Research Article
Microstructures of Reduced Graphene Oxide/Sulfur Nanocomposites and Their Impacts on Lithium Storage Performances

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1. Introduction

Sulfur is an attractive and emerging cathode alternative in lithium batteries for its high theoretical energy density and low cost [1–3]. The Li/S couple, based on the complete reduction of S to form Li2S, has a theoretical specific capacity of 1672 mAh g$^{-1}$ S corresponding to a theoretical specific energy of over 2600 Wh kg$^{-1}$ [4–6]. However, considerable technological challenges that are attributed to the intrinsic properties of S and lithium sulfide prevent rapid commercialization of Li/S batteries. For instance, elemental S is an electronic insulator by nature, which demands appropriate conducting additives. Secondly, lithium reaction with S occurs via lithium polysulfide (Li2Sx) intermediates, among which the high-order lithium polysulfides (Li2Sx, x ≥ 4) are readily dissolved in the commonly used organic electrolyte. While the liquid phase Li2Sx facilitates rapid kinetics beneficial to high rate capability, the soluble Li2Sx can diffuse through the electrolyte to the Li anode leading to gradual capacity degradation upon charge/discharge cycling.

Recent efforts have demonstrated success in attenuating the dissolution of Li2Sx and overcoming sulfur’s insulating problems via embedding S into various carbon-based additives [7], such as mesoporous carbon [8, 9], microporous carbons [10], porous or hollow carbon nanofibers [11, 12], nanotubes [13], graphene, and reduced graphene oxide [14–28]. Table 1 lists a set of representative graphene/sulfur composites, synthesis approaches, and their electrochemical performance data which were reported lately. It is seen that S has been incorporated into graphene via ball milling [14], melting/gasification at elevated temperatures [15–20], chemical reaction [21–24], or emulsion in CS2 solution [25–27]. Graphene and reduced graphene oxide (rGO) nanosheets have received much attention because (1) they have relatively high electronic conductivities and lithium-ion diffusion coefficients; (2) the ultrathin and flexible nanosheets can accommodate the volume changes of S upon electrochemical cycling; (3) the reactive functional groups on the nanosheets can immobilize S via moderate chemical interaction [28] and act as growth points for S during charge, thereby diminishing
Table 1: Comparison of a set of reported studies on graphene/sulfur and graphene oxide/sulfur composites with their corresponding electrochemical performances.

