GRAPHENE-SULFUR COMPOSITES: A NOVEL METHOD IN DEVELOPING ADVANCED LITHIUM-SULFUR BATTERIES

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Graphene-based sulfur composites are currently the subject of a great deal of scientific study, due to their ability to significantly improve the performance and efficiency of Lithium-Sulfur battery systems. This article reviews the recent advances made in the field, with some discussion on the future and practicality of the development of these new composites. There are many potential applications to these composite battery systems, including more efficient large-scale energy storage, longer-lasting rechargeable electronic devices, and the improved proposition for electrical vehicles as a popular mode of transport. It is thought that many of the issues that Li-S battery systems currently have, including the high resistivity of sulfur and the loss of polysulfides into the electrolyte, can be improved upon or solved using nanomaterials such as graphene. Many different methods have been explored in an attempt to integrate graphene into the sulfur cathode. These include the creation of sulfur-graphene nanosheets; the development of a functionalized graphene-sheet sulfur (FGSS) nanocomposites, the use of graphene oxide, and the integration of graphene into MOF derived nanoporous carbon.

Introduction

In recent times, scientific interest has grown considerably in the area of energy storage, in particular large-scale rechargeable storage systems that can be utilized over an extended period of time. These systems, if developed sufficiently, will enable major advances in areas such as renewable energy distribution, and practical electric vehicular transport (Bruce *et al.* 2008). One such rechargeable system that has garnered recent attention is the lithium-sulfur (Li-S) battery. This is due to the fact that elemental sulfur has the highest theoretical energy capacity (the amount of electrical charge it can deliver at a specific voltage) (1672 mA h g^{-1}), and power density (2600 W h kg^{-1}) of all discovered cathodes (Wang *et al.* 2011). In addition to this, sulfur is naturally abundant and would therefore be a highly cost-effective battery material, in addition to it being non-toxic and environmentally friendly.

Despite these major advantages, however, there are a number of challenges in Li-S batteries that must be overcome before any functional, long-term prototype can be developed. These include the high resistivity of elemental sulfur (which hinders ion transport between the electrodes and reduces the battery capacity), and the high solubility of polysulfide ions that are discharged into the electrolyte as the cathode is cycled (charged/discharged) (Cao *et al.* 2011). This loss of sulfur ultimately leads to a gradual decrease in the battery capacity, as less sulfur atoms are available for the electrochemical reaction. The tendency for the sulfur component to change volume as it is converted to polysulfides is also a major issue, as this leads to the gradual damage of the cathode from repeated expansion and contraction (Ji *et al.* 2011). These problems lead to a decrease in initial battery capacity and efficiency, as cycling progresses.

Much research over the past few decades has been conducted in an attempt to address these problems, in particular through the integration of sulfur into chemical structures known as *composites*. These are essentially materials that are comprised of two or more constituent materials that when combined, yield a novel material with different chemical and physical properties to its components. Such research includes the investigation of conductive polymers in improving the conductivity of sulfur composites (Liang *et al*. 2009, Ji *et al.* 2009, Lai *et al.* 2009). As well as this, significant progress has been made recently in the use of sulfur-carbon composites as the cathode in Li-S batteries, in an attempt to reduce the dissolution of polysulfides (Liang *et al.* 2009).

Previously, research into other types of electrochemical storage systems, including lithium-ion batteries (Yoo *et al.* 2008, Wang *et al.* 2009, Wang *et al.* 2010) has shown that graphene has the correct chemical properties to improve the lifetime and quality of certain battery systems. This is due to its high conductivity, chemical resilience, large surface area (approx. 2600 m^2 g^{-1}) and wide-ranging electrochemical window (Choucair *et al.* 2009).

In the case of lithium-sulfur batteries, a number of novel methods have been approached in recent years in an attempt to integrate graphene into the structure of the sulfur cathode, in the form of a composite. Current research and study into this area is of huge interest to many areas of the scientific community, due to the potential applications of such systems. The question should therefore be raised as to how successful these methods have been at overcoming some of the fundamental issues of Li-S batteries. A number of these recent methods will now be analyzed in detail.

