The correlation between carbon structures and electrochemical properties of sulfur/carbon composites for Li-S batteries

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HIGHLIGHTS

- S/RGO-CYS cathode exhibits high rate capability and low capacity decay rate.
- How the carbon structure affects the sulfur/carbon cathode property is elucidated.
- Sulfur-containing groups’ role in immobilizing lithium polysulfides is elucidated.
- Surface chemistry of the carbon host is more important for excellent Li-S battery.

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ABSTRACT

The structures of carbon materials greatly affect the electrochemical properties of sulfur/carbon composites for lithium-sulfur (Li-S) batteries. Understanding the effect of carbon structure factors on the electrochemical properties of sulfur/carbon composites helps in rational designing of the cathode material for optimized battery performance. We prepare reduced graphene oxide (RGO), cysteine-modified RGO (RGO-CYS), microwave-expanded graphite oxide (MEGO) and activated-MEGO (aMEGO) with specific surface areas (SSA) of 58–3010 m² g⁻¹, C/O atomic ratios of 2.41–10.81, pore sizes of 0.9–5.6 nm and pore volumes of 0.14–2.03 cm³ g⁻¹. The electrochemical performance researches S/RGO-CYS > S/RGO > S/MEGO > S/aMEGO when it is listed in the order of their specific capacity, rate capability and cyclic life. And the S/RGO-CYS delivers a high reversible capacity of 455 mA h g⁻¹ at 8 C. The excellent performance of S/RGO-CYS composite is ascribed to the sulfur-containing functional groups of the RGO-CYS, which helps the sulfur dispersion and stabilizes the dissoluble lithium polysulfides. Our results demonstrate that the surface chemistry of carbon materials plays a more important role than the SSA, pore size and pore volume for the electrochemical properties of sulfur/carbon composites for Li-S batteries.

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1. Introduction

Lithium-sulfur (Li-S) batteries offer a high theoretical energy density of 2567 W h kg⁻¹ by the multi-electron-transfer cathode reaction between elemental sulfur and lithium ions, and are a focus
of post lithium-ion batteries technology [1–6]. Yet, there are challenging obstacles standing in the way of the large-scale application of the Li-S technology in the market, which include the potential safety risk of Li-dendrite formation, the low cyclic life as a result of the dissolution of the lithium polysulfides (Li2Sx, 4 ≤ x ≤ 8) in the electrolyte and the volume change (~80%) of the sulfur during lithiation/delithiation, and the poor rate capability due to the low electrical conductivity of sulfur (5 × 10−3 S cm−1 at 25 °C) [7–9].

Carbon materials are commonly used as the host to accommodate sulfur to address these issues relevant to the sulfur-cathode owning to their diversity, conductivity, robust stability and chemistry, and their ready abundance and cost [10–12]. The carbon structure features including the porosity, specific surface area (SSA) and surface chemistry are the keys to optimized sulfur/carbon cathode [10,13,14]. Pioneering studies have focused on tailoring the carbon pore structure to obtain pores with diameter in the range of one half to hundreds of nanometers which contain elemental sulfur at the charged state and restrain the dissolution of lithium polysulfides formed during discharge process [15–25]. A larger SSA of the carbon host that is usually accompanied with a higher porosity provides more sitting sites for sulfur, thus reduces the particle size and sulfur, hence the charge/discharge reaction of the battery favors [26,27]. Carbon has a weak interaction with dissolvable lithium polysulfides, which is unsatisfactory to limit the shuttle effect and self-discharge when operating a Li-S battery. Therefore, decorating the carbon surface with functional groups or inorganic nanoparticles has been becoming an active direction in recent research to stabilize the sulfur cathode [28–31].

The electrochemical performance of the sulfur/carbon composite depends on a complex synergy between the above structural factors of carbon, yet should be more closely related to the major ones. Understanding the effect of carbon structure on the electrochemical properties of sulfur/carbon composites is of great importance to guide future rational design of the sulfur/carbon composite for optimized cathode of Li-S batteries. However, it is a challenging task due to the complexity and diversity of the carbon structures. Graphene, a sp2-hybridized carbon, has a tunable SSA of tens to thousands square meters per gram, and is ready for functional groups decoration and micropores creation. Therefore, it is a promising model material for studying the relevant of the carbon structure to the electrochemical performance of the sulfur/carbon composite as a cathode of Li-S batteries.

