The ever-growing demand and consumption of energy as well as the depletion of fossil fuels and its associated environmental pollution have driven scientists to pursue renewable energy alternatives. Photovoltaic panels and wind farms are being installed worldwide. However, to fully utilize the electricity generated by these inherently intermittent sources, rechargeable battery systems are a vital part of the system, enabling grid-scale electric storage and benefitting electric and hybrid-electric vehicular transport.1

Amongst all the rechargeable battery systems that have serviced mankind for decades, lithium-ion batteries (LIBs) have dominated the commercial battery market, owing to their high cell voltage, low self-discharge rate, and stable cycling performance.2–4 However, the applications of these batteries have been somewhat limited due to their low energy density (100–220 W h kg−1) and high cost.5,6 These battery systems—which consist of a graphite anode and a lithium metal oxide cathode and rely on a Li-ion intercalation mechanism—are very attractive for the electric vehicle market. Nonetheless, they do not enable a long driving range unless very large battery packs are utilized, which comes at very high cost and weight. Thus the goal of traveling 500 km per charge is still unattainable. Electrochemical systems that offer a higher capacity and energy density as well as a longer life-time at a lower cost are becoming promising options, but are definitely challenging to bring into practice.

Lithium-sulfur (Li-S) batteries are considered as one of the most promising candidates for the next-generation energy storage systems, because of their high theoretical energy density and the natural abundance of sulfur.7–10 A conventional Li-S cell consists of a lithium metal anode and an elemental sulfur cathode in an ether-based electrolyte. The coupling of the high-capacity electrodes of lithium (3840 mAh g−1) and sulfur (1675 mAh g−1) affords an average cell voltage of 2.2 V and a theoretical energy density of 2570 W h kg−1. The reversible conversion reaction between sulfur and lithium sulfide (Li2S) is accompanied by a series of intermediate lithium polysulfides (LiPSs, Li2Sn, 2 ≤ n ≤ 8). The electrochemical reactions of Li-S batteries are completely different than the conventional LIBs because the LiPSs are soluble in the ether-based electrolytes. Thus it involves dissolution-precipitation transitions that are difficult to control. Upon discharge/charge, the dissolved intermediates diffuse to the anode side to be reduced and then shuttle back to the cathode. This parasitic reaction, called the polysulfide shuttle, continuously occurs in the cell unless means are provided to shut it down. It results in self-discharge, low Coulombic efficiency as well as active material loss and rapid capacity fading. This is one of the major hurdles that limit the practical realization of the Li-S system, although others include low sulfur utilization ratio, high volume expansion, and lithium anode degradation.

To solve the LiPS shuttle problem, much effort has been devoted to physical confinement of LiPSs using carbonaceous materials in the past decade. A variety of 3D porous carbon materials, including CMK-3,11 porous hollow carbon spheres,12–15 carbon nanotubes16 and nanofibers,17,18 and microporous carbons19,20 have been developed to host the sulfur and suppress the diffusion of LiPSs into the electrolyte by retaining them in the nanostructured pores. A similar effect was also achieved by wrapping sulfur particles with 2D graphene nanosheets21,22 or conductive polymers.23 More recently, interlayer carbon paper has been shown to be effective in inhibiting the diffusion of polysulfide to the lithium anode.24 The porous architecture enables these carbon interlayers to act as a pseudo-current collector as well as a layer for polysulfide retention while providing good electronic conductivity.25 Along with suppressing the polysulfide shuttle, these carbonaceous materials provide additional electron conduction and pathways for electrolyte and Li+ ion diffusion, resulting in improvement in the cycling performance of Li-S batteries. However, Li-S cell cathodes made from non-polar carbonaceous hosts still generally suffer from rapid capacity fading over long-term cycling (> 300 cycles). This is fundamentally because the very weak interactions between the non-polar carbon and the polar LiPSs species can only confine the LiPSs based on diffusion limitation. Eventually, the LiPSs still migrate out of the cathode host upon long-term cycling. This causes not only loss of active materials, but also unspecific deposition of discharged products and the associated cathode passivation and deterioration. Therefore, materials with stronger adsorption/binding for LiPSs are desired in achieving stable long-term cycling performance for the Li-S cell.

