achieved 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.

#### 3. Results and discussion

The morphology of CNT/S composites prepared by a facile ball-milling without any heating treatment is shown in Fig. 1a, b, and S1. CNTs with an outer diameter of 8–15 nm were employed as three-dimensional conductive scaffolds. The sulfur content of CNT/S composite materials was determined as 50% by TGA (Fig. S2). The weight loss peak of sulfur in CNT/S composites shifted to higher temperature range from 200 to 320 °C compared to pure sulfur, indicating the high efficiency of such a room-temperature strategy for incorporation of sulfur into nanocarbon scaffolds [34,35]. As shown in Fig. 1a and S1, the sulfur particle with a size of 5–500 nm was closely attached to the surface of the CNTs and even occupied the pores among CNTs. A few large sulfur particles can also be observed in the CNT/S cathode materials. The high-magnification TEM image of CNT/S composites (Fig. 1b) reconfirmed the close attachment of sulfur particle onto the surface of the CNTs, which facilitated the electron transportation between the sulfur active materials, the current collectors, and the outer circuits through conductive CNT networks. Meanwhile, the legible lattice fringes with an interplanar spacing of 0.269 nm were detected, very similar to the standard value of (331) planes of orthorhombic S (Fig. 1b). As presented in Fig. 1c, no distinct difference between the diffraction peaks of the XRD patterns of the pure sulfur and that of CNT/S composites was detected, neither on position nor on intensity, reconfirming the sulfur in the composite of good crystallization. In contrast, the sulfur peak in the composite was hardly identified on the Raman spectra (Fig. S1b), which was ascribed to the weaker scattering of sulfur phase compared with that of CNTs. According to the N<sub>2</sub> sorption isotherms (Fig. 1d), a hysteresis loop was observed in the  $N_{\rm 2}$  adsorption isotherm of CNTs. There were large amount of mesopores attributed to the intertubular space of agglomerated CNTs. However, the hysteresis loop almost disappeared after loading of sulfur. The CNT pore volume decreased from 0.27 to  $0.12 \text{ cm}^3 \text{ g}^{-1}$  and the specified surface area decreased from 79.3 to 26.3  $m^2 g^{-1}$  after sulfur loading as well. Most of the sulfur particles were filled into the intertubular spaces, and also a few sulfur particles were infiltrated into the internal spaces of CNTs. Therefore, most of the pores in the range of 2–50 nm were occupied by sulfur during ball milling (inset of Fig. 1d).

A family of CNT/S cathodes with a sulfur loading amount ranging from 0.32 to 4.77 mg cm<sup>-2</sup> were fabricated by controlling the thickness of the CNT/S electrodes on the Al foil during the doctor blade process. The top and side views of the CNT/S cathode with different sulfur loading amounts are



Fig. 1 – (a) SEM and (b) TEM images of the CNT/S composites, (c) XRD patterns of pure S and CNT/S composites and (d)  $N_2$  adsorption–desorption isotherms and corresponding pore size distributions (inset) of CNT and CNT/S composites. (A colour version of this figure can be viewed online.)

illustrated in Fig. 2. The CNT/S cathode offered a compact surface in large area domain (Fig. 2a). No crack or protuberance was observed in large area electrode. However, there were still a lot of interconnected macro-/meso-pores (Fig. 2b-d) in the electrode, which served as ion channels for rapid ion transportation during cycling even the axial transfer distance was much longer as the thickness increasing. Such uniform electrode provided a close contact with the separator and could be easily infiltrated by the electrolyte. The thickness of the CNT/S electrode was determined by the side view images. As shown in Fig. 2b, CNT/S based electrode with a thickness of 15 µm was available by controlling the blade thickness and corresponding sulfur loading amount as  $0.32\,mg\,cm^{-2}\!.$  Also, the CNT/S composite cathodes with thicknesses of 100 and 215  $\mu m$  were also obtained (Fig. 2c and d). The corresponding sulfur loading amounts were determined to be 2.02 and 3.72 mg  $cm^{-2}$ , respectively.

