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New Approaches for High Energy Density Lithium–Sulfur Battery Cathodes

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CONSPECTUS

The goal of replacing combustion engines or reducing their use presents a daunting problem for society. Current lithium-ion technologies provide a stepping stone for this dramatic but inevitable change. However, the theoretical gravimetric capacity ($\sim$300 mA h g^{-1}) is too low to overcome the problems of limited range in electric vehicles, and their cost is too high to sustain the commercial viability of electrified transportation. Sulfur is the one of the most promising next generation cathode materials. Since the 1960s, researchers have studied sulfur as a cathode, but only recently have great strides been made in preparing viable composites that can be used commercially. Sulfur batteries implement inexpensive, earth-abundant elements at the cathode while offering up to a five-fold increase in energy density compared with present Li-ion batteries.

Over the past few years, researchers have come closer to solving the challenges associated with the sulfur cathode. Using carbon or conducting polymers, researchers have wired up sulfur, an excellent insulator, successfully. These conductive hosts also function to encapsulate the active sulfur mass upon reduction/oxidation when highly soluble lithium polysulfides are formed. These soluble discharge products remain a crux of the Li–S cell and need to be contained in order to increase cycle life and capacity retention. The use of mesoporous carbons and tailored designs featuring porous carbon hollow spheres have led to highly stable discharge capacities greater than 900 mA h g^{-1} over 100 cycles. In an attempt to fully limit polysulfide dissolution, methods that rely on coating carbon/sulfur composites with polymers have led to surprisingly stable capacities ($\sim$90% of initial capacity retained). Additives will also play an important role in sulfur electrode design. For example, small fractions ($>$ 3 wt%) of porous silica or titania effectively act as polysulfide reservoirs, decreasing their concentration in the electrolyte and leading to a higher utilization of sulfur and increased capacities.

1. Introduction

In the next 25 years, energy demand will increase by at least 35% from our present usage with the consumption of fossil fuels slated to grow, not decline. This will put increasing pressure on the world's reserves of nonrenewable energy sources and will also greatly affect climate disruption. Electrical energy storage systems can allow more widespread use of intermittent renewable energy generators (wind, solar, wave) and reduce the consumption of fossil fuels for transportation. Conventional lithium-ion (Li-ion) batteries utilize a cathode with a crystalline structure that features both electronic and ionic conductivity that can reversibly intercalate lithium ions with minimal structural change. Present research is reaching the theoretical energy density limits of these cathodes and leaves no room for satisfying our needs in electric/plug-in hybrid vehicles. Higher limits must be introduced, which potentially can be realized through redox-driven phase-transformation chemistry that involves sulfur or oxygen as cathodes. These future generation systems offer increased energy densities, reduced cost factors, and more benign environmental factors due to their use of nontoxic elements.

Sulfur is a promising cathode for lithium batteries because its chemistry is vastly different from that which

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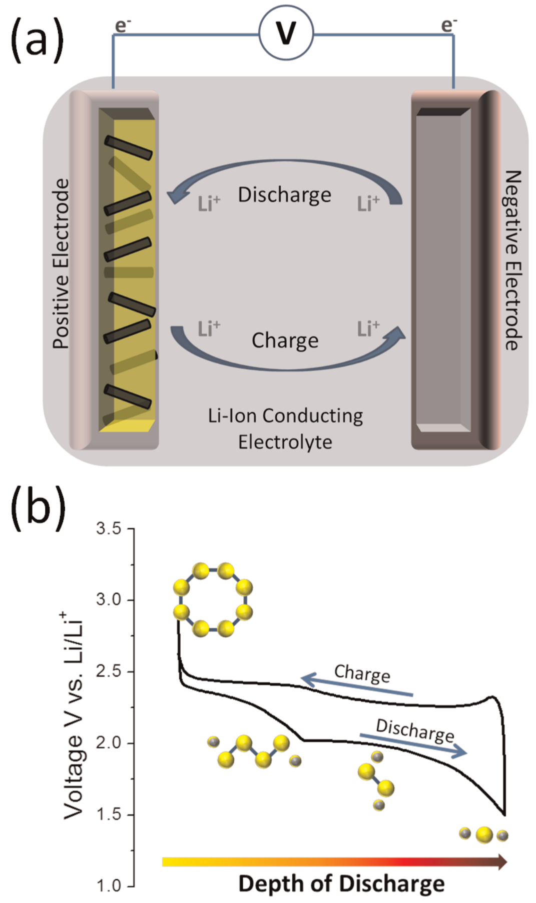