Recently, a wide spectrum of studies have been reported on developing sulfur host materials with strong chemical binding for LiPSs along with mechanistic investigation into the underlying principles of these materials. Utilizing chemical adsorption—rather than solely relying on the high surface area or pore structure of the host materials—as the case for the physical confinement—benefits from the strong interaction between the host materials and LiPS species. Li-S batteries with improved cycling stability have been achieved by using these materials in the cathodes. This review article focuses on the various types of chemical interactions with LiPSs realized by different sulfur hosts. Comprehensive reviews on nanostructured carbon host materials, electrolytes and anode materials for Li-S batteries have been published elsewhere, and hence are not included here.10,26–29
was carried out by Zhou et al. Compared to pristine graphene, the functional groups by density functional theory (DFT) calculations the formed LiPSs also chemically interact with the GO. Discussed later below, we believe upon discharge of the bonded sulfur, interaction of GO with sulfur rather than polysulfides. However, as capacity fading. These early studies focused mostly on probing the understanding into the electronic structure and chemical bonding of GO-S composites. A follow-up study by the same group reported a mesoporous N-doped carbon with high surface area (824 m²·g⁻¹). Excellent capacity retention of 95% over 100 cycles was achieved, which was ascribed to the improved chemical adsorption for LiPSs from N-doping. The strong interaction with LiPSs was probed using pair distribution function analysis on the polysulfide-contacted N-doped carbon, although the assignments of these peaks are not completely clear (Figure 2). Other studies have also introduced N-doped graphene or porous hollow nanospheres to confine LiPSs.

A comprehensive DFT calculation study on pyridinic and quaternary nitrogen doped carbon by Peng et al. provides important insights into the underlying mechanism for polysulfide binding (Figure 3). It was found that the positive Li⁺ ions bind directly to the electron-rich pyridinic nitrogen that possesses a lone electron pair, whereas for the quaternary nitrogen, Li⁺ ions are prone to bind to the neighboring carbon atoms due to the distribution of N-donated electrons in the delocalized π-system. In short, this coupled interface is related to the electron donating/accepting behavior between polysulfides and the N-doped carbon.

Grafting amphiphilic polymers on carbon materials represents another approach in this category. This concept was first adopted by Zheng et al. by coating a polyvinylpyrrolidone (PVP) layer onto carbon nanofiber (CNF) walls. Transmission electron microscopy (TEM) analysis (Figure 4) showed that the PVP coating can alleviate the Li₂S detachment from the CNF walls upon discharge. The improved polysulfide binding was further confirmed by DFT calculations showing a Li⁺–O (in pyrrolidone) interaction. Ma et al. introduced another facile method to incorporate nitrile-containing molecules into carbon/sulfur composite by alkoxy-silane grafting. It was calculated that amine and imidazolium chloride molecules exhibit higher LiPS binding energy than polyacrylonitrile. Amino groups have also been covalently bonded to a graphene oxide substrate. The authors demonstrated not only the binding ability of polysulfides with amino groups, but also that of the amino groups onto the graphene oxide substrate.

**Metal oxide based electrodes.**— Metal oxides, in contrast to carbon materials, are intrinsically polar materials that can strongly interact with polar polysulfide species. No further surface modification is needed to achieve a greater polarization and stronger electrostatic interactions between Sₓ²⁻ and functionalized graphene.

However, GO exhibits a much lower conductivity than graphene due to the presence of the oxygenated groups. Doping carbon with nitrogen is an alternative method to enhance the chemisorption towards LiPSs without compromising the conductivity. Song et al. has introduced a mesoporous N-doped carbon with high surface area (824 m²·g⁻¹). Excellent capacity retention of 95% over 100 cycles was achieved, which was ascribed to the improved chemical adsorption for LiPSs from N-doping. The strong interaction with LiPSs was probed using pair distribution function analysis on the polysulfide-contacted N-doped carbon, although the assignments of these peaks are not completely clear (Figure 2). Other studies have also introduced N-doped graphene or porous hollow nanospheres to confine LiPSs.

**Polar-Polar Chemical Interactions with Polysulfides**

Lithium polysulfides are inherently polar molecules and do not engage in strong interaction with typical non-polar carbons. Therefore, various approaches based on a polar-polar interaction with LiPSs have been utilized, mostly using modified carbonaceous materials and metal oxides as outlined below.

