Effective Strategies for Stabilizing Sulfur for Advanced Lithium-Sulfur Batteries

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A Revised Review Article submitted to Journal of Materials Chemistry A
Abstract: The lithium-ion battery, with a relatively small energy density of \(~250 \text{ Wh/kg}\), has dominantly powered many devices requiring small energy demands. However, there remains a need for a cheaper and smaller type of battery with higher energy density for energy-intensive storage purposes in the automotive, aircraft, and household energy sectors. With its higher specific capacity (1675 mAh/g) and lower costs, the lithium-sulfur (Li-S) battery represents the most promising next generation batteries. The main focus of scientific inquiry surrounding Li-S batteries lies at the cathode where sulfur chemically bonds to lithium. Current challenges pertaining to the high performance cathode such as the dissolution of sulfur into the electrolyte and electrode volume changes are highlighted. This review focuses on recent developments in the last three years of various sulfur integration methods at the cathode that result in improved electrochemical performance, increased energy density, cyclic stability, and a higher capacity over the mainstream lithium-ion battery. In particular, the most recent approaches were systematically examined and compared including the use of carbon and non-carbon composites to stabilize sulfur. Ideal material hosts for sulfur atoms in the cathode for outstanding Li-S batteries were outlined and thoroughly discussed. Critical understanding and relevant knowledge were summarized aiming to provide general guidance for rational design of high-performance cathode for advanced Li-S batteries.
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1. Introduction

Battery technology, first emerged in the late 19th century, has since grown to become an integral member in the greater energy ecosystem. While there have been a number of developments within the area of battery technology, the most popular one is the Li-ion battery, which have significantly contributed to the energy infrastructure of society. It ushered in a new age and variety of products, with small energy needs, thus becoming indispensable to everyday existence. However, with growing interest to generate sustainable energy for automobile and household uses, novel battery designs that have significantly increased energy density are being sought out. The Li-S battery, first introduced in the early 21st century, is a type of lithium ion battery that uses sulfur as the active material in the cathode. It possesses a theoretical specific capacity of 1675 mAh/g and gravimetric energy density of 2500 Wh/kg, which is significantly higher relative to the widely used Li-ion battery (~250 Wh/kg).\(^1\)\(^2\) Compared to cathode materials (e.g., oxides) utilized in current Li-ion batteries, sulfur is relatively light, inexpensive, and readily sourced. Although both Li-ion and Li-S batteries rely on the same ion transport mechanism, they utilize different electrode materials, electrolytes and hence have different battery reactions.\(^2\)\(^-\)\(^6\) Energy density of conventional Li-ion batteries relies on the amount of Li\(^+\) that can be intercalated or inserted into an electrode, in which the cathode material is typically a lithium metal oxide (e.g., LiCoO\(_2\) and LiFePO\(_4\)). These oxides or phosphates have very limited capability to accommodate Li, thus showing low capacity and greatly limiting battery performance. One important characteristic of the Li-S battery is the occurrence of octatomic S\(_8\) molecules, which can bind 2 Li atoms per S atom. Therefore, energy density of sulfur cathode can be significantly increased.

Increased volumetric and specific energy density are directly related to the surface chemistry occurring at the cathode/electrolyte interface where sulfur is reduced and chemically bonds to
lithium ion. Upon discharge, the sulfur cathode undergoes three main stages: (i) solid to solution reduction of $S_8$ into long chain polysulfides, (ii) the solution phase reduction of long chain polysulfides to short chain polysulfides, and (iii) solution to solid reduction of short chain polysulfides to insoluble and insulating $Li_2S_2$. Figure 1 highlights the major electrochemical characteristics of the Li-S battery. Figure 1a depicts a typical discharge voltage profile of the Li-S battery. The open circuit voltage of the battery occurs at 2.3-2.4 V. As the battery discharges, solid state octatomic $S_8$ binds with Li ions, migrated from the anode, to form high order long chain lithium polysulfides. This initial reduction reaction corresponds to the first plateau region that occurs at 2.3-2.4 V as the energy derived from the battery is obtained from this conversion step. The transformation of high order polysulfides to intermediate polysulfides occurs in the dark brown region whereby $Li_2S_6$ is converted to $Li_2S_4$. This conversion step does not produce a significant amount of energy; as a result, there is a noticeable drop in voltage to 2.0-2.1 V. The yellow region whereby $Li_2S_4$ is further converted to $LiS_2$, where the majority of the energy derived from the Li-S battery is obtained. The further bonding of $Li^+$ ions form short chain and low order lithium polysulfides. The illustration below the diagram in Figure 1a highlights the sulfur being converted to $Li_2S$. Figure 1b highlights the reaction stages sulfur undergoes from solid state sulfur to lithium sulfide. There are no specific phase changes that occur with sulfur upon cycling. Electrolyte access in the cathodic region is necessary for proper $Li^+$ diffusion, however, lithium polysulfide diffusion loss into the electrolyte is a major concern as well.
**Figure 1.** General characteristics of the Li-S battery: (a) electrochemical cycling profile of a typical Li-S battery and detailed schematic of sulfur bonding chemistry upon discharge and charge cycles and (b) multiple step reduction of sulfur upon battery discharge. Reprinted with permission from Ref [8]. Copyright 2013, Nature Publishing Group.
Li-S batteries, as discussed thus far, have a positive outlook, however they are not without their drawbacks. The long chain intermediate polysulfide compounds are highly soluble in the traditional organic electrolyte and can diffuse through the separator towards the anode. Once at the anode, the polysulfides are reduced to lower order polysulfide and then diffuse back towards the cathode where they are reformed into their original long chain polysulfides. This leads to the low utilization of the active sulfur at the cathode, a phenomenon known as the “shuttling effect”. Another issue is the volume expansion known to occur in lithium batteries. Upon insertion of lithium ions, electrodes containing sulfur will more than double their volume possibly leading to cracks in the solid electrode.

Therefore, amongst the issues faced with the Li-S battery, the low electron conductivity of sulfur and its dissolution represent the biggest challenge in limiting its practical applications. Current efforts involve combining sulfur with a high, electrically conductive carbon material within cathodes. This technique integrates the excellent conductivity of carbon to ensure electrons transfer to all active sulfur. Generally, overcoming the inherent challenges associated with the development of Li-S batteries will be solved in the following ways: (1) creating a minimal transport pathway for lithium ions and electrons to achieve high energy/power density, (2) using a highly porous media to allow for sulfur expansion, (3) effective polysulfide trapping through physical or chemical means, and (4) a nanostructured matrix to diminish the effect of pulverization. The major focal point in this review is to provide a discussion of how sulfur can be stabilized within a cathode. Included in the following section is an examination of the variety of pathways that have been employed to develop next generation composite sulfur cathode electrodes for the Li-S battery. We will emphasize novel synthesis methods; unique nanostructures and morphology; significantly improved battery performance, capacity, cycling stability, and rate
performance; and acquired mechanistic understanding to promote the cathode performance. In particular, the direct correlation between cathode morphology and energy density are examined. To this end, we focus on elucidating correlation of materials synthesis/process, structures, and performance, thereby summarizing the new knowledge to society.