FIGURE 1. (a) Schematic illustration of a typical Li−S cell. The cathode consists of sulfur (yellow) and a conductive additive (black, for example, carbon) separated from the negative electrode lithium (gray) by an ion-conducting electrolyte. Lithium ions propagate through the electrolyte during charge and discharge and the electrons travel through an external circuit. (b) A typical voltage vs capacity plot for a Li−S cell. During discharge sulfur, S_8 (yellow ring) is reduced by lithium (gray sphere), and the sulfur ring is opened and shortened until the final discharge product Li_2S is formed.

governs typical intercalation materials (i.e., $LiFePO_4$, $LiMn_2O_4$). In its most stable form, sulfur forms a molecular structure with a density of 2.07 g/cm^3 comprised of stacked eight atom rings (S_8). In typical lithium−sulfur (Li−S) cells (Figure 1a), lithium metal is used as the negative electrode and is separated from the positive sulfur electrode by an ion conducting liquid or solid electrolyte. During discharge of the cell, the sulfur−sulfur bonds are cleaved to open the S_8 ring, and subsequent shortening of the sulfur chain length is thought to occur as shown in Figure 1b. The overall redox couple of a Li−S cell is described by the reaction $S_8 + 16Li \leftrightarrow 8Li_2S$ and occurs at a potential of 2.15 V vs Li/Li$^+$, which is ~2/3 lower than typical intercalation transition metal oxide electrode materials. This lower potential is not detrimental for practical applications because the gravimetric capacity of sulfur is the highest of any solid cathode material at 1675 mA h g^{-1}. It correlates to theoretical energy densities of 2500 W h kg^{-1} or 2800 W h L^{-1} based on weight or volume, respectively.[1] This affords the Li−S cell up to 5 times greater energy densities compared with conventional lithium-ion batteries at a significantly lower cost.

1.1. Challenges of a Sulfur Cathode. The significant advantages of sulfur as a cathode are evident, but wide-scale commercial use is so far limited because of some key challenges that must be addressed. The first main issue is that sulfur is both ionically and electrically insulating.[2] The insoluble low-order lithium polysulfide discharge products are also expected to be electronic insulators, although their properties are uncertain because they have not been isolated as single phases. To overcome the insulating nature of these materials, intimate contact of conductive additives such as carbon or metals with high surface areas (i.e., nanosizing) augment the electrical conductivity, and organic electrolytes that wet the sulfur create pathways for ionic transport. Through reducing the sulfur particle size, the diffusion path for electrons and lithium ions is greatly reduced and leads to a higher utilization of the active sulfur mass.

These are not the only challenges in the Li−S cell. Most of the problems arise because of the intermediate discharge products (Li_2S_x, $2 < x < 8$). Upon reduction by lithium in an organic electrolyte, sulfur is reduced stepwise to a sequence of highly soluble lithium polysulfide intermediates. These intermediates can take part in the well described "sulfur shuttle mechanism" whereby sulfur active mass is lost through redox reactions of polysulfides at both the positive and negative electrode surfaces.

In this Account, attention will be given to recent published work from the previous few years that has focused on the Li−S battery cathode. Owing to space limitations, we highlight some design approaches to cathodes that aim to achieve complete containment of sulfur and limit dissolution of polysulfides in the electrolyte. These include the creation of porous carbons/polymers/metal oxides and functionalized graphenes that limit sulfur dissolution through both physical and chemical interactions. Entrapment through surface modification or additives will also be discussed, such as using polymer coatings as a physical barrier to retard polysulfides or porous oxide additives to physically sorb soluble polysulfides.

2. Contained Cathodes

2.1. Macro-, Meso- and Microporous Carbon. In order to effectively house sulfur, the host must contain the sulfur without significantly diminishing the overall practical properties of the cell, that is, the gravimetric/volumetric energy density. The optimal material to satisfy these conditions is lightweight, conductive, and can "wire-up" the insulating sulfur, such as one made predominately of carbon. This configuration was used in the earliest reports, but it failed to harness the potential of carbons to limit polysulfide dissolution by trapping sulfur and its reduced species at the cathode owing to primitive carbon architecture.

Carbon is highly effective as an electronic conduit to enable redox accessibility of the sulfur, but it can also act as a framework to encapsulate the redox products. A straightforward solution is to introduce pores in the carbon that sulfur can impregnate. Pore size is defined by the IUPAC as being either macro (>50 nm), meso (2−50 nm), or micro (<2 nm). Various carbons embodying these pore structures and their combinations have been employed in the last 2 years with varying degrees of effectiveness.