Here, we prepared four types of graphene-based carbon materials. The reduced graphene oxide (RGO) has a relatively low SSA of 58 m2 g−1, a high concentration of oxygen-containing functional groups (C/O atomic ratio of 2.41) with an average pore diameter of 2.9 nm and pore volume of 0.14 cm3 g−1. The microwave-expanded graphite oxide (MEGO) has a moderate SSA of 440 m2 g−1, an increased C/O atomic ratio of 3.57, an average pore size of 5.6 nm and pore volume of 1.43 cm3 g−1. The activated-MEGO (aMEGO) possesses a high SSA of 3010 m2 g−1, a low concentration of functional groups of C/O atomic ratio of 10.81, the lowest average pore diameter of 0.9 nm and the highest pore volume of 2.03 cm3 g−1. We further decorated the RGO with cysteine (RGO-CYS) to obtain sulfur-containing groups with a SSA (60 m2 g−1), C/O atomic ratio (2.50) and pore structure (average diameter of 2.8 nm and volume of 0.21 cm3 g−1) similar to those of the RGO. The electrochemical test of the sulfur/carbon composites with a sulfur content of 70 wt% researched S/RGO-CYS > S/RGO > S/MEGO > S/aMEGO when listed in order of their specific capacity, rate capability and cyclic life. The excellent electrochemical performance of the S/RGO-CYS comparing to the other sulfur/carbon composites in this study is ascribable to the sulfur-containing species of the S/RGO-CYS that is able to help the distribution of sulfur and to stabilize the dissoluble lithium polysulfides, and suggests that the surface chemistry of graphene-based carbon materials plays a more important role than the SSA, pore diameter, and pore volume for the sulfur/carbon cathode.

2. Experimental section

2.1. Synthesis of RGO, RGO-CYS, MEGO and aMEGO

The GO was made from the modified Hummers method [32]. The RGO was synthesized by heating GO under Ar flow at 155 °C.
and atmospheric pressure for 10 h. The RGO-CYS was obtained via a liquid-phase method. Typically, the GO was dispersed in deionized water by ultrasonication for 1.0 h to obtain the well-dispersed GO suspension (1 mg ml\(^{-1}\)). 320 mg of cysteine was then added to the GO suspension, and stirred for 4 h to obtain the GO-CYS suspension. The RGO-CYS sample was collected via freeze-drying technique and finally by heating at 155 °C under Ar atmosphere for 10 h. MEGO and aMEGO were synthesized according to the previous research [33,34].

2.2. Synthesis of sulfur/carbon composites

1600 mg of sodium sulfide (Na\(_2\)S) was dissolved in 160 ml of NaOH solution (10 wt%) to form a Na\(_2\)S solution. Then, 800 mg of sublimed sulfur powder was added into the Na\(_2\)S solution and stirred for 2 h at 60 °C to obtain sodium polysulfide (Na\(_2\)S\(_x\)) solution. The as-obtained Na\(_2\)S\(_x\) solution was added to the suspension of graphene-based carbon materials and stirred for 2 h under vigorous magnetic stirring to obtain Na\(_2\)S\(_x\)/carbon suspension. Then 2 M of HCOOH solution was dropwise added into the Na\(_2\)S\(_x\)/carbon suspension until the pH value reached 2 and stirred for another 2 h. The S/C composite was collected after filtration, washing with deionized water, freeze-drying and finally heating at 155 °C under Ar flow for 10 h.

2.3. Synthesis of Li\(_2\)S\(_4\)/carbon composites

0.25 M of Li\(_2\)S\(_4\) solution was prepared by dissolving stoichiometric amounts of Li\(_2\)S and sulfur in DOL/DME at 60 °C for 12 h. RGO, RGO-CYS, MEGO and aMEGO powders were then added to four vials containing 10 ml of Li\(_2\)S\(_4\) solutions, respectively. We adjusted the amounts of the graphene-based carbon powder to ensure that the total surface area of the powders are identical. The suspensions were then stirred for 24 h, and finally centrifuged, dried at room temperature in an Ar-filled glovebox to obtain the Li\(_2\)S\(_4\)/carbon composites for XPS analysis.