2. Current Achievement of Li-S Batteries.

Arguably, the conventional lithium-ion type battery is approaching its capacity limits. There remains ongoing research to improve the cycle stability and charging rate performance of Li-ion batteries; however, they correspond to marginal improvements in energy density. The potential for significantly increased energy density over the Li-ion battery is where the Li-S battery serves as a great alternative. Many groups have made great contributions to Li-S batteries in terms of enhanced capacity, rate performance, and cyclic stability. For example, Chen et al. utilizes a multi-chamber/micro/mesoporous carbon nanocube substrate to generate a suitable Li-S cathode. The presence of different nano-sized pore structures allowed for a high initial capacity of 1078 mAh/g and a long cycle stability (1004 mAh/g after 1000 cycles). Li et al. utilizes a novel 3D developed porous carbon to generate a high initial capacity of 1115 mAh/g with an extended cycle stability of 750 mAh/g after 1000 cycles. Other important progresses in last three years were highlighted in Table 1, providing a comprehensive comparison of the most recent novel sulfur cathode structures and their respective performance metrics.
Table 1. Novel sulfur cathode structures and their corresponding battery performance metrics.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Sulfur loading/percentage in composite (wt%)</th>
<th>Electrolyte</th>
<th>Discharge rate (C)</th>
<th>Voltage range (V)</th>
<th>Discharge capacity (mAh/g)</th>
<th>Initial</th>
<th>After n cycle</th>
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<tr>
<td>Reduced Graphene Oxide wrapped MOF cobalt doped carbon polyhedrons</td>
<td>1mg/59</td>
<td>1M LiTFSI; 1:1 v/v DOI:DME 0.1M LiNO₃</td>
<td>0.3</td>
<td>1.8-2.6</td>
<td>1218</td>
<td>949</td>
<td>949 (300)</td>
</tr>
<tr>
<td>Dense Graphene Sheet</td>
<td>1.1mg/69.6</td>
<td>1M LiTFSI; 1:1 v/v DOI:DME 0.1M LiNO₃</td>
<td>0.5</td>
<td>1.6-2.8</td>
<td>1300</td>
<td>770</td>
<td>770 (300)</td>
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<tr>
<td>Polypyrrole/Graphene</td>
<td>2mg/52</td>
<td>1M LiTFSI; in TEGDME</td>
<td>0.1</td>
<td>1.0-3.0</td>
<td>1415.7</td>
<td>641</td>
<td>641 (50)</td>
</tr>
<tr>
<td>NiS₂ Shell</td>
<td>1mg/63</td>
<td>0.8M LiTFSI; 1:1 v/v DOI:DME 0.2M LiNO₃</td>
<td>0.1</td>
<td>1.8-3</td>
<td>1238</td>
<td>954</td>
<td>954 (1200)</td>
</tr>
<tr>
<td>Hierarchical Free-Standing Carbon Nanotube Paper</td>
<td>&gt;2.0mg/54</td>
<td>1M LiTFSI; 1:1 v/v DOI:DME 0.25 M LiNO₃</td>
<td>0.05</td>
<td>1.7-2.8</td>
<td>995</td>
<td>~700</td>
<td>~700 (150)</td>
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<td>Lithium Sulfide/Microporous Carbon</td>
<td>1mg/37.5</td>
<td>1 M LiPF₆, 1:1 v/v EC:DEC</td>
<td>0.1</td>
<td>1.0-3.0</td>
<td>700</td>
<td>650</td>
<td>650 (900)</td>
</tr>
<tr>
<td>Amylopectin/Graphene Oxide</td>
<td>2mg/56</td>
<td>1M LiTFSI; 1:1 v/v DOI:DME</td>
<td>0.125</td>
<td>1.5-2.8</td>
<td>1200</td>
<td>900</td>
<td>900 (100)</td>
</tr>
<tr>
<td>Mesoporous Titanium Nitride</td>
<td>1mg/58.8</td>
<td>1M LiTFSI; 1:1 v/v DOI:DME 2wt% LiNO₃</td>
<td>0.5</td>
<td>1.6-2.8</td>
<td>988</td>
<td>644</td>
<td>644 (500)</td>
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<tr>
<td>Hierarchical Porous Carbon Rod</td>
<td>1.5mg/80</td>
<td>1M LiTFSI; 1:1 v/v DOI:DME 1wt% LiNO₃</td>
<td>1</td>
<td>1.6-2.8</td>
<td>970</td>
<td>700</td>
<td>700 (300)</td>
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<tr>
<td>Shaddock Peel Carbon Sheet</td>
<td>2.0mg/62</td>
<td>1M LiTFSI; 1:1 v/v DOI:DME 0.1 M LiNO₃</td>
<td>0.2</td>
<td>1.8-2.8</td>
<td>1099.2</td>
<td>722.5</td>
<td>722.5 (100)</td>
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<tr>
<td>Structure Type</td>
<td>Composition</td>
<td>Current Density (mg/1 M LiTFSI)</td>
<td>CTE (10^-6 K^-1)</td>
<td>Reaction Temp (°C)</td>
<td>Ref.</td>
<td></td>
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<tr>
<td>MXene(Transition metal carbide(e))</td>
<td>1.0 mg/70</td>
<td>1 M LiTFSI; 1:1 v/v DME; DOL 2 wt% LiNO₃</td>
<td>0.5</td>
<td>1.8-3.0</td>
<td>723 (650)</td>
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<td></td>
</tr>
<tr>
<td>TiO₂ inverse opal Structure</td>
<td>0.8 mg/45</td>
<td>1 M LiTFSI; 1:1 v/v DOL:DME 1 wt.% LiNO₃</td>
<td>0.2</td>
<td>1.8-2.6</td>
<td>1100</td>
<td>890 (200)</td>
<td></td>
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<tr>
<td>Thin Film Polypyrrole Structure</td>
<td>1.0 mg*/86</td>
<td>1 M LiTFSI; 1:1 v/v DOL:DME 1 wt.% LiNO₃</td>
<td>0.2</td>
<td>1.8-2.6</td>
<td>1126</td>
<td>822 (400)</td>
<td></td>
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<tr>
<td>Multichamber/ Micro/Mesoporous Carbon Nanocubes</td>
<td>1.62 mg/72</td>
<td>1 M LiTFSI; 1:1 v/v DOL:DME 0.1 M LiNO₃</td>
<td>0.5</td>
<td>1.6-2.6</td>
<td>1078</td>
<td>1004 (1000)</td>
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<tr>
<td>Li₂S/Reduced Graphene Oxide Paper</td>
<td>0.8mg-1.5 mg*/50</td>
<td>0.6 M LiTFSI; 1:1 v/v DOL:DME 0.4 M LiNO₃</td>
<td>0.2</td>
<td>1.7-2.8</td>
<td>1119</td>
<td>816 (150)</td>
<td></td>
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<tr>
<td>Polydopamine coated Carbon Spheres</td>
<td>1.5mg/65</td>
<td>1 M LiTFSI; 1:1 v/v DOL:DME 2 wt.% LiNO₃</td>
<td>0.2</td>
<td>1.5-3.0</td>
<td>1070</td>
<td>900 (150)</td>
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<tr>
<td>Nitrogen Doped Carbon Nanotube Web</td>
<td>0.9mg-1.0 mg/77.01</td>
<td>1 M LiTFSI; 1:1 v/v DOL:DME 0.1 M LiNO₃</td>
<td>0.5</td>
<td>1.8-2.8</td>
<td>1146.1</td>
<td>714 (200)</td>
<td></td>
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<tr>
<td>Single Layer Graphene Sheet</td>
<td>0.76mg-0.97mg*/80</td>
<td>0.7 M LiPF₆ in PYR₁₄TFSI/DOL/DME(2:1:1) 0.5 M LiNO₃</td>
<td>2</td>
<td>1.5-3.0</td>
<td>1062</td>
<td>606 (100)</td>
<td></td>
</tr>
<tr>
<td>3D Coral like, Nitrogen Doped Carbon</td>
<td>0.8mg-1.2mg/54</td>
<td>1 M LiTFSI; 1:1 v/v DOL:DME 0.2 M LiNO₃</td>
<td>2</td>
<td>1.5-3.0</td>
<td>~800</td>
<td>621 (250)</td>
<td></td>
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<tr>
<td>3D Porous Carbon</td>
<td>2.36mg/90</td>
<td>0.38 M LiTFSI; 1:1 v/v DOL:DME 0.31 M LiNO₃</td>
<td>2</td>
<td>1.5-3.0</td>
<td>1115</td>
<td>750 (1000)</td>
<td></td>
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</table>
3. Methods to Stabilize Sulfur within Cathodes

3.1 Carbon composites

Amongst the issues facing a future of commercially available Li-S battery, one of the most challenging might be the creation of a suitable cathode. A sulfur cathode, capable of minimizing the polysulfide shuttle process and volume changes during charge and discharge, is highly demanded. A number of methods have been employed to approach this dilemma. A very popular pathway to a high capacity sulfur electrode is the use of a carbon sulfur composite as illuminated in Figure 2. Most composites are formed from a melt diffusion method where sulfur is deposited into the pores/shells/tubes of a carbon matrix. In addition, novel approaches to the design of the cathode include the use of lithium sulfide whereby sulfur is inherently present in the composite. In the following proceedings, a number of techniques used by researchers to develop next generation Li-S batteries are explored.

![Figure 2](image_url)  
**Figure 2.** Novel approaches using to encapsulate sulfur and its related polysulfides into various carbon materials to fabricate robust sulfur cathodes. Reprinted with permission from Ref [40]. Copyright 2014, American Institute of Physics.
3.1.1 Porous carbon for sulfur composite cathodes

In contrast to the variety of complex carbon sulfur composites, one of the simpler introductions into a composite structure for the Li-S battery comes by the way of highly porous carbon/sulfur composites. Scientists have utilized carbon sources of varying surface areas and porosities to serve as substrate hosts. With the melt diffusion technique, where sulfur and carbon are mixed into a specific ratio and then hydrothermally treated, they have obtained a suitable composite structure that allows for notable cyclic stability. Jayaprakash et al. introduced porous hollow carbon sulfur composites for high performance Li-S batteries. The composite represents a relatively simple and scalable approach for creating mesoporous hollow carbon capsules that encapsulate and retain sulfur at the cathode and within the pores of the carbon. The unique mesoporous carbon is synthesized by a pyrolysis step where a carbon precursor is evenly deposited onto porous metal oxide nanoparticles (silica template). It is then calcined at 1300°C for 12 hours to form the carbon host, decomposing the metal oxide template into a gas phase that generates a highly porous carbon matrix. It’s followed by a dissolution step of the metal oxide nanoparticle, where hydrofluoric acid is used to remove the template. Subsequently, sulfur vapor infusion at an elevated temperature (600°C) allows for a high sulfur loading (~70%). The characteristics of the mesoporous carbon (2-50 nm), i.e. interior void space, mesoporous shell structure, and composition of the shell, were designed to increase the amount of sulfur retained by the capsules. This minimized lithium polysulfide dissolution and the shuttling effect while still maintaining fast transport of lithium ions to the sulfur. The fabricated battery demonstrated a capacity of ~1000 mAh/g over 100 cycles and had excellent charge rate capabilities. It was able to retain most of its initial capacity after exposure to a relatively high charging rate (e.g., 3C) and reduced back to its original rate. This method
employs the use of a high temperature synthesis step to infuse sulfur vapor deep into the carbon matrix. However, this method is not always desired as it is energy intensive. Other techniques that utilize a thin film coating to restrain sulfur movement are sought after if the carbon sulfur mix temperature can then be lowered.

