

Challenges and current development of sulfur cathode in lithium–sulfur battery

Chengyin Fu¹ and Juchen Guo^{1,2}



Rechargeable lithium–sulfur (Li–S) batteries have exceptional theoretical capacity; however, the practical applications are still elusive to date due to many critical challenges. This review summarizes the technical issues of the sulfur cathode and the strategies in recent years to address these issues from the aspects of lithium polysulfides sequestration, new mechanism of Li–S reactions, organosulfur cathode materials, functionality of binders, and the role of the electrolytes.

Addresses

¹ Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, United States

² Materials Science and Engineering Program, University of California, Riverside, CA 92521, United States

Corresponding author: Guo, Juchen (jguo@engr.ucr.edu)

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Introduction

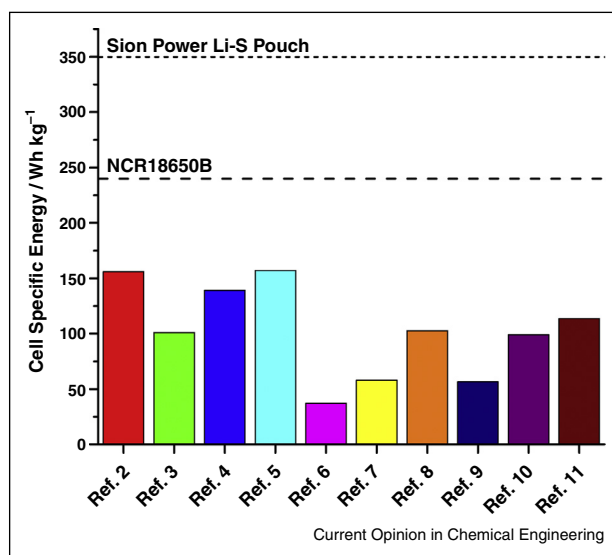
The most intriguing property of Li–S batteries is the assumed high practical specific energy extrapolated from the theoretical value at $\sim 2450 \text{ Wh kg}^{-1}$, which is based on the theoretical capacity of sulfur and Li with a nominal voltage of 2.1 V. As a comparison, the theoretical specific energy of Li-ion batteries is less than 600 Wh kg^{-1} , and the practical specific energy of Li-ion batteries at cell-level is typically 40–50% of the theoretical value. If using the same material-to-cell ratio, the practical specific energy of Li–S batteries could be estimated at around 1000 Wh kg^{-1} , which would be a revolutionary improvement from Li-ion technologies. However, whether Li–S batteries indeed have such a promising future requires closer scrutiny.

Hagen and coworkers reported a detailed analysis on the specific energy of NCR18650B manufactured by Panasonic, one of the state-of-the-art Li-ion batteries [1^{*}]. Their analysis shows that one NCR18650B cell contains

11.4 g anode materials and 17.4 g cathode materials (including all binders and carbon additives), 4.3 g electrolyte and 14.0 g inactive mass. Assuming a Li–S battery has the same inactive mass, the practical specific energy of Li–S batteries can be calculated, as shown in Figure 1, using the published information including specific capacity of sulfur, areal sulfur loading, sulfur content in the cathode, and the amount of electrolyte being used. A number of statements about Figure 1 are as follows: first, the 18650 cylindrical configuration may not be ideal for Li–S batteries for maximum specific energy, and the volumetric energy density cannot be estimated due to the lack of necessary information in the publications. Second, only publications with unambiguous description of electrolyte/sulfur (E/S) weight ratio are included. Third, the reported E/S ratios are all from coin cell configuration, which generally requires more electrolyte than in pouch cells. Therefore the calculation may underestimate the specific energy that can be achieved in pouch cells to some extent. Finally, in addition to the assumption of 14.0 g inactive mass, we also assume 100% excess of Li anode, which is a very optimistic assumption, due to the non-ideal coulombic efficiency of Li deposition-stripping.

Despite these approximations, Figure 1 can illustrate the gap between the current developmental stage of Li–S batteries and expectations for the future. Figure 1 includes the Li–S cell-level specific energy calculated from 10 publications since 2014 with an areal loading of sulfur $\geq 4 \text{ mg cm}^{-2}$ [2–10,11^{*}]. All the calculated cell-level specific energies are not only significantly lower than the benchmark 350 Wh kg^{-1} achieved by a prototype Li–S pouch cell from Sion Power (2.8 Ah, 1260 mAh g^{-1} of sulfur, 25 wt.% carbon content in cathode, and 400% Li excess) [12^{*}], but also below that of the NCR18650B Li-ion cell. Our calculation suggests that the decisive factor resulting in low specific energy is the high E/S ratio used in these publications. To the best of our knowledge, the majority of published Li–S works used E/S ratios higher than 10, which would significantly increase the overall weight of the full cells and thus reduce the practical specific energy. On the other hand, this ratio (electrolyte to cathode) in Li-ion batteries is typically only 1/4. It is worth noting that relatively high E/S ratio may be an inherent requirement in Li–S batteries for two possible reasons: first, the high surface area of the nanoporous cathode structure and second in-depth sulfur utilization by dissolving lithium polysulfides. Nevertheless, minimizing the E/S ratio is crucial to the future of

Figure 1



Calculated cell-level specific energy of Li-S batteries from published works using NCR18650B configuration and inactive components assuming 100% Li excess.

Li-S batteries, and the investigation of practical E/S ratio must be performed in pouch cells assembled with industrial standards.

The brief estimate and analysis above may illustrate a more realistic picture of the current development of Li-S batteries. To achieve high practical specific energy, the three components including the Li anode, electrolyte, and sulfur cathode have to be considered and designed in synergy, and each of them is facing steep challenges. In this review, we only focus on the recent developments of sulfur cathodes from the aspects of lithium polysulfides sequestration, new mechanisms of Li-S electrochemical reaction, cathode materials based on organosulfur compounds, new functionality of polymeric binders, and the role of electrolytes.

Polysulfides sequestration strategies

A significant challenge to Li-S batteries is a complex process during discharge and charge: since sulfur typically exists as cyclo-S₈ molecules, the Li-S electrochemical reaction generates a number of intermediate products named lithium polysulfides (Li₂S_{*n*}, 3 ≤ *n* ≤ 8). Li₂S_{*n*} are soluble in the electrolytes so that they can diffuse into the bulk electrolyte resulting in capacity fading. The dissolved Li₂S_{*n*} also directly reacts to Li anode to form insoluble lithium sulfide (Li₂S) precipitate and lower order polysulfides Li₂S_{*m*} (*m* < *n*). The Li₂S_{*m*} can diffuse back to the cathode (driven by concentration gradient) and being electrochemically oxidized to Li₂S_{*n*} again during charging. Therefore, a steady state during charging,

namely ‘polysulfide shuttle’, can reach between the polysulfides electrochemical oxidation at the cathode and the polysulfides chemical reduction at the anode. The polysulfide shuttle not only severely impairs the coulombic efficiency of the battery but also consuming the active materials. On the other hand, it is recognized that electrolytes capable of dissolving polysulfides are actually required for a functioning Li-S battery with S₈ cathode. The reason is that both S₈ and Li₂S are inferior electrical conductors, so the discharge reaction would be terminated at a shallow state if sulfur covered by an insoluble and insulating sulfide shell. Therefore, exposing the fresh sulfur surface by forming soluble lithium polysulfides is necessary for the in-depth discharge and reversible charge reactions.