2.4. General characterizations

SEM was performed on a JSM-2100F (JEOL Ltd.) operated at 5.0 kV, and TEM was performed using a JEM-ARM200F (JEOL Ltd.) at an accelerating voltage of 200 kV. EDAX mapping was employed for elemental distribution analysis of the sulfur/carbon composites. XRD patterns were collected using a D/max-TTR III with Cu K\(_\alpha\) radiation of \(\lambda = 1.54178\) Å operating at 40 kV and 200 mA. Thermogravimetric analysis (TGA, TGAQ5000IR) was performed in a Nitrogen atmosphere by heating from RT to 700 °C at a rate of 10 °C min\(^{-1}\). EA was performed on a Vario EL cube (Elementar Analysensysteme GmbH). XPS analysis was conducted with a Thermo ESCALAB 250 instrument using a magnesium anode (monochromatic K\(_\alpha\) X-rays at 1486.6 eV) as the source. Nitrogen adsorption/desorption isotherms were performed on a Quantachrome Autosorb-IQ to determine the pore structures and SSA of the graphene-based carbon materials.

2.5. Electrochemical tests

Sulfur cathode comprised of 75 wt% active materials, 15 wt% Super-P carbon and 10 wt% poly(vinylidene fluoride) binder was

| Table 1: Structure features of the four carbon materials. |
|----------|---------|--------|-------|
|          | RGO     | RGO-CYS| MEGO  | aMEGO |
| SSA (m\(^2\) g\(^{-1}\)) | 58      | 60     | 440   | 3010   |
| Pore volume (cc g\(^{-1}\)) | 0.14    | 0.21   | 1.43  | 2.03   |
| Average pore width (nm) | 2.9     | 2.8    | 5.6   | 0.9    |
| C/O atomic ratio from EA | 2.41    | 2.50   | 3.57  | 10.81  |
| S/C atomic ratio from XPS (× 10\(^{-2}\)) | 0.6     | 1.54   | 0.4   | 0.2    |

Fig. 2. SEM images and sulfur elemental mappings of (a) S/RGO, (b) S/RGO-CYS, (c) S/MEGO and (d) S/aMEGO. For each material, the SEM and elemental mapping were acquired at the same area. TEM images and histograms of sulfur nanoparticle size distribution of (e, i) S/RGO, (f, j) S/RGO-CYS, (g, k) S/MEGO and (h, l) S/aMEGO.
slurry-cast onto an aluminium current collector. CR2032 coin-type cells were then fabricated in an Ar-filled glovebox to examine their electrochemical performances. The electrolyte was 1.0 M LiTFSI in a mixture (volume ratio of 1:1) of DOL and DME with 1 wt% LiNO₃ as the additive. The metallic lithium foil was used as the anode, and the battery separator was a Celgard 2400 membrane. Galvanostatic charge/discharge behavior of the samples was performed using a CT2001A battery test system (LAND Electronic Co.) at various current densities between 1.5 and 2.8 V. EIS was performed on a PARSTAT4000 electrochemical workstation by applying an AC amplitude of 5 mV in the frequency range from 0.01 to 10⁵ Hz. The polysulfide entrapment studies for RGO-CYS and aMEGO were conducted in two in-site batteries using 2 ml of electrolyte and the same total sulfur loading (2 mg).