**Modified carbonaceous materials.**— Owing to graphene oxide’s (GO) high surface area and its ability to chemically interact with the sulfur/poly sulfide species, it has been one of the most studied functionalized carbon materials used as sulfur hosts. Ji et al. has prepared a GO based sulfur electrode by chemically depositing a nanosized sulfur layer onto the GO nanosheets. C K-edge X-ray absorption spectroscopy (XAS) studies revealed a strong chemical interaction between sulfur and the GO functional groups along with the formation of C-S bonds (Figures 1a, 1b). Another study using various spectroscopy techniques, including X-ray photoelectron spectroscopy (XPS) and X-ray emission spectroscopy (XES), provides a comprehensive understanding into the electronic structure and chemical bonding of GO-S composites. A follow-up study by the same group reported a Li-S cell with greatly improved cycling performance (0.039% capacity fading per cycle over 1500 cycles) enabled by further modification with cetyltrimethyl ammonium bromide (CTAB) along with an ionic liquid-based electrolyte and an elastomeric binder system. CTAB, a polar ionic surfactant, affords additional binding of outer-layer sulfur and is suggested to be one of the reasons for the improvement in capacity fading. These early studies focused mostly on probing the interaction of GO with sulfur rather than polysulfides. However, as discussed later below, we believe upon discharge of the bonded sulfur, the formed LiPSs also chemically interact with the GO.

A thorough study on polysulfide binding with the inherent GO functional groups by density functional theory (DFT) calculations was carried out by Zhou et al. Compared to pristine graphene, the functionalized graphene shows much greater binding energy towards Sₓ²⁻, Sₓ⁻, Sₓ² moieties (Sₓ²⁻ binding is shown in Figure 1c). The calculations demonstrated that the hydroxyl groups are bound more strongly than epoxy groups, and that polysulfide anion species (Sₓ⁻, Sₓ²⁻) exhibit stronger binding than neutral Sₓ⁰ molecules. This was ascribed to the induced asymmetric charge distribution over the Sₓ²⁻ that causes a greater polarization and stronger electrostatic interactions between Sₓ²⁻ and functionalized graphene.

Figure 1. Representative pattern of GO immobilizing S. Yellow, red, and white balls denote S, O, and H atoms, respectively, while the others are C atoms. Note that the C atoms bonding to S or O are highlighted as blue balls. (b) C K-edge XAS spectra of GO and GO-S nanocomposites after heat treatment in Ar at 155 °C for 12 h. Reprinted from Ref. 31. (c) Geometry configuration (side and top view) of Sₓ⁻ on graphene, EO-graphene, and HO-graphene surfaces via DFT calculations, with the electron exchange and binding energy values shown. Reprinted from Ref. 34.
synthesized in the presence of adsorption of Li$_2$S$_6$. These observations represent the first spectro-altered chemical environment around the titania surface following the bond. As well, the peak shift in the Raman spectrum indicates an appeared in the FTIR spectrum, corresponding to formation of a S-Ti-O

electrode for the electro-deposition of Li$_2$S and S$_8$ from a polysulfide electrolyte, by discharge to 1.7 V and recharge to 2.6 V, respectively. After discharge (Figure 7d), the EDX sulfur mapping overlays well with that of indium, indicating the preferred Li$_2$S deposition on the polar oxide due to the much stronger polysulfide/Li$_2$S binding. A similar conclusion can be drawn after charge (Figure 7e).

**Lewis Acid-Base Interaction with Polysulfides**

The lone electron pairs of the polysulfide anion, S$_x^{2−}$ render it a soft Lewis base. Sulfur host materials that have Lewis acid characteristics, in principle, are able to interact strongly with LiPSs and thus trap spectroscopic evidence for the chemical interactions between polar oxides and polysulfides.