The most common strategy to sequester lithium polysulfides is to use a conductive porous medium as the sulfur host [13]. Because of good electrical conductivity and their low weight, porous carbon materials are the most rational choice, although their porous structure and low tap density may not be ideal to maximize the volumetric energy density. Nowadays, it is well recognized that solely relying on the physical adsorption from the carbon hosts is not effective enough to sequester lithium polysulfides. The polysulfides sequestration (i.e. capacity retention) is determined by a dynamic competition between the time scale of two processes: the electrochemical Li-S reaction versus the lithium polysulfides diffusion. Although high discharge-charge currents can accelerate the Li-S reaction to favor the polysulfides sequestration, practical approaches to slow the lithium polysulfides diffusion are required since Li-S batteries should be able to operate at the full range of current. Therefore, the host materials and/or additives must possess strong attraction to the lithium polysulfide species.

In recent years, there have been two emerging approaches to achieve polysulfides attraction: One is to utilize functional groups containing heteroatoms, particularly nitrogen and oxygen, in carbon hosts or additives to attract lithium polysulfides. The most straightforward mechanism is based on the electrostatic attraction between the electronegative heteroatoms (due to the lone pairs of electrons) to the positively charged Li⁺ ions [14–18]. She *et al.* [19] and Park *et al.* [20] independently observed the shift of Li 1s spectrum when electron-donating functional groups are presented using X-ray photoelectron spectroscopy (XPS) analysis on the lithiated sulfur cathodes, indicating the electrostatic attraction. Song and coworkers investigated the polysulfides sequestration mechanism on nitrogen-doped carbon with X-ray absorption near edge structure spectroscopy (XANES) and density functional theory (DFT) computation [21]. Their results suggest that nitrogen atoms promote oxygen-containing functional groups to chemically bond with sulfur, which immobilizes polysulfides in the cathode. Zhang and

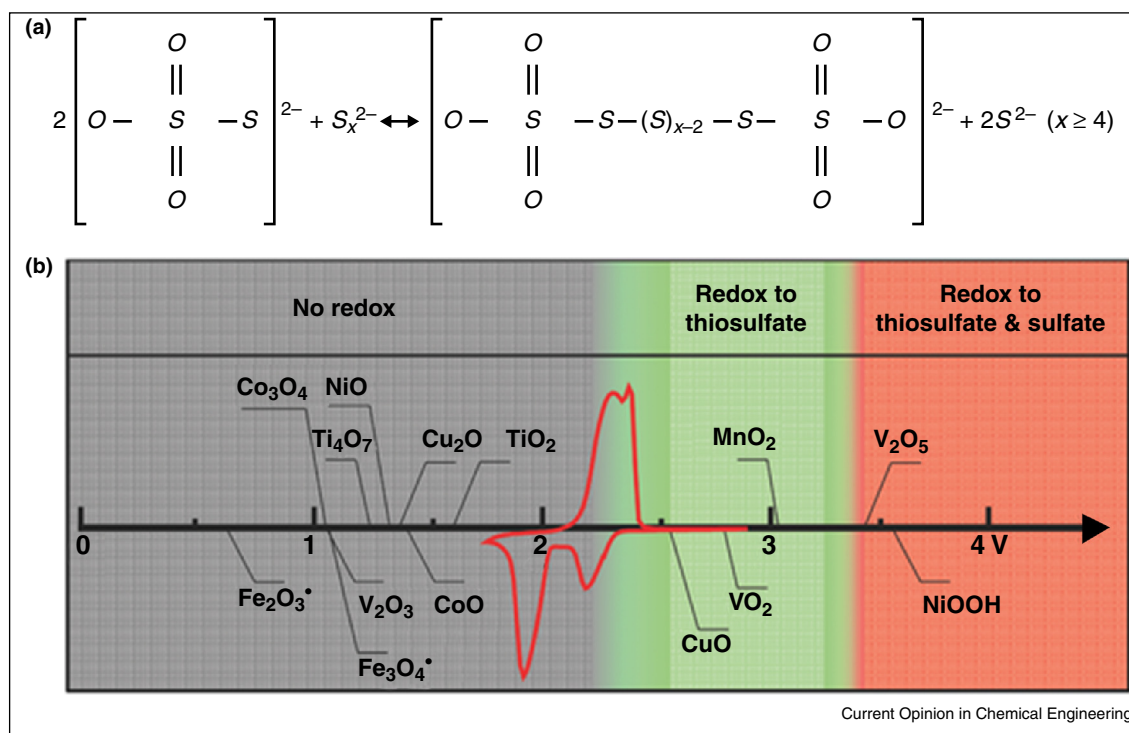
coworkers utilized the oxygen-containing functional groups in graphene oxide as polysulfides immobilizers [22]. According to their *ab initio* calculations and X-ray absorption spectroscopy (XAS) results, epoxy and hydroxyl groups in graphene oxide can enhance the binding of sulfur to the C–C bonds due to the induced ripples.

The second polysulfides sequestration approach is to use certain metal oxides as additives, which were demonstrated as effective polysulfides adsorbers including SiO₂ [23], TiO₂ [24–26], Ti₄O₇ [27,28], NiFe₂O₄ [29], MnO₂ [30,31], and metal organic framework (MOF) [32]. Although polysulfide-adsorbing functionality was found in various metal oxides more than a decade ago [33], the detailed mechanisms were only revealed recently with advanced spectroscopic and computational technologies such as XPS and DFT. It was found that the adsorption of polysulfides on metal oxides is due to the electrostatic attraction between the electronegative polysulfide anions and the positively charged metal sites on the metal oxide surface or the MOF frameworks. Tao and coworkers further discovered that the attraction between polysulfide anions and Magnéli phase titanium oxide (Ti₄O₇) is stronger than that with TiO₂ due to the low coordinated Ti sites on the Ti₄O₇ surface for preferential polysulfides adsorption [28]. In light of the excellent polysulfides

sequestration property of MnO₂ demonstrated in their earlier works [30,31], Liang and coworkers very recently proposed a novel mechanism of polysulfides mediation through the formation of polythionates on the surface of metal oxides based on ‘Wackenroder reaction’ [34*]. Through the proposed reaction, polythionate chains can be covalently tethered by the surface S₂O₃²⁻ groups as shown in Figure 2a. Liang and coworkers further revealed that this mechanism is determined by the redox potential of the metal ions, since the surface metal sites need to be capable of oxidizing polysulfides to form polythionates. The metal oxide surface can be regenerated in delithiation (charge). As shown in Figure 2b, only metal oxides such as MnO₂, VO₂ and CuO within a certain redox potential window can be polysulfide mediators based on this surface redox mechanism.

Between these two different approaches, that is utilizing heteroatoms or metal oxides to sequester lithium polysulfides, the latter approach seems to be preferable. Because the polysulfides are directly attracted to metal oxides either electrostatically or covalently, the binding is strong. On the other hand, the attraction of polysulfides to the heteroatoms is through the connection of Li⁺ ions, thus resulting in relatively weaker binding. Although there is no direct comparison of these two approaches

Figure 2



(a) The proposed polythionates formation mechanism on a transition metal oxide surface; (b) chemical reactivity of different transition metal oxides with lithium polysulfides as a function of redox potential versus Li/Li⁺. Source: adopted from Ref. [34*].

in open literature, our survey of published works indicates better capacity retention of sulfur cathodes using metal oxide additives. However, a potential disadvantage of metal oxide additives is the introduced electrochemical 'inactive' mass. Since the functional sites of metal oxides are located on the surface, the particle size needs to be minimized to reduce the required mass and enhance the polysulfide adsorbing sites.