Macroporous carbons have been the least utilized for Li−S cells owing to their open architecture, which is highly ineffectual at containing soluble polysulfides. However, if the macroporous carbon is coupled to a high viscosity electrolyte, the lithium polysulfides are limited in mobility and will predominately remain at the cathode. Watanabe et al. used an ordered inverse opal carbon to house sulfur and replaced the commonly used low viscosity organic electrolytes with a high viscosity glyme-Li salt.[3] This electrolyte is similar to a room temperature ionic liquid in that it consists purely of $[\mathrm{Li(glyme)}]^+$ cations and TFSI^- anions. It afforded relatively stable cell cycling with a reversible capacity of over 700 mA h g^{-1} after 50 cycles and a coloumbic efficiency of 97%. While the results are promising, the current density was low (139 mA g^{-1}), and the poor scalability of inverse opal carbons is problematic for large-scale applications.

Most of the recent reported research on porous carbon cathodes has focused on mesoporous carbons (MCs), following on early work by our group where small carbon mesopores (3−4 nm) and a hydrophilic polymer coating provided effective confinement of sulfur and its reduction products to yield high reversible capacities up to 1320 mA h g^{-1}.[4] A question concerns what pore size and distribution are optimal. Liu et al. have used a systematic approach to determine the effect that both pore size and sulfur loading have on the cycling stability and overall capacity of the Li−S cell.[5] A series of MCs with tunable pore sizes (3, 7, 12, and 22 nm) and pore volumes up to ~4.8 cm^3/g were synthesized using a hard template approach. The sulfur was infiltrated into the various MCs at different weight ratios using a two-step infiltration technique. Sulfur dissolved in CS_2 was mixed with the MC, and once dry, the composite was heated at 155 °C where the low sulfur viscosity permits flow into the carbon pores. The weight fraction of sulfur gradually increased as the pore size of the MC increased, and a sulfur content of 83 wt % was reported for the 22 nm MC material. Surprisingly, all of the sulfur/carbon composites exhibited almost identical initial sulfur utilization even though the weight ratio of sulfur was significantly different (56−84 wt %) between MCs. Contrary to other reports, this suggests there is no influence on the battery performance even if the MC is fully "stuffed" with sulfur. The MC with the largest pore size and volume clearly should be used to optimize both gravimetric and volumetric capacities were this to be the case.

Another method of sulfur entrapment is to utilize a bimodal MC as the sulfur host. The first demonstration of this concept by Dudney et al. used a hierarchically structured sulfur−carbon (S/C) nanocomposite material as the high surface-area cathode.[6] A porous carbon with a uniform distribution of mesopores of 7.3 nm was synthesized through a soft-template synthesis method, followed by KOH activation to result in a bimodal porous carbon with added microporosity of less than 2 nm to the existing mesopores while maintaining integrity of the original carbon. More recent work has created bimodal carbons using a double template approach to directly fabricate highly ordered carbons with pore size split between ~6 and ~2 nm pores.[7,8] Each pore contributes an equal amount of pore volume with the smaller pores existing in the walls of the carbon framework that houses the larger pores. When sulfur was impregnated into the carbon host, the smaller pores preferentially filled first (Figure 2a). This optimized the use of the smaller supermicropores to entrap the sulfur while the larger pores facilitated electrolyte ingress throughout the structure. An improvement on this concept was demonstrated by creating spherical bimodal-carbon particles around 300 nm in dimension with the same pore distribution (Figure 2b). Nazar et al. were able to cycle these sulfur/carbon electrodes at a high current rate of 1 C and maintain a high and relatively stable discharge capacity of 850 mA h g^{-1} at the 100th cycle (Figure 2c).[9]

Another approach similar to creating a bimodal pore structure has been achieved by Archer et al. with the synthesis of hollow carbon spheres that exhibit a porous outer shell with small 3 nm pores and a large interior cavity around ~200 nm.[10] While this may not be considered bimodal in most respects, it effectively creates an enclosed area where the sulfur can be stored and polysulfides have difficulty