<table>
<thead>
<tr>
<th>Composite</th>
<th>S content in G/S powder (wt)</th>
<th>Electrolyte</th>
<th>1st discharge capacity (mAh g⁻¹)</th>
<th>Capacity at the nth cycle (mAh g⁻¹)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG – a-S ball milling</td>
<td>73 wt% 82 wt%</td>
<td>1 M LiTFSI/DOL/DME</td>
<td>1503@0.1 C 835@1 C</td>
<td>615@100th 530@100th</td>
<td>[14]</td>
</tr>
<tr>
<td>rGO + a-S melting infiltration</td>
<td>22 wt%</td>
<td>1 M LiPF₆/EC/DMC</td>
<td>1598@0.16 A g⁻¹</td>
<td>670@80th</td>
<td>[15]</td>
</tr>
<tr>
<td>TG + c-S melting infiltrating</td>
<td>20 wt% 40 wt% 60 wt% 80 wt%</td>
<td>1 M LiTFSI/DOL/DME</td>
<td>962@0.28 A g⁻¹ 1021@0.28 A g⁻¹ 1210@0.28 A g⁻¹ 854@0.28 A g⁻¹</td>
<td>602@70th 728@70th 880@70th 449@70th</td>
<td>[16]</td>
</tr>
<tr>
<td>TG + a-S melting infiltration</td>
<td>67 wt%</td>
<td>N/A</td>
<td>1290@0.025 A g⁻¹</td>
<td>421@100th</td>
<td>[17]</td>
</tr>
<tr>
<td>rGO + S melting infiltration</td>
<td>66.7 wt%</td>
<td>1 M LiTFSI/DOL/DME</td>
<td>1093@0.2 C</td>
<td>435@60th</td>
<td>[18]</td>
</tr>
<tr>
<td>TG + a-S rGO coated</td>
<td>63 wt%</td>
<td>N/A</td>
<td>1588@0.025 A g⁻¹</td>
<td>928@100th</td>
<td>[17]</td>
</tr>
<tr>
<td>rGO + S + PEG GO/CB wrapped</td>
<td>70 wt% (34–46%)</td>
<td>1 M LiTFSI/DOL/DME</td>
<td>960@0.2 C</td>
<td>520@100th</td>
<td>[19]</td>
</tr>
<tr>
<td>pGNs + a-S melting infiltration</td>
<td>22 wt%</td>
<td>1 M LiTFSI/PEGDME</td>
<td>1611@0.05 A g⁻¹</td>
<td>539@40th</td>
<td>[20]</td>
</tr>
<tr>
<td>pGNs + S melting infiltration</td>
<td>66.7 wt%</td>
<td>1 M LiTFSI/DOL/DME</td>
<td>1379@0.2 C</td>
<td>1007@60th</td>
<td>[18]</td>
</tr>
<tr>
<td>rGO + c-S Na₂S oxidation</td>
<td>87 wt%</td>
<td>1 M LiCF₄SO₃ + 0.2 wt% LiNO₃ / DME/DOL</td>
<td>705@0.33 A g⁻¹</td>
<td>492@50th</td>
<td>[21]</td>
</tr>
<tr>
<td>rGO + c-S Na₂S + NaSO₃</td>
<td>75.2 wt%</td>
<td>1 M LiCF₄SO₃ + 0.2 wt% LiNO₃ / DME/DOL</td>
<td>1300@0.2 A g⁻¹</td>
<td>930@50th</td>
<td>[22]</td>
</tr>
<tr>
<td>rGO + S Na₂SO₃ + Na₂S + rGO</td>
<td>63.6 wt% 50.9%</td>
<td>1 M LiTFSI/DOL/DME</td>
<td>1267@0.314 A g⁻¹</td>
<td>804@80th</td>
<td>[23]</td>
</tr>
<tr>
<td>p graphene + c-S Na₂S₂O₃ + H₂SO₄</td>
<td>83.3 wt% 66.6%</td>
<td>1 M LiTFSI + 0.1 M LiNO₃ / EGDME/DOXL</td>
<td>1237@0.1 C</td>
<td>810@50th</td>
<td>[24]</td>
</tr>
<tr>
<td>TG + c-S S dissolve in CS₂</td>
<td>71.8 wt%</td>
<td>1 M LiTFSI/DOL/DME</td>
<td>923@0.1 C</td>
<td>490@50th</td>
<td>[25]</td>
</tr>
<tr>
<td>rGO + S chemical microemulsion</td>
<td>66 wt%</td>
<td>1 M LiTFSI/PYR₁₄TFSI / PEGDME</td>
<td>1320@0.168 A g⁻¹</td>
<td>735@50th</td>
<td>[26]</td>
</tr>
<tr>
<td>Nafton coated TG + c-S S dissolve in CS₂</td>
<td>71.8 wt%</td>
<td>1 M LiTFSI/DOL/DME</td>
<td>923@0.1 C</td>
<td>750@50th</td>
<td>[25]</td>
</tr>
<tr>
<td>rGO + S wrapped, S in CS₂</td>
<td>65 wt% (52%)</td>
<td>1 M LiTFSI/DOL/DME</td>
<td>725@1 C</td>
<td>622@60th</td>
<td>[27]</td>
</tr>
</tbody>
</table>

*a-S: amorphous sulfur; c-S: crystalline sulfur.