Solid-state Li-S electrochemical reactions in liquid electrolytes

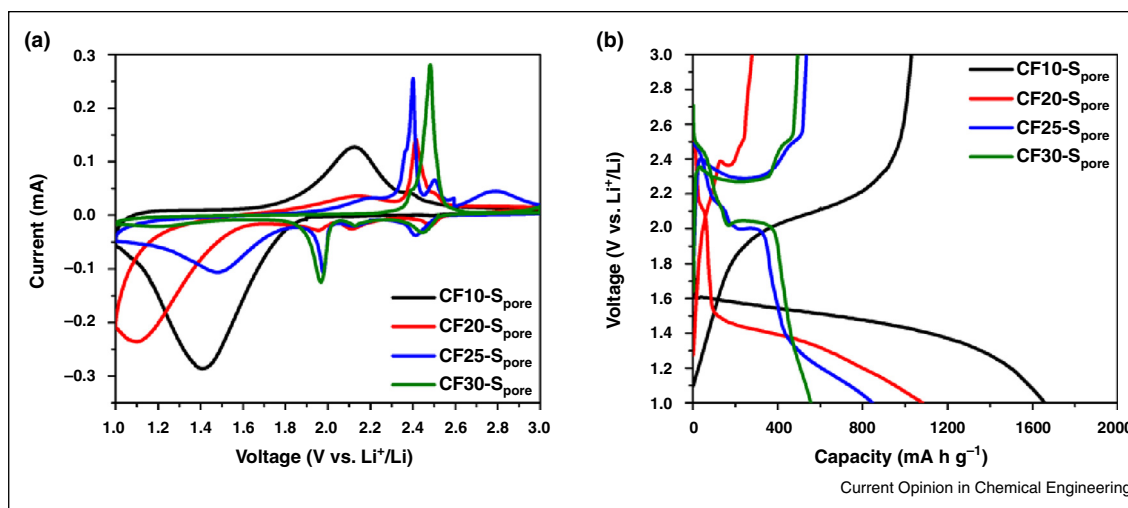
In addition to the fundamentally different electrochemical reactions, one crucial difference between Li-S and Li-ion batteries is that the lithiation–delithiation of conventional sulfur cathodes involves liquid phase reactions; due to the highly insulating nature of sulfur, it has been recognized that electrolytes capable of dissolving lithium polysulfides must be employed to achieve high sulfur utilization involving reactions of dissolved polysulfides. Unfortunately, this prerequisite also severely impairs the cycle stability and is the reason that the majority of the investigations on sulfur cathodes focus on polysulfides sequestration as described above. On the other hand, a solid-state Li-S electrochemical reaction with in-depth sulfur utilization without polysulfide intermediates would be highly desirable. Fu and coworkers recently proposed a new solid-state Li-S electrochemical reaction enabled by the sub-nano confinement of sulfur [35]. Their study demonstrated a clear correlation between Li-S electrochemical characteristics and the size of sulfur confinement; when the size of the confinement was smaller than 1 nm, distinctly different Li-S electrochemical characteristics are demonstrated by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) as shown in Figure 3. Furthermore, such

anomalous behaviors (single pair redox peaks in CV and single sloping plateau in GCD curves) were identical in both tetraethylene glycol dimethyl ether (TEGDME) electrolyte and ethylene carbonate/diethyl carbonate (EC/DEC) electrolyte, which does not work for conventional sulfur cathodes. Their hypothesis is that due to the limitation of the pore size, Li⁺ ions could only enter the pores through desolvation. As a result, Li-S reactions within the sub-nano pores occur in solid-state or quasi solid-state. The small size of the sulfur clusters or molecules in the sub-nano confinement enable in-depth lithiation. Their observed Li-S behaviors are actually consistent with a number of previous investigations using microporous (sub-nano pore size) carbon materials as sulfur hosts [36–38]. The well-accepted mechanism to explain these anomalous Li-S behaviors is that smaller sulfur allotropes (such as S₄) other than cyclo-S₈ are confined in the micropores due to the size limitation so that the low order lithium polysulfides can be directly generated without soluble high order polysulfides [37]. However, whether small sulfur allotropes exist in the sub-nano pores under ambient temperature and pressure is still under debate without unambiguous evidence either way [35]. Nevertheless, the solid-state Li-S reaction mechanism should be valid regardless of the form of sulfur in the sub-nano pores. Also, electrolytes not compatible with conventional sulfur cathodes, particularly the ones based on carbonate solvents, should work with sub-nano confined sulfur due to the desolvation mechanism.

Polymeric organosulfur cathode materials

Polymeric organosulfur is a category of compounds that emerged recently as new sulfur cathode materials. The concept is to crosslink long sulfur chains (cyclo-S₈

Figure 3



CV scans (a) and GCD curves (b) of sulfur confined in different pore sizes including 1.0 nm, 2.0 nm, 2.5 nm and 3.0 nm (denoted CF10-S_{pore}, CF20-S_{pore}, CF25-S_{pore}, and CF30-S_{pore}, respectively) in TEGDME electrolyte. Source: adopted from Ref. [35].

polymerize at temperatures between 100 °C and 200 °C as diradicals) using monomers with multiple polymerizable groups enabled by free radical polymerization. Since the resultant organosulfur polymers consist of mainly sulfur chains and a small portion of polymers as crosslinker, this polymerization method is called ‘inverse vulcanization’; vulcanization refers to the process of crosslinking natural rubber (mainly polyisoprene) with a small portion of sulfur chains as crosslinker. A representative synthesis route of inverse vulcanization and the resultant organosulfur polymer structure is shown in Figure 4a. Monomers that have been used as crosslinkers typically have two or three polymerizable groups including vinyl [39–42], ethynyl [43,44], sulfhydryl [45], and nitrile [46]. The obvious advantage of organosulfur compounds from inverse vulcanization is the high sulfur content. However, also due to the long-chain sulfur network, lithium polysulfides from chain cleavage can still be generated during lithiation. As shown in Figure 4c, the electrochemical behaviors of inverse vulcanized organosulfur polymers are almost identical to those of conventional sulfur cathodes. Therefore, issues originating from polysulfides dissolution may not be effectively addressed.

Another type of polymeric organosulfur compound is synthesized by tethering sulfur to polyacrylonitrile backbones (S-PAN) [47–49]. Its molecular structure is shown in Figure 4b. The structure of S-PAN is fundamentally different from that of the inverse vulcanized organosulfur polymers, that is polymer chains with sulfur crosslinkers (or side chains) versus sulfur chains with polymer crosslinkers. Therefore, its electrochemical behaviors are distinctly different as shown in Figure 4d. More interestingly, the electrochemical behaviors of S-PAN are almost identical to those of sulfur in sub-nano confinement (Figures 3 and 4d), indicating similar lithiation–delithiation processes despite seemingly different molecular/composite structures. One can speculate that the tightly crosslinked structure with shorter sulfur chains in S-PAN compounds strongly resembles that of the sulfur in sub-nano confinement. It is also worth noting that carbonate-based Li-ion electrolytes also work for S-PAN compounds with identical electrochemical behaviors in ether-based electrolytes. Both sub-nano confined sulfur and S-PAN derived compounds demonstrated exceptional cycle stability up to one thousand cycles without capacity decay. However, both materials suffer from the same disadvantages, including low sulfur content and large irreversible discharge capacity in the first cycle, which has not been well understood to date.