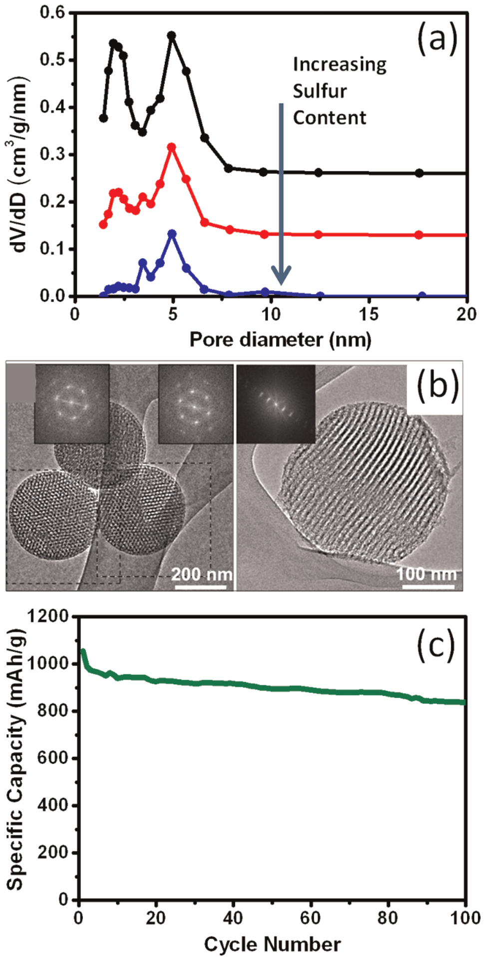

FIGURE 2. (a) Pore size distribution of the bimodal mesoporous carbon (BMC) with different sulfur loadings. (b) TEM micrographs of spherical BMC nanoparticles showing the 2-D hexagonal structure. (c) Cycling performance of BMC nanoparticles with 70 wt % sulfur at a 1 C rate.

diffusing out because of the small pores in the carbon shell. The hollow carbon spheres were reported to hold 70 wt % sulfur, and they retained 91% of their initial capacity (1071 mA h g^{-1}) after 100 cycles at a moderate C/5 rate. Possible drawbacks to the hollow carbon spheres are the fragility of the porous carbon shell and scalability of the process. A vapor infusion method is required for sulfur impregnation involving three separate passes to obtain a high sulfur loading.

Microporous carbons have also been used as hosts for sulfur in Li–S cells. Gao et al. used sucrose as a carbon precursor to form microporous carbon spheres with a very narrow pore size distribution of less than 1 nm.[11] Their material exhibited highly stable cycling with 42 wt % sulfur loading and high capacity above 900 mA h g^{-1}. However, an increase in sulfur content to just 51 wt % dramatically decreases the discharge capacity by ~600 mA h g^{-1}. The material also exhibited an unusual discharge profile that did not have the characteristic two voltage plateau evident in most other Li–S reports. This may be due to reaction of the carbon with sulfur to form a bonded C–S composite owing to heat treatment or the alkyl carbonate electrolyte mixture chosen for this work. Recent studies performed by Abruña et al. show that carbonate based solvents undergo side reactions in the presence of nucleophilic sulfide anions.[12] Activated carbon (in the form of fibers woven into a cloth) has also been examined by Aurbach, Garsuch, et al., as a microporous host for sulfur that, uniquely, does not require binder.[13] An inexpensive commercial AC cloth with high surface area (2000 m^2/g) and narrow pore size distribution (<2 nm) was impregnated with 33 wt % sulfur and cycled at an intermediate current density of 150 mA g^{-1}. A large, stable discharge capacity of 1057 mA h g^{-1} was obtained with a very high Coulombic efficiency. The latter is aided by the use of $LiNO_3$ in the electrolyte to passivate the negative electrode and limit the sulfur shuttle mechanism.

2.2. Graphene. It was only a matter of time before arguably the most popular material of the past decade was coupled to sulfur in a Li–S battery. Graphene's advantageous properties of very high conductivity, large surface area, and the ability to tune the hydrophobicity/philicity with surface functionalization has led to a few different methods of marrying it with sulfur to make effective electrodes.[14–19] Two different designs for sulfur/graphene composites have been employed with each having its positive characteristics. The first method utilizes large sulfur particles enveloped by graphene/graphene oxide sheets with either a polymer layer buffering the sulfur[15] or the sulfur particles simply in intimate contact with the graphene.[17,18] The sulfur particles grown through a one-pot *in situ* acid oxidation of sodium polysulfide species (Figure 3a) proved effective at producing a sulfur composite with 87 wt % sulfur that exhibited relatively stable cycling at a C/5 rate.[18] A similar procedure was used to form a graphene oxide/sulfur composite, employing a final heat treatment step to melt sulfur into the 3D disordered GO sheets.[17] This composite exhibited extremely stable cycling using an ionic liquid/PEGDME electrolyte at C/10 rate with a reversible capacity of 950 mA h g^{-1} over 50 cycles (Figure 3b).

Another approach to combine sulfur and graphene is to sandwich sulfur particles between functionalized graphene sheets and apply a Nafion coating. This is proposed to significantly limit sulfur loss from the cathode owing to repulsive interactions of the Nafion SO_3^- moieties with the