Other than being used as additives, metal oxides have also been employed as coated layers on carbon/sulfur composites or sulfur particles. Our group first coated CMK-3/S composite particles with a thin oxide (SiO$_x$, VO$_x$) layer through a surface initiated growth method. The thin oxide coating layer functions not only as a physical barrier towards LiPS diffusion, but also a polarophilic layer to chemically adsorb the LiPSs. Using a more sophisticated nanostructure design, Seh et al. coated amorphous TiO$_2$ onto sulfur nanoparticles to create a yolk-shell structure. This cathode material yielded a long-life Li-S battery with 0.033% capacity fading per cycle over 1000 cycles. Although the chemical interaction of LiPSs with metal oxides was not directly mentioned in either report, we believe this was one of the major contributions to the improved cycling performance using metal oxides. Another interesting work by Xiao et al. demonstrated the use of a hybrid TiO$_2$/graphene interlayer between the sulfur cathode and the separator, as a polysulfide reservoir layer. The TiO$_2$ nanoparticles anchored between the graphene sheets chemically bind the dissolved polysulfides, while the graphene conducts electrons to reactivates them. In addition, mesoporous TiO$_2$ has also been used directly as a sulfur host, demonstrating improved cycling performance.

As the underlying drawbacks of the highly insulating nature of these metal oxides hinders their overall electrochemical performance, our group has recently developed a bifunctional sulfur host material – nanostructured Ti$_4$O$_7$ – which combines metallic conductivity with a strong chemical binding ability for LiPSs. The high surface area Ti$_4$O$_7$ (290 m$^2$·g$^{-1}$) is shown to adsorb more LiPSs than the non-polar carbon materials. The underlying mechanism of the chemical interaction was probed by analyzing S 2p XPS spectra of the material (Figures 6d–6f). The two 2p$_{3/2}$ components of pristine Li$_2$S$_x$ at 161.6 and 163.1 eV, correspond to the terminal and bridging sulfur atoms (S$_t^{−1}$ and S$_b^0$), respectively. Upon contact of Li$_2$S$_x$ with Ti$_4$O$_7$, the two sulfur components shift to higher binding energies by 2.7 and 1.7 eV, respectively, indicating the polarization of electrons away from the terminal and bridging sulfur atoms to the Ti$_4$O$_7$ surface. Different from an insulating TiO$_2$ host where the trapped LiPSs cannot engage in redox behavior, on the metallic surface of Ti$_4$O$_7$ the electron transfer to chemically bounded LiPSs is enhanced, resulting in surface-mediated deposition of the discharged product Li$_2$S. This was evidenced by the significantly lessened concentration of LiPS intermediates in the operando cell and the much earlier precipitation of Li$_2$S than in the case of carbon electrodes, as proved by operando X-ray absorption near-edge spectroscopy (XANES) (Figure 6g). This conclusion was further supported by the conformal deposition of Li$_2$S onto the host, and the two-fold lowered charge-transfer resistance on the discharged electrodes. Tao et al. has also studied the Ti$_4$O$_7$ material and provided understanding of LiPSs binding via DFT calculations. Using the Ti$_4$O$_7$ (1−20) surface as an test substrate, the optimized geometry indicated that the small sulfur clusters S$_x$ (x = 1,2,4) are preferentially bonded to low coordinated Ti sites.

Visual evidence for the controlled deposition of Li$_2$S on indium tin oxide (ITO), another conductive metal oxide, was presented in a model study by Yao et al. As seen in Figure 7, a glassy carbon planar electrode that was patterned with ITO was used as a current collector for the electro-deposition of Li$_2$S and S$_8$ from a polysulfide electrolyte, by discharge to 1.7 V and recharge to 2.6 V, respectively. After discharge (Figure 7d), the EDX sulfur mapping overlays well with that of indium, indicating the preferred Li$_2$S deposition on the polar oxide due to the much stronger polysulfide/Li$_2$S binding. A similar conclusion can be drawn after charge (Figure 7e).
them within the hosts. Examples of these materials are metal-organic frameworks (MOFs) and MXene phases.

**Metal-organic frameworks.**— Beyond porous carbon, MOFs represent another class of host materials with high surface area and tunable porosity. Because of this, some MOFs, including ZIF-8, and MIL-101(Cr), were used directly as a host material to encapsulate sulfur/polysulfides, and showed promising cycling performance. More importantly, MOFs can trap the soluble polysulfides owing to their binding to the transition metal ions and the functional groups on the surface. A Li-S battery using a mesoporous Cr-based MOF, MIL-100(Cr), achieved a remarkable increase in the capacity retention. Aside from the LiPSs confinement in the meso- and micropores, the improvement also benefits from the oxygen rich surface groups, which provides additional adsorptivity via chemical interactions. Nonetheless, the functional groups in the MOF structure may not always make a positive contribution. For example, the amino groups in NH₂-MIL-53(Al) are unfavorable for the generation and stabilization of the LiPSs due to their soft Lewis-basic character. Moreover, they raise the energy barrier for charge transfer and hinder the ion diffusion by blocking the MOF channels.