New functionality of binders

Polymer binder was often an overlooked component in Li–S investigations, since its traditional role is merely to bind the electrode to the current collector. However, considering the low overall sulfur utilization and

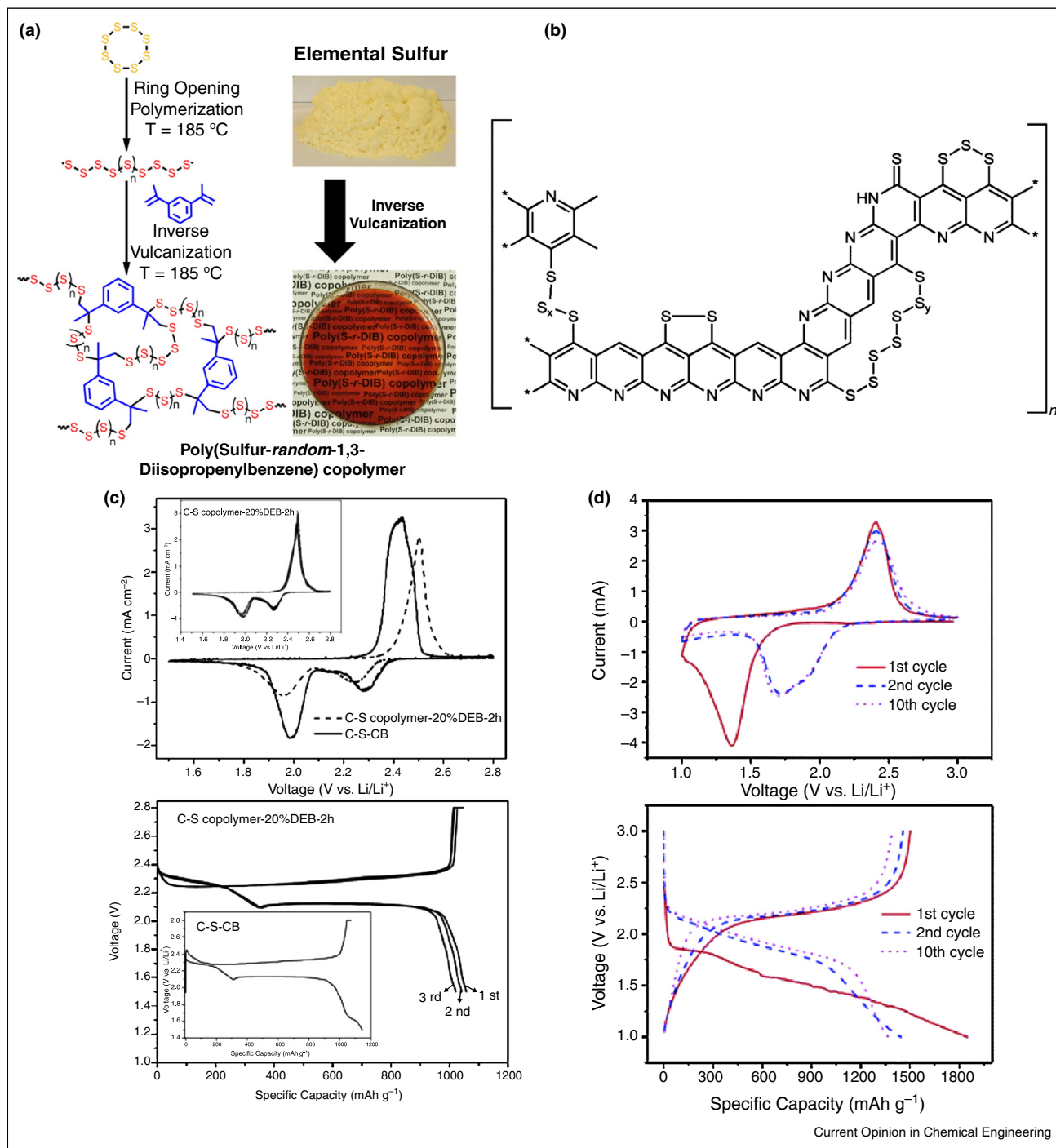
considerable amount of binder in the sulfur cathode, it is highly desirable that polymer binders can serve multiple functions to improve capacity and capacity retention. Early sulfur cathode investigations mostly used polyvinylidene fluoride (PVDF) as binder, adopted from Li-ion batteries. More recently, poly(vinylpyrrolidone) (PVP) largely replaced PVDF as the designated binder owing to its strong affinity with lithium polysulfides through electrostatic attraction between heteroatoms (N and O) and Li⁺ ions as shown in Figure 5a [50]. Poly(ethylene glycol) (PEG), a common polymeric electrolyte based on its affinity to Li⁺ ions with ether linkage, was also demonstrated as an effective binder as it locally modifies the electrolyte system, suppresses passivation of the cathode, and improves reaction kinetics [51]. More recently, poly(acrylamide-co-diallyldimethylammonium chloride) (PAMAC), poly(diallyldimethylammonium chloride) (PDDAC), β -cyclodextrin polycation (shown in Figure 5b) and gum arabic, which is a mixture of polysaccharides and glycoproteins, have also been investigated as binders showing capability to improve the cycle stability of sulfur cathodes [52–55]. It seems that the ionomer binders with positively charged backbones (polycations) such as PAMAC, PDDAC and β -cyclodextrin polycation could be more effective due to the electrostatic interaction between the positively charged backbones and the negatively charged polysulfide anions.

Despite the increasing attentions from the community, investigations on polymer binders are still in their infancy. The polymer binders containing heteroatoms seem to have the same functionality as the sulfur host materials decorated with heteroatoms. Their interaction to polysulfides is through the coulombic attraction to the Li-ions, which may be less effective than the direct attraction to polysulfide anions. On the other hand, two types of ionomer binders, polycations (positively charged backbones) and polyanions (negatively charged backbones), are both studied in the literature and demonstrating improved Li–S performance. However, the negatively charged backbones of polyanions (such as Li-ion exchanged Nafion) should repel polysulfide anions instead of attracting. Moreover, the affinity to polysulfides is only one of the many parameters characterizing the effectiveness of polymer binders: the affinity to carbon (uniform distribution of binders in sulfur cathodes), the swelling behavior in the electrolytes and the electrical conductivity all are important parameters and affecting each other. Therefore, the exact functionalities of the polymer binders must be systematically investigated with careful cross-comparison to optimize their performance.