Li₂S₄ leaching; and (4) ubiquitous cavities can be created on the surface of graphene sheets via oxidation activation to facilitate the intimate electrical contact and S immobilization. Due to the large variety of synthesis conditions, S compositions, and choice of electrolyte as shown in the table, it is difficult to quantitatively correlate the microstructure of S with electrochemical performances. To this end, the focus of this paper is to report the one-to-one comparison to show the differences of GO/S composites in the aspects of structure, phase, microstructure, and their impacts on lithium storage/removal electrochemical performances. The microstructure of S is tuned via two distinct compositing approaches, that is, physical mixing via mechanical grinding (MGO/S) and chemical reaction via in situ surface sulfurization (CGO/S).

The structure and morphology of MGO/S and CGO/S were analyzed with the help of X-ray diffractometer (XRD) and scanning electron microscopy (SEM). The sulfur contents and their thermal stability were studied with the help of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Raman spectroscopy has emerged as a powerful analytical technique for the microstructural characterization of a variety of graphitic nanocomposites [29–32]. Despite the wealth of information now available
from a single Raman measurement of a nanographite system, the data obtained from such experiments is limited to the localized carbon structure at the focal point of the laser. Hyperspectral Raman mapping allows the acquisition of Raman spectra across a relatively large region of the sample, which provides for a more representative understanding of the overall specimen. Recent developments in advanced chemometric algorithms, for example, partial least squares (PLS), can greatly simplify the postacquisition data analysis and extraction of structural information [33–36]. In this research, we investigated the chemical state and distribution of S in MGO/S and CGO/S with the help of both point and PLS Raman mapping.

2. Experimental

2.1. Fabrication of GO/S Composites. The MGO/S composite powders were prepared by mechanically milling the mixture of rGO and S (Aldrich) for 15 minutes with an agate mortar and pestle. The rGO nanosheets were fabricated using the modified Hummer's method, which has been described elsewhere [37–39]. The S content in the MGO/S was tuned in the range of 20–70 wt%.

The CGO/S composite was synthesized via a chemical route. The rGO was dispersed in the sodium polysulfide (Na$_3$S$_x$) aqueous solution with a 5 wt% cetrimonium bromide (CTAB) and sonicated for 4 h to ensure complete dispersion. Afterwards, 2 M acetic acid was slowly titrated into the solution. Acetic acid was chosen for its gentle reaction rate with sodium polysulfide, resulting in a better distribution and finer S particle size. After filtering and washing, the rGO/S precipitates were dried under vacuum at 50°C for 12 h and further thermally treated under nitrogen flows at 155°C for 12 h. The S content in the CGO/S powders was tuned between 20 and 70 wt% by adjusting the volume of the Na$_3$S$_x$ solution to the mass of rGO.

2.2. Electrochemical Characterization. The rGO/S powders were mixed with 5 wt% polyvinylidene fluoride (PVdF) binder solution in N-methyl-2-pyrrolidone (NMP) in a 90:10 mass ratio. The slurries were applied to aluminum current collectors via a doctor blade and dried at 50°C under vacuum for 12 h. The electrode thickness was 120 μm on average. The cathode membrane was cut into a disk of 1 cm diameter with the help of a precision disc cutter (MTI Corp.). The electrode surface densities (active material only) of the MGO/S and CGO/S cathodes were on average, 1.0 mg/cm$^2$.

The rGO/S cathode discs were tested in three Swagelok-type cells or button cells (CR2016) with lithium foil as counter electrode. The electrolyte solution was 1 M lithium bis(tri-fluoromethane)sulfonimide (LiTFSI) in tetraethylene glycol dimethylether (TEGDME):1,3-dioxolane (DOL) (3:7 v/v). The solvents TEGDME and DOL were dehydrated over 4 Å molecular sieves prior to use. Commercial polypropylene membranes were used as separators, having a thickness of 25 μm and an average pore size around 30–40 nm. The cells were assembled in an argon-filled glove box (Omni VAC), with a purifying system controlling the moisture content below 0.5 ppm. The cells were galvanostatically cycled at a constant 0.05 C or 0.1 C rate on a LAND CT-2001A battery test system at ambient temperature.