3. Results and discussion

The RGO, RGO-CYS, MEGO and aMEGO were prepared by the method described in the experimental section. All the samples show a randomly crumpled carbon sheets in the scanning electron microscopy (SEM) images (Fig. 1a–d). The N₂ adsorption/desorption isotherms were tested (Fig. 1e) and analyzed by the Density Functional Theory model (Fig. S1) to determine the SSA and the pore structures of the four graphene-based carbon materials. The RGO and RGO-CYS have a similar SSA of 58 and 60 m² g⁻¹, respectively, which are significantly lower than those of the MEGO (440 m² g⁻¹) and aMEGO (3010 m² g⁻¹). All the graphene-based carbon materials have micro/mesopores with the values of the average diameter and volume summarized in Table 1. The elemental analysis (EA) shows a C/O atomic ratio of 2.41, 2.50, 3.57 and 10.81 for the RGO, RGO-CYS, MEGO and aMEGO, respectively, indicating different concentrations of the oxygen-containing functional groups which is in accordance with the X-ray photoelectron spectra (XPS) of the C 1s signal (Fig. S2) of the carbon materials. The XPS of the S 2p signal of the RGO (Fig. 1f) suggests the existence of the SOₓ species which is very likely the residual left when synthesizing the graphite oxide (GO) with sulfuric acid. And the moderate reduction process (heat treatment at 155°C) for preparing the RGO allows the SOₓ preserved. The SOₓ signals of the MEGO and aMEGO are much weaker and even non-detectible, which is ascribable to the high temperature for synthesizing these two materials. On the other hand, the XPS of the RGO-CYS shows an intensive signal of SOₓ and S–S bonds, which is indicative of the successful decoration of the cysteine to the RGO. We summarized the C/O atomic ratio, the S/C atomic ratio, the SSA, and the average diameter and volume of the micro/mesopores of the four carbon materials in Table 1.

The elemental sulfur was loaded on the RGO, RGO-CYS, MEGO and aMEGO by the method described in the previous literature [35,36]. The X-ray diffraction (XRD) patterns of the four sulfur/carbon composites (Fig. S3) are identical in the characteristics of orthorhombic S₈ [30,37]. The thermogravimetric analysis (TGA) in Fig. S4 indicates that the sulfur contents are around ~70 wt% for all of the four sulfur/carbon composites. The SEM images and the energy-dispersive X-ray spectroscopy analysis (EDAX) mappings in Fig. 2a–d of the four composites indicate a uniform distribution of sulfur in carbon. Yet the transmission electron microscopy (TEM) images (Fig. 2e–h) and SEM images (Fig. S5) show that the sulfur nanoparticles have a different average diameters of 152 ± 45, 27 ± 7, 15 ± 4 and 11 ± 4 nm on the RGO, RGO-CYS, MEGO and aMEGO (Fig. 2i–l), respectively. The significantly larger SSA of MEGO (440 m² g⁻¹) and aMEGO (3010 m² g⁻¹) than RGO (58 m² g⁻¹)
The electrochemical performance of the four sulfur/carbon composites were tested with identical parameters in CR2032 coin-type cells with a lithium foil as the anode and 1.0 M LiTFSI in a mixture of DOL and DME (volume ratio of 1:1) with 1 wt% LiNiO3 as the cathode of Li-S batteries [38,39]. The Coulombic efficiency and capacity decay rate as shown in Fig. 4. The aMEGO has the largest SSA and pore volume of 3010 m2 g⁻¹ and 2.03 cm³ g⁻¹, respectively, and the smallest pore size of 0.9 nm among the four graphene-based carbon materials, yet the S/aMEGO delivers the lowest specific capacity and rate capability, showing the strongest shuttle effect and the poorest cyclic life (Fig. 4a–f). On the contrary, the S/RGO-CYS delivers the best electrochemical performance while the RGO-CYS has a low SSA of 60 m² g⁻¹, a moderate pore volume of 0.21 cm³ g⁻¹ and pore size of 2.8 nm. Moreover, the specific capacity and rate capability, Coulombic efficiency and capacity decay rate of the four sulfur/carbon composites change randomly with the SSA of the four sulfur/carbon composites change randomly with the SSA (Fig. 4a, b), pore size (Fig. 4c, d) and pore volume (Fig. 4e, f), indicating that a larger SSA and pore volume and a smaller pore width of MEGO and aMEGO do not help in improving the electrochemical performance of the sulfur/carbon composites. Though the oxygen-containing functional groups may help in stabilizing the polysulfides [29,44,49], the correlation between the C/O atomic ratio and S/C atomic ratio and the electrochemical performance of the sulfur/carbon composites (specific capacity, rate capability, Coulombic efficiency and capacity decay rate) and between the graphene-based carbon structure features (SSA, pore width, pore volume, C/O atomic ratio and S/C atomic ratio) and the electrochemical performance of the sulfur/carbon composites (specific capacity and the rate capability of the sulfur/carbon composites (specific capacity, rate capability, Coulombic efficiency and capacity decay rate). The correlation between the graphene-based carbon structure factors, (a, b) SSA, (c, d) pore width, (e, f) pore volume, (g, h) C/O atomic ratio and (i, j) S/C atomic ratio and the electrochemical performance of the sulfur/carbon composites (specific capacity, rate capability, Coulombic efficiency and capacity decay rate).