Role of electrolytes

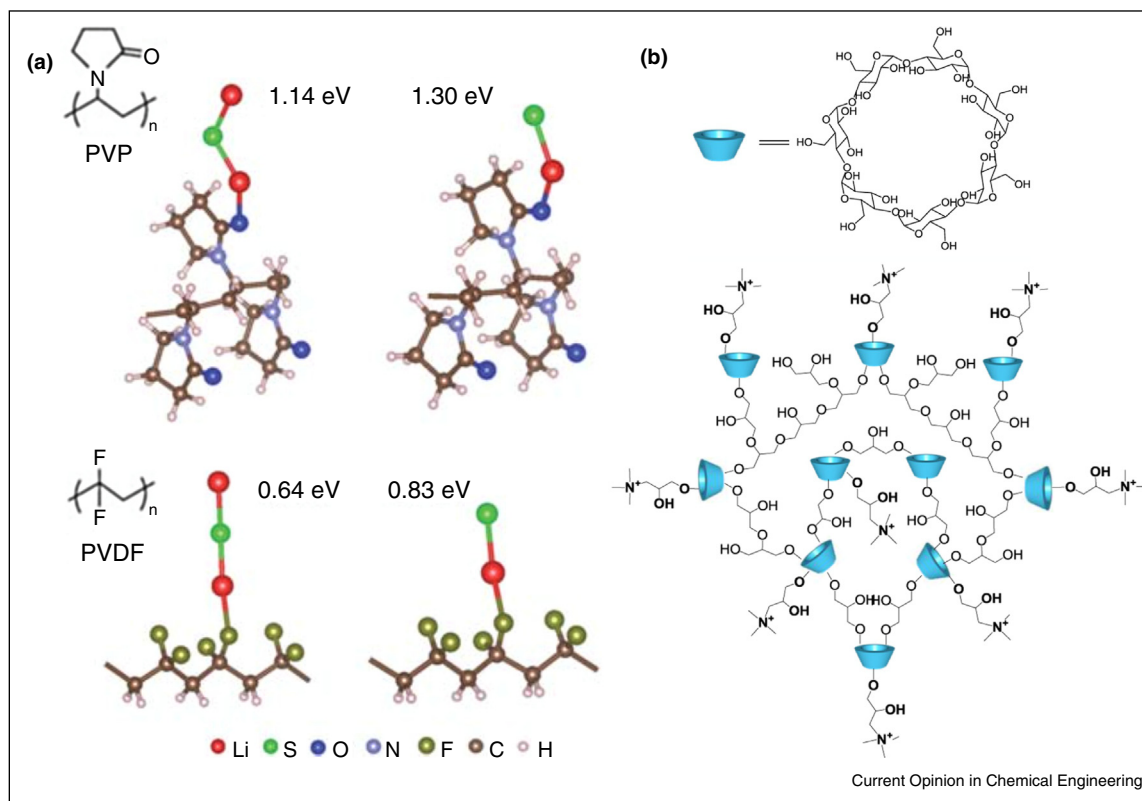
Ether-based electrolytes are commonly used in Li–S batteries due to their good stability, high ion conductivity, and, most importantly, high polysulfides solubility. The

Figure 4



(a) The synthetic scheme of inverse vulcanization using 1,3-diisopropenylbenzene as crosslinker and the resultant organosulfur polymer, adopted from Ref. [40]; **(b)** schematic structure of S-PAN compound, adopted from Ref. [47]; **(c)** typical electrochemical characteristics, CV scans (top) and GCD curves (bottom), of inverse vulcanized organosulfur, which are almost identical to conventional sulfur cathodes, adopted from Ref. [43]; **(d)** typical electrochemical characteristics, CV scans (top) and GCD curves (bottom), of S-PAN, which is distinctly different from inverse vulcanized organosulfur but identical to the sulfur in sub-nano confinement, adopted from Ref. [48].

Figure 5



(a) ab initio simulations indicate the binding energy of PVP to lithium polysulfides is superior to that of PVDF, adopted from Ref. [50]; (b) schematic structure of β -cyclodextrin polycation, adopted from Ref. [54].

most common etheral solvents are TEGDME and a mixture of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL). DME has high polysulfides solubility, and DOL can provide a relatively stable solid electrolyte interphase (SEI) on the lithium anode surface. The most common salt in ether-based electrolytes is lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) because of its high dissociation constant and compatibility with ethers despite the potential corrosion of the aluminum current collector [56]. Lithium hexafluorophosphate (LiPF₆), which is a commonly used salt in Li-ion batteries, is rarely used in ether-based electrolytes due to the lower dissociation in ethers.

Lithium nitrate (LiNO₃) has recently been used as the common additive in electrolytes for Li-S batteries due to its ability to improve cycle stability. Aurbach and coworkers propose that LiNO₃ is able to react with Li anode and form a passivation layer of Li_xNO₃, which prevents further reactions between the Li anode and polysulfides [57]. On the contrary, Zhang has reported that the passivation film on the Li anode grows continuously with the consumption of LiNO₃, and LiNO₃ will be irreversibly reduced on the cathode when the discharge (lithiation) potential is lower than 1.6 V [58].

Ionic liquids (ILs) are another category of electrolyte additives used to suppress the solubility of lithium polysulfides. Yuan and coworkers first suggested using a room temperature ionic liquid, *N*-methyl-*N*-butyl-piperidinium bis(trifluoromethanesulfonyl) imide (PP14-RTIL), as the electrolyte additive [59]. Park and coworkers have investigated several different aprotic mixtures of ILs and lithium salts as Li-S electrolytes [60]. They propose that the solubility of polysulfides is governed by the donor ability of the ILs, and IL electrolytes containing ([TFSI]⁻), bis(pentafluoroethanesulfonyl)amide ([BETA]⁻), and PF₆⁻ anions can effectively suppress the polysulfides solubility. In contrast, tetrafluoroborate (BF₄⁻) and bis(fluorosulfonyl)amide ([FSA]⁻) anions can chemically react with lithium polysulfides. It is also worth noting that addition of ILs may increase the viscosity of the electrolyte, thus undermining the rate performance of the batteries.

A new concept of Li-S electrolytes is 'solvent-in-salt' (SIS), which refers to a high concentration of salt in the solvent. Suo and coworkers reported that SIS electrolytes with high concentrations of LiTFSI (up to 7 M) in DME/DOL could effectively alleviate the dissolution of lithium polysulfides and protect the Li anode by forming lithium

fluoride (LiF) [61]. A similar mechanism was also speculated from the SIS investigation by Kim and coworkers [62]. However, two critical issues of the SIS electrolytes are the relatively high density and the high cost associated with the high quantity of Li salts. The high density of SIS electrolytes could reduce the full cell specific energy. In addition to the conventional roles, novel electrolyte systems can also bring new functionalities. Gordin and coworkers investigated bis(2,2,2-trifluoroethyl) ether as a co-solvent to suppress the self-discharge of Li–S batteries by forming protective layer on the Li anode [63]. Chen and coworkers studied dimethyl disulfide as a co-solvent, which is electrochemically active thus providing significantly improved capacity [64]. It is worth pointing out that the separator also plays an important role in polysulfides sequestration: a recent work by Chang and coworker demonstrated that the commercial separator coated with a layer of single-walled carbon nanotubes on the cathode side could serve as an effective polysulfides barrier [65].

Although current sulfur cathode investigations overwhelmingly use electrolyte solvents with good solubility of lithium polysulfides, Cuisinier and coworkers reported a very interesting study on using a nonsolvent for lithium polysulfides, namely hydrofluoroether (HFE), as a co-solvent for Li–S electrolytes [66]. Their operando XANES results indicated the formation of polysulfides during the lithiation process. However, the low solubility due to the HFE co-solvent effectively limited the polysulfides' mobility to the vicinity of the cathode, thus achieving good cycle stability. It is also worth noting the HFE-added electrolyte resulted in a sloping lithiation potential profile, which is similar to the ones observed in the sub-nano confined sulfur and S-PAN compounds, indicating a quasi solid-state reaction mechanism.