The use of Sulfur-Graphene Nanosheets (S-GNS)

One particular strategy at integrating the useful properties of both graphene and sulfur is the creation of what are known as *Sulfur-Graphene Nanosheets (S-GN*S). These consist of elemental sulfur that has been physically mixed into graphene nanosheets (GNS), and heated to allow the infiltration of sulfur into the graphene layers. Wang *et al*. (2010) successfully synthesized a S-GNS composite, using a graphene-sulfur weight ratio of 1:1.5. Using various methods of spectroscopic analysis, such as Raman spectrum (fig. 1), it was found that the sulfur particles coated the graphene in a uniform fashion, which is ideal for ensuring that the sulfur has as much exposure to the graphene interface as possible, and maximum electrical conductivity is achieved throughout the cathode. This was confirmed by SEM images (fig. 2(c)), which show that the sulfur particles had melted, and had evenly distributed throughout the GNS.

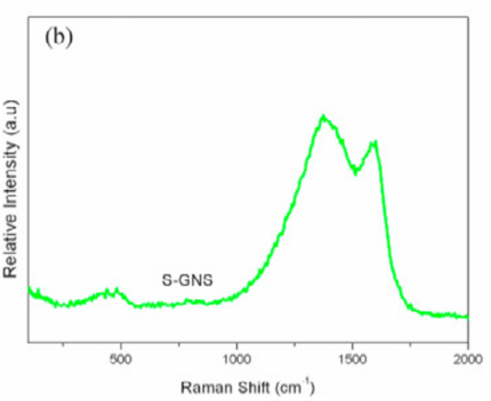

Figure 1: *Raman Spectrum of S-GNS composite. No characteristic peak for sulfur was observed (normally found at 259, 412 cm^{-1} (White, S. N., 2008)), indicating that the sulfur was in a highly dispersed state throughout the composite (Wang, J. Z. et al 2010).*

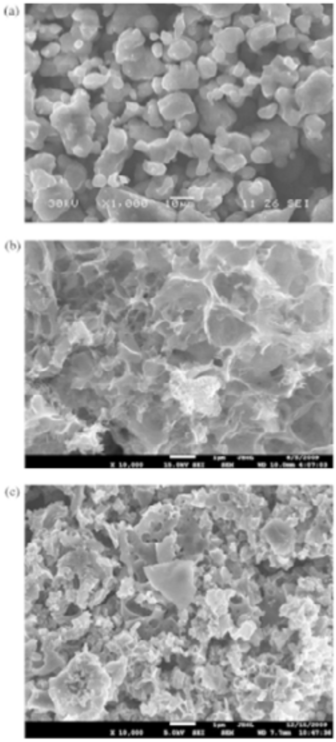

Figure 2: *SEM imagery of pure sulfur (a), the GNS (b), and the S-GNS composite (c). It can be observed that the solid structure of pure sulfur has entirely disappeared in the S-GNS composite, indicating excellent dispersion. (Wang, J. Z. et al 2010).*

During this experiment, a number of performance tests were conducted on the resulting S-GNS cathode, in comparison to a conventional cathode of pure sulfur. One of these tests involved the measurement of the cycling stability of the cathode. This is defined as a measure of the ability of a battery to retain a fraction of its initial capacity over a number of charge-discharge cycles. When the measurements were conducted (using a lithium anode, with a constant current density of 50 mA g $^{-1}$), it was found that the S-GNS nanocomposite retained a higher level of capacity as the cycles progressed (see fig. 3) (Wang *et al.* 2010). It was also noted that the initial capacity of the S-GNS electrode was significantly higher than that for pure sulfur (1611 mA h g^{-1} for S-GNS in comparison to 1100 mA h g^{-1} for pure sulfur), indicating greatly improved conductivity. It can therefore be concluded from these results that the S-GNS nanocomposite leads to a significant performance and lifetime improvement, when compared to a bare sulfur electrode.