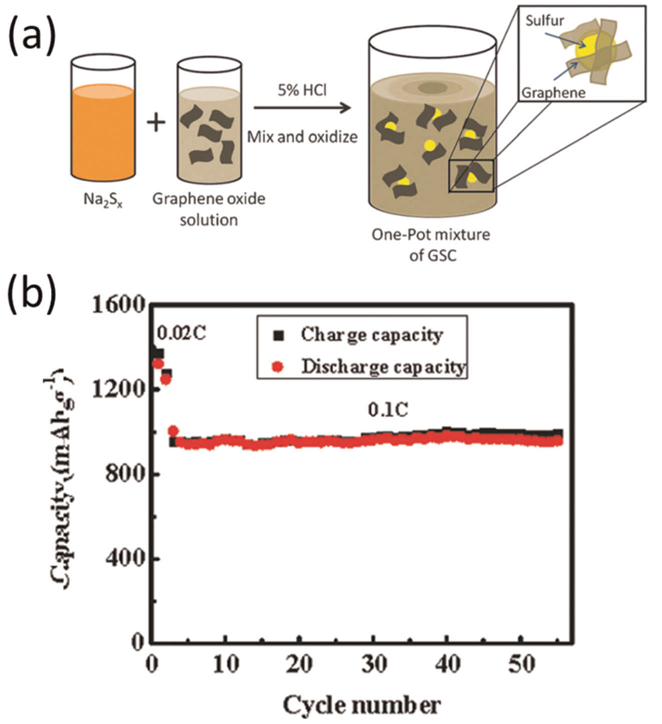

FIGURE 3. (a) Schematic illustration of the one-pot synthesis technique of a graphene–sulfur composite. (b) Cycling performance of a graphene oxide/sulfur composite using an ionic liquid/PEGDME electrolyte at 0.1 C rate. Adapted and reproduced with permission from refs 17 and 18. Copyright 2012 Royal Society of Chemistry. Copyright 2011 American Chemical Society.

polysulfide anions that restrict diffusion into the electrolyte.[16] Thermally expanded graphite oxide is also effective as a 3D network; we note that 60 wt % sulfur that is melt-infiltrated exhibits a high initial discharge capacity of 1210 mA h g^{-1} and maintains 73% capacity retention over 70 cycles at a current density of 280 mA g^{-1}.[19] Graphene and graphene oxide are very promising hosts for sulfur because of the wide range of compositions that can be produced through functional chemistry as well as the different architectures that can be constructed around sulfur particles or melt-diffused sulfur to form sandwiched/interleaved composites.

2.3. Carbon Nanotubes/Fibers. Multiwalled carbon nanotubes (MWCNT) in a Li–S cell have long been investigated as a highly conductive form of carbon that might provide an encapsulation effect for sulfur due to their 1D porous structure. Jin et al. used a precipitation technique to infiltrate sulfur into the large pore of MWCNTs by oxidation of sodium polysulfide species in the presence of MWCNTs.[20] The composite exhibited high initial sulfur utilization but had fairly rapid capacity fading over 30 cycles with only 63% capacity retention. This may suggest that MWCNTs have a very limited effect at retaining soluble polysulfides. Limitations occur because of their 1D structure and a typical length on the order of a few micrometers, which limits Li-ion diffusion compared with a more open 3D network. However, recent work that features a new method of infiltrating sulfur into disordered carbon nanotubes (DCNT) holds promise. Wang et al. formed DCNTs from polyaniline deposited in an anodized alumina membrane (AAO).[21] The sulfur was incorporated into the DCNTs through a vapor infusion method whereby smaller sulfur molecules (S_2) could theoretically penetrate further into the carbon structure and possibly even penetrate graphitic layers. Various impregnation temperatures under vacuum were attempted, with 500 °C proving optimum for stable cycling and providing composites with 40 wt % sulfur active mass. Several hurdles remain as there is a significant irreversible capacity in the first few cycles which is due to excess sulfur on the surface of the DCNTs.

Carbon nanofibers (CNFs) have also been investigated as conductive additives[22] to carbon/sulfur composites or more importantly, utilized in a similar fashion to the DCNTs discussed previously. Zhang et al. used porous CNFs synthesized by electrospinning a polyacrylonitrile/poly(methyl methacrylate) mixture followed by carbonization to remove PMMA and create pores in the fiber walls.[23] Sulfur was introduced by precipitation from aqueous solution with further heat treatment at 155 and 160 °C to infiltrate sulfur and remove any excess that is present on the surface. At low rates (0.05 C), using a viscous electrolyte comprised of an ionic liquid (Pyr_{14}TFSI) and PEGDME, the CNF/sulfur composite (42 wt % sulfur) exhibited an initial discharge capacity of nearly 1400 mA h g^{-1} and retained 82% capacity after 30 cycles.

CNF networks have also been synthesized through a templating method using an AAO membrane similar to the previous DCNTs.[24] The premise for the study was to obtain a material with sulfur residing only in the interior of the fibers so that polysulfide diffusion was limited to the ends of the fibers. This was accomplished by coating the cylindrical pores of an AAO membrane with carbonized polystyrene and subsequently infiltrating the carbon pores with sulfur. The AAO template was removed with H_3PO_4, which left CNFs with only sulfur in the interior. Upon cycling of the material in a low viscosity organic electrolyte, it showed signs of polysulfide dissolution, with an ~50% capacity fade over 150 cycles at a C/5 rate, although a specific capacity of about 730 mA h g^{-1} was still retained. Active mass loss may be attributable to the less than ideal sulfur confinement with such large pore substrates, but architectural improvements will undoubtedly be forthcoming soon.

