Graphene-enveloped sulfur in a one pot reaction: a cathode with good coulombic efficiency and high practical sulfur content†

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Graphene–sulfur composites with sulfur fractions as high as 87 wt% are prepared using a simple one-pot, scalable method. The graphene envelops the sulfur particles, providing a conductive shrink-wrap for electron transport. These materials are efficient cathodes for Li–S batteries, yielding 93% coulombic efficiency over 50 cycles with good capacity.

The lithium–sulfur (Li–S) battery has garnered significant attention in recent years due to sulfur's large theoretical capacity (1675 mA h g⁻¹) and the battery's small environmental impact given the high availability of resource materials for the cathode. In a typical Li–S cell, sulfur is reduced in stages from S₈ to Li₂Sₓ (x = 1 or 2). There are two main concerns with the Li–S cell that limit its immediate use in commercial applications. A pure sulfur cathode is highly insulating (5 × 10⁻³⁰ S cm⁻¹) and can only be reduced efficiently if a conductive material is added. The issues of bulk and surface conductivity in sulfur composites have been recently outlined in sophisticated studies. Also, the intermediate reduction species Li₂Sₓ (3 ≤ x ≤ 6) are highly soluble in typical non-aqueous organic electrolytes which leads to active mass loss and lowered coulombic efficiency through the well known sulfur shuttle mechanism. In order to address these issues, recent research on the Li–S cell has focused on the addition of conductive porous carbon matrices that can effectively "wire-up" and house elemental sulfur. These materials have proven to be highly effective at containing lithium polysulfides, but their scalability has yet to be proven in large-scale production of Li–S batteries.

Graphene is a viable carbon matrix material for the Li–S cell since it is highly conductive and can envelope sulfur to hinder polysulfide dissolution. Previous work has shown that graphene can be used as a conductive support for polymer wrapped sulfur particles, melt-infiltrated sulfur and interstitial sulfur particles. While these materials are promising, they do not address the issue of large-scale technology for commercial applications and practical sulfur loading. This is a challenge. In general, the lower the sulfur content, the higher the sulfur capacity owing to factors such as electrolyte accessibility within the porous carbon, and electronic contact. Many papers focus on cells that exhibit very high capacity per gram of sulfur, but which contain sulfur contents well below 50% which greatly reduces their overall energy density per gram of cathode. Herein, we report a highly scalable graphene–sulfur composite (GSC) cathode material that exhibits the highest sulfur loading level (87 wt%) reported. Reduced graphene oxide (rGO) is used to envelope micron sized sulfur particles, to form a highly conductive network around the sulfur particles and trap the polysulfides through favourable hydrophilic–hydrophilic interactions. Larger sulfur particles with a lower surface area to volume ratio are more advantageous than nano-sized particles because they reduce the amount of rGO required to fully envelope the particles.

The synthesis of the graphene–sulfur composite (GSC) was easily accomplished by combining a mixture of graphene oxide and soluble polysulfide (Na₂S₆₋₂₄), and carrying out oxidation in situ as a one pot reaction as described in Scheme 1 (and see ESIF). The GSC composite was obtained after filtration and drying.

The XRD patterns of graphite, graphene oxide, sulfur and GSC are shown in Fig. 1a. The graphite starting material is clearly oxidized by the modified Hummer's method: the d-spacing increases from 3.35 Å for natural graphite to 8.42 Å for the graphene oxide which is in good agreement with previously reported data for graphene oxide. The synthesis relies on the in situ oxidation of the polysulfides with acid in the presence of the exfoliated graphene oxide, which simultaneously forms the sulfur particles and wraps them with the conductive agent. On fabrication of the GSC, a characteristic sulfur XRD pattern is obtained. It is noteworthy that no graphite or graphene oxide peaks appear in the GSC pattern which proves that the graphene sheets are in a substantially

Scheme 1 The one-pot synthesis step for the production of GSC.
exfoliated state and do not restack upon the oxidation of sulfur in the synthesis. The one-pot synthesis of GSC also aids in the intimate contact between the sulfur particles and the graphene sheets, and provides synthetic synergy. When the two solutions are initially mixed before HCl oxidation, the strongly basic sodium polysulfides can undergo a redox reaction with the graphene oxide to form a slightly more graphitic carbon. A decrease in resistance of the GSC electrode compared to pure graphene oxide is demonstrated by AC impedance spectroscopy (see S2, ESI†). The polysulfides will be slightly oxidized on the rGO surface and this can form nucleation sites for further sulfur particle growth by HCl oxidation of the remaining sodium polysulfides in solution.

The nature of the carbon and sulfur in the GSC composite was analyzed by Raman spectroscopy and the spectrum is shown in Fig. 1b. The sulfur particles exhibit a characteristic peak at ~520 cm\(^{-1}\) which is due to the A\(_1\) symmetry mode of the sulfur–sulfur bond.\(^{16}\) The relative intensity of the D peak at ~1350 cm\(^{-1}\) which represents disordered carbon and the G peak at ~1590 cm\(^{-1}\) which represents graphitic carbon are indicative of the degree of graphitization of a carbon sample.\(^{17}\) The intensity ratio of the D and G peaks is \(I_D/I_G = 1.22\). This means that the average distance between defects is <4 nm in the graphene that envelops the sulfur.\(^{18}\) The graphene sheets that envelope the sulfur particles in GSC therefore have both disordered and graphitic domains as expected from the synthesis method. High temperatures and strong reducing conditions are necessary to reduce graphene oxide to “graphene”, which are incompatible with the sulfur moiety in the composite.