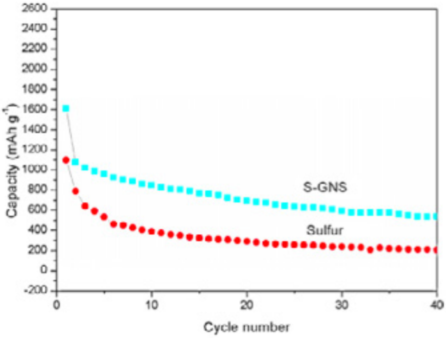

Figure 3: *Capacity of pure sulfur, S-GNS battery systems vs. cycle number. It can be observed that the S-GNS composite had a higher initial capacity than the pure sulphur, and maintained better cycling stability. (Wang, J. Z. et al 2010)*

Improvement of GNS capacity through development of Functionalized Graphene Sheet-Sulfur (FGSS) nanocomposite

The experimental results obtained using a S-GNS nanocomposite are clearly a major improvement on the conventional Li-S battery type. However, another experimental report (Cao *et al.* 2011) notes that the sulfur loading (i.e. the amount of sulfur that is successfully absorbed into the composite) is extremely low, at approximately 17-22 wt% (Wang *et al.* 2010). It also notes that there is a large decrease in the capacity of the S-GNS battery as the charge/discharge cycles progress (approx. 1100 to 600 mA h g^{-1} in 40 cycles, see fig. 3), which is partially due to the dissolution of polysulfides into the electrolyte. It is therefore clear that a more efficient method to integrate sulfur into the composite should be explored, and to better protect the polysulfides from dissolving into the electrolyte.

One particular type of composite that has shown improvement in these areas is a *functionalized graphene sheets-sulfur nanocomposite (FGSS)* (Cao *et al.* 2011). This consists of sheets and stacks of functionalized graphene (graphene with various oxide groups attached) (Schniepp *et al*. 2006, Wang *et al*. 2011), with interlocking layers of sulfur atoms. This is commonly referred to as a sandwich-type layout (see fig. 4). The major advantage of this arrangement is that the sulfur loading is much higher, and the distribution of sulfur nanoparticles is more uniform. An experiment by Cao *et al.* (2011) analyzes the effectiveness of this arrangement, and finds that although the performance of the battery is improved, there is still significant migration of polysulfides into the electrolyte.

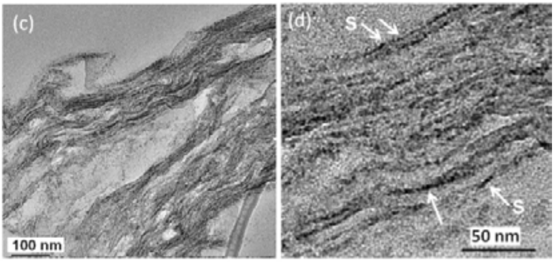

Figure 4: *TEM images of Nafion-coated FGSS nanocomposite, at scales of 100nm (c) and 50nm (d). The sandwich structure of interlocking dark (sulphur) and bright (graphene) lines can clearly be seen (Cao, y. et al 2011).*

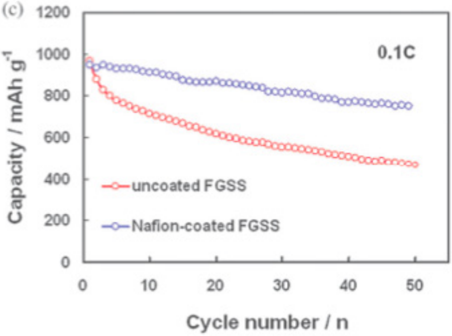

Figure 5: *Graph of cycle performance of pure FGSS, and with Nafion coating. Current kept at 0.1 C. The improvement capacity and cycling stability when the Nafion coating is added can be observed (Cao, y. et al, 2011).*

