C–S Bonds in Sulfur-Embedded Graphene, Carbon Nanotubes, and Flake Graphite Cathodes for Lithium–Sulfur Batteries

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ABSTRACT: Lithium–sulfur (Li–S) batteries are excellent rechargeable battery candidates which are extraordinarily promising as they exhibit superior specific capacity and well-known energy density; they are cost-effective and environmentally benign. Nevertheless, a few technical issues pose a significant challenge on the path to industrial applications, namely, capacity fade and Coulombic efficiency decay, which are inherent in the soluble polysulfide shuttle effect during charge/discharge cycling. Carbon materials which have excellent conductive scaffold and flexible structure with a variety of morphologies can serve as a remedy to this issue. Herein, with a well-designed melt-diffusion procedure, we prepared three carbon-based sulfur-embedded cathodes with diverse structures [graphene, carbon nanotubes (CNTs), and flake graphite]. Sulfur loading varies between 60 and 73 wt %. Among these three carbon/S cathodes, beyond 100 cycles, the graphene/S cathode showed a discharge capacity of 840 mA h g⁻¹ at 0.2 A g⁻¹ current density and its average Coulombic efficiency was above 99.4%, demonstrating the best cycle stability and reversibility. While at a higher current rate, 1 A g⁻¹, CNT/S reaches the best capacity of 518 mA h g⁻¹ among these three cathodes, revealing excellent sulfur utilization under high rate conditions. The X-ray photo spectroscopy shows evidence for chemical bonding between graphene/CNTs surfaces and carbonyl, hydroxyl, and ether groups, resulting in well-confined polysulfides in the cathode side, which significantly restrain the movement of soluble polysulfide in the charging process and efficiently decreases the capacity fading of sulfur. This unique structure is a potential explanation for the outstanding electrochemical performance.

1. INTRODUCTION

The lithium–sulfur battery is an emerging star for next-generation electrochemical energy storage, with superior theoretical specific capacities of 1675 mA h g⁻¹ and overwhelming 2600 Wh kg⁻¹ theoretical specific energy.¹–³ Sulfur, which comprises the cathode material, is abundant in nature, environment friendly, and of low cost. Despite these advantages, its industrialization is still facing two basic obstacles. One is low electric and ionic conductivity of both sulfur and its discharge products, Li₂S, which leads to poor active material utilization and inferior reversibility. The other obstacle is the loss of active material via dissolution of long chain polysulfide intermediate products to the electrolyte, namely, “shuttle effect”, in which soluble polysulfides transfer to the anode side, where the reaction with metallic lithium ultimately yields shorter and insulated polysulfides, resulting in capacity fading, inferior Coulombic efficiency, and anode corrosion.¹⁻⁶ In addition, the volume expansion for complete lithiation of sulfur can be as high as 80%, which leads to severe pulverization and delamination of the active material from the current collector.⁷⁻⁸

Multiple strategies have been considered to solve these problems of the sulfur cathode, such as (1) introduction of a conductive network to enhance electron mobility; (2) design a suitable cathode network to facilitate the lithium ion diffusion channel and immobilize polysulfides; (3) establishment of an easily accessible and sufficient surface area to lower the deposition of insulated Li₂S₂ or Li2S; (4) construction of robust and electrochemical reactive porous structures to alleviate the volume expansion and buffer the resulting stress. All these solutions share the same idea: rational construction of the suitable sulfur cathode is the pivotal factor to address the abovementioned Li–S batteries drawbacks.⁹⁻¹⁰

Carbon materials comes with an excellent conductive scaffold and flexible structure [such as graphene and carbon nanotubes (CNTs)] and diverse morphology, which can work efficiently as the sulfur and polysulfide confinement cage in cathodes for the Li–S battery system. Many recent reports on sulfur-embedded carbon cathodes exhibited significant reduction of the shuttle effect for lithium sulfur batteries and hence alleviate the capacity fading dramatically.¹¹⁻¹⁶ Seeking promising sulfur substrates for lithium–sulfur battery applica-