Recently, Zheng et al. introduced the Ni-based metal organic framework (Ni-MOF), Ni₆(BTB)₄(BP)₃, as a sulfur host: very significant improvement in cycling stability was achieved. Besides the LiPSs confinement in the pores of the Ni-MOF, the soluble LiPSs are further immobilized by the Lewis acid-base interaction. The Lewis acidic Ni(II) center is inclined to coordinate with a soluble Sₓ₂⁻ anion (soft Lewis base, as axial ligand), which can effectively capture the soluble LiPSs within the cathode, as shown in Figure 8. High capacity retention of 89% was demonstrated after 100 cycles at a rate of 0.1 C. The Lewis acid-base interaction between the open metal sites of the MOF and sulfur was also reported for HKUST-1, in which the Cu(II)–S interactions in the composite resulted in the S 2p peaks shifted to lower energies.

**Two-dimensional MXene phases.**— In spite of their very good polysulfide adsorptivity, the MOFs are highly electronically insulating hosts, resulting in low sulfur utilization, and poor rate performance of Li–S cells. Recently, we reported a new class of sulfur host materials — delaminated MXene phases (Figures 9a, 9b) — that capitalize on a combination of inherently high conductivity and a highly active two-dimensional surface to chemically bind LiPSs by metal-sulfur bonding interactions. The existence of S-Ti-C bonding at the interface, as determined by XPS analysis, is suggestive of strong interaction and chemisorption of LiPSs onto the Lewis acid Ti sites and hydroxyl surface groups, as shown in Figure 9c. These active centres that exhibit strong interaction with LiPSs provide multiple Li₂S nucleation sites. This effectively mitigates the dissolution of LiPSs into the electrolyte and results in very good cycling performance with a capacity fade rate of 0.05% per cycle. Other family members of the
MXene phases (with over 60 members known) having good LiPSs absorptivity as well as high conductivity have also been demonstrated to be highly promising candidates for high performance Li-S batteries.66

Thiosulfate-polythionate conversion to trap polysulfides.— The previously discussed interaction between the host materials and LiPSs rely on surface affinity, either from polar-polar interactions or Lewis acid-base interactions. Recently, we have reported that δ-MnO2 nanosheets chemically trap soluble LiPSs by a new mechanism – thiosulfate-polythionate conversion – which has its foundation in the “Wackenroder reaction” reported for aqueous sulfur species over a century ago.67,68 We demonstrated that this mechanism originates from a redox reaction between MnO2 and the LiPSs formed on discharge. The XPS evidence shows that the surface Mn(IV) oxidizes the Sx2−, thereby forming Mn(II) in the process and decorating the MnO2 nanosheet surfaces with functional thiosulfate groups, S2O32−. These species anchor ‘higher-order’ Sx2− (x > 4) by catenating them into the S-S bond in thiosulfate [O3S-S]2− to form polythionate complexes of the type [O3S-Sx-S]2−, leaving insoluble ‘lower-order’ polysulfides in electrical contact with the MnO2 host, as shown in Figures 10a–10b.67 This curtails active mass loss during the discharge/charge process, suppresses the polysulfide shuttle and provides a good interface for the Li2S deposition, resulting in a Li-S battery with long cycling (up to 2000 cycles; Figure 10c). The high LiPSs adsorptivity of MnO2 contributes to a low self-discharge rate of only 5% irreversible capacity loss over 3 days shelf time. This is far superior to that of materials with low affinity for LiPSs (e.g. Super P carbon, which exhibits a 42% loss under the same conditions).69 Furthermore, the thiosulfate-polythionate conversion may also account in part for the excellent properties of another Li-S host material, graphene oxide, based on observation of the same thiosulfate and polythionate groups on the GO surface after contact with polysulfides.66 The GO is proposed to function in the same manner by oxidizing the polysulfides to surface thiosulfate groups while undergoing partial reduction to graphene.