provide more space for adhering sulfur, which is favored for forming smaller sulfur particles. Moreover, the average diameter of the sulfur on RGO-CYS is much smaller than on the RGO though the SSA of RGO-CYS (60 m² g⁻¹) and RGO (58 m² g⁻¹) are very close, which may be ascribable to the sulfur-containing cysteine that helps in sulfur dispersing.

The electrochemical performance of the four sulfur/carbon composites were tested with identical parameters in CR2032 coin-type cells with a lithium foil as the anode and 1.0 M LiTFSI in a mixture of DOL and DME (volume ratio of 1:1) with 1 wt% LiNiO3 as the electrolyte. Fig. 3a depicts the galvanostatic charge/discharge curves measured at 0.1 C (1 C = 1675 mA h g⁻¹), both here and below in the voltage range of 1.5–2.8 V of the four composites. The S/RGO, S/RGO-CYS, S/MEGO and S/aMEGO deliver reversible capacities of 1070, 1260, 850, and 758 mA h g⁻¹, respectively, in the first cycle. When at higher C-rates, the S/RGO-CYS delivers the highest specific capacity compared to the other sulfur/carbon composites in this study (Fig. 3b and Fig. S6), and still preserves a specific capacity of 455 mA h g⁻¹ at 8 C, which is much higher than that of the S/RGO (334 mA h g⁻¹) and significantly higher than those of the S/MEGO (30 mA h g⁻¹) and S/aMEGO (20 mA h g⁻¹). This result indicates a much better rate capability of the S/RGO-CYS compared to the other sulfur/carbon composites. Fig. 3c shows the cyclic stability of the four sulfur/carbon composites tested at 0.5 C for 200 cycles. The specific capacities of the S/RGO, S/RGO-CYS, S/MEGO and S/aMEGO in the first cycle are 849.5, 976, 612 and 677 mA h g⁻¹, respectively, and retain the specific capacities of 471, 655, 380 and 352 mA h g⁻¹ in the 200th cycle, corresponding to the capacity decay rates of 0.29%, 0.21%, 0.24% and 0.33% per cycle, respectively. This result indicates the best cyclic stability of the S/RGO-CYS comparing to the other three sulfur/carbon composites. A Coulombic efficiency of closer to 100% indicates a weaker shuttle effect of the dissolved lithium polysulfides which is preferred for the cathode of Li-S batteries [38,39]. The Coulombic efficiencies are 100.93%, 100.01%, 100.66%, 101.4%, respectively, for the S/RGO, S/RGO-CYS, S/MEGO and S/aMEGO at the 200th cycle. We note that the S/RGO-CYS exhibits the highest specific capacity and rate capability, the weakest shuttle effect of the polysulfides and the best cyclic stability among the four types of sulfur/carbon composites in this study. It is noteworthy that the rate capability of the S/RGO-CYS composite exceeds those of many other graphene-based sulfur composites of a similar sulfur content in previous reports [28,36,39–47].