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tions, researchers have investigated mesoporous carbon,\textsuperscript{17–20} CNTs,\textsuperscript{21–23} graphene or graphene oxide,\textsuperscript{24–30} mixture of CNTs\textsuperscript{31} and graphene,\textsuperscript{32–34} carbon fiber cloth,\textsuperscript{35} carbon floc,\textsuperscript{35} and carbon onion.\textsuperscript{36}

To further investigate the sulfur-embedded carbon cathodes, we prepared three cathodes with sulfur embedded in different carbon allotropes (graphene, CNTs, and flake graphite) and compared their cycling and high-rate performances at identical charge/discharge conditions. In addition, we use the X-ray photoelectron to investigate the C–S interaction mode in the three carbon/S composite cathodes. We expect that the interaction between carbon and sulfur specifies an important effect on electrochemical performance of these carbon/S cathodes, which can guide the improvement of carbon-based Li–S cathodes.

2. RESULTS AND DISCUSSION

We fabricated carbon/S composites using sulfur melt-diffusion, in which Graphene, CNTs, and flake graphite host sulfur as confines. This procedure is described in detail in the Experimental Section. The morphologies of graphene, CNTs, flake graphite and their sulfur composites are examined by scanning electron microscopy (SEM). Figure 1 presents the photography. From Figure 1a, the graphene sheets are corrugated and wrinkled with scrolled edges. As a result of sulfur melt diffusion at temperature of 155 °C, the deficient pores of the graphene sheets are filled with abundant sulfur particles and the surface and edges of graphene are covered by an amount of agglomeration of sulfur, which is shown in Figure 1b. The same phenomena were also found in CNT/S and graphite/S composites. Before sulfur melt diffusion, CNTs organization are unordered and featured with the three-dimensional network of bundles, as shown in Figure 1d. The flake graphite has layered structures with smooth surfaces, as shown in Figure 1g. After melt diffusion, the sulfur particles were agglomerated on the surfaces of CNTs to form CNT/S bulks (Figure 1e). While in the graphite/S composites, many graphite layers agglomerated together to form large bulks with sulfur covering all the surfaces of graphite (Figure 1h). The sulfur particle homogeneously covers the surfaces of these three carbon/S composites, and further elemental mapping of sulfur in Figure 1c,i measurement confirms it.

The X-ray diffraction (XRD) patterns of graphene, CNT, graphite, graphene/S, CNT/S, graphite/S, and pure S materials are shown in Figure 2a. There is no distinct peak in the XRD pattern of graphene, which indicates low crystallinity or amorphous structure. The featured diffraction peaks of CNTs and flake graphite are at 26.5°, which indicates the typical structure of graphite crystals. The peak of CNTs is broader than that of flake graphite, revealing their lower crystallinity. After sulfur melt-diffusion, the sulfur diffraction peaks can be observed in three carbon/S composites with decreased intensity compared to pure sulfur. In contrast to the graphite/S composite, the featured peaks of graphite are observed in CNT/S and graphene/S composites because of the low crystallinity of CNTs and graphene themselves.

To investigate the sulfur weight ratio in the three composites, we performed thermogravimetric analysis (TGA). From Figure 2b, it is apparent that pure sulfur features one-step weight loss in the temperature range 190–300 °C. At the same temperature range, the three carbon/S composites reproduce the weight loss profile of pure sulfur, therefore, it is reasonably attributed to the loss of sulfur. Thus, the loss in 190–300 °C is a good approximation to the sulfur weight ratio in the composites. Based on the above assumption, the weights of sulfur in the graphene/S, CNT/S, and graphite/S are calculated as 72.94, 59.63, and 62.80 wt %, respectively.