The Li–S batteries with different sulfur loading amounts ranging from 0.32 to 4.77 mg cm<sup>-2</sup> were assembled in an argon-filled glove-box at 25 °C. The relationship between the initial discharge capacities (based on sulfur (red), CNT/ S + PVDF binder (olive), and CNT/S + PVDF binder + Al current collector (blue)) and the sulfur loading amount is shown in Fig. 3a. A significant improvement of sulfur utilization was observed when the sulfur loading amount was 0.32 mg cm<sup>-2</sup>, with the 1st discharge capacity of 1288 mAh  $g_s^{-1}$  (577 mAh  $g_{C/S+PVDF}^{-1}$ , 84 mAh  $g_{C/S+PVDF+Al}^{-1}$ ) at 0.2 C (1.0 C = 1672 mAh  $g^{-1}$ ). The electrode with low sulfur loading amount presented a perfect lithium ion storage performance when calculated based on the active sulfur materials or CNT/S composite/PVDF binder, whereas an extremely low discharge capacity was available based on CNT/S composite/PVDF/Al current collector. With the increase in the sulfur loading on the electrode, the discharge capacity based on the total mass of the electrodes became larger, although the sulfur utilization began to decrease slightly when the sulfur loading was higher than 0.32 mg cm<sup>-2</sup>. A cell with an initial discharge capacity of 280 mAh  $g_{C/S+PVDF+Al}^{-1}$  (1215 mAh  $g_s^{-1}$ , 547 mAh  $g_{C/S+PVDF}^{-1}$  at 0.2 C could be achieved when the sulfur loading amount was increased to 2.02 mg cm<sup>-2</sup>.

The areal discharge capacities of the 1st and 100th cycle for different sulfur loading amounts are shown in Fig. 3b. When the sulfur loading amount was  $3.72 \text{ mg cm}^{-2}$ , a higher 1st and 100th discharge capacity were achieved as  $3.21 \text{ mAh cm}^{-2}$  and  $1.33 \text{ mAh cm}^{-2}$ , respectively. In contrast, the 1st and 100th discharge capacity were only  $0.41 \text{ mAh cm}^{-2}$  and  $0.27 \text{ mAh cm}^{-2}$ , respectively, for the sulfur loading amount of  $0.32 \text{ mg cm}^{-2}$ . With the sulfur loading on the electrode rising to  $3.72 \text{ mg cm}^{-2}$ , the areal density of electrodes became larger. The over loading of sulfur on the



Fig. 2 – (a) The top and (b–d) side views of the CNT/S composite electrodes. The sulfur loading amounts were (a) 0.32, (b) 0.32, (c) 2.02, and (d)  $3.72 \text{ mg cm}^{-2}$ . (A colour version of this figure can be viewed online.)



Fig. 3 – (a) The relationship between the initial discharge capacities (based on sulfur (red), CNT/S composites (C/S) + PVDF binder (olive) and C/S + PVDF binder + current collector (blue), respectively) of Li–S cells and the sulfur loading amount; (b) the discharge capacities of the 1st and 100th cycle with different sulfur loading amounts. (c) The cycling performance and (d) coulombic efficiency at a current density of 0.2 C (1.0 C = 1675 mA g<sup>-1</sup>) with the sulfur loading amount of 0.32, 2.02, and 3.72 mg cm<sup>-2</sup>, respectively. (A colour version of this figure can be viewed online.)

electrode induced a very thick layer of electrode, which provoked overlong diffusion length for ions in the electrolyte, and more polysulfides were generated and dissolved into the buck electrolyte during discharging process. Therefore, the shuttle of polysulfide tended to be more severe and the sulfur utilization became poorer, leading to the relatively fast degradation in the areal discharge capacity. The cycling performance and coulombic efficiency of electrodes with the sulfur loading amount of 0.32, 2.02, and  $3.72 \text{ mg cm}^{-2}$  are shown as Fig. 3c and d, respectively. The Li-S cell with higher sulfur loading amount afforded a higher areal discharge capacities initially; however, the coulombic efficiency was lower as the result of the above-mentioned shuttle of polysulfides when a large amount of sulfur was encapsulated in the cell. The decay rates in the initial 100 cycles of cells with the sulfur loading amount of 0.32, 2.02, and 3.72 mg cm<sup>-2</sup> were 0.33%, 0.43%, and 0.58%, respectively. The initial coulombic efficiencies for cells with sulfur loading amounts of 0.32, 2.02, and 3.72 mg cm<sup>-2</sup> were about 96%, 84%, and 83%, corresponding to shuttle factors (defined as ratio of the sulfur amount caused by the diffusion of polysulfides between cathode and anode and by the charge/discharge current) of 12%, 47%, and 50%, respectively.