In addition, emerging from Nazar’s group, a new alternative for a highly porous carbon/sulfur cathode was developed. The novelty lies in the originality of the carbon structure that was generated in the experiment. It utilizes CMK-3, a popularly known member of the mesoporous carbon family, which exhibits a uniform pore diameter, high pore volume, and high electrical conductivity. In particular, CMK-3 was synthesized by a nano-casting technique, whereby sucrose was mixed with a mesoporous silica hard template (SBA-15) in a sulfuric acid solution and sonicated for 1 hour. The mixture was then carbonized at 900°C for 5 hours in an inert argon atmosphere to form the porous CMK-3 carbon nano-rods. Removal of the SBA-15 silica template utilized a 5% HF solution, which was mixed with the composite for 4 hours at room temperature. To form the carbon/sulfur composite a melt diffusion strategy was enacted as previously mentioned earlier. A 3:7 mass ratio of CMK-3 to sulfur was heated to 155 °C in order to melt the sulfur and allow it to infuse into the carbon host. Upon cooling, it solidifies to form sulfur nanotubes that are in close proximity with the nearby conductive carbon wall. Polyethylene glycol (PEG) polymer served as a final thin film coating on the surface of the cathode composite, binding to the functional groups on the surface of the composite introduced by nitric acid oxidation (80°C, 30 mins). The PEG serves to diminish the loss of active sulfur to the electrolyte by forming a hydrophilic region in between the cathode and electrolyte phase. This in turn solubilizes formed polysulfides over the electrolyte while still facilitating fast ion diffusion. As a result, a stable capacity of 1005 mAh/g was achieved over 20 cycles.
Another similar method was developed to synthesize a highly porous carbon/sulfur composite structure (HPC). Polyacrylonitrile (PAN) as the carbon precursor was mixed with sodium carbonate, which acted as a porogen, to facilitate the creation of HPC upon decomposition at 750°C. This approach demonstrates conductive additives and strong adsorbing agents with a large surface area, such as mesoporous carbon, which are viable options to increase capacity of the cathode electrode. The carbon/sulfur was also synthesized by a simple melt diffusion technique with an additional high temperature treatment at 300°C. This was to vaporize the sulfur on the outside surface of the carbon matrix and either remove it or infuse it deeper into the carbon support. The surface area of the carbon material was determined to be 1472.9 m²/g, which is high enough to account for effective electrochemical reactions to occur. In relation to the carbon to sulfur ratio, 57% would be the optimal ratio for the best performing battery. Increased sulfur content resulted in lower charge/discharge efficiency as active sulfur would begin to exist outside the porous structure. In Figure 3a, a suggested electrochemical reaction mechanism is shown. Due to the promising electron conductivity that occurs at the interface between the sulfur and carbon, an irreversible reaction is most likely to occur there. As such, the increase in contact area between the sulfur and carbon could improve the energy density of the electrode. The high electrical conductivity of the carbon is related to highly conjugated nature stemming from the carbonization of PAN at 750°C. The developed meso/microporous structure can diminish the dissolution of sulfur related reaction products into the organic electrolyte, as well as promote the diffusion of lithium ions within the electrolyte, thus increasing the electrochemical characteristics of the cathode. Figure 3b illustrates the structure of the carbon HPC and the mixed composite with sulfur in a melt diffusion technique. There is no significant difference between the initial porous carbon and the 57% sulfur in the carbon sulfur composite, however an increase to 75% corresponds to a
major change in the pore structure of the carbon. This is most likely caused by in situ high sulfur vapor pressure. As a result, the battery demonstrated an initial high capacity of 1155 mAh/g at a current density of 40 mA/g, stabilizing at 750 mAh/g after 84 cycles.

**Figure 3.** (a) Suggested reaction scheme for the electrochemical reaction of the sulfur/HPC composite cathode, (b) SEM of HPC (left), sulfur/HPC composite with 57 wt.% sulfur (middle), and sulfur/HPC composite with 75 wt.% sulfur (right). Reprinted with permission from Ref [51]. Copyright 2009, American Chemical Society.

In addition, Choi et al. provided a new method to synthesize a hierarchical ordered porous carbon/sulfur composite. In the configuration, the majority of the sulfur is encapsulated in the inner meso/micropores surrounded by a microporous carbon shell. Stable cycling was achieved because
of the presence of the outer shell that minimized polysulfide dissolution. The novelty of this concept lies in the preparation of the porous carbon, where spray pyrolysis, used to apply a thin film onto a heated surface to form a specific compound, was used to create the substrate. To synthesize the porous carbon, a mixture of sucrose (carbon source) and sodium carbonate (Na$_2$CO$_3$) (base catalyst) were thermally decomposed, and the gaseous bubbles that were formed served to control the size and rate of formation of porous carbon. The prepared sulfur electrode demonstrated a high initial capacity of 1412 mAh/g and excellent capacity retention after 500 cycles (77%) at 2 A/g current density. Thermal gravimetric analysis (TGA) determined that the sulfur content obtained from the pore volume is 66%, which was calculated from the pore volume of the HPC (0.93 cm$^3$/g) and density of sulfur (2.97 g/cm$^3$). By introducing a sulfur amount equivalent to 50 wt % doping to accommodate for volume expansion, sulfur was infused into the inner pores of the carbon matrix by capillary motion, whereby liquid sulfur diffused through narrow spaces created by the porous carbon.

A pea-pod like porous carbon matrix to create an effective carbon/sulfur cathode composite for the Li-S battery was proposed by Li et al.$^{53}$ The pea-pod like carbon combined the advantages of large pore volume (4.69 cm$^3$/g) and bimodal pore size (2 and 22 nm) structure. Due to the large pore size and volume, sulfur loading can be as high as 84%, which allowed for enhanced electrochemical performance. The mesoporous carbon was prepared by a mixture of resorcinol (carbon precursor) and colloidal silica spheres. The solution was heat treated to 800°C to form the mesoporous carbon following aqueous removal of the silica template. Polypyrrole, a conductive polymer, was added as a final thin film coating to the cathode in order to aid in cycle stability and high rate discharge capacity of the battery. The pea-pod structure increased electrical contact for higher electronic conductivity of active sulfur. However, the unique morphology did not correlate
to a significantly high current capacity (1000 mAh/g) with rapid capacity fading after 50 cycles. This poor performance can be attributed to the inability of the pea-pod structure to mitigate the loss of active sulfur species. To effectively improve the capacitative stability of the cathode conductive polymer coatings, additional functional groups or surface modifications are deemed necessary.

Although the use of singular porous carbon structures have been proven to be an effective sulfur host, the combination of different pore size carbon materials can yield a promising composite cathode. Li et al. developed an ordered meso/microporous core shell carbon (MMSC) with a pore volume of 2.07 cm³/g that allowed for suitable sulfur loading and excellent retention of the active material. A combination of the two types of porous carbon is a supported view, as mesoporous hosts are typically used for sulfur encapsulation. The cycle stability is poor however, because organic electrolytic solvents can still infiltrate the structure. Microporous carbon utilizing a pore size less than 0.5 nm has been proven to minimize the polysulfide shuttle effect due to volume constraint, however loading is limited. Therefore, a combination of both types of porous carbon is necessary to create a novel carbon/sulfur composite. The meso-microporous core-shell carbon-sulfur cathode is able to achieve a stable capacity of 837 mAh/g at 0.5C after 200 cycles with a corresponding capacity retention of 80%, reflecting the minimized capacity loss. To fabricate the effective carbon matrix, SBA-15 (mesoporous silica hard template) and sucrose (carbon precursor) were physically mixed before being carbonized at 900°C for 5 hours in an inert argon atmosphere, followed by silica removal with HF. These steps are outlined in Figure 4a-b. Figure 4d demonstrates the cycle stability of the formed meso/microporous structure as it compares to the individual carbon matrix, while Figure 4e highlights the great charge rate characteristics of the fabricated battery from 0.1-2 C. A sulfur/meso-carbon cathode undergoes a
solid liquid solid mechanism while sulfur/micro-carbon demonstrates a solid/solid reaction mechanism. Employing sulfur/micro carbon as a physical means to retain soluble polysulfides outside the sulfur/meso-carbon allows for complete encapsulation of sulfur within the carbon matrix, improving cycle stability. Such phenomena are appreciated in Figure 4b-c, with the corresponding representative discharge profile and electrochemical reaction at the cathode for a sulfur/meso-microporous electrode.

It should be noted that metal organic frameworks (MOFs), otherwise considered porous coordination polymers, are of particular interest as nanostructured materials for Li-S batteries. Their intrinsic large pore volume and high surface area can serve as a suitable precursor to develop novel carbon structures for the Li-S battery. MOFs can thus be utilized indirectly as a sacrificial template to construct carbon nanostructures or directly carbonize to form highly nanoporous carbon. Carbon structures developed in these respective synthesis steps can then be further functionalized to improve electrochemical performance.
Figure 4. (a) Illustration detailing the preparation of ordered meso-microporous core shell (MMCs) carbon and sulfur/carbon composites. (b) Suggested lithiation process inside the meso/micropores structure and diagram of the cathode structure. (c) Voltage profile of the Li-S battery and related electrochemical reactions of the electrode. (d) Cycle stability of S/MMCS at 0.5 C. (e) Rate Capability at various rates of S/MMCS in 3.0-1.0 V voltage range vs Li⁺/Li. Inset of (e) is the discharge voltage profiles at current densities from 0.1 to 2C. Reprinted with permission from Ref [54]. Copyright 2014, American Chemical Society.

3.1.2 Carbon nanotubes/sulfur composite

Due to the volume changes sulfur undergoes through delithiation-lithiation, it is desired that a suitable matrix to encapsulate sulfur can accommodate the expansion of sulfur related product upon cycling, which is an important characteristic of Li-S batteries. A highly porous form of carbon is therefore necessary. However, simple methods of carbon particle encapsulation of sulfur
have been unable to demonstrate an effective pathway for completely eliminating the polysulfide shuttle effect without some additional functionalization. Chemical bonding to the polysulfides produced or other modifications must be employed. The porous carbon structure can be easily doped with heteroatoms to increase cycle stability, or as previously reported, combined with other forms of porous carbon to reduce the shuttle effect. Compared to traditional highly porous carbon blacks, carbon nanotubes can provide easily controlled functionalization, thereby leading to further improved battery performance.

As a matter of fact, carbon nanotubes in combination with sulfur presents itself as one solution to the development of a stable cathode material.\textsuperscript{55,60} Carbon nanotubes have a variety of distinct qualities as reflected by their current interest. High aspect ratios, increased surface area over porous carbon, and a significantly high surface to volume ratio are some of its major benefits.\textsuperscript{20,61-63} Recently, a cathode from amine functionalized carbon nanotubes was developed by attaching polyethyleneimine (PEI) polymers, which have a large number of amine per molecular unit to every hydroxyl and carboxyl functionalized multiwall carbon nanotube.\textsuperscript{64} The CNT-PEI was prepared by heating a mixture of CNT suspension and PEI solution at 80 °C for 12 hours. The product was subsequently combined with sulfur, and the general fabrication steps are shown in Figure 5. The main purpose of the amine groups is to effectively anchor lithium polysulfides as they are formed. The PEI is covalently bonded to the carbon nanotubes, allowing for a more permanent control of the movement of the polysulfides. At a charging rate of 0.5C the optimal carbon/sulfur composite, CPS-70 (sulfur content wt%), demonstrated an initial capacity of close to 1000 mAh/g with minimal capacity fade after 100 cycles. In batteries that use CNT-PEI composites, PEI is clearly seen as a strong inhibitor to lithium polysulfide (LiPS). Dissolution through binding to form polysulfides are reflected by an increase in cathode conductivity. These features, combined with
other positive features of CNT’s such as excellent conductivity, good mechanical properties and great physical trapping of LiPS, all give promise to the continued development of this type of Li-S battery. Even after exposure to charging rates as high as 2C, the cathode was still able to retain its original electrochemical performance at 0.5C.