Summary and perspectives

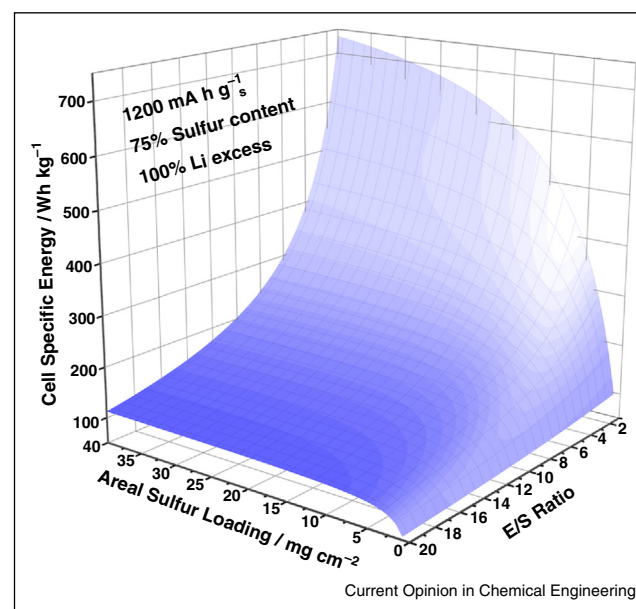
With regard to conventional sulfur cathodes, liquid-phase reactions involving polysulfides are inevitable. Therefore, the cycle stability is essentially dependent on the affinity of the cathode with lithium polysulfides. Cathode components, including the sulfur host, additive, and binder, should all be active to attract lithium polysulfides. Because polysulfide anions are the active species, the sequestration functionality should be specifically designed to directly attract polysulfide anions. Metal oxides show promising properties in attracting polysulfides, but the electrochemically 'inactive' mass associated with their use needs to be minimized. Polycation binders also seem effective to attract polysulfide anions due to the electrostatic attraction, but systematic investigations on binders are currently lacking. In addition to the polysulfides affinity, other properties of polymer binders, including mechanical strength, solubility, and long-term stability in specific electrolytes, are all important to the optimization of the binder systems. Furthermore, active binders, that is polymers capable of reversible lithiation–delithiation

reactions within the Li–S potential window without sacrificing their mechanical properties, may be a concept worth pursuing. All the cathode components also should promote the in-depth sulfur utilization, which is critical to achieving high full cell capacity. Although the theoretical capacity of sulfur is 1675 mAh g^{-1} , the achievable capacity demonstrated by the literature is only typically around 1200 mAh g^{-1} .

Although solid-state Li–S reactions are an attractive concept, the realization of such a concept faces critical challenges, including low sulfur content and large irreversible capacity in the first cycle despite the excellent stability in following cycles. Also, the solid-state Li–S electrochemical potential seems inherently low at $\sim 1.8 \text{ V}$ versus Li/Li^+ [35]. Host material/structure design and synthesis will be critical to achieve the solid-state Li–S reaction with both superior cycle stability and high sulfur content. Meanwhile, novel electrolyte systems, such as the one reported by Cuisinier and coworkers, are critically important and require further investigations to achieve a well-balanced Li–S 'quasi-solid-state' reaction with in-depth sulfur utilization. Moreover, the E/S weight ratio needs to be watched carefully since almost all studies in open literature used an E/S ratio too high to ever achieve full cell capacity to surpass the state-of-the-art Li-ion batteries.

Figure 6 shows the calculated Li–S full cell specific energy as a function of areal sulfur loading and E/S weight ratio. The calculation is based on a 14.0 g inactive mass and 18650-cell configuration with the following optimistic

Figure 6



Calculated Li–S full cell specific energy as a function of areal sulfur loading and electrolyte/sulfur weight ratio.

assumptions: 1200 mAh g⁻¹ specific capacity of sulfur, 75 wt.% sulfur content in the cathode, and 100% excess of Li anode. It is clear that the development of practical high capacity Li-S batteries still has a long winding road ahead to travel.