Note that the severer shuttle occurred with the increase in the sulfur loading amounts. Several strategies had been proposed to control the shuttle of polysulfides. For instance, the incorporation of polymer chains (such as polyethylene glycol [14,16,18,36], and polyvinylpyrrolidone [37]) or porous polysulfide reservoirs [38-40] that afforded the highly hydrophilic surface and a chemical gradient. In addition, the use of electrolyte with a highly concentrated lithium salt [22,41], solvent-in-salt electrolyte with ultrahigh salt concentration and high lithium-ion transference number [42], and electrolyte containing lithium nitrate [43], tetrabutylammonium triflate or N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide [44] effectively suppressed the redox shuttle of the dissolved lithium polysulfides. Besides, the use of a cation permselective membrane rendered the electrostatic interaction and further allowed lithium ions to diffuse, whereas prevented the permeation and thus restrained the shuttle of polysulfide anions across the membrane, i.e. suppressed the shuttle of polysulfides [45]. The addition of nanocarbon (e.g. graphene [46] or CNT [47]) paper acting as a pseudo-upper current collector localizes and retains the dissolved active material during cycling. An applicable way to recharge Li-S cells by a facile charge operation control that inhibits the electrochemical reactions along with severe polysulfide dissolution and thus offers outstanding improvement [48]. The rational combination of these concepts with high loading CNT/S cathode is expected to further suppress the shuttle effect and greatly improve the cycling stability of Li–S cells.

The electrochemical characteristics of CNT/S cathode were also evaluated by galvanostatic charge–discharge profiles, CV curves, rate performance test, and EIS measurement. Fig. 4a shows the normalized galvanostatic charge–discharge curves (by dividing the discharge capacity) with sulfur loading

amount of 0.32, 2.02, and  $3.72 \text{ mg cm}^{-2}$ , respectively. The curves possessed a typical two-plateau feature of Li-S multielectron-transfer chemistry. The ratio of the length of highand low-stage kept almost constant; however, the polarization of the reduction of polysulfides into Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S became severe with the increase in the sulfur loading amount. It was inferred that there were outstanding increases in internal resistance on both ion diffusion and electron transfer with higher loading of active materials on the electrode. The typical CV profiles of the CNT/S electrode with a loading amount of 2.02 mg cm $^{-2}$ is shown in Fig. 4b. It still presented a typical two-step discharging behaviors. Two main reduction peaks at around 2.27 and 1.93 V were detected during the first cathodic scan, which corresponded to the reduction of element sulfur to lithium polysulfides (nS + 2Li^+ + 2e^-  $\rightarrow$  Li\_2S\_n, (4  $\leqslant$  n  $\leqslant$  8)) and the reduction of lithium polysulfides to lithium sulfides (Li<sub>2</sub>S<sub>n</sub> +  $2(n-1)Li^+ + 2(n-1)e^- \rightarrow nLi_2S$  (n < 4)), respectively [5,16]. Two oxidation peaks at 2.33 and 2.45 V in the subsequent anodic scan were also identified, which were correlated to the oxidation of lithium sulfide to lithium polysulfide and further oxidation to element sulfur, respectively [5,16]. The reduction and oxidation peaks were well maintained at the sequent cycles, and no obvious changes on the intensity and position of the peaks in the process of cathodic and anodic scan were observed, except the minor shift of oxidation peak of the lithium sulfide to low voltage. Fig. 4c describes the rate performance of the Li–S cell with a sulfur loading amount of  $2.02 \text{ mg cm}^{-2}$ . The areal discharge capacities of 2.26, 1.96, 1.80, and  $1.76 \text{ mAh cm}^{-2}$  were achieved at a current density of 0.1, 0.2,

0.5, and 1.0 C, respectively. The perfect rate performance was ascribed to the high effective electron pathways provided by the CNTs and interconnected macro-/mesopores as ion channels in the cathode.