Figure 5. (a) Schematic process for creating amine functionalized carbon nanotubes (b) Extended cycle stability of Li-S cells with CPS-70 cycled a 0.5C (838 mA/g), 1C (1675 mA/g), and 2C (3350 mA/g). Reprinted with permission from Ref [64]. Copyright 2015, American Chemical Society.
Mi et al. proposed the idea of hierarchical microporous-mesoporous carbonaceous nanotubes (HMMCNT), which features a thick microporous wall and an inner hollow channel. The unique structure of the carbon based support served two functions: (1) the available micropores formed a thick outer layer carbon matrix, increasing conductivity of the composite cathode and allowing for better confinement of sulfur molecules and any formed polysulfides, and (2) the inner hollow cavity could allow for more sulfur deposition, accommodate volume changes and provide pathways for lithium ion diffusion upon prolonged cycling. The carbon nanotubes were synthesized by heating a tellurium/carbon nano-cable in an inert atmosphere, acting as the sulfur host matrix. The tellurium (Te/C) nano-cables were synthesized by a modified hydrothermal treatment method where two separate solutions containing the carbon and metal precursors were mixed. The resultant solution was dried before being calcined at 900°C for 3 hours in an argon atmosphere to generate carbon nanotubes. The carbon was mixed with sulfur in a subsequent hydrothermal step to allow for proper sulfur diffusion into the pores of the prepared carbon nanotubes. They report on the abundance of micro-pores found in the thicker outer layer of the carbon matrix, reflected in the increased conductivity of the composite cathode, through high contact areas between the conductive carbon material and the sulfur. Inner hollow surfaces created by the researchers could store more sulfur to increase capacity, as well as account for volume changes between charge and discharge cycles. Therefore, excellent rate capability and reversible capacity of 800 mAh/g were realized.

Sulfur encapsulated carbon nanotubes for the Li-S battery was also recently proposed to address issues relating to the polysulfide detainment at the cathode, sulfur-electrolyte contact, and required space for sulfur expansion. A vertically aligned hollow carbon nanotube structure with melted sulfur was prepared by utilizing anodic aluminum oxide membranes as templates for the design of
the carbon nanotubes through a process known as the polystyrene carbonization. In the process outlined above, the anodic aluminum oxide (AAO) served as both a template for the nanotube formation and barrier to prevent sulfur from coating the exterior wall of the nanotube. As a result, sulfur is effectively contained in the high aspect ratio carbon nanotubes, and its contact with electrolyte is minimized. The hollow space provides for sufficient sulfur expansion and contraction during repeated cycling. The characteristics of the hollow carbon nanotube structure is important for guaranteeing high specific capacity and stable cycle life of the sulfur cathode in the Li-S battery. A stable discharging capacity of 800 mAh/g was maintained after 160 cycles at 0.2C.

The use of carbon nanotubes to restrain sulfur inside the cathode have primarily involved heating a physical mixture of carbon matrix and sulfur to 155°C for an extended time. At that temperature, liquid sulfur is at its lowest viscosity and can therefore easily diffuse into the carbon, providing a cathode structure with evenly dispersed sulfur particles. A potential issue that arises from such an experimental procedure is that liquid electrolyte can still access the sites where sulfur diffused into. A new technique, briefly mentioned in the discussion involving porous carbon, suggests that increasing temperature, when infusing sulfur into carbon, results in improved battery electrochemical performance. In the effort of mitigating the electrolyte accessibility to active sulfur in a carbon host, Guo et al.\textsuperscript{67} developed a high temperature synthesis procedure. The in situ physical mixture of carbon and sulfur was heated to 500°C, which is high enough to vaporize sulfur and infuse it into carbon voids and even into graphitic layers where possible. It is known that sulfur vapor at 200°C is primarily composed of S\textsubscript{8} molecules. At higher temperature, the main constituents of sulfur vapor become S\textsubscript{6} and S\textsubscript{2} which are smaller, more reactive molecules. These can infuse deeper into the micro-pores of the carbon. The resulting composite cathode formed from
precursors heated to 500°C showcased improved cycle stability (750 mAh/g after 100 cycles) than samples heated to only 300°C and 160 °C, respectively.

Overall, carbon nanotubes represent one avenue to the development of the cathode for the Li-S battery. They are relatively easy to synthesize, and can modifying with functional groups, which make them very appealing for application. However, in placing sulfur into the carbon nanotubes, there still faces challenges due to the lack of efficiency. High thermal energy or time intensive treatment steps add to the complexity of synthesis. Carbon nanotubes dependent on the pore size or diameter play a vital role in determining the maximum amount of sulfur atoms that can be placed within the tubes.

3.1.3. Carbon nano-shell/sulfur composite.

Similar to the carbon nanotube sulfur composite mentioned beforehand, the shell/sulfur composite has allowed scientists to generate a new structure that might potentially offer increased battery performance.\textsuperscript{33,68,69} The main idea behind the use of the shell is to coat or wrap the sulfur particle in an electrically conductive material in the overall cathode structure. Sun \textit{et al.}\textsuperscript{70} developed a hollow core shell carbon structure that resulted in a battery with excellent electrochemical properties. The approach stemmed from the conclusion that hollow carbon spheres with significant interior void space are likely to retain high amounts of active sulfur and polysulfides, minimizing the loss of capacity. However, due to low adsorption potential of the interior of the porous shell, an added carbon micropore into the shell structure was devised to immobilize sulfur and it’s cycling products. The carbon matrix was prepared through a number of solution stage and pyrolysis steps as seen in Figure 6a that converted polymer spheres into a carbon core shell
structure. This cathode structure was able to allow for long-term charge/discharge cycles with minimal capacity loss (900 mAh/g after 200 cycles) as shown in Figure 6b and 6c.

Figure 6. (a) Illustration of the preparation of the hollow core-shell interlinked carbon spheres (b) Cycling performance of carbon/sulfur composite at current density of 0.5 and 4.0 C (c) Rate capability of carbon/sulfur composite. Reprinted with permission from Ref [70]. Copyright 2015, American Chemical Society.
Nano-shells or spheres, being primarily of carbon origin, are also considered a viable option for the synthesis of stable cathode material for the Li-S battery. They are easily modified and demonstrate good life cycle capacity. Drawbacks derive from a potential obstacle where lithium ion diffusion into the cathode could be minimized by the presence of the carbon layer, which results in lower energy storage, as capacities above 1000 mAh/g for over 100 cycle are difficult to obtain. Further research is being conducted to determine whether nano-shell/nano-spheres can be improved in regards to capacity and cycle stability.\textsuperscript{71,72} Rehman \textit{et al.}\textsuperscript{73} proposed silicon/silicon dioxide hierarchal porous carbon spheres as an efficient polysulfide retainer. It was theorized that there was a need for an advanced sulfur cathode, with a combined structure of conductive carbon and metal oxide that can support a high amount of sulfur and possess strong adsorption potential to contain polysulfides into the cathode structure via chemical and physical binding. Slightly different from mainstream porous carbon structures, this cathode material has an increased surface area that promotes polysulfide absorption, but also through excellent electrostatic interactions between the negatively charged polysulfide anion and positively charged Si/SiO\textsubscript{2}. The increased surface area with a defined pore size distribution, allows for easier Li\textsuperscript{+} insertion/extraction, reflected in the high rate capability. To synthesize the material initial solid cross link materials were made using polyhedral; octaphenyl, oligomeric silsequioxane (Ph-POSS) as both carbon and Si/SiO\textsubscript{2} precursor. High temperature annealing at 900\textdegree C for 3 hours in N\textsubscript{2} produced Si/SiO\textsubscript{2}C, which lead to the Si/SO\textsubscript{3}C-S following a melt diffusion technique to impregnate sulfur into the silicon/carbon material. 600 mAh/g after 500 cycles demonstrated the effective sulfur stabilization within the carbon matrix.
Xu et al.\textsuperscript{74} provided yet another example of the benefit of utilizing carbon spheres for enhanced Li-S battery performance. They created mesoporous carbon-sulfur composite microspheres by a technique known as evaporation induced self-assembly process (EISA), where the solvent evaporation allows for the development of pores within the carbon structure. The formed microspores were then incorporated within carbon spheres and a capacity stabilized around 750 mAh/g was realized. Furthermore, to investigate pathways for increasing sulfur content in the cathode material, additional carbon source derived from sucrose was introduced via an annealing treatment at 1000°C. The prepared carbon spheres were mixed with a certain amount of sulfur. The sulfur was consequently pushed into the porous structure of the carbon by the general melt-diffusion technique at 149 °C for 6 hours. The temperature was then increased to 300 °C for 2 hours to vaporize extra sulfur on the outer surface of the carbon spheres. Carbon spheres, similar to carbon shells previously reported, are effective as physical restraints for the sulfur atoms. However, like the shells and porous carbon, they do not form well when dispersed contact between the carbon and the sulfur occurs. As a result, decreased coulombic efficiency and current capacity is still apparent in many of the cathode composites studied.