Interestingly, in order to solve this issue of polysulfide loss the FGSS composite was also coated with Nafion®, a highly conductive polymer which is intended to act as a protective film to hinder polysulfide dissolution. This is shown to have a significant effect on the capacity and cycling stability of the battery system (see fig. 5). It was found that the uncoated FGSS electrode had 52% of its initial capacity remaining after 50 cycles. On the other hand, the Nafion coated FGSS electrode retained 79.4% of its original capacity after 50 cycles, and approx. 74.3% after 100 cycles (Cao *et al*. 2011) (at constant rate of 0.1 C, see fig. 5). In addition to the Nafion acting as a protective barrier against polysulfide dissolution between the graphene sheets, this is also due to its ability to act as a cation exchange material. This arises due to the polytetraflouroethylene component of the polymer, which allows the Li^+ cations to enter the cathode, while simultaneously preventing the polysulfides from leaving due to static repulsion. This particular use of a graphene-based composite, in combination with the protective polymer coating, yields significant improvement in battery performance and capacity. It should be noted that when compared to the previous method (Section 2), the FGSS design is a far better candidate for integration into a practical battery system. The multilayered structure is far more efficient at sulfur loading, and performs significantly better at protecting the dissolution of polysulfides.

Use of Oxides of Graphene as Polysulfide Traps

As mentioned previously, finding a method to hinder the escape of polysulfides from the cathode is of extreme importance in the attempt to develop an efficient Li-S battery system, with minimal capacity fading. One such method that has been attempted makes use of graphene oxide (GO) as a sulfur immobilizer (Ji *et al.* 2011).

The basic idea behind this concept is that the hydroxyl groups (and various other oxygen-based functional groups that are present on the graphene oxide) positively contribute to the chemical bond between the carbon and sulfur atoms, which significantly hinders any polysulfide discharge from the cathode into the electrolyte. It has been observed previously that the GO composite also has the capability to withstand the volume changes that occur as sulfur is converted into the polysulfides, and as it reverses back to elemental sulfur upon recharging of the battery (Lai *et al*. 2009, Chen *et al*. 2011). The expansion and contraction of the sulfur can lead to the disintegration of the composite as cycling progresses. The larger surface area of the graphene oxide (due to the functional groups) also provides a well-established electron transfer network between the ions, facilitating better conductivity.

In an experiment conducted by Ji *et al.* (2011), a graphene oxide-sulfur (GO-S) nanocomposite is synthesized, through the use of chemical deposition to deposit sulfur atoms onto layers of 2D graphene oxide. The resulting composite is then heat treated to remove any excess sulfur atoms that were not attached to the composite. A notable advantage in using this method of synthesis is that it is cheap and environmentally friendly, which enables a higher suitability for mass production.

The cycling efficiency of the composite was experimentally tested as a cathode of an electrode system, with a lithium anode. It was found that after 50 cycles (at a constant rate of 0.1 C), the capacity of the system remained constant at approximately 954 mA h g^{-1}. This consistency indicates that there is very little dissolution of polysulfides occurring in the system, and even surpasses the levels of polysulfide protection achieved in method 3. The Coulumbic efficiency (the efficiency by which charges are transferred during an electrochemical reaction) was measured to be around 96.7% (Ji *et al.* 2011). This indicates that the cathode is highly stable as the reversible electrochemical reactions progress with each cycle (see fig. 6) These results show that using functional groups as immobilizers in the GO-S composite is an effective way of confining sulfur to the conducting matrix, and hindering any dissolution into the electrolyte.

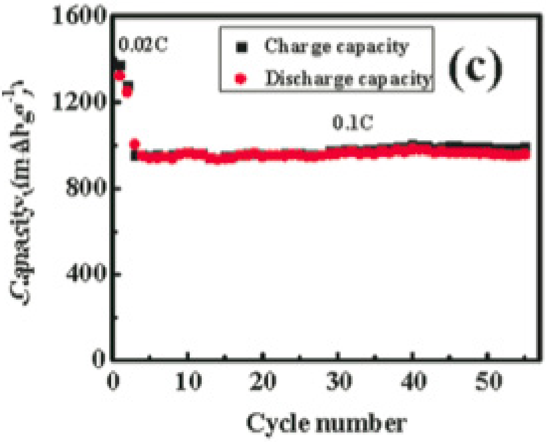

Figure 6: *Graph depicting the cycle performance at constant rate of 0.1 C. Can be seen that the capacity remains near initial levels, even during the final cycles (Ji, L. et al 2011).*