Acknowledgement

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest

- Hagen M, Hanselmann D, Ahlbrecht K, Maca R, Gerber D, Tübke J: **Lithium-sulfur cells: the gap between the state-of-the-art and the requirements for high energy battery cells.** *Adv Energy Mater* 2015, **5**:1401986.
- Detailed analysis of state of the art NCR18650B Li-ion batteries and extrapolation of the requirements for high capacity Li-S full batteries.
- Yuan Z, Peng HJ, Huang JQ, Liu XY, Wang DW, Cheng XB, Zhang Q: **Hierarchical free-standing carbon-nanotube paper electrodes with ultrahigh sulfur-loading for lithium-sulfur batteries.** *Adv Funct Mater* 2014, **24**:6105-6112.
- Zu C, Manthiram A: **High-performance Li/dissolved polysulfide batteries with an advanced cathode structure and high sulfur content.** *Adv Energy Mater* 2014, **4**:1400897.
- Qie L, Manthiram A: **A facile layer-by-layer approach for high-areal-capacity sulfur cathodes.** *Adv Mater* 2015, **27**:1694-1700.
- Strubel P, Thieme S, Biemelt T, Helmer A, Oschatz M, Brückner J, Althues H, Kaskel S: **ZnO hard templating for synthesis of hierarchical porous carbons with tailored porosity and high performance in lithium-sulfur battery.** *Adv Funct Mater* 2015, **25**:287-297.
- Sun Q, Fang X, Weng W, Deng J, Chen P, Ren J, Guan G, Wang M, Peng H: **An aligned and laminated nanostructured carbon hybrid cathode for high-performance lithium-sulfur batteries.** *Angew Chem Int Ed* 2015, **54**:10539-10544.
- Schneider A, Weidmann C, Suchomski C, Sommer H, Janek J, Brezesinski T: **Ionic liquid-derived nitrogen-enriched carbon/sulfur composite cathodes with hierarchical microstructure – a step toward durable high-energy and high-performance lithium-sulfur batteries.** *Chem Mater* 2015, **27**:1674-1683.
- Zhou G, Paek E, Hwang GS, Manthiram A: **Long-life Li/polysulfide batteries with high sulphur loading enabled by lightweight three-dimensional nitrogen/sulphur-codoped graphene sponge.** *Nat Commun* 2015, **6**:7760.
- Li Z, Zhang J, Chen Y, Li J, Lou X: **Pie-like electrode design for high-energy density lithium-sulfur batteries.** *Nat Commun* 2015, **6**:8850.
- Ding YL, Kopold P, Hahn K, Aken PA, Maier J, Yu Y: **Facile solid-state growth of 3D well-interconnected nitrogen-rich carbon nanotube-graphene hybrid architectures for lithium-sulfur batteries.** *Adv Funct Mater* 2016, **26**:1112-1119.
- Qie L, Zu C, Manthiram A: **A high energy lithium-sulfur battery with ultrahigh-loading lithium polysulfide cathode and its failure mechanism.** *Adv Energy Mater* 2016, **6**:1502459.
- Cathodes with ultrahigh sulfur loading and very low electrolyte/sulfur weight ratio.
- Eroglu D, Zavadil KR, Gallagher KG: **Critical link materials chemistry and cell-level design for high energy density and low cost lithium-sulfur transportation battery.** *J Electrochem Soc* 2015, **162**:A982-A990.
- Technical and economical requirements for Li-S batteries for electric vehicles.
- Ji X, Lee KT, Nazar LF: **A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries.** *Nat Mater* 2009, **8**:500-506.
- Zheng G, Zhang Q, Cha JJ, Yang Y, Li W, She ZW, Cui Y: **Amphiphilic surface modification of hollow carbon nanofibers for improved cycle life of lithium sulfur batteries.** *Nano Lett* 2013, **13**:1265-1270.
- Ma L, Zhuang H, Lu Y, Moganty SS, Hennig RG, Archer LA: **Tethered molecular sorbents: enabling metal-sulfur battery cathodes.** *Adv Energy Mater* 2014, **4**:1400390.
- Wang Z, Dong Y, Li H, Zhao Z, Wu H, Hao C, Liu S, Qiu J, Lou X: **Enhancing lithium-sulphur battery performance by strongly binding the discharge products on amino-functionalized reduced graphene oxide.** *Nat Commun* 2014, **5**:5002.
- Pang Q, Nazar LF: **Long-life and high-areal-capacity Li-S batteries enabled by a light-weight polar host with intrinsic polysulfide adsorption.** *ACS Nano* 2016, **10**:4111-4118.
- Ma L, Zhuang HL, Wei S, Hendrickson KE, Kim MS, Cohn G, Hennig RG, Archer LA: **Enhanced Li-S batteries using amine functionalized carbon nanotubes in the cathode.** *ACS Nano* 2016, **10**:1050-1059.
- She ZW, Wang H, Hsu PC, Zhang Q, Li W, Zheng G, Yao H, Cui Y: **Facile synthesis of Li₂S-polypyrrole composite structures for high-performance Li₂S cathodes.** *Energy Environ Sci* 2014, **7**:672-676.
- Park K, Cho JH, Jang JH, Yu BC, Hoz AT, Miller KM, Ellisona CJ, Goodenough JB: **Trapping lithium polysulfides of a Li-S battery by forming lithium bonds in a polymer matrix.** *Energy Environ Sci* 2015, **8**:2389-2395.
- Song J, Xu T, Gordin ML, Zhu P, Lv D, Jiang YB, Chen Y, Duan Y, Wang D: **Nitrogen-doped mesoporous carbon promoted chemical adsorption of sulfur and fabrication of high-areal-capacity sulfur cathode with exceptional cycling stability for lithium-sulfur batteries.** *Adv Funct Mater* 2014, **24**:1243-1250.
- Ji L, Rao M, Zheng H, Zhang L, Li Y, Duan W, Guo J, Cairns EJ, Zhang Y: **Graphene oxide as a sulfur immobilizer in high performance lithium/sulfur cells.** *J Am Chem Soc* 2011, **133**:18522-18525.
- Ji X, Evers S, Black R, Nazar LF: **Stabilizing lithium-sulphur cathodes using polysulphide reservoirs.** *Nat Commun* 2011, **2**:325.
- Evers S, Yim T, Nazar LF: **Understanding the nature of absorption/adsorption in nanoporous polysulfide sorbents for the Li-S battery.** *J Phys Chem C* 2012, **116**:19653-19658.
- Liang Z, Zheng G, Li W, She Z, Yao H, Yan K, Kong D, Cui Y: **Sulfur cathodes with hydrogen reduced titanium dioxide inverse opal structure.** *ACS Nano* 2014, **8**:5249-5256.
- Yu M, Ma J, Song H, Wang A, Tian F, Wang Y, Qiu H, Wang R: **Atomic layer deposited TiO₂ on a nitrogen-doped graphene/sulfur electrode for high performance lithium-sulfur batteries.** *Energy Environ Sci* 2016, **9**:1495-1503.
- Pang Q, Kundu D, Cuisinier M, Nazar LF: **Surface-enhanced redox chemistry of polysulphides on a metallic and polar host for lithium-sulphur batteries.** *Nat Commun* 2014, **5**:4759.
- Tao X, Wang J, Ying Z, Cai Q, Zheng G, Gan Y, Huang H, Xia Y, Liang C, Zhang W, Cui Y: **Strong sulfur binding with conducting Magnéli-phase Ti_nO_{2n-1} nanomaterials for improving lithium-sulfur batteries.** *Nano Lett* 2014, **14**:5288-5294.
- Fan Q, Liu W, Weng Z, Sun Y, Wang H: **Ternary hybrid material for high-performance lithium-sulfur battery.** *J Am Chem Soc* 2015, **137**:12946-12953.
- Liang X, Hart C, Pang Q, Garsuch A, Weiss T, Nazar LF: **A highly efficient polysulfide mediator for lithium-sulfur batteries.** *Nat Commun* 2015, **6**:6682.
- Liang X, Nazar LF: **In situ reactive assembly of scalable core-shell sulfur-MnO₂ composite cathodes.** *ACS Nano* 2016, **10**:4192-4198.