The porosity of the three carbon/S composites was employed by adsorption–desorption isotherms with N\textsubscript{2}, as shown in Figure 2c. With relative pressure ranges from 0.8 to 1.0, all the three samples demonstrate no hysteresis loop, suggesting that the materials have a large number of homogeneous pores.\textsuperscript{37} The distribution of the pore size can be deduced with Barrett–Joyner–Halenda (BJH)’s adsorption variants, as shown in Figure 2d. From the figure, we can see the pore size distribution of graphene and CNTs spreads over a range from 2 to 11 nm, while there is no significant pore in flake graphite. The Brunauer–Emmett–Teller surface areas of graphene, CNT, and graphite materials are 113.3, 178.7, and 10.2 m\textsuperscript{2} g\textsuperscript{−1}, respectively, which indicates that the graphene and CNTs come with larger surface area than flake graphite. This is because there are a lot of defects and porous structures on the rough graphene sheet surface, which leads to high surface areas. The porous and defective structures provide spaces and interfaces to restrain soluble sulfur chains in cycling and improve the intercalation between the electrolyte and cathode, which leads to high reversible capacity and fast charge transfer of lithiation/delithiation.\textsuperscript{38}

The C 1s X-ray photoelectron spectroscopy (XPS) spectra of graphene, graphene/S, CNT, CNT/S, graphite, and graphite/S are shown in Figure 3. The C 1s spectra of pristine graphene and CNTs reveal the presence of C–O (287.5, 285.3 eV) and C=O (288.3, 287.6 eV) groups, which indicates that graphene and CNTs were partly oxidized. After sulfur melt diffusion, the binding energies of C=O (286.6, 286.5 eV), respectively, in graphene/S and CNT/S composites became
smaller than the pristine graphene and CNTs. This indicates that the carbon surface-attached carbonyl, hydroxyl, and ether groups are expected to have chemical bonds with sulfur, which can contribute to well-confined polysulfides in the side of the cathode. In addition, the S 2p spectra in Figure 4b (graphene/S) and 4c (CNT/S) show the broad high binding energy peak at the position around 169 eV, which strongly supports chemical bond in play. However, for graphite, either the C 1s or S 2p spectrum of graphite does not show such characteristic, which indicates no chemical binding between graphite and sulfur species.

Intensive electrochemical characterization was applied to estimate the function of the three carbon/S cathodes with metallic lithium as anodes. The long-term stability for cycling up to 100 cycles was further investigated with 200 mA g\(^{-1}\) current density. As Figure 5a presented, all the three cathodes exhibit better cycle stability than pure sulfur. Among three cathodes, discharge capacity of graphene/S remains to be above 840 mA h g\(^{-1}\) up to 100 cycles. Moreover, the average Coulombic efficiency of the graphene/S cathode reveals to be above 99.4\%, which demonstrates the best cycle stability and excellent reversibility. The increasing in capacity in the first few cycles is because of the electrode activity process. The lithium ion gradually enters the electrode materials, so the lithiation channels become much smoother after first few cycles resulting in increasing capacity. Figure 5b–d presents cycle dependence of charge/discharge performance of the three carbon/S cathodes. The CNT/S cathode is able to deliver the high capacity from the very beginning, while graphene/S and graphite/S capacity peaks can only be obtained after 10–20 warm-up cycles, which indicates that the CNT/S cathode represents fastest electrochemical active kinetics among the tested cathodes. The rate capability, for all of them, was estimated under a wide range of current density. As can be seen from Figure 5e, the graphene/S cathode exhibits a high discharge capacity at 1600 mA h g\(^{-1}\) at beginning few cycles at 100 mA g\(^{-1}\) current density. In case that current density elevates to 200, 400, 800, and 1000 mA g\(^{-1}\), the cathodes exhibited capacities of 1196, 1023, 713, and 448 mA h g\(^{-1}\), respectively. Furthermore, the graphene/S cathode shows good recovery of the capacity of 945 and 798 mA g\(^{-1}\) as current rate drops to 200 and 100 mA g\(^{-1}\). It is worth mentioning that CNT/S and graphite/S cathodes have better capacities of 518 and 557 mA h g\(^{-1}\) than the graphene/S cathode when it comes to the high current rate (1 A g\(^{-1}\)), which can be explained by the fact that the CNTs and graphite provide faster sulfur utilization under high rate charge/discharge conditions. Figure 5f–h displays the charge rate dependence of charge/discharge behaviors of the three carbon/S cathodes. There are two prominent plateaus at the high charge rate which reveals excellent electrical conductivity resulting in rapid charge transfer.