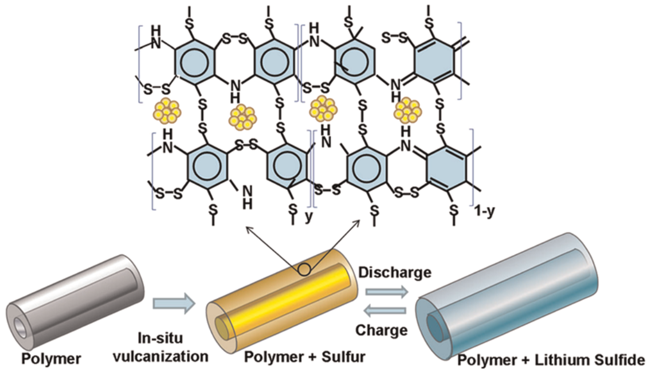

FIGURE 4. Schematic illustration of the construction and discharge/charge process of the polyacrylonitrile nanotube/sulfur composite. Adapted and reproduced with permission from ref 28. Copyright 2012 Wiley-VCH.

2.4. Tubular Porous Polymers. Porous polymers have also been researched as hosts for sulfur, which mimic the structure of carbon nanotubes and fibers.[25−27] Liu et al. have performed interesting studies using polyaniline nanotubes to host sulfur both in its elemental form and as part of the polymer backbone.[28] Sulfur was reacted with polyaniline nanotubes at 280 °C in order to chemically incorporate sulfur carbon bonds in the polymer through an *in situ* vulcanization as shown in Figure 4. Elemental sulfur was still present in the sample (62 wt %) and was postulated to be present in the pores of the polymer structure. The composite exhibited an initial capacity of 755 mA h g^{-1} at a C/10 rate but the capacity increased in the next few cycles before suffering a slight capacity fade to 837 mA h g^{-1} after 100 cycles. The increase in capacity was reasoned to be due to the low surface area of the composite that initially did not allow electrolyte to penetrate the full structure. Upon cycling, some of the sulfur is reduced to soluble polysulfides so the additional porosity allows for higher accessibility and capacity. The capacity fading may be due to degradation of the polymer–sulfur backbone because the disulfide bonds in the polymer may not reform upon oxidation.

MWCNTs have also been used as a support to create a porous polyacrylonitrile/sulfur composite.[29] PAN was coated on the exterior surface of MWCNTs, and the material was treated with varying amounts of sulfur (30, 48, and 63 wt %). The best overall results were obtained for the 48 wt % sulfur composite, which exhibited 85% capacity retention, amounting to ~590 mA h g^{-1} after 50 cycles at a C/10 rate. The composite has good rate capabilities and is able to be discharged up to 4 C while maintaining a discharge capacity above 400 mA h g^{-1}, but the average discharge voltage is low at 1.8 V and, when coupled to the marginal capacity, significantly hinders the gravimetric energy density of the material.

2.5. Porous Metal Oxides. Carbonaceous materials are not the only hosts for sulfur that have been researched in the past few years for the Li–S battery. Tarascon et al. have taken guidance from approaches to carbon coat $LiFePO_4$ to overcome its insulating nature, by carbon coating an insulating host that serves to contain the sulfur.[30] Their work utilized an insulating metal–organic framework (MIL-100) consisting of an open framework of small mesopores (~2.5–2.9 nm) and micropores (~0.5 and ~0.9 nm). Sulfur was impregnated through the well-known melt diffusion technique,[4] affording a composite with 48 wt % sulfur. Since MIL-100 is insulating, up to 50 wt % carbon was necessary to coat the particles to ensure good electrical conductivity. The material (amounting to 24 wt % sulfur in the electrode) was compared with an electrode containing mesoporous carbon CMK-3 with similar sulfur filling (52 wt %) and 20 wt % Ketjen Black (total 42 wt % sulfur in the electrode). The MIL-100/S composites exhibited high capacity, and also more stable cycling, suggesting that the oxidic framework helps to retain polysulfide. This concept, using oxide additives, has a similar effect to that reported by other researchers and discussed below (*vide infra*). The drawback is the low overall capacity of the MIL-100/S after 50 cycles at C/10 (~500 mA h g^{-1}) and the low sulfur content, which makes the system less practical.

3. Physical Barrier Containment

The previous discussion overviewed work that focused on providing a host for sulfur that contains the soluble polysulfides through architectural effects combined with chemical restraints. Another method of containment is to apply coatings to the sulfur host structure that physically blocks polysulfides from escaping from the cathode, while still allowing ingress of the electrolyte to the sulfur/carbon mass.