A larger SSA and pore volume of the carbon materials provide more sites for the sulfur sitting, therefore, will yield a smaller sulfur particle size and more uniform dispersion (Fig. 2d) which is critical for Li-S batteries [48]. And a small pore size of less than 1 nm was suggested to be important for suppressing the shuttle effect [16]. To understand the difference of the electrochemical performance of the four sulfur/carbon composites, we studied the correlation between the graphene-based carbon structure features (SSA, pore width, pore volume, C/O atomic ratio and S/C atomic ratio) and the electrochemical performance of the sulfur/carbon composites (specific capacity, rate capability, Coulombic efficiency and capacity decay rate) as shown in Fig. 4. The aMEGO has the largest SSA and pore volume of 3010 m² g⁻¹ and 2.03 cm³ g⁻¹, respectively, and the smallest pore size of 0.9 nm among the four graphene-based carbon materials, yet the S/aMEGO delivers the lowest specific capacity and rate capability, showing the strongest shuttle effect and the poorest cyclic life (Fig. 4a–f). On the contrary, the S/RGO-CYS delivers the best electrochemical performance while the RGO-CYS has a low SSA of 60 m² g⁻¹, a moderate pore volume of 0.21 cm³ g⁻¹ and pore size of 2.8 nm. Moreover, the specific capacity, rate capability, Coulombic efficiency and capacity decay rate of the four sulfur/carbon composites change randomly with the SSA of the four sulfur/carbon composites change randomly with the SSA (Fig. 4a, b), pore size (Fig. 4c, d) and pore volume (Fig. 4e, f), indicating that a larger SSA and pore volume and a smaller pore width of MEGO and aMEGO do not help in improving the electrochemical performance of the sulfur/carbon composites. Though the oxygen-containing functional groups may help in stabilizing the polysulfides [29,44,49], the correlation between the C/O atomic ratio and the electrochemical performance is not clear in this study. This phenomenon may be ascribable to the largest sulfur particle size of the S/RGO among the four sulfur/carbon composites which hinders the charge transfer in the S/RGO (Fig. S7). Fig. 4i and j show that the specific capacity and the rate capability of the sulfur/carbon composites increase with the S/C atomic ratio of the graphene-based carbon material. We note that the S/RGO-CYS shows a specific capacity of 18% higher and a decay rate of 28% lower than that of the S/RGO. The Coulombic efficiencies are 100.01% and 100.93% for the S/RGO-CYS and S/RGO, respectively, indicating a weaker shuttle effect of the S/RGO-CYS composite. Considering that the RGO-CYS...
Fig. 5. XPS showing the S 2p signals of (a) Li$_2$S$_4$/RGO, (b) Li$_2$S$_4$/RGO-CYS, (c) Li$_2$S$_4$/MEGO and (d) Li$_2$S$_4$/aMEGO.

Fig. 6. In-situ polysulfides entrapment study of (a) S/RGO-CYS, (b) S/aMEGO.
and RGO have a similar SSA, pore size and pore volume (Table 1), the improved electrochemical performance of the S/RGO-CYS should be ascribable to the sulfur-containing functional groups (Fig. 1f) introduced by cysteine.

To further study the effect of cysteine on the electrochemical performance of the sulfur/carbon composites, we selected Li2S4 as the representative polysulfide species to probe the interaction between the graphene-based carbon materials and the polysulfides. The XPS S 2p of Li2S4 shows two peaks centered at 161.7 eV and 163.1 eV with an intensity ratio of ~1:1 (Fig. 5b), which represent the terminal (S=S, connecting to Li) and bridging sulfur (S=S, connecting to only S), respectively [50]. We blended the four types of graphene-based carbon materials in the Li2S4 solution for 24 h and filtrated and dried for XPS measurement. The intensity ratio of the S=S peak over the S=S peak reduces to less than 1 for the Li2S4/RGO and Li2S4/RGO-CYS, which features the XPS of the four types of Li2S4/carbon composites suggest that the polysulfides are adsorbed by direct interaction with the carbon surface on the MEGO and aMEGO, and by forming polythionates on the RGO and RGO-CYS. The polythionates species is a result of the interaction between the thiosulfate species on the carbon surface and the soluble lithium polysulfides [49]. This reaction favors for the adsorption of lithium polysulfides onto the carbon host and prolongs the contact time of the lithium polysulfides on carbon surface, which results in suppressed shuttle effect.