SEM images of the graphene/S, CNT/S, graphite/S, and pure sulfur cathodes before and after charge/discharge cycling are shown in Figure 6. For the SEM data, the cells before cycling and after cycling are both 50% DOD discharged. For the graphene/S cathode, there is a sign of film formation approximately at the nanoscale on the cathode surface after cycling (Figure 6b), while CNT/S (Figure 6c) and graphite/S (Figure 6e) cathodes still have plenty of porous surfaces, comparable to its stand-alone counterpart (Figure 6d,f). All the three carbon/S cathodes exhibited no evidence for passivation film formation, indicating a robust structural stability of the cathode leading to high reversible capability. The fabricated electrode achieves outstanding rate capability, Coulombic efficiency, stability, and sulfur utilization.

To further look into the sulfur confinement in the three carbon/C cathodes compared with the pure sulfur cathode, Table 1 presents the EDX result of percentage change for the graphene/S, CNT/S, graphite/S, and pure sulfur cathodes surface. As the table shows, there is 6.38, 13.41, and 14.89 wt % loss of sulfur for the graphene/S, CNT/S, and graphite/S cathodes, respectively. The results indicate that sulfur is efficiently confined in the nanoscale graphite/S and CNT/S cathodes due to their high sulfur retention. In contrast, the graphene/S cathode exhibits lower sulfur confinement, which could be attributed to the lower sulfur retention observed in the EDX analysis.
Figure 3. XPS spectra of C 1s in (a) graphene, (b) graphene/S, (c) CNT, (d) CNT/S, (e) graphite, and (f) graphite/S materials.

Figure 4. XPS spectra of S 2p in (a) pure S, (b) graphene/S, (c) CNT/S, and (d) graphite/S materials.
cathodes after 100 cycles, compared to 19.79 wt % loss from the pure sulfur cathode, indicating the best sulfur confinement ability for graphene hosts than CNTs and graphite cathodes. The increasing oxygen ratio after cycles is coming from the electrolyte loading in the surface of the anode.

3. CONCLUSIONS

Graphene, CNTs, and flake graphite were introduced as sulfur host/confinements by using the sulfur melt-diffusion procedure to fabricate carbon-supported sulfur cathodes. It makes construction of sulfur loading of 60−73 wt % possible for Li−S batteries. We prepared three sulfur-embedded carbon cathodes (graphene, CNTs, and flake graphite) and compared their cycling and high-rate performances at the identical experimental setup. Among the three cathodes, the graphene/S cathode demonstrates the best cycle stability and high reversibility at low rate charge/discharge conditions, while the CNT/S cathode has better capacities at high rate charge/discharge conditions. The C−S interaction was thoroughly characterized to explain the excellent electrochemical performances of graphene/S and CNT/S cathodes. The functional groups containing oxygen are proved to chemically bond with sulfur, preventing the shuttle effect of soluble polysulfide in the cycling process, and in turn improves the cycle stability of the sulfur cathodes.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Graphene/S, CNT/S, Graphite/S Materials. Graphene and flake graphite were bought from XFNano Co. Ltd., Nanjing, China. CNTs were purchased from...
New Materials Co. Ltd., Shenzhen, China. The electronic conductivities of graphene, CNTs, and graphite are recorded using the SDY-5 four-point probe meter (Guangzhou, China) with the four-electrode approach. The electronic conductivities of graphene, CNTs, and graphite are 25, 105, and 620 S cm$^{-1}$, respectively. Graphene, CNTs, and flake graphite were blended with sulfur by a weight ratio of 1:3, which were manually ground in an argon-protected glovebox. An Al$_2$O$_3$ crucible is used to hold and transfer the samples to a furnace in an alumina tube, where the samples were heated in a flowing argon environment at 155 °C for 10 h. When annealed to room temperature, it results in homogeneous black powders. Finally, we used pestles and mortars to grind the products. The obtained carbon/sulfur composites were labeled as graphene/S, CNT/S, and graphite/S.