Hybridization of Graphene and Microporous Carbon-based Metal Organic Frameworks (MOFs)

As of recently, another promising method that has been developed for the containment of polysulfides is a process that involves the use of *Metal Organic Frameworks (MOFs).* These porous, crystalline structures are composed of coordination bonds between metal ions, and multidentate organic ligands (Nature publishing group, 2014). Under the correct conditions, they are able act as a template in the formation of nanoporous carbon, which supports sulfur diffusion throughout its structure (Xi *et al.* 2013).

This nanoporous carbon structure, derived from a MOF, is highly suited for containing polysulfides. This is due to the small pore sizes of the carbon matrix that trap the sulfur atoms by adsorption onto the surface. This allows the cycling stability of the system to be maintained at a high level for an extended period of time. Previous scientific study has also found that variation of the pore size of *carbon-based* MOFs affects their electrochemical suitability as a cathode in a Li-S battery. Smaller pore sizes (<2 nm) are found to improve the cycle stability of the cathode, while larger pore sizes (2-50 nm) cause an increase in initial discharge capacity (Xi *et al*. 2013). Carbon-based MOFs also have a large surface area, which greatly encourages efficient ion transfer during the electrochemical reaction.

It has been found, however, that the capacity of the MOF derived microporous carbon is quite low. This is due to the fact that there are many grain boundaries and interfaces throughout the composite (Chen *et al*. 2014). These lead to poor electrical conductivity, as there are many possible electron scattering centers that impede the efficient transition of ions throughout the cathode.

One particular study has taken a novel approach to addressing this problem (Chen *et al*. 2014). Due to the low resistivity of graphene, it can be used as a structural intermediate to increase the electrical conductivity between each component of the composite. In this study, a composite known as graphene sheet-sulfur/zeolithic imidazolate framework-8 derived carbon (GS-S/

$C_{ZIF8\text{-}D}$) was synthesized. This consists of a carbon host that is derived from a MOF known as Zeolitic Imidazole Framework-8 (ZIF-8). The carbon host is then infused with sulfur, to produce a composite. The resulting composite is then wrapped with graphene sheets (*see figure 8 for illustrated production process*). Due to the high flexibility of graphene, it easily wraps around the S/$C_{ZIF8\text{-}D}$. This ensures that the improved conductive effects are well applied throughout the composite (see fig 9 for SEM image) (Chen *et al*. 2014).

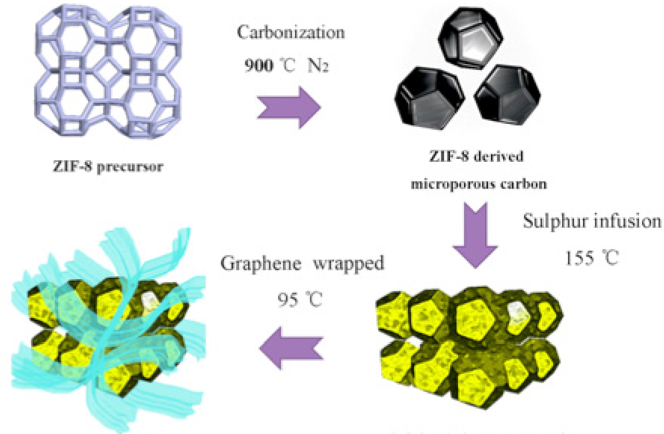

***Figure 7:** Synthesis process for GS-S/$C_{ZIF8\text{-}D}$ nanocomposite (Chen, R. et al, 2014)*

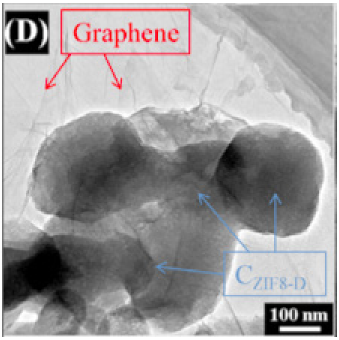

***Figure 8:** SEM image of graphene-wrapped MOF derived microporous carbon framework. Due to the flexibility of graphene, it can easily wrap around the GS-S/$C_{ZIF8\text{-}D}$ nanocomposite. (Chen, R. et al, 2014)*