32. Zheng J, Tian J, Wu D, Gu M, Xu W, Wang C, Gao F, Engelhard MH, Zhang J, Liu J, Xiao J: **Lewis acid–base interactions between polysulfides and metal organic framework in lithium sulfur batteries.** *Nano Lett* 2014, **14**:2345–2352.
33. Song M, Han S, Kim H, Kim J, Kim K, Kang Y, Ahn H, Dou SX, Lee J: **Effects of nanosized adsorbing material on electrochemical properties of sulfur cathodes for Li/S secondary batteries.** *J Electrochem Soc* 2004, **151**:A791–A795.
34. Liang X, Kwok CY, Lodi-Marzano F, Pang Q, Cuisinier M, Huang H, Hart CJ, Houtarde D, Kaup K, Sommer H, Brezesinski T, Janek J, Nazar LF: **Tuning transition metal oxide–sulfur interactions for long life lithium sulfur batteries: the ‘Goldilocks’ principle.** *Adv Energy Mater* 2016, **6**:1501636.
- A novel mechanism of lithium polysulfides sequestration enabled by formation of polythionate covalently tethered on metal oxide surface.
35. Fu C, Wong BM, Bozhilov KN, Guo J: **Solid state lithiation–delithiation of sulphur in sub-nano confinement: a new concept for designing lithium–sulphur batteries.** *Chem Sci* 2016, **7**:1224–1232.
36. Zhang B, Qin X, Li GR, Gao P: **Enhancement of long stability of sulfur cathode by encapsulating sulfur into micropores of carbon spheres.** *Energy Environ Sci* 2010, **3**:1531–1537.
37. Xin S, Gu L, Zhao N, Yin Y, Zhou L, Guo Y, Wan L: **Smaller sulfur molecules promise better lithium–sulfur batteries.** *J Am Chem Soc* 2012, **134**:18510–18513.
38. Zheng S, Han P, Han Z, Zhang H, Tang Z, Yang J: **High performance C/S composite cathodes with conventional carbonate-based electrolytes in Li–S battery.** *Sci Rep* 2014, **4**:4842.
39. Chung WJ, Griebel JJ, Kim ET, Yoon H, Simmonds AG, Ji HJ, Dirlam PT, Glass RS, Wie JJ, Nguyen NA, Guralnick BW, Park J, Somogyi A, Theato P, Mackay ME, Sung Y-E, Char K, Pyun J: **The use of elemental sulfur as an alternative feedstock for polymeric materials.** *Nat Chem* 2013, **5**:518–524.
40. Simmonds AG, Griebel JJ, Park J, Kim KR, Chung WJ, Oleshko VP, Kim J, Kim E, Glass RS, Soles CL, Sung Y-E, Char K, Pyun J: **Inverse vulcanization of elemental sulfur to prepare polymeric electrode materials for Li–S batteries.** *ACS Macro Lett* 2014, **3**:229–232.
41. Griebel JJ, Li G, Glass RS, Char K, Pyun J: **Kilogram scale inverse vulcanization of elemental sulfur to prepare high capacity polymer electrodes for Li–S batteries.** *J Polym Sci Part A: Polym Chem* 2015, **53**:173–177.
42. Arslan M, Kiskan B, Yagci Y: **Combining elemental sulfur with polybenzoxazines via inverse vulcanization.** *Macromolecules* 2016, **49**:767–773.
43. Sun Z, Xiao M, Wang S, Han D, Song S, Chen G, Meng Y: **Sulfur-rich polymeric materials with semi-interpenetrating network structure as a novel lithium–sulfur cathode.** *J Mater Chem A* 2014, **2**:9280–9286.
44. Dirlam PT, Simmonds AG, Kleine TS, Nguyen NA, Anderson LE, Klever AO, Florian A, Costanzo PJ, Theato P, Mackay ME, Glass RS, Char K, Pyun J: **Inverse vulcanization of elemental sulfur with 1,4-diphenylbutadiene for cathode materials in Li–S batteries.** *RSC Adv* 2015, **5**:24718–24722.
45. Kim H, Lee J, Ahn H, Kim O, Park MJ: **Synthesis of three-dimensionally interconnected sulfur-rich polymers for cathode materials of high-rate lithium–sulfur batteries.** *Nat Commun* 2015, **6**:8278.
46. Talapaneni SN, Hwang TH, Je SH, Buyukcakir O, Choi JW, Coskun A: **Elemental–sulfur-mediated facile synthesis of a covalent triazine framework for high-performance lithium–sulfur batteries.** *Angew Chem Int Ed* 2016, **55**:3106–3111.
47. Fanous J, Wegner M, Grimminger J, Andresen A, Buchmeiser MR: **Structure-related electrochemistry of sulfur-poly(acrylonitrile) composite cathode materials for rechargeable lithium batteries.** *Chem Mater* 2011, **23**:5024–5028.
48. Yin L, Wang J, Lin F, Yang J, Nuli Y: **Polyacrylonitrile/graphene composite as a precursor to a sulfur-based cathode material for high-rate rechargeable Li–S batteries.** *Energy Environ Sci* 2012, **5**:6966–6972.
49. Kim J-S, Hwang TH, Kim BG, Min J, Choi JW: **A lithium–sulfur battery with a high areal energy density.** *Adv Funct Mater* 2014, **24**:5359–5367.
50. She ZW, Zhang Q, Li W, Zheng G, Yao H, Cui Y: **Stable cycling of lithium sulfide cathodes through strong affinity with a bifunctional binder.** *Chem Sci* 2013, **4**:3673–3677.
51. Lacey MJ, Jeschull F, Edström K, Brandell D: **Functional, water-soluble binders for improved capacity and stability of lithium–sulfur batteries.** *J Power Sources* 2014, **264**:8–14.
52. Zhang SS: **Binder based on polyelectrolyte for high capacity density lithium/sulfur battery.** *J Electrochem Soc* 2012, **159**:A1226–A1229.
53. Ma Z, Huang X, Jiang Q, Huo J, Wang S: **Enhanced cycling stability of lithium–sulfur batteries by electrostatic–interaction.** *Electrochim Acta* 2015, **182**:884–890.
54. Zeng F, Wang W, Wang A, Yuan K, Jin Z, Yang Y: **Multidimensional polycation β -cyclodextrin polymer as an effective aqueous binder for high sulfur loading cathode in lithium–sulfur batteries.** *ACS Appl Mater Interfaces* 2015, **7**:26257–26265.
55. Li G, Ling M, Ye Y, Li Z, Guo J, Yao Y, Zhu J, Lin Z, Zhang S: **Acacia senegal – inspired bifunctional binder for longevity of lithium–sulfur batteries.** *Adv Energy Mater* 2015, **5**:1500878.
56. Xu K: **Nonaqueous liquid electrolytes for lithium-based rechargeable batteries.** *Chem Rev* 2004, **104**:4303–4417.
57. Aurbach D, Pollak E, Elazari R, Salitra G, Kelley CS, Affinito J: **On the surface chemical aspects of very high energy density rechargeable Li–sulfur batteries.** *J Electrochem Soc* 2009, **156**:A694–A702.
- Discovery of LiNO₃ as an effective Li–S electrolyte additive.
58. Zhang SS: **Role of LiNO₃ in rechargeable lithium/sulfur battery.** *Electrochim Acta* 2012, **70**:344–348.
- Irreversible LiNO₃ cathodic decomposition under 1.6 V versus Li/Li⁺.
59. Yuan LX, Feng JK, Ai XP, Cao YL, Chen SL, Yang HX: **Improved dischargeability and reversibility of sulfur cathode in a novel ionic liquid electrolyte.** *Electrochem Commun* 2006, **8**:610–614.
60. Park JW, Ueno K, Tachikawa N, Dokko K, Watanabe M: **Ionic liquid electrolytes for lithium–sulfur batteries.** *J Phys Chem C* 2013, **117**:20531–20541.
61. Suo L, Hu Y-S, Li H, Armand M, Chen L: **A new class of solvent-in-salt electrolyte for high-energy rechargeable metallic lithium batteries.** *Nat Commun* 2013, **4**:1481.
62. Kim H, Wu F, Lee JT, Nitta N, Lin H-T, Oschatz M, Cho WI, Kaskel S, Borodin O, Yushin G: **In situ formation of protective coatings on sulfur cathodes in lithium batteries with LiFSI-based organic electrolytes.** *Adv Energy Mater* 2014, **4**:1401792.
63. Gordin ML, Dai F, Chen S, Xu T, Song J, Tang D, Azimi N, Zhang Z, Wang D: **Bis(2,2,2-trifluoroethyl) ether as an electrolyte co-solvent for mitigating self-discharge in lithium–sulfur batteries.** *ACS Appl Mater Interfaces* 2014, **6**:8006–8010.
64. Chen S, Dai F, Gordin ML, Yu Z, Gao Y, Song J, Wang D: **Functional organosulfide electrolyte promotes an alternate reaction pathway to achieve high performance in lithium–sulfur batteries.** *Angew Chem Int Ed* 2016, **55**:4231–4235.
65. Chang C, Chung S, Manthiram A: **Effective stabilization of a high-loading sulfur cathode and a lithium-metal anode in Li–S batteries utilizing SWCNT-modulated separators.** *Small* 2016, **12**:174–179.
66. Cuisinier M, Cabelguyen P-E, Adams BD, Garsuch A, Balasubramanian M, Nazar LF: **Unique behaviour of nonsolvents for polysulfides in lithium–sulphur batteries.** *Energy Environ Sci* 2014, **7**:2697–2705.
- Unique Li–S electrochemical properties demonstrated in electrolyte with a non-solvent (hydrofluoroether) of lithium polysulfides as co-solvent.