2.3. Material Characterizations. TGA was used to determine the sulfur content in the rGO/S powders and was performed on a 2050 Thermogravimetric Analyzer (TA Instruments) at temperatures ranging from room temperature to 600°C at a ramping rate of 5°C min$^{-1}$. The thermal stabilities of the rGO/S powders were examined by means of DSC (DSC 2010, TA Instruments). The DSC pan was sealed in ambient atmosphere and the temperature range was set from room temperature to 200°C at a ramping rate of 5°C min$^{-1}$. The XRD spectral data were collected on a MD-10 Precision Mini X-ray Diffractometer (MTI Corp.) with Cu Kα radiation, between scattering angles (2θ) of 18 and 72°. SEM images were obtained at 20 kV acceleration voltage in secondary electron mode (Topcon Positioning Systems, Inc.).

Raman point spectra and maps were obtained using a LabRamHR 800 system (Horiba Jobin Yvon) equipped with a confocal scanning Raman microscope (High Stability BX41) and a diode-pumped solid-state, frequency-doubled Nd:YAG laser (Laser Quantum) operating at 532 nm and 15 mW of power at the sample. The Stokes scattered photons were collected in a 180° backscattering geometry through a long working distance 100x objective (Olympus) and were captured via a back-illuminated, thermoelectrically cooled, Andor CCD camera (1.024 × 106 pixels). The integration time of each measurement was 10 s, and signals were averaged for three accumulations to improve the spectral clarity. The spot size of the laser in each measurement was ~1 μm$^2$, and the spectral resolution was ~1 cm$^{-1}$ under this set-up. Two-dimensional spectral maps of the samples were collected by scanning the laser focus over a 10 μm × 10 μm area in a raster fashion, using a step size of 1 μm. The resulting hyperspectral datasets were imported into MATLAB for further processing via PLS regression analysis. A 32-point bicubic interpolation function was utilized to reduce pixilation of the final chemical images.

3. Results and Discussion

Figure 1 presents the XRD profiles of the two different specimens, that is, MGO/S and CGO/S, with rGO and pristine S powders for comparison. No traces of impurities were found within the detection limit of the instrument. Elemental S exists in the orthorhombic phase (α-S) (phase group fddd). There are no characteristic diffraction peaks for rGO powders, confirming the transition of graphite’s 3D long-range order stacking into 2D disordered nanosheets as a result of the chemical exfoliation process. In the MGO/S composites, the characteristic α-S peaks are clearly observed. This suggests that elemental S crystallites exist freely throughout the composite. The baseline of the XRD peaks around 25° is raised for MGO/S indicating a coexistence of S and rGO, and inhomogeneity of the composite as others have indicated. In contrast, the XRD pattern of the CGO/S nanocomposite reveals no strong diffraction peaks corresponding to elemental S. This suggests either that the S particles exist in an amorphous phase or that the crystallite size has become...
too small to generate diffraction peaks due to the nanosizing effect of the acetic acid coupled with the surfactant CTAB.

The DSC profiles of MGO/S and CGO/S specimens are shown in Figure 2. Elemental S exhibits two endothermic peaks at 113.3° C and 119.7° C. The first peak corresponds to either the solid phase transformation from orthorhombic (α-S) to monoclinic (β-S) or the α-S phase melting, while the second peak represents the transformation from solid to liquid state (β-S melting) [40]. The pristine S peaks are relatively sharp and well resolved. The weak peaks in the range of 157–165° C reflect λ-phase transition and polymerization [41, 42]. For MGO/S, all the peaks have reduced in intensity, which correlates linearly with the reduced amount of S in the composite. It is also observed that the second peak has shifted approximately 2 degrees lower (117.8° C). The two-degree shift of the liquidation peak of S in the MGO/S composite might correlate with the reduction of S particle size after mechanical grinding. It is interesting to notice that, for the CGO/S nanocomposite spectrum, the peak corresponding to the α-S melting and/or α-S to β-S transition becomes less detectable. The λ-transition and polymerization peaks have also diminished significantly. By contrast, the β-S phase peak becomes dominant at 117.8° C. This phenomenon would be attributed to the effective dispersion of the β-phase sulfur nanoparticles throughout the graphene surface. The confinement of S would result in a masking of the weak phase transition and/or melting occurrence as the capillary action between sulfur and graphene would allow the semi-liquidized sulfur to move freely throughout the graphene structure. The DSC results suggest that the present S phase in CGO/S nanocomposites differentiates from pristine S as well as sulfur presented in MGO/S.