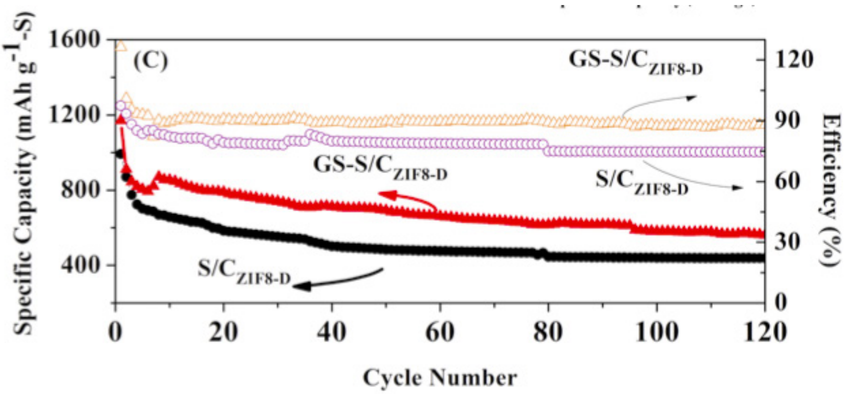

Figure *Cycling performance of GS- S/C_{ZIF8-D} composite compared to the S/C_{ZIF8-D} composite. Can be observed that the capacity retention is significantly improved for the GS- S/C_{ZIF8-D} composite compared to the S/$C_{ZIF8-D.}$ (Chen, R. et al 2014).*

The resulting composite was performance tested as a cathode in a Li-S cell, in comparison to the same composite without the graphene wrapping. It was found that the initial discharge capacity of GS-S/C_{ZIF8-D} was significantly higher than that of the S/C_{ZIF8-D} composite (1171 mA h g^{-1} vs. 982 mA h g^{-1} respectively). This initial discharge value is also significantly higher than any of the previous methods (2-4). The S/C_{ZIF8-D} composite was also found to have both a lower capacity and cycling stability than that of the graphene wrapped composite over 120 cycles (see figure 10) (Chen *et al.* 2014)**.** This improvement is due to the increase in charge-transfer speed, due to the highly conductive graphene sheet network. It should also be noted from these results that when compared to the previous methods, this is the most efficient composite system. The improvements made in this experiment, through the use of graphene as a conductive intermediate, clearly indicate that such a structure is a very promising design for a rechargeable Li-S electrode system.

Conclusions

It can be seen from the experimental results above that the integration of graphene-based composites into Li-S batteries leads to a significant improvement in performance and efficiency, when compared to conventional Li-S designs. The varieties of novel approaches that have been developed, which incorporate graphene into their composite structure, indicates how important the nanomaterial has become in the development of composite battery systems. It should also be noted, however, that the sheer variety of experimental methods highlights how the integration of 2D nanomaterials such as graphene into these systems is still highly experimental. Therefore, assuming current research continues at a similar pace, even more efficient composite systems will be produced in the very near future, which will quickly surpass the achievements of these recent developments.

In terms of the production of practical applications using these composite batteries, these are still a number of years away. This is due to the rapidly changing and purely experimental nature of current developments, both in graphene synthesis and Li-S composite battery design. One issue that will likely arise is how these methods will be industrialized for mass production, in particular the current issue of the large-scale manufacturing of advanced nanomaterials (Kim *et al.* 2009). However, as noted previously the fast pace of current research in the area indicates that it may not be long before Li-S batteries become an attractive alternative to conventional battery systems already in use, and could one day revolutionize many important energy systems of the modern world.

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