The effectiveness of graphene as a well dispersed, flexible conductive agent is evident from the scanning electron micrographs in Fig. 2a and b, where the sulfur particles are highlighted by red squares. Sulfur is present as large micron sized particles that are completely enfolded by sheets of graphene without the use of polymers or additives. The well known strong binding of sulfur and carbon aids in driving this interaction. The TEM image in Fig. 2c clearly shows a sulfur particle that is approximately 1.5 \(\mu\)m in size enfolded by sheets of graphene. The carbon and sulfur elemental mapping demonstrates that sulfur is present as discrete particles embedded in the carbon tissue matrix, unlike other methods of synthesis that rely on melting of the sulfur into the graphene framework.\(^{12}\) Although that approach is viable (in principle), only a 22 wt% sulfur content was reported. Our method also differs from other reports that utilized polyethylene glycol as an interface between the sulfur particles and the graphene wrap, where composites containing 50–60 wt% sulfur were obtained in a two-step process.\(^{11}\) Through the \textit{in situ} one pot approach described here, a reduction in the amount of graphene required to envelope the sulfur is achieved. The sulfur content, measured by both elemental analysis and thermogravimetric analysis (see S1, ESI†), was 87 wt%. This greatly increases the overall gravimetric capacity of the material with respect to total mass of cathode, especially as no additional carbon was used to prepare the cathode in our case.

The electrochemical properties of the GSC cathode were examined in a coin cell configuration using 1 M LiTFSI in a
mixed solvent of 1,3-dioxolane and tetraethylenglycol dimethyl ether (1:1) as the electrolyte. Li foil was used as the counter electrode. The batteries were cycled between 1.5 and 3 V using a discharge/charge rate of C/5 (334 mA g\(^{-1}\)) which corresponds to a current density of 0.4 mA cm\(^{-2}\) (see ESI†). The discharge/charge profile is typical of a Li–S cell (Fig. 3a). Two voltage plateaus are observed at \(\sim 2.4\) V for the reduction of \(\text{S}_8\) to \(\text{Li}_2\text{S}_2\) and at \(\sim 2.0\) V for the further reduction to \(\text{Li}_2\text{S}_4\) and \(\text{Li}_2\text{S}\). Significantly, almost no overcharge is observed on the second cycle which indicates that the sulfur shuttle mechanism has been eliminated. The favourable hydrophilic–hydrophilic interactions between the lithium polysulfides and slightly oxidized graphene play a crucial role in reducing the loss of active mass. The long term cycling and coulombic efficiency of the GSC is shown in Fig. 3b. An initial discharge capacity of 705 mA h g\(^{-1}\) at a C/5 rate (full discharge in five hours) is obtained, and the capacity only fades 8\% over the first 15 cycles. The cycling stabilizes after 30 cycles and a very small capacity fade of 11\% is observed over the last 20 cycles. The overall capacity fade over 50 cycles is most likely due to the formation of insulating domains of Li2S that are not fully oxidized upon charge of the cell. The decrease in capacity is not due to active mass loss from polysulfide dissolution, because the sulfur shuttle mechanism is minimal as evidenced by the overcharge (difference in charge capacity and discharge capacity) which is quite low and only reaches 38 mA h g\(^{-1}\) at the 50th cycle. This leads to a relatively high coulombic efficiency (for a Li–S cell) at the 50th cycle of \(-93\%\). Although previous reports on graphene–sulfur composites have not reported this value, and hence comparison is not possible, other sulfur/carbon cathodes have been reported with coulombic efficiencies as high as 94\% after 50 cycles.\(^{18}\)

These materials were prepared by a complex, albeit clever vapour diffusion method which could make scale-up challenging. Most importantly, the overall cathode capacity (S + C + binder) is 550 mA h g\(^{-1}\); over a 50\% increase compared to graphene–sulfur materials recently reported.\(^{11}\)

In summary, a novel sulfur cathode composite has been synthesized that is easily scalable for large-scale production. The use of partially oxidized graphene as both an electrical conduit for insulating sulfur and as a barrier to retard polysulfide dissolution has led to an effective cathode material. The GSC is very important for realistic commercial Li–S batteries due to its extremely high sulfur content of 87 wt\% and its respectable initial discharge capacity of 705 mA h g\(^{-1}\). Further improvements are envisioned by using novel electrolytes such as ionic liquids,\(^{19}\) and solid polymers.\(^{20}\) We have shown that large amounts of conductive carbon additives are not required to obtain an efficient working Li–S cell. We attribute these promising properties to the fabrication process and the graphene composition which lies midway between highly graphitic (i.e. highly conductive) and slightly hydrosol as a result of oxo-groups on the carbon surface, which aid in polysulfide binding. Future research is being devoted to increase the overall capacity by modifying the morphology so that more complete reduction of sulfur can be obtained.

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Notes and references