Figures 3(a) and 3(b) show representative Raman point spectrum and PLS mapping results for MGO/S. A strong peak ca. 505 cm$^{-1}$ corresponds to the $A_{1g}$ symmetric stretching mode of S [43]. Interestingly, this phonon mode experienced a large frequency shift (∼35 cm$^{-1}$) compared to that observed in the bulk S precursor (see the inset in Figure 3(a)). Although unusual, such energetic shifts have been observed for the $A_{1g}$ mode of S in other similarly prepared GO/S [21]. The presence of only the bulk S vibrational mode in the MGO/S spectra confirms that the mechanical mixing process only results in the inclusion of bulk S which does not chemically interact with the rGO substrate. The PLS image generated from the hyperspectral data set shows a small, localized inclusion of S. Figures 3(c) and 3(d) show representative Raman point spectrum and PLS mapping results for CGO/S. A peak centered at 648 cm$^{-1}$ emerges in nearly all of the acquired pixels. This new peak is likely due to the formation of C-S bonds [21]. In some region, weak peaks centered around 1040 cm$^{-1}$ representing O-S bands are also observed. These extra bonds are probably formed during the chemical deposition of S onto the rGO surface. Ideally, the chemical approach to synthesizing the CGO/S composite should result in a thin layer of S completely covering the entire GO topology. Indeed, the PLS image generated from the raw hyperspectral data shows a large, nearly homogeneous distribution of chemically incorporated S, which further supports the conclusion of covalently bound S onto the rGO lattice.

Figures 4(a)–4(e) exhibit SEM images of S powder before and after mechanical grinding, rGO, MGO/S, and CGO/S. Comparing Figures 4(a) and 4(b), it is seen that the mechanical grinding condition used in the present experiment has effectively reduced the S particle size from approximately 100–350 μm to 2–15 μm agglomerates, resembling submicron-sized, fine flakes in appearance. While comparing Figures 4(c) and 4(d), it is apparent that the surface morphology of rGO is altered after mechanical mixing with S. Particularly, the pure rGO nanosheets are curled and have smooth surfaces, whereas the MGO/S surfaces are covered with scattered amounts of S particle agglomerates. The presence of the GO nanosheets has effectively distributed S fine particles and alleviated S agglomeration. The nonuniform distribution of S in MGO/S is also clearly observed, that is, some regions with scarce S, while others contain...
many S aggregates. The existence of free S agglomerates and nonhomogeneity is anticipated to have adverse effects on the electrochemical performances. As stated previously, the S aggregates can freely diffuse in the organic solvent and commence the polysulfide shuttle, resulting in capacity loss and cycle fading.

In the CGO/S nanocomposites (see Figure 4(e)), it is difficult to distinguish the S particles from the rGO nanosheets except that the micrograph is much brighter due to the coverage of the electronically insulating S. Apparently, no S particles or agglomerates are observed, suggesting homogeneous distribution of nanosized S. Moreover, the CGO/S morphology exhibits no significant difference from pristine rGO, maintaining a curly, thin flake-like appearance. This may indicate that the S coverage is very thin. The EDX mapping (see Figures 4(f) and 4(g)) confirms the homogeneous distribution of S throughout the specimen. The homogeneous mixing will enhance the electrical contact area between S and conductive graphene and thereby improve the sulfur utilization and cyclability.