3.1. Polymer Coatings. In the recent literature, a variety of different approaches have been utilized in order to limit polysulfide dissolution with the use of polymer coatings that go far beyond polyethylene glycol, which was initially used as a hydrophilic barrier.[4] Zhao et al. circumvented the use of a host material for sulfur and simply coated sulfur particles with a conducting polymer, polythiophene.[31] They were able to synthesize a polythiophene/sulfur composite with ~72 wt % sulfur that performed extremely well electrochemically. Using a low viscosity electrolyte of DOL/DME, the composite was cycled at a current density of 100 mA h g^{-1} and retained 74% of its initial capacity (1120 mA h g^{-1}) after 80 cycles.

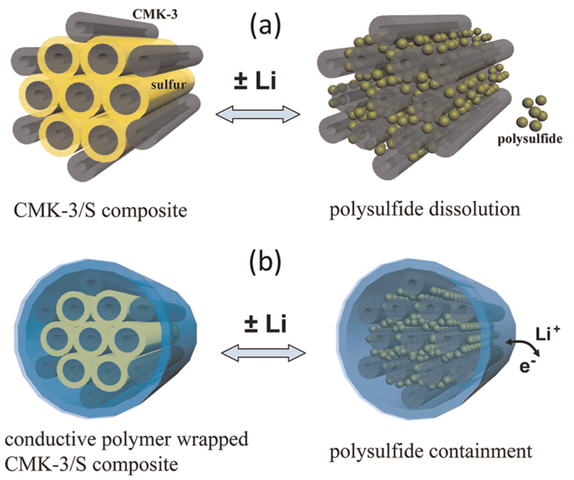

FIGURE 5. Scheme of polymer-coated CMK-3/sulfur composite for improving the cathode performance. (a) In bare CMK-3/S particles (gray, CMK-3; yellow, sulfur), polysulfides (green color) still diffuse out of the carbon matrix during lithiation/delithiation. (b) With conductive polymer coating layer (blue color), polysulfides could be confined within the carbon matrix. Lithium ions and electrons can move through this polymer layer. Adapted and reproduced with permission from ref 32. Copyright 2011 American Chemical Society.

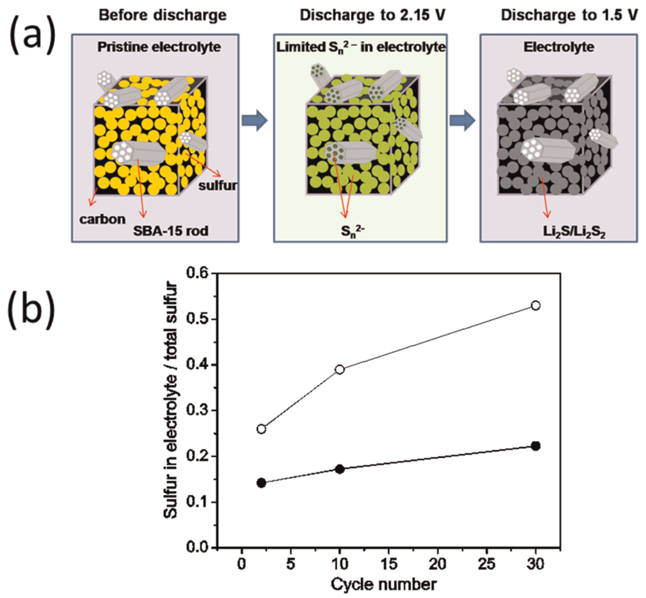

FIGURE 6. (a) Schematic diagram showing the effect of SBA-15 rods in the electrode on reversibly absorbing/desorbing polysulfide anions. (b) Percentage of sulfur dissolution into the electrolyte, from the SCM/S cathode (open dot curve) and from the SBA-15 added SCM/S cathode (solid dot curve). Adapted and reproduced from ref 34. Copyright 2011 Nature Publishing Group.

Cui et al. have used a carbon host (CMK-3) that is highly effective at retaining polysulfides itself,[4] because of its small ~3–4 nm pores as a substrate to polymer coat in order to limit polysulfide dissolution even further as shown in Figure 5.[32] CMK-3/S composites were prepared and mixed with the conductive polymer PEDOT/PSS, which forms a thin 10–20 nm coating. While the effect of the polymer coating on electrochemical performance was not considerable, a slight increase in capacity stability was observed over bare CMK-3/S. The PEDOT/PSS coated CMK-3/S was able to retain an overall capacity greater than 600 mA h g^{-1} after 150 cycles at a C/5 rate.