The capability of RGO-CYS in retaining polysulfides was demonstrated by discharging the S/RGO-CYS and S/aMEGO composites in glass cells to visually observe the color change of the electrolyte. The photographs of the two cells discharged at different stages are shown in Fig. 6. Though the two electrodes contained a same amount of sulfur of 2 mg and discharged at a same current of 320 µA, the color change of the electrolyte for the S/RGO-CYS was non-detectable after 0.5 h (Fig. 6a) while the electrolyte around the S/aMEGO cathode was yellow (Fig. 6b). After 8 h when the two electrodes reached fully discharged state, the electrolyte for the S/RGO-CYS was significantly lighter than that for the S/aMEGO. The yellow color represents the dissolution of the lithium polysulfides generated upon discharge process, and the lighter color indicates a lower concentration [49], which suggests a higher capability in retaining the polysulfides for the RGO-CYS.

We also note that the average particle size of sulfur on the RGO-CYS is 1/6 that on the RGO though both the RGO-CYS and RGO have a similar SSA, pore size and pore volume, suggesting that the sulfur-containing functional groups on the graphene surface helps in sulfur dispersion to form nanometer-size particles which is critical for shortening the charge transfer distance inside the nonconductive sulfur [48], therefore the S/RGO-CYS shows a lower charge transfer resistance (Fig. 5e). Besides, the thiosulfate species on the RGO-CYS surface promotes the adsorption of lithium polysulfides thus accelerates the charge transfer between the lithium polysulfides and the RGO during charge/discharge. These two factors yield a higher rate capability (Fig. 3b) of the S/RGO-CYS.

In addition, the electrochemical impedance spectra (EIS) of the S/RGO-CYS acquired before and after 300 charge/discharge cycles (Fig. S8) indicate a minor change of the charge transfer resistance from 80 to 65 Ω after cycling. The SEM images and EDAX mappings of the cycled cathodes (Fig. S10) show that the carbon mappings match the morphologies for the four sulfur/carbon composites, yet, the sulfur mappings disperse uniformly in the area where the EDAX mappings and SEM images are acquired for the S/RGO, S/MEGO, and S/aMEGO. Only the sulfur mapping of S/RGO-CYS shows a pattern that matches the morphology. And the higher magnification SEM images show particles with diameter of ~200 nm on the cathode surface for the S/RGO, S/MEGO, and S/aMEGO, which may be attributed to the detachment of active materials from the carbon host. The above analysis indicates that RGO-CYS possesses an improved capability in holding the soluble polysulfides upon cycling. The S/RGO-CYS shows the best electrochemical performance comparing to the other three sulfur/carbon composites. To further study the effect of cysteine on the electrochemical performance of the sulfur/carbon composites, and our study on the structure features of the graphene-based carbon materials suggests that the sulfur-containing functional groups at the carbon surface can yield a small sulfur particle size of tens of nanometers and significantly hold the soluble polysulfides by forming polythionates, therefore, assists in charge transfer between the carbon and the sulfur and lithium polysulfides, consequently, leads to an improved cyclic life and rate capability.

4. Conclusions

We studied the correlation between the structure features (SSA, pore size, pore volume, C/O atomic ratio and S/C atomic ratio) of graphene-based carbon materials and the electrochemical performance of the sulfur/carbon composites. The specific capacity, rate capability, Coulombic efficiency and capacity decay rate change randomly with the SSA, pore size and pore volume. The S/RGO-CYS delivers the best electrochemical performance among the four sulfur/carbon composites while RGO-CYS has a low SSA of 60 m² g⁻¹, a moderate pore volume of 0.21 cm³ g⁻¹ and pore size of 2.8 nm. Polysulfides entrapment study and XPS analysis indicate that the excellent electrochemistry performance of the S/RGO-CYS composite can be ascribed to the sulfur-containing functional groups which help in dispersing the elemental sulfur and stabilizing the soluble polysulfides by forming polythionates. This study demonstrates that the surface chemistry of the graphene-based carbon host plays a more important role than the SSA, pore size and pore volume in improving the electrochemical performance of the sulfur/carbon composites, and evidenced the rational design of the sulfur/carbon composite for optimized cathode of Li-S batteries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2016.11.102.

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