Figure 5(a) shows the 1st and 10th discharge-charge profiles of MGO/S and CGO/S composites, both of which contain 50 wt% rGO content. The initial discharge capacities were 1077 and 1211 mAh g\(^{-1}\) S for MGO/S and CGO/S, respectively, which correspond to approx. 64.4% and 72.4% S utilization, respectively. The slight difference in the initial capacity arises from the presence of some free isolated S particles which exhibit poor electronic contact with rGO and hence the lower utilization. This fact can be correlated with the shape of the initial discharge profiles where there exists the presence of a high-voltage (2.2–2.4 V) plateau during discharge of the CGO/S electrode. The lack of retention of this high-voltage plateau for the MGO/S electrode suggests poor control of the polysulfide shuttle. Figure 5(b) shows the
fact that the capacity fades rapidly for MGO/S. Upon discharge/charge cycling, the unbonded S particles in MGO/S react with lithium to form polysulfides which then readily dissolve into the electrolyte and migrate to the anode. As a result, the MGO/S capacity is reduced to 240 mAh g\(^{-1}\) at the 25th cycle which is only 22\% retention of its initial capacity. As for CGO/S, due to effective interaction between S and rGO, the capacity retention is improved significantly. At the 25th cycle, the reversible capacity is maintained at 640 mAh/g which is 2.5 times better than that of MGO/S.

Figures 5(c) and 5(d) plot the reversible capacity (at the 5th cycle) as a function of the rGO percentage. Both the specific capacities in terms of net sulfur and the total electrode composite, that is, \(Q_S\) and \(Q_T\), are presented. Compared with \(Q_S\), \(Q_T\) is more practically meaningful in the lithium-battery configuration. In MGO/S, \(Q_S\) is only 100 mAh/g at 20 wt\% rGO but reaches up to 900 mAh/g with 75 wt\% rGO. The high value in the latter case lies in the improvement of electrical conductance and contact and hence the sulfur utilization. In the range of 40–50\%, the \(Q_S\) changes insignificantly in MGO/S suggesting the percolation threshold. As for CGO/S, both \(Q_S\) and \(Q_T\) values at each composition increased by 100–200 mAh/g throughout the entire range. Additionally, the general trend shows the continuous increase of \(Q_S\) with the rGO content. These phenomena are attributed to the effective nanosizing of the S particles and enhanced the electrical contact between S and rGO. It is noteworthy that no percolation threshold is observed for CGO/S in the experimental composition range. The values of \(Q_T\) decrease continuously with the rGO content because rGO is an inactive component for lithium storage. The maximum \(Q_T\) reaches 400 mAh/g which is 2-3 times the cathode materials like LoCoO\(_2\) and LiFePO\(_4\).

Although our material characterization techniques have indicated a homogeneous dispersion of S throughout the rGO host structure as well as the formation of a covalent bond between C and S, the liquid electrolyte used in this research was still capable of penetrating into accessible voids within the CGO/S microstructure and inducing the polysulfide shuttle. Consequently, the first Coulombic efficiency of the
CGO/S cathode in 1 M LiTFSI-TEGMDE/DOL (30:70 v/v) electrolyte was only 79% and the effects of this process were manifested in the significant capacity fade observed during the first five cycles. As elucidated by this work, C-S composite enhancements alone offer limited room for the improvement of battery performance unless an appropriate electrolyte is used, and liquid electrolytes will inevitably lead to some extent of active material dissolution and capacity fade upon cycling.

4. Conclusions

Homogenous distribution of amorphous/nanocrystalline sulfur was achieved throughout a reduced graphene oxide matrix by utilizing a one-step chemical synthesis route. The resulting CGO/S electrode consistently exhibited enhanced sulfur utilization and improved cyclability compared to the mechanically mixed composite containing the same amount of sulfur. This was attributed to the enhanced interaction between rGO and nanosized S as well as increased electrical contact. The CGO/S nanocomposites showed no percolation threshold within the experimental composition range (30–70 wt% rGO) and the maximum specific capacity per total electrode composite reached 400 mAh/g which is 2-3 times the cathode materials like LoCoO$_2$ and LiFePO$_4$.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
References


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