3.1.4 Graphene /sulfur composite

Amongst the variety of carbon structures combined with sulfur, one of the more interesting composite structures is related to the use of graphene.\textsuperscript{75-79} Graphene, which exists as a sheet like molecule, is composed of carbon in a hexagonal structure. It can be combined with sulfur to make sandwich or sponge like structures that display good electrochemical performance. Gu et al.\textsuperscript{73} also highlighted the excellent properties of graphene, where they developed a graphene-based sulfur composite cathode for energy storage in Li-S batteries. Ahn et al.\textsuperscript{80} recently reported the use of a
three dimensional graphene sponge to serve as a film coating for sulfur (Figure 7a). Their interest lied with the notion that graphene based sulfur/carbon composites prepared by different chemical reaction routes have shown high rate ability. They created a novel film consisting of an assembly of tiny sulfur nano-granules coated on a three-dimensional graphene sponge, where the overall morphology is a consistent sulfur film place over the surface of graphene sheets (Figure 7b). They believed that the composite material allowed for a more intimate contact between the sulfur film and underlying graphene layer, which was reflected in an increased electro-conductivity of sulfur. They also believed that aligned 3D structure minimized the dissolution of sulfur. As shown in Figure 7c, a stable capacity of ~900 mAh/g was achieved at a current rate of 1C after 500 cycles indicative of effective sulfur stabilization.
Figure 7. (a) General synthesis procedure for formation of 3D–rGO. (b) Illustration of the various stages incorporated to generate the composite structure. (c) Cycle stability and corresponding coulombic efficiency tested at 0.1C rate. Reprinted with permission from Ref [80]. Copyright 2016, American Chemical Society.
A graphene oxide/sulfur nanocomposite cathode was developed via an environmentally friendly chemical reaction–deposition strategy to immobilize sulfur on quasi two dimensional graphene oxide in an ionic liquid based electrolyte. They deposited nano-sulfur on graphene sheets by chemical reaction in a micro emulsion system, followed by heating the samples in an argon environment at a 155°C for 12 hours. This was in order to remove bulk sulfur not immediately attached to GO layers, as well as to assist diffusion of the sulfur into pores of the GO. The low temperature heat treatment also serves the added benefit of improving the electronic conductivity of the in situ prepared GO-S nanocomposites. Graphene oxide was clearly demonstrated to perform very well as a means to stabilize the cathode electrode. It provides highly reactive functional groups on the surface of the graphene oxide that can serve as strong footholds for sulfur. Also, by limiting the concentration of polysulfide anions formed, the redox shuttle is mostly avoided. The distinctive structure of the GO-S composite is seen in its physical and chemical properties. It has enough free void space to allow for volume changes that occur during cycling. The large surface area of the partially reduced graphene oxide can provide more electrical contact with sulfur and the current collector. The synthesis of the reduced graphene oxide generates a plethora of surface bound functional groups, which have the binding power to retain sulfur atoms effectively and diminish formed lithium polysulfides from dissolving into the electrolyte. Due to the strong interaction between the formed graphene oxide and sulfur, a high initial capacity of 950-1400 mAh/g at 0.1 C after 50 cycles is obtained.

3D graphene foam reduced graphene oxide (rGO) hybrid nested hierarchal networks was applied to the Li-S battery. It was reported that a 3D hybrid graphene hierarchical network macrostructure utilizing a chemical vapor deposition, highly conductive graphene foam combined with rGO aerogel, as a current collector to solve what they termed as the “double low” issue of
inherent low sulfur content (< 70 wt.%) and low sulfur loading (< 2 mg/cm²) found in conventional sulfur electrodes. The pores generated in structure serve as an electrolyte reservoir, facilitating electrolyte ion diffusion to the sulfur and improved absorption ability of the cathode toward soluble polysulfide ions. Even with significantly high sulfur loading (9.8 mg/cm²) and sulfur content (83%), a specific capacity of 10.3 mAh/cm² was generated. Lin et al.\textsuperscript{78} proposed an effective technique for graphene/sulfur composites by utilizing a scotch tape like exfoliation method to generate a cathode material. The idealized structure of graphene/sulfur cathodes involves the uniform dispersion of sulfur molecules onto a graphene sheet. According to the structure of sulfur (S\textsubscript{8}) molecules, the lone pairs that exist on S 3pz, 2 electrons interact with antibonding conjugated orbitals of graphene. The increased electron density of the formed polysulfides have a stronger attraction to graphene than sulfur. The novel structure exhibits key advantages, such as polysulfide confinement ability, ample space to accommodate volume expansion, and short transport pathway for electrons and Li\textsuperscript{+}. The developed cathode composite contained 73 wt % sulfur, demonstrating notable cyclic stability (615 mAh/g for 100 cycles) and coulombic efficiency of 96%. At 2C, the capacity was 570 mAh/g after 10 cycles. Song et al.\textsuperscript{83} studied an advanced sulfur cathode enabled by highly crumpled nitrogen-doped graphene sheets for high energy density Li-S batteries. They adopted nano-porous structures to hold sulfur and maintain proximate contact between the electro-conductive carbon matrix and sulfur. Through several annealing steps they were able to form a crumpled nitrogen doped graphene sheet. A high initial capacity of 1000 mAh/g and excellent cycle stability after 300 cycles was found with 80% and 90% sulfur loading respectively. Figure 8 highlights the cycle rate stability of the sample after increasing the discharging rate to 1C; returning back to 0.1C, the fabricated battery was able to realize its original capacity.
Figure 8. (a) Synthesis Procedure of highly crumpled nitrogen doped graphene. (b) Microscopy images and EELS mapping of the highly crumpled NG sheets. (c) Cycling stability and coulombic efficiency of NG-based cells with NG-S80 and NG-S90 cathodes at a current density of 0.39 mA/cm^2 for the first cycles and 1.17 mA/cm^2 for subsequent cycles. Sulfur loading is 1.5 mg-sulfur/cm^2. (d) Cycling stability and coulombic efficiency of the NG based cells with NG-S80 cathodes with sulfur loading of 5 mg-sulfur/cm^2 at current density of 0.45 mA/cm^2 for the first few cycles and 1.3 mA/cm^2 for subsequent cycles. (e) Rate capability of NG based cells with NG-S80 cathode at different sulfur loading. Reprinted with permission from Ref [83]. Copyright 2016, American Chemical Society.

Graphene can be combined with other forms of carbon to fabricate carbon-sulfur composite cathode. Ding et al. 80 utilized a similar approach to develop a hybrid carbon nanotube/graphene
architecture for the Li-S battery. They considered the utilization of both materials as a stepping stone for enhanced electrochemical performance. They reported that 3D hybrid structures created from CNTs and graphene show synergistic effects and improved properties as it’s related to energy storage. Because they utilize graphene, the chemical properties of that form of carbon allow for heteroatom doping, specifically nitrogen. Nitrogen is often sourced for doping in graphene structures because of its small atomic radius and high electronegativity. With the use of nickel foam, glucose, and dicyandiamide, they are able to use a solid growth technique to create the nitrogen doped 3-D CNT/graphene hybrid structures. In detail, the 3-D framework is synthesized by a solid state pyrolysis of a mixture of glucose, dicyandiamide and nickel foam at 800 °C in an inert argon atmosphere, followed by nickel foam removal with HCl leaving the resulting 3-D NCNT/NG substrate. Dicyandiamide (DCDA) serves a multifunctional role in providing a nitrogen source, layered graphitic carbon nitride for graphene deposition, and ammonia (NH₃) etchant for the production of nickel nanoparticles. The formed layered graphitic carbon nitride first binds to the surface of the nickel foam, while binding to aromatic carbon intermediates produced by glucose pyrolysis. This ultimately produces graphene layers, the carbon nitride intermediate decomposing at ~750°C. CNTs are formed in tandem with the formation of graphene layers, reflecting the catalytic effect of nickel nanoparticles derived from nickel foam etching that originated from DCDA pyrolysis. Sulfur was subsequently infused into the carbon host by the melt diffusion technique, where a sample of mass ratio of 1:4 (carbon: sulfur) was physically mixed before being heated to 155°C for 20 hours in an argon atmosphere. The porous, unique 3-D structure of the obtained carbon composite allows for excellent electron transport and Li⁺ diffusion into the cathode. According to the authors, the composite architecture allowed for reversible
capacities of 1314 and 922 mAh/g at 0.2 and 1C, respectively, with a capacity retention of 97% after 200 cycles at 2C rate.

Graphene, a sheet like carbon structure, is best combined with sulfur in a sandwich type effect, where sulfur is encased between layers of graphene.\textsuperscript{18,77,84-88} That effect alone seems to generate a long cycle life as the capacity fade is minimized. SEM and TEM images also highlight good sulfur encapsulation by graphene, which is potentially derived from the good contact surface interaction between graphene and sulfur. In addition, graphene can be heteroatom doped or functionalized with oxygen groups (carbonyl, carboxyl \textit{etc.}) to allow for chemical bonding with polysulfides.

\textbf{3.1.5 Heteroatom doped carbon for improved cathode performance}

The cathode of the Li-S battery is primarily made of sulfur, and its derivatives are intermixed with a highly conductive substrate such as carbon. The role of carbon is already known, however, it is just as popular in its use of heteroatoms, primarily nitrogen. The interactions between polysulfides created through charging and discharging and the present nitrogen aids in retaining long chain polysulfides at the cathode.\textsuperscript{89-92} Here, we discuss a number of advances made to the Li-S battery, where heteroatom doping played a major role in improving the electrochemical performance of the cell. The creation of new functional groups with the ability to chemically adhere sulfur or lithium sulfide is highly promising as well. Song \textit{et al.}\textsuperscript{93} utilized nitrogen doping in the promotion of chemical adsorption and synthesis of a high capacity sulfur cathode with exceptional cycling stability for the Li-S battery. A nitrogen doped mesoporous carbon was synthesized to effectively create chemical adsorption of the sulfur molecule onto high surface area carbon framework. The mesoporous carbon contained oxygen functional groups in which nitrogen can facilitate the sulfur – oxygen containing functional group bond by lowering the enthalpy of formation. Typically, the mesoporous nitrogen doped carbon is fabricated by using poly (melamine-co-formaldehyde) resin
as the carbon source intermixed with triblock copolymer Pluronic F127, TEOS, and colloidal silica particles as porogens. After a series of processing steps, the product is heat treated in 900°C for 2 hours, followed by an acid leaching in hydrofluoric acid, to form the 3-D mesoporous nanocarbon structure. In detail, the authors explored the mechanism by which nitrogen served to support oxygen containing functional groups binding with sulfur atoms through density functional theory (DFT) calculations.\textsuperscript{93} Enthalpy changes of sulfur between different carbon substrates were determined as the difference between adsorbed state and the individual substrate, as well as sulfur atom adsorbate. Negative values of $\Delta H$ infer a favorable reaction step. The $\Delta H$ of the carboxyl group of pyridinic N-doped carbon was seen to be $\sim$56.88 kCal/mol, the lowest among all three carboxyl groups of both the N-doped and un-doped carbons. The $\Delta H$ of the carbonyl group of pyrrolic N doped carbon was seen to have the overall lowest enthalpy (117 kcal/mol). These results indicate that the lowest $\Delta H$ of sulfur adsorption on the oxygen functional of the N-doped carbon substrates demonstrates enhanced stabilization of sulfur on their surface. The results also point to the effectiveness of nitrogen in N-doped carbon to accommodate sulfur bonding with oxygen rich functional groups.