The EISs of the fresh cell and cells after 500 cycles are shown in Fig. 4d and S3. The EIS curves of fresh cells were with two semicircles, corresponding to the Li-ion migration through the surface film on the lithium anode (high frequency semicircle) and the charge transfer across the interface (low frequency semicircle) respectively. The impedance decreased with the increase in the sulfur loadings (Fig. S3a). After cycling, the continuous reduction of sulfur and diffusion of polysulfide induced the changes on the equivalent series resistance of electrolyte and cell components, such as the resistance contributed by the charge transfer, as well as the resistance caused by the diffusion of lithium ions into the bulk cathode. Consequently, due to the formation of solid electrolyte interfaces on the Li anode and irreversible insulate Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> layer on cathode electrode, the EIS was quite different from those collected on fresh cells. With more sulfur loading in one cell, more insulate Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> were generated after cycling test. The equivalent series resistance caused by electrolyte and cell components was 3.75, 4.39, and 17.61  $\Omega,$  corresponding to the sulfur loading of 0.32, 2.02, and 3.72 g cm<sup>-2</sup>, respectively. The high sulfur loading in cathode also resulted in vast dissolution of polysulfides into the electrolyte and the irreversible deposition of Li<sub>2</sub>S and/or Li<sub>2</sub>S<sub>2</sub> on cathode, anode and poor ion pathway in the cell, which was responsible for the increased impedance.



Fig. 4 – (a) The galvanostatic charge–discharge curves of Li–S cells showing the polarization and over-charging; (b) The cyclic voltammetry curves at a scan rate of  $0.1 \text{ mV s}^{-1}$  with a sulfur loading amount of 2.02 mg cm<sup>-2</sup>; (c) The reversible charge–discharge processes of rate performance at 0.1, 0.2, 0.5, and 1.0 C; (d) The electrochemical impedance spectra of the fresh cell and that with a sulfur loading amount of 2.02 mg cm<sup>-2</sup> after 500 cycles. (A colour version of this figure can be viewed online.)

#### 4. Conclusions

The CNT/S composites fabricated by a facile room-temperature ball-milling strategy were employed as cathode materials. The sulfur loading amounts of the electrodes were altered from 0.32 to 4.77 mg cm<sup>-2</sup> by tuning the thickness of CNT/S composites coated onto the Al foil. A high initial discapacity of 1288 mAh  $g_{\rm S}^{-1}$  (577 mAh  $g_{C/S+PVDF}^{-1}$  , charge 84 mAh  $g_{C/S+PVDF+Al}^{-1}$ ) at 0.2 C was achieved with the sulfur loading amount of  $0.32 \text{ mg cm}^{-2}$ . The as-obtained Li–S cell afforded the highest sulfur utilization compared to the other cells with different loading amount. A cell with an initial discharge capacity of 1215 mAh  $g_S^{-1}$  (280 mAh  $g_{C/S+PVDF+Al}^{-1}$ , 547 mAh  $g_{C/S+PVDF}^{-1}$ ) at 0.2 C was achieved with the sulfur loading amount increasing to 2.02 mg cm<sup>-2</sup>. When the sulfur loading amount was  $3.77 \text{ mg cm}^{-2}$ , a high initial areal discharge capacity of 3.21 mAh cm $^{-2}$  (864 mAh g $^{-1}$ ) was achieved. The CNTs acting as conductive scaffolds provided a robust electrochemical environment, high effective electron pathways and ion channels for the electrochemical process of Li-S batteries, which are promising candidates for the construction of high energy density Li-S batteries.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon. 2014.03.049.

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