Another conducting polymer, polyaniline, has also been utilized as a coating for a MWCNT/S composite.[33] The MWCNTs were impregnated with sulfur before oxidative polymerization of polyaniline. The sulfur content remained high in the composite at 70 wt % and also retained a crystalline structure. The material showed very stable cycling over 80 cycles and not surprisingly had less capacity fade than uncoated MWCNT/S. The rate capability of the material was also quite good with ~90% capacity retention after 80 cycles at current densities ranging from 200 to 1000 mA g^{-1}.

4. Additives To Retain Polysulfides

4.1. Porous Metal Oxides. Containing soluble polysulfides has been discussed through both physical and chemical barriers of the host material or coatings on the host material for sulfur. Another method of containment at the cathode is to provide additives in the cathode matrix that can attract and hold polysulfides so that they do not diffuse to the negative electrode. To employ this concept, we utilized mesoporous silica as an additive to a large pore mesoporous carbon/sulfur electrode (Figure 6a).[34] The main interaction that the polysulfides have with the additive is through surface sorption, and therefore the surface area is increased significantly by synthesizing the additive with a mesoporous structure. At a C/5 rate, the capacity versus a cell without additive was both increased and much more stable over 40 cycles. The silica additive was able to sorb polysulfides during intermediate discharge and release them near the end of discharge so that they could be further reduced in the mesoporous carbon with ~94% of the sulfur being reversibly sorbed in the silica at the 40th cycle. The amount of sulfur present in the electrolyte after 30 cycles decreased by more than 30% compared with a cell consisting of no silica additive (Figure 6b).

5. Conclusions

The goal of introducing a next generation battery technology that outperforms present lithium-ion batteries may indeed be met by a sulfur cathode. This Account highlighted the innovative research on Li–S batteries that is being undertaken from scientists around the globe toward that aim. The Li–S battery has experienced a revival in the past few years from its fundamental studies in the 1960s and great strides have been made. Containment of sulfur within the cathode (as opposed to a different, lower volumetric energy density catholyte cell design where polysulfides are dissolved in the electrolyte) is critical for use with an unprotected, or even a protected, Li metal anode. Much research has been devoted to solving this issue. Three main avenues have been used to date: impregnating sulfur in a porous carbon or polymer, coating the host material with a polymer, and altering the cathode composition with additives. Porous hosts for sulfur have experienced the greatest level of research activity. Stable capacities at ~1000 mA h g^{-1} have been reached over 100 cycles using porous hollow spheres and 850 mAh g^{-1} over 200 cycles for bimodal nanospherical carbons. These alone still allow polysulfide dissolution, which requires a second tier of containment that can be found with coatings or porous oxide additives.

The prospectus of Li–S batteries has improved remarkably over the past few years, but more improvements are still needed at the cathode. The containment of polysulfides is critical to increase cycle life and minimize capacity fading. Achieving full, reversible reduction of Li_2S_2 to Li_2S, which accounts for half of the theoretical capacity, is vital to improving energy density. Fundamental studies are necessary to understand and control this process better. While some research is informative, a more realistic, scalable approach to materials design is important. Tailored hosts for sulfur need to be optimized to provide high tap densities, large pore volumes for increased sulfur loading while still containing the sulfur. Commercially viable additives or coatings for cathodes may prove essential for operation, but they must be efficient in both weight and volume so that they do not drastically decrease the performance of the hosts for sulfur. Finally, innovations at the negative electrode are critical to reduce concerns of dendritic growth. With these considerations in mind, however, sulfur is unquestionably a viable cathode material, and scientists are proving that with the recent research outlined here.

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BIOGRAPHICAL INFORMATION

Scott Evers received his B.Sc. in Honours Chemistry with Materials Chemistry Specialization from the University of Waterloo in 2010. He is currently a graduate student in Chemistry/Nanotechnology at the University of Waterloo, under the supervision of Prof. Linda F. Nazar. His research interests focus on the optimization of the cathode in the Li–S battery through tailored designs of porous carbons and graphenes as hosts for insulating sulfur.

Linda Nazar is a Professor of Chemistry and Electrical Engineering at the University of Waterloo, Canada, and holds a Senior Canada Research Chair in Solid State Energy Materials. She received her Ph.D. in Chemistry from the University of Toronto and then joined Exxon Corporate Research (USA) as a postdoctoral fellow. She was awarded the Electrochemistry Society Battery Division Research Award in 2009, the International Battery Association award in 2011, and the 2011 IUPAC Distinguished Women in Chemistry/Chemical Engineering award and was the 2010 Moore Distinguished Scholar at the California Institute of Technology. She was also recently elected to the Royal Society of Canada. Her solid state electrochemistry research is focused on energy materials with research spanning Li-ion and Na-ion batteries, Li–sulfur and Li–air batteries, and energy conversion materials.

FOOTNOTES

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The authors declare no competing financial interest.

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