Achieving a high capacity and a long-term stability with high content sulfur is one of the challenges for current Li-S batteries. Using lightweight 3D nitrogen/sulfur co-doped graphene sponge, Manthiram \textit{et al.}\textsuperscript{94} developed an idea to increase sulfur loading in cathodes (up to 4.6 mg/cm$^2$). The doping by nitrogen allows for quick electron transfer and increases attraction between the polysulfide species and the carbon based framework. It works to immobilize polysulfide ions and promote lithium sulfide/polysulfide/sulfur reversible conversion to enhance the electrochemical performance of Li-S batteries. To obtain the nitrogen – sulfur co-doped graphene sponge, 50 mL of GO aqueous dispersion and 0.01 M of thiourea were mixed. The
mixture stirred for 30 min and then sealed in 100 mL Teflon lined stainless steel autoclave for hydrothermal reaction at 180 °C for 12 hours seen in Figure 9 a-c. Excellent rate performance and a stable capacity of 800 mAh/g were obtained, even after 200 cycles shown in Figure 9d-f.

Figure 9. (a) Photograph of rGO/S-doped graphene, N-doped graphene and N, S-co-doped graphene sponges after hydrothermal reaction and freeze drying. (b) Lightweight N, S co-doped graphene sponge standing on dandelion. (c) Diagram of the formation process of N, S co-doped
graphene electrode and schematic of fabrications of typical Li/polysulfide cell with N, S-co-doped graphene electrode after adding polysulfide catholyte. (d) Galvanostatic charge/discharge profiles of N, S co-doped graphene electrode with graphene coated separator at various rates with potential window 1.5-2.8 V. (e) Rate Characteristics of the N, S-co-doped graphene electrode at different current densities. (f) Cycling stability and coulombic efficient of the lithium polysulfide batteries with N, S co-doped graphene electrodes and graphene coated separator at 0.5C rate for 200 cycles. Reprinted with permission from Ref [94]. Copyright 2015, Nature Publish Group.

Heteroatom doping, in particular nitrogen doping into surface-functionalized carbon, can aid in the formation of carbon functional group - sulfur bonds that limit the polysulfide shuttle effect. Nitrogen, with high electronegativity, attracts electrons around it, making nearby carbon electropositive. This enables carbons to be susceptible to bond formation. Heteroatom doping is generally considered a supporting technique in combination with carbon or some other electrically conductive host material in the development of high performance cathodes for the Li-S battery. Pore structure and overall carbon morphology play a pivotal role in determining electrochemical performance of the Li-S battery. Introductory porous carbon containing high surface area and pore volume can easily hold sulfur, although significant degradation occurs after extended cycling. Carbon nanotubes (CNT) have also been looked at as a viable candidate for a Li-S cathode. Unless the surface is functionalized or combined in a carbon hierarchical structure CNT show little improvement to high energy density batteries. Graphene sheets have been explored because of the unique “sandwich” like structure that can be employed to retain sulfur and its active species. Even though many carbon based hosts show similar material properties, differences in electrochemical
performance can arise from the amount of sulfur species actually present in the carbon host during experimentation, which can be derived from different sulfur carbon intermixing strategies.

As highlighted in the manuscript, there are a variety of cathode designs that have shown remarkable electrochemical performance. Among carbon based cathode composite structures, high surface area and pore volume generate the highest energy density as sulfur deposition is relatively easy. This is if the model is following the melt diffusion strategy, whereby liquidized sulfur is allowed to infiltrate the void spaces of the carbon host. The research direction among carbon based supports needs to follow this trend of high pore volume and high surface area. Functionalization of the carbon support also has been demonstrated to further improve the electrochemical storage capacity of the battery. Amongst non-carbon based structures, minimization of active sulfur loss by chemisorption, or by altering the formation of lithium polysulfides so as to minimize their presence in the electrolyte, is of growing interest. In the future a mixed metallic and carbon based supports for the Li-S battery are very promising as they are more electrochemically stable than their carbon counterparts and can combine physical and chemical means to minimize active sulfur species loss.

3.2. Non-Carbon Approach for Stabilization

The shift away from a carbon matrix to encapsulate sulfur molecules at the cathode has been explored because of the inability of a suitable carbon matrix to retain sulfur and its related products at the cathode during cycling. New insights stem from the use of transitional metal oxides, sulfides, organic polymers and other approaches to minimize or eliminate the use of a carbon source to fabricate a next generation Li-S battery. Non carbon based material are unique because of the vast variety of structures that exist. Polymers and metallic nanostructure have different properties other
than physical detainment of active sulfur species, such as chemisorption properties or volume expansion properties, which allow them to generate high performance lithium sulfur batteries.

3.2.1 Polymer coating/sulfur composite

Despite the variety of carbon sulfur composites and their inherent derivatives, polymer combinations with sulfur have been increasingly sought out for their use in the development of next generation Li-S batteries. Polymers, specifically those that allow for ionic diffusion, can act as physical barriers to the loss of sulfur reaction products during discharge, therefore reducing capacity loss. A number of approaches have been explored to synthesize a stable polymer for Li-S battery cathode. Kim et al. demonstrated the use of a layer by layer polymer deposition technique to develop a high capacity Li-S battery. They reported a technique of depositing thin films based on a single poly-(allylamine hydrochloride)/poly-(acrylic acid) PAH/PAA priming bi-layer with over coated bilayers of (polyethylene oxide) (PEO/PAA(A)) directly applied to S₈ cathodes for Li-S batteries as seen in Figure 10a. The author previously reports the benefit of PAH and PAA coated onto separators in batteries as minimizing the polysulfide diffusion rate. To fabricate such cathodes and enable stable layer by layer (LbL) thin films, primer adhesion layers were essential. A PAA/PAH initial layer was formed by a spin coating of an aqueous solution containing PAH (pH 7.5) and pAA (pH 3.5) in the presence of lithium bis(trifluoromethanesulfonyl)-imide salt (LiTFSI). Following the deposition of the priming bilayer (PAH/PAA), (PEO/PAA)ₙ multilayers were sequentially deposited onto primed S₈ cathodes by successive dipping depositions from PEO/PAA solutions. Each solution was prepared by adding LiTFSI (0.1 M) and adjusting the solution pH to allow for hydrogen bonding between ether oxygen of PEO and proton rich carboxylic acids of PAA. It was determined that a sequentially adsorbed PAH/PAA bilayer on the S₈ cathode effectively served as a priming layer for further LbL deposition of (PEO/PAA(A)
multilayers. The PEO/PAA pairing was selected for LbL deposition to encourage high ionic conductivity. A specific capacity of 806 mAh/g after 100 cycles for a 3 bilayer composite was obtained, and superb rate performance was also demonstrated as seen in Figure 10 b-c.

**Figure 10.** (a) Diagram illustrating the layer by layer (LbL) deposition of single (PAH/PAA) priming bilayer and (PEO/PAA) \( n \) multilayers on \( S_8 \) cathodes. (b) Cycle Stability and Coulombic efficiency of \( S_8 \) cathode and (PAH/PAA)/(PEO/PAA)\( n \) multilayer coated \( S_8 \) cathodes \( (n = 1, 3, \text{ and } 5) \) at 0.5C without LiNO\(_3\) salts in the electrolytes. (c) Cyclic rate stability of \( S_8 \) cathode and PAH/PAA(PEO/PA(A))\( n \) \( (n = 1, 3, \text{ and } 5) \) multilayer – coated \( S_8 \) cathodes with different C-rates from 0.1 to 2.0 C, with 10 cycles for each respective rate. Reprinted with permission from Ref [97]. Copyright 2016, American Chemical Society.
Alternative to design composite sulfur cathode, utilization of polymer solid-state electrolyte was suited as an effective method to mitigate the sulfur loss from cathodes.\textsuperscript{98} Instead of conventional Celgard membranes as the separator, a Nafion\textsuperscript{®} ionic conductive membrane was employed. This acts as a cation selective electrolyte for Li-S batteries to suppress polysulfide diffusion. Although utilized in this research, the idea of a cation exchange polymer is not a novel concept. Cation exchange polymer membranes are applied in variety of industry processes. Polymer chemistry, to develop either a stable coating for the cathode electrode or as a building block for the cathode itself, are an effective solution to preserving the electrochemical activity of sulfur while limiting the polysulfide shuttle reaction. Such synthesis led to promising electrochemical performance (500 mAh/g for 500 cycles). Polymer chemistry discussed thus far has played a secondary role in acting as a thin film coating to a carbon/sulfur composite. However, sulfur itself can undergo an “inverse vulcanization” reaction where it forms a stable polymer that can be directly used as a cathode. Vulcanization refers to the cross-linkage of polydiienes with a small amount of sulfur to form rubber. Inverse vulcanization stabilizes polymeric sulfur from depolymerization by co-polymerizing large amounts of sulfur with relatively small dienes. By process of co-polymerization, the transformation of elemental sulfur into a stable polymer with high sulfur loading can be realized. Chung \textit{et al.} utilized the inverse vulcanization technique for the direct reaction of 1,3-diisopropenylbenzene (DIB), a divinylic monomer, with liquid sulfur at 185 °C.\textsuperscript{99} This enables the sulfur molecules (S\textsubscript{8}), which exist as octatomic rings, to break and form linear chains that enable free radical co-polymerization with DIB. Co-polymerization was conducted in liquid sulfur at 185 °C to allow for an adequate concentration of sulfur radicals from the ring opening phase and sufficient reaction with DIB. Originally developed for a different purpose, the fabricated sulfur rich polymer was seen to have great cycle life, maintaining 800
mAh/g even after 100 cycles. Understood for quite some time is the fact that at room temperature, sulfur exists as an eight membered ring ($S_8$) that is converted into a “yellowish” liquid phase above 120-124°C. Further heat treatment unravels the sulfur rings into linear polysulfanes that can be processed further to stable semi-crystalline polymeric sulfur, suitable for battery testing.