Chemical Bonding within Polymer Chains

Functional polymers that can anchor sulfur/LiPSs are also of interest as an alternative cathode hosts to realize long-term cycling. Since sulfur can be incorporated into polymer chains using different
Figure 6. (a) A schematic showing the electron density transfer between Li$_2$S$_4$ and TiO$_x$ (yellow = S, green = Li, blue = Ti, red = O). (b,c) Sealed vials of a Li$_2$S$_4$/THF solution (1), and after contact with graphite (2), VC carbon (3) and Ti$_4$O$_7$ (4), immediately upon contact (b) and after 1 h stirring (c); (d–f) High-resolution XPS S 2p spectra of (d) Li$_2$S$_4$, (e) Li$_2$S$_4$/Ti$_4$O$_7$ and (f) Li$_2$S$_4$/VC (black dotted line = experimental data, red line = overall fitted data, solid/dotted lines in other colors = fitted individual components); (g) Data for Ti$_4$O$_7$/S-6 (solid lines + symbols) compared with VC/S-6 (dashed lines) show the much lower concentration of LiPS in solution. (Black = Li$_2$S; blue = LiPS, shown as the sum of Li$_2$S$_6$ and Li$_2$S$_4$; red = elemental sulfur.) Reprinted from Ref. 55.

Figure 7. (a) Schematic illustration of the fabrication of polysulfide-ITO micropattern glassy carbon cathode to show the nature of polysulfide deposition. (b,c) The corresponding SEM images of a fresh ITO micropattern, and Li$_x$S-ITO micropattern, respectively. Scale bar, 20 μm. (d,e) EDX mapping of ITO glassy carbon electrode after discharging to 1.7 V and charging to 2.6 V, respectively, showing clearly patterned distributions of carbon (red), indium (blue) and sulfur (green). Scale bars, 50 μm. Reprinted with permission from Ref. 57.
techniques, a variety of sulfurized polymer composites have been explored in the past decade. These polymer-based studies can be divided into two main categories: sulfurization with conjugated polymers and inverse-vulcanization polymerization.

Sulfurization with conjugated polymers.— Polyaniline (PANi) has been widely studied in Li-S batteries because of its facile preparation, good mechanical stability and good electronic conductivity in its p-doped state. What is often not recognized, however, is that PANi will be in its reduced state in the normal operating voltage window of a Li-S cell, and hence would be highly insulating. Ma et al. developed the very first PANi-sulfur cathode composite for Li-S battery via an in situ chemical oxidative polymerization technique.\(^7\) The conjugated repeating unit of PANi and the amino groups is reported to allow the polymer to be used as an electric conduit and a chemical trap for LiPSs.

Most of the earlier studies of this material simply relied on using PANi as a conductive coating for sulfur to try to improve its conductivity while alleviating the diffusion of LiPSs.\(^71\),\(^72\) A more effective utilization of PANi as conductive matrix to impede the LiPS dissolution was introduced by Xiao et al. where novel three-dimensionally cross-linked S-PANi nanotubes were synthesized via in situ sulfurization at 280\(^\circ\)C.\(^73\) During the sulfurization process, a fraction of sulfur reacted with PANi allowing the polymer backbones to be interconnected with disulfide bonds, whereas the rest remain as elemental sulfur within the structure, as shown in Figure 11a. Therefore, sulfur is both physically and chemically confined within the nanotubes at a molecular level without significantly altering the chemical structure of PANi. Furthermore, some of the disulfide bonds can be split to form dithiolates on discharge, which allows the polymer to expand concurrently to alleviate the mechanical stress. Zhou et al. further improved the performance of such materials by developing a yolk-shell...
Figure 10. (a) A schematic showing entrapment of soluble polysulfides by the MnO2 nanosheet surface via the thiosulfate-polythionate conversion, (b) High resolution S 2p spectrum of Li2S4 after contact with MnO2, showing the appearance of thiosulfate and polythionate; (c) Long term cycling performance of the 75S/MnO2 composite. Reproduced from Ref. 67.