4.2. Materials Characterizations. Rigaku D8A X-ray diffractometer (Bruker, Germany) was used to perform the XRD measurements. The radiation source is Cu K$_\alpha$ ($\lambda = 0.154$ nm) with 2$\theta$ from 5° to 80°. We used N$_2$ gas in the TGA Q600 system (TA, USA) to analyze thermogravimetric properties, starting at room temperature and ending at 600 °C. The heating rate was set to 20 °C min$^{-1}$. Isotherms were measured by using an ASAP 2020 analyzer (Micromeritics, USA) at liquid nitrogen temperature for N$_2$ adsorption—desorption. We also deduced distribution of the pore size by the BJH method with isotherms data. SEM is performed using the FEI Nova Nano 230 system to characterize the sample morphologies. An accelerating voltage of 15 kV is used in the SEM experiment. We employed an X-ray photoelectron spectrometer (PHI-5000, USA) to implement XPS measurements with an emission current of 10 mA. A radiation source (Al K$_\alpha$) of 1486.7 eV is used. The SDY-5 four-point probe meter (Guangzhou, China) is used to carry out four-electrode conductivity measurement for graphene, CNT, and graphite materials.

4.3. Electrochemical Measurements. The cathodes were fabricated by a mixture of carbon/S powders with acetylene black (ENSACO Co. Ltd., Switzerland) and polytetrafluoroethylene (Alfa Aesar Co. Ltd., USA) binder with ratio 5:3:2 in terms of weight. The mixtures were stirred with ethanol into homogeneous slurry at room temperature. Next, we coated them onto a current collector of aluminum foil, which was then vacuum-dried at 70 °C for 24 h. Pure sulfur follows the same steps. The sulfur areal loadings in the graphene/S, CNT/S, and graphite/S cathode slides are 0.86, 0.70, and 0.74 mg cm$^{-2}$, respectively. These cathodes were further assembled to battery cells in the following procedures.

In a glovebox protected by argon, the 2032 coin cells were used to assemble cathodes, the counter electrodes—Li foil (Zhongneng Lithium Products Co. Ltd., Tianjin, China), a cell separator—Celgard 2400 film (Celgard Co. Ltd., USA), and

![Figure 6. SEM photography for cathodes before and after cycling: (a,b) graphene/S; (c,d) CNT/S; (e,f) graphite/S; (g,h) pure.](image)

Table 1. Surface Elemental Percentage in Terms of Weight and Atom Count for Graphene/S, CNT/S, Graphite/S, and Pure S, Measured by Energy-Dispersive X-Ray Spectroscopy (EDX), Samples Taken from Cathodes before Cycling and after 100 Cycles

| cathodes   | wt %    | at. %   | wt %    | at. %   | wt %    | at. %   |
|------------|---------|---------|---------|---------|---------|---------|
|            | C       |         | O       |         | S       |         |
| graphene/S | before   | 66.13   | 82.69   | 3.07    | 2.88    | 30.81   | 14.43   |
|            | after    | 33.21   | 44.78   | 42.36   | 42.88   | 24.43   | 12.34   |
| CNT/S      | before   | 74.40   | 87.60   | 2.50    | 2.21    | 23.10   | 10.19   |
|            | after    | 75.67   | 83.80   | 14.64   | 12.17   | 9.69    | 4.02    |
| graphite/S | before   | 72.11   | 86.29   | 2.69    | 2.41    | 25.20   | 11.30   |
|            | after    | 65.92   | 75.22   | 23.77   | 20.37   | 10.31   | 4.41    |
| pure S$^{10}$ | before     | 56.69   | 76.41   | 3.62    | 3.66    | 39.25   | 19.82   |
|            | after    | 33.55   | 44.21   | 46.59   | 46.08   | 19.46   | 9.61    |
the electrolyte—1 M lithium bis(trifluoromethane sulfone)-imide + 1 wt % LiNO₃ in 1,3-dioxolane and dimethoxyethane (1:1 in volume) mixture together. The electrolyte from Guotai-Huang New Chemical Materials Co. Ltd., Zhangjiagang, China was used.

A battery testing system—LAND 2001A (Landian Corp., Wuhan, China)—was used to perform the galvanostatic charge/discharge cycle tests.

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**Notes**

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