Meanwhile, a unique pathway in creating such sulfur rich polymers was explored by using trithiocyanuric acid (TTCA) crystals as a precursor. TTCA was subjected to solvent purification steps before being physically mixed with sulfur and thermally annealed at 160-245 °C to stimulate the ring opening phase of sulfur. Linear polysulfanes formed from the ROP could easily bond to the thiol functional groups on the TTCA, generating a stable polymer structure. Excellent electrochemical characteristics are obtained from the fabricated Li-S cell, with a high initial capacity of 945 mAh/g after 100 cycles at 0.2C. Interestingly, the crystals are thought to increase the lithium ion transfer rate within cathode structures, allowing for excellent rate performance at 0.1C (1210 mAh/g) and 5C (730 mAh/g).

Polymers are able to form a thin coating on the surface of the cathode, and depending on their modification, can effectively retain active sulfur at the cathode. Polymer chain structure and functionalization on their surface can allow for physical or chemical trapping of formed polysulfides while maintaining good physical contact, much like carbon alternatives. However, there remains concern over the ionic conductivity of the thin film and how it affects overall energy density. Its use for viable cathode structures is contingent upon further research.

3.2.2 Metal sulfide/carbon-composite structure

Scientists have utilized pure sulfur combined with a variety of substrates to propose next generation battery types. The role of sulfur and its inherent problems have been tackled from a
myriad of angles. One avenue being recently explored is the use of lithium sulfide.\textsuperscript{101-103} By replacing sulfur with lithium sulfide, destructive volume expansion known to occur at the cathode is reduced as lithium sulfide is already at the maximum volume obtainable relative to sulfur. Hence, the vacant space present in the structure is ample for volume changes due to cycling.\textsuperscript{104-109} However, lithium sulfide still suffers from low electron conductivity as well as the “shuttle effect”. Lithium sulfide cathodes are already pre-lithiated; they can therefore be combined with non-lithium metal anodes for battery fabrication. Use of Li$_2$S for a stable Li-S battery has recently been successfully demonstrated.\textsuperscript{102,110} In the battery, the use of Li$_2$S/graphene nanospheres with carbon coating could withstand a high charge and discharge rate along with a long cycling stability. The Li$_2$S composite cathode were prepared by dissolving sulfur powder into toluene, followed by the addition of single layered graphene oxide well mixed in tetrahydrofuran (THF) to prepare the composite solution. Lithium precursor was added in the form of lithium triethylborohydride while heating and stirring to form stable Li$_2$S spheres. The formed Li$_2$S/GO cathode exhibited a high discharge capacity of 650 mAh/g (942 mAh/g-sulfur) with a low capacity decay rate of 0.046% per cycle. The added carbon coating minimizes polysulfide loss, and graphene oxide acts as another polysulfide inhibitor. Similarly, metal sulfides can be used for increasing electrochemical performance by acting as a catalyst to quickly convert high order long chain polysulfides into smaller chains, therefore reducing the propensity for long chain polysulfides to enter the electrolyte. Yuan \textit{et al.}\textsuperscript{18} proposed increasing Li-S battery performance by modifying the polysulfide reactions that occur at the cathode. The interfacial area that exits between cobalt sulfide (CoS$_2$) and the liquid electrolyte are strong absorption and activation sites for polar polysulfides. The amount of polysulfides in a cell is not only governed by diffusion, but also to the conversion of polysulfide and corresponding accumulation in the electrolyte. The high polarity of polysulfide
reduces their interaction with retainers in such carbon structures. An example of a flood is used to explain the concept. Instead of placing blocks to hinder the deluge, one widens and deepens the existing channels. The same can be said for the role of CoS$_2$ where instead of blocking the movement of polysulfide, it accelerated the conversion of sulfur to lithium sulfide through an accelerated redox process. CoS$_2$ is synthesized through hydrothermal treatment. The CoS$_2$ was further processed by a physical mix with graphene to form a CoS$_2$/graphene composite. **Figure 11** highlights the reaction mechanism undergone at the cathode interface upon cycling the battery. With a 15% concentration of CoS$_2$ in the composite, a stable capacity of 500 mAh/g was achieved after 2000 cycles at 0.2C, indicating the excellent functionality of CoS$_2$. 
Figure 11. Illustration of the discharge process in sulfur composite cathodes. (a) Carbon sulfur cathode reaction and (b) CoS$_2$ – mixed carbon/sulfur cathode where polysulfide shuttle reduction is accelerated. (c) Cycling performance (d) Galvanostatic charge-discharge profiles during 1$^{st}$ cycle. (e) Energy and Coulombic efficiency of graphene, CoS$_2$ (15%) + G, and CoS$_2$ (30%) + G based sulfur cathode at current density of 0.5C. (f) Cycling performance of CoS$_2$ (15%) + G-based
sulfur cathode at a current density of 2.0C for 2000 cycles, followed by 10 cycles at 0.2C. Reprinted with permission from Ref [18]. Copyright 2015, American Chemical Society.

A similar idea was used to design the Li$_2$S composite cathode, in which carbon coated Li$_2$S particles were dispersed onto a graphene support. To improve the performance of the lithium sulfide cathode, a layer of conductive carbon was added to the surface of the micron sized lithium sulfide particles. Lithium sulfide, in combination with dried graphene powder, formed the initial composite structure, followed by further chemical vapor deposition of a carbon shell layer. It’s the combined effect of a protective surface layer that was vapor deposited on the materials and in situ formed a protective layer that lead to an initial capacity of 1040 mAh/g at 0.5C for 700 cycles. These showed very promising results for the continued development of such batteries. Metal catalysts that can form bonds with polysulfide or quickly convert sulfur into lower order polysulfides achieve the same purpose of reducing loss of active sulfur to the electrolyte. They are however additives to the cathode material, which do not directly participate in lithium ion storage, adding mass to the cathode and hence lowering battery efficiency. Replacing lithium at the anode with a lithium sulfide cathode electrode avoids inherent safety issues. Because of lithium sulfides compatibility with other material, such as silicon and carbon based materials, high energy density batteries can be fabricated. Lithium sulfide is also the fully expanded form of sulfur; cathode composites fabricated with lithium sulfides do not undergo the same volume stress that typical Li-S batteries do. However, techniques to utilize lithium sulfide are met with challenges similar to the challenges of the Li-S battery, such as dismal cycle stability and severe capacity degradation.
3.2.3 Metal oxide-sulfur composite

Up to this point we have regarded the discussion of significant improvements to the Li-S battery primarily around the use of carbon supports to aid in the stability and electron conductivity of the cathode.\textsuperscript{111-115} Certain metal oxides can be utilized in situ with a carbon support to generate a high performance Li-S battery as the oxides can facilitate chemisorption of the formed lithium polysulfides. In the other unique case of completely using a metal oxide support, unique hosts such as TiO\textsubscript{2} are of note because they possess a high electron conductivity. Using metal oxide in Li-S batteries strongly depends on its chemical and physical properties. Metal oxide doping as an additive to the sulfur cathode has picked up recent interest because these specific materials can retain polysulfides at the cathode through chemical bonding, hence affording good cycle stability.\textsuperscript{116-120} Zhang \textit{et al.}\textsuperscript{121} reported the use of double shelled nano-cages utilizing cobalt hydroxide and layered double hydroxides as the outer shells. Layered double hydroxides (LDHs) represent a family of anionic 2D structure clays, commonly used for catalysis as catalysis precursors. Their chemical formula generalized as $[\text{M}^{2+}_{-1-x}\text{M}^{3+}_x\text{O(H)}_2]\text{A}^{x/-}\text{mH}_2\text{O}$. $\text{M}^{2+}$ represents a divalent cation, $\text{M}^{3+}$ a trivalent cation and $\text{A}^{x/-}$ a charge equilibrating interlayer anion. From the presence of an array of hydrophilic and hydroxyl groups, LDH could serve as a great polysulfide mediator by retaining sulfur at the cathode. The double shell structure of CH/LDH highlights two main advantages. The outer LDH and inner Co(O(H))\textsubscript{2} constitute a hollow structure, which allows for encapsulating a significant amount of sulfur. Secondly, high surface area of the metal oxide composite allows for increased chemical bonding with polysulfides to minimize their dissolution. To create the shell, a rhombic dodecahedral zeolitic imidazolate framework ZIF-67 particle is experimentally used to form hollow polyhedral layered double hydroxide (LDH) shells by using nickel nitrate, a catalyst, in the presence of ethanol. Double shelled cobalt hydroxide and
layered double hydroxide nano-cages are thus made from reacting the single shelled ZIF-67 with LDH and an aqueous solution of Na₂MoO₄. Sulfur is then chemically combined with the nano-cages by a melt diffusion process. An initial capacity of 1014 mAh/g at 0.1C was realized and 736 mAh/g was demonstrated even after 100 cycles. Indication of the effectiveness of the metal oxide composite in minimizing polysulfide diffusion. With a sulfur loading of 3 mg/cm² and rate cycling between 0.1-1C, high reversible capacities of 800 mAh/g was achieved at 0.1C. The notable performance is a reflection of the hollow structure, which allows for sufficient sulfur loading. The surface with hydroxyl functional polar groups have strong affinity towards lithium polysulfides, allowing for long cycle life stability by minimizing polysulfide diffusion into electrolyte. The metal oxide cathode has also proven to enhance the rate kinetics of the battery demonstrated in its rate performance even after high charging rate.