Figure 11. (a) Schematic illustration of the construction and discharge/charge process of the S-PANi nanotubes. Reprint from Ref. 72. (b) Schematic illustration of the synthesis of the S-PANI yolk-shell structure and (c) comparison of the S-PANI core-shell and yolk-shell SEM images after five cycles in cells. Reprint from Ref. 74.

nano-composite of S-PANI with a buffer void space for alleviating the volumetric expansion (Figures 11b–11c).74

Aside from PANi, polyacrylonitrile (PAN) can also form conductive conjugated polyacrylpyridine through pyrolysis in the presence of sulfur at 200–300 °C. Wang et al. discovered that elemental sulfur could be used as a dehydrogenating and doping agent during PAN pyrolysis.75,76 Specifically, the sulfur molecule reacts with PAN to form a heterocyclic polymeric matrix by attaching to the acryl-backbone (Figure 12a), while the sp2-hybridized carbon becomes sp2-conjugated with the cyclized nitrile group.77 The formation of S-S, C-S and C≡C bonds is evidenced by FTIR spectroscopy (Figure 12c).78,79 This structure bypasses the polysulfide shuttle by avoiding the formation of the soluble LiPSs (Li2Sx, 4 ≤ x ≤ 8). During the discharge process, the continuous breakdown of cyclic S-S and C-S bonds results in a mixture of the conjugated polymer and Li2S. The subsequent charging/oxidation process forms delocalized radicals in the polymer backbone that traps Li2S for growth of cyclic sulfur (Figure 12b).77 In order to further improve the conductivity of the overall cathode, activated-MWCNTs and reduced graphene oxide were also added to synthesize a 3D electronically conductive matrix.80,81 However, Doan et al. pointed out that the sulfur saturation point in the pyrolyzed-PAN matrix is roughly 56 wt. % via TGA.82 This applies a limit on the sulfur loading fraction in PAN-based composite materials.

Inverse-vulcanization polymerization.— Inverse vulcanization involves the use of molten elemental sulfur as co-monomer in a free-radical polymerization to afford hyper-branched polymers. Chung et al. depolymerized α-sulfur to a sulfur di-radical species, which co-polymerizes with 1,3-diisopropenylbenzene (DIB) to obtain sulfur-random-DIB (S-r-DIB) with 90 wt. % sulfur content, as shown in Figure 13a.83 Upon discharge, the organosulfur-DIB units go through high-order, low-order and fully discharged stages (species 1, 3 and 5 in Figure 13b), which proceeds along with the conventional sulfur speciation (species 2, 4 and 5 in Figure 13b).84 These organosulfur species act as plasticizers and co-deposit onto the cathode framework along with other low-order LiPSs during discharge. A few other co-monomers, such as diethynylbenzene (DEB),85 oleyamine,86 styrenic
propylenedioxythiophene and 1,4-diphenylbutadiyne (DiPhDY) have also been attempted for inverse-vulcanization. In particular, S-r-DiPhDY has shown good performance with an initial capacity of 1500 mA·h·g⁻¹ and a decay rate of 0.085% per cycle over 800 cycles.

Conclusions and Perspectives

Here we have provided a broad overview of the recent approaches that have been utilized to chemically bind LiPSs in various ways. Modifications of pristine carbons that include graphene oxide, N-doped carbons or grafted amphiphilic polymers have the advantages of being lightweight, high surface area materials, but the mechanical and chemical stability of these modified materials over long-term cycling are under-investigated. Polar-polar interaction with LiPSs realized by using metal oxides has recently been shown to contribute to greatly improved cycling performance. In particular, the demonstrated surface-controlled polysulfide redox behavior and Li₂S deposition on a conductive and polar oxide surface has provided an exciting perspective for not only conventional “contained” cathodes but also catholyte-type Li-S cells. Among different cathode host materials, 2D or 3D carbonaceous supports, such as free-standing carbon nanotube paper or reduced graphene-oxide sponges with advanced electrode configurations, have opened up new possibilities in achieving sulfur loadings up to 10 mg·cm⁻². These free-standing thick carbonaceous electrodes do not require the use of other electrochemical inactive components such as carbon additives or polymeric binders, allowing them to be used directly. However, with increased areal sulfur loading, the cell capacity typically degrades faster than that of a lower loading cell upon long-term cycling. This may be related to the lengthened electrolyte penetration path, cathode structure collapse due to large volume expansion, increased parasitic reactions of largely dissolved LiPSs with lithium anode, and increased anode/cathode resistance. Future work should focus on designing smart cathode architectures...
for high sulfur loading, understanding cell failure mechanisms, and on protecting the lithium anode in order to realize the goal of commercializing Li-S cells.

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