The use of hierarchical hydrogenated TiO₂ (HTS) mesoporous spheres derived from anatase nano-sheets was proposed by Yuan et al.¹²² Due to the highly exposed (001) facets of the anatase nano-sheets, highly efficient sulfur hosts were fabricated with significantly high coulombic efficiency, cycling performance and a notable discharge capacity of 579 mAh/g. In particular, TiO₂ structures were chosen as hosts over carbon type precursors because of the intense chemical bonding between Sn²⁻ and reduced (001) facets of HTSs. The void space in the hierarchical mesoporous metal oxide compound contributed as a reaction chamber to encapsulate high levels of sulfur deposition, minimize volume changes and retain sulfur and its derivative compounds at the cathode. Thus far, attention has been directed towards the sole use of a metal oxide to encapsulate sulfur atoms. The combination of a metal oxide with a carbon matrix can also generate a suitable cathode structure. Apart from TiO₂, combination of zinc oxide and sulfur incorporated with carbon nanotubes were explored for high performance Li-S batteries.¹¹² The composite was
prepared by ball milling sulfur and carbon followed by a subsequent drying stage as shown in Figure 12.

Figure 12. (a) A synthesis procedure highlighting the ball milling process for ZnO-S/CNT and Ni(OH)$_2$-S/CNT. Cycle life of ZnO-SCNT, Ni(OH)$_2$-SCNT – 45% composite cathode at (b) 160 mA/g and (c) 1600 mA/g. Reprinted with permission from Ref [112]. Copyright 2016, Elsevier Ltd.

In detail, the composite was formed by ball milling a mixture of Zn (CH$_3$COO)$_2$·2H$_2$O, ethanol, and a sulfur carbon nanotube S/CNT – 60% in a specific weight ratio and then filtering and drying the obtained sample. Ni(OH)$_2$-S/CNT was prepared similarly. As an additive, ZnO was proven through DFT to possess a stronger binding ability to formed polysulfides than that of Ni (OH)$_2$. 
For the cathode composite derived from ZnO, an initial discharge capacity of 942 mAh/g is highlighted after 70 cycles (160 mA/g current density), retaining a capacity of 698 mAh/g after 200 cycles upon the increase of current density to 1600 mA/g (Figures 12 b-c). An additional example of the benefits derived from metal oxide used in batteries is given by Seh et al.\textsuperscript{123} in which they demonstrated the effectiveness of sulfur-TiO\textsubscript{2} yolk shell nano – architecture for a Li-S battery that is capable of a long cycle life. The theorized advantage of the yolk shell resides in the functionality of internal void space in accommodating large volumetric changes of sulfur upon lithiation. This serves to protect the structural integrity of the shell, minimizing polysulfide dissolution. To prepare the composite material, sulfur nano particles were formed from a reaction between sodium thiosulfate and hydrochloric acid. TiO\textsubscript{2} is then coated on the outside of the nanoparticles, followed by an effective toluene sulfur dissolution effect to make the “yolk shell” illustrated in Figure 13a. Even after 1000 cycles, a stable capcity of 800 mAh/g is demonstrated reflecting the ability of TiO\textsubscript{2} to effectively encapsulate the sulfur molecule seen in Figure 13b.

![Figure 13](image.png)

**Figure 13.** (a) Yolk shell structure effective at trapping polysulfides. (b) Charge-discharge current capacity and Coulombic efficiency of the proposed battery for 1000 cycles at 0.5 C. (c)
A composite cathode consisting of sulfur and hollow–mesoporous TiO$_2$ titanium intercalated within carbon nanotubes was also developed.\textsuperscript{23} The hollow mesoporous titanium is able to confine sulfur and also ensure high electrical conductivity. Due to severe volume expansion experienced by typical Li-S batteries, hollow mesoporous titanium-CNT composites enhance both the electrode conductivity and the mechanical strength of the cathode. The battery was able to maintain a cycle capacity of 1000 mAh/g for over 100 cycles. Consequent treatment of the battery to different charging rates minimally affected the battery; at 5 C the battery was able to maintain above 600 mAh/g after 100 cycles. Encapsulation of sulfur atoms by a metal oxide particle is just one aspect of the multifunctional role that they can have in minimizing sulfur loss to electrolyte. Liang \textit{et al.}\textsuperscript{124} provided yet another explanation for the use of metal oxides in Li-S batteries through important metrics, such as cyclic voltammetry and surface spectroscopy. Through their work, it is shown that materials with redox potentials in a targeted window react with polysulfides to form activated surface – bound polythionate species. For example, MnO$_2$ exhibits a redox potential of 3.05 V, higher than the polysulfide reduction potential of 2.4 V. Therefore, upon discharge of the battery MnO$_2$ will trigger the formation of thiosulfate/polythionate species. Metal oxides with reduction potentials above that of the optimal window, such as V$_2$O$_5$, are able to repetitively re-oxidize polysulfides to inactive sulfate species leading to poorer cycle life than metal oxides similar in reduction potential to MnO$_2$. Cells using a S/VO$_2$-graphene substrate as a cathode exhibit an initial discharge capacity of 1180 mAh/g at C/20 and a corresponding decay rate of 0.058\% per cycle over 1000 cycles; stabilization occur at 400 mAh/g. Metals oxides that are known to have a
lower reduction potential than optimal do form strong bonds with lithium polysulfides, and hence do not demonstrate a stable capacity through this mechanism. Therefore, good polar surface interactions and acid-base interactions still enables these metal oxides to form promising Li-S batteries. Thus, the use of metal oxides to encapsulate sulfur particles or facilitate increased electrochemical performance through their binding ability with polysulfides and high electron conductivity have led to promising cathode structures that portray excellent energy storage abilities. The potential challenge is the industrial scalability of such products as rare earth metals and precious metals such as vanadium and magnesium represent a focal point to their fabrication.

4. Summary and Perspective

Recently, sulfur cathode of Li-S batteries has received considerable attention for improving overall battery capacity and cyclic stability. Determining an effective way to stabilize sulfur and its related products at the cathode will lead to the creation of a battery capable of retaining a high current capacity after numerous cycles. Hosting nanostructures that can encapsulate sulfur atoms have proven to be the current best method for generating batteries with a more optimal electrochemical performance. In general, fine tuning the structure allows for precise placement of sulfur particles inside these host structures, which have high electrical conductivity yet enough free volume space to accommodate the volume expansion of the lithiated sulfur particles. Among others, sulfur encapsulation, whether by carbon film, shell, nanotube or graphene sheet, is a viable direction for a long cycle life Li-S battery. Porous carbon films that can provide ample space for sulfur expansion is an effective way of minimizing the loss of active sulfur species. Carbon shells offer an improvement to porous carbon as they can physically retain sulfur at the cathode and offer increased electrical conductivity; however, cycle stability above 1000 mAh/g has proven challenging. Graphene has proven to be one of the best carbon sources for creating a suitable
cathode for Li-S batteries. Apart from its high electrical conductivity and unique morphology that allows the graphene sheets to have intimate contact with sulfur, it can be partially reduced easily to form rGO that has an abundance of oxygen rich functional groups. It’s these functional groups that can bind to sulfur in lithium polysulfide, hence minimizing the current capacity loss challenge endemic to Li-S batteries. Heteroatom doping in combination with other surface modification to carbon materials can further help with reducing the shuttle effect by making nearby oxygen containing functional groups electronegative, and therefore susceptible to sulfur bonding. Therefore, these processes by using carbon materials to stabilize sulfur have been demonstrated to be effective at generating batteries with excellent electrochemical characteristics. A specific capacity around 1000 mAh/g for 100 cycles can be readily attainable. Yet there still remains a need to continue to optimize their structure. Therefore, significant efforts in by modifying the carbon host structure through high temperature, acid treatment, or some other physical means to create a homogenous mixture and stable composite material are ongoing.

Alternative, methods by using metal sulfide catalysts to quickly convert sulfur to its reduction products, and hence avoid polysulfide dissolution are being explored. For example, cobalt sulfide can quickly convert long chain polysulfides formed upon the discharge cycle to short chain polysulfides. This reduces the amount of inactive sulfur dissolved into the electrolyte, which is reflected in minimized capacity fade. In addition, metal oxide nanoparticles such as MnO₂, that can encapsulate sulfur atoms and have a reduction potential above that of lithium polysulfide, can significantly reduce the capacity fade due to the shuttle effect by minimizing the amount of inactive sulfur species present in the electrolyte.

It should be noted that modifications to the fabrication of Li-S batteries, such as utilizing lithium sulfide in the cathode material instead of a carbon-sulfur mix, represent a potential avenue
for a high performance battery. Lithium sulfide, which already contains lithium ions at the cathode, can then be paired with anodes of a much higher energy density, creating batteries that are superior in longevity to that of Li-ion batteries. Also solid-state electrolytes utilized in the Li-S battery are very promising as they minimize the initial loss in capacity due to the polysulfide shuttle effect. These electrolytes possess an increased chemical stability in comparison to organic electrolytes and are less susceptible to polysulfide dissolution, which is the major factor in current capacity loss. However, the low ionic conductivity of solid electrolytes, particularly at room temperature, makes them not optimal for use in many commercial products.\textsuperscript{125,126} Therefore, further research is needed.

Overall, among currently studied lithium batteries, a Li-S battery with an improved cathode is the most promising option to meet those optimizations of cheap, light, energy dense batteries for various applications. In the near term, Li-S battery research should be targeted to an energy density of > 250 Wh/kg over 1000 cycles. The long term goal of such battery technology is consumer product. For that to occur, the Li-S battery should be able to be cycled with minimal capacity loss. Also, in line with U.S. DOE targets set at reducing the cost of electric vehicle batteries from $500/kWh to <$100 kWh over the next decade, the Li-S battery hold significant potential at realizing commercial success. While there are very few examples of the present commercial use of Li-S batteries, there remains significant promise of the development of such energy storage devices. With current research efforts globally, the production of a Li-S battery commercially competitive with Li-ion batteries should less than ten years away.

Acknowledgements

G. Wu acknowledges the financial support from the start-up funds of University at Buffalo along with National Science Foundation (CBET-1511528). This work was also partially supported by
the U.S. Department of Energy under Contract DE-AC0206CH11357 from the Vehicle Technologies Office, Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE). We are grateful Mr. Matthew Smith from University at Buffalo for editing the text.

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