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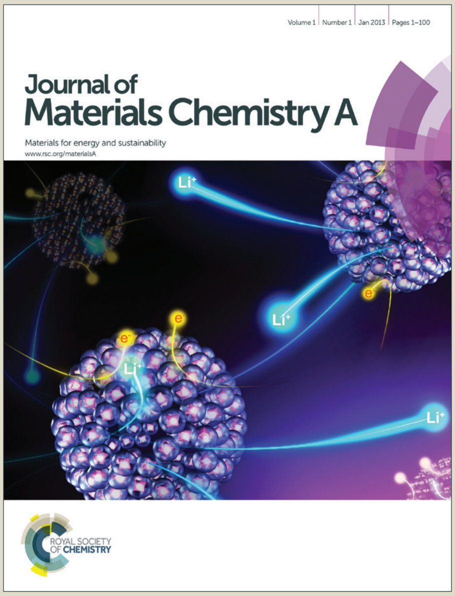

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ARTICLE

Recent progress in polymer/sulphur composites as cathodes for rechargeable lithium-sulphur batteries

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Currently, studies with sulphur electrode materials are focused primarily on carbon/sulphur and polymer/sulphur composites. Because carbon/sulphur composites are a more popular research interest than polymer/sulphur composites, improving the cycle performance of sulphur by using polymers is also a major research focus. Therefore, we review the latest developments for polymer/sulphur composites in Li-S batteries. The various polymer/sulphur composites and their impacts on the electrochemical performance are discussed. Meanwhile, the synthetic approaches toward the various polymer/sulphur composites are also summarised. Finally, the future research directions involving polymer/sulphur composites are addressed.

Introduction

Due to their appealing features, lithium-sulphur cells are a next-generation power source for emerging advanced technologies, such as electric vehicles; the theoretical specific capacity of these cells far exceeds that of the current-generation lithium-ion cells, and the relevant electrochemical parameters are shown in Table 1.[1-3] However, lithium-sulphur cells are not new electrochemical energy storage systems. They have been studied for almost 50 years, beginning when Herbet and Ulam first introduced elemental sulphur as a positive electrode material in 1962.[4] However, few developments with room temperature Li-S batteries have been accomplished in the subsequent decades because several major problems remain unsolved.

Due to its high reactivity of Li metal and its tendency to form dendrites, the use of Li metal as an anode material is associated with numerous safety concerns.[5] Tremendous efforts have been made toward producing lithium-metal free sulphur-based batteries.[6-9] Unfortunately, because the lithium metal anode and the lithium sulphide anode can both react with moisture, a dry and inert environment is necessary when fabricating and assembling electrodes. These could potentially increase the practical industrial cost of Li-S batteries.

The other issue hindering the large-scale uptake of Li-S batteries involves the sulphur cathode. 1) Sulphur is an electronic insulator with a conductivity of approximately 5×10^{-30} S cm^{-1} at 25 °C, leading to low electrochemical utilisation and limited rate capabilities, requiring carbon materials as a conducting additives.[10, 11] 2) One critical issue is the "polysulphide shuttle". When a Li-S cell discharges, the elemental sulphur is not reduced directly to lithium sulphide; instead, a complex and multiphase process within a multistep reaction is required. The elemental sulphur first reacts with Li^+ to generate soluble a high-order polysulphide, Li_2S_n ($4\leq n<8$). Afterwards, the long chain polysulphide undergoes a sluggish process that forms the final products, which are low-order polysulphides (Li_2S_2 and Li_2S). During the entire process, the dissolved PS ions diffuse easily from the cathode to the anode through a concentration gradient. This material can diffuse toward

Table 1 Comparison of a typical lithium-ion cells and lithium/sulphur cells

System	Average discharge potential/ V	Cathode specific Capacity/ mA h g^{-1}	Theoretical specific Energy/ Wh Kg^{-1}	Practical specific energy (obtainable)/ Wh Kg^{-1}	Theoretical energy density/ Wh L^{-1}	Cycle life (current status)
Graphite/LiM_xO_y[a]	3.4-4.0	140-200	500-600	150-200	~1800	300-1000
Lithium/sulphur	2.15	1675	2600	200-700	~2800	<200

(Based on typical lithium-ion cells, LiM_xO_y =$LiCoO_2$, $LiMnO_2$, $LiFePO_4$）

the negative electrode, causing self-charging if the lithium metal electrode is not protected. Consequently, the shuttling phenomenon decreases the active mass utilised during the discharge process and markedly reduces the coulombic efficiency during the charging process.[12, 13] 3) Another issue associated with the sulphur cathode is the variable volume. The active mass of the sulphur (ρ=2.07 g cm^{-3}) expands (~80%) when discharging due to the lower density of Li_2S (ρ=1.66 g cm^{-3}) and contracts again when charging. The performance of lithium/sulphur cells is often limited by the deterioration of the electrode structure and the morphological changes in the active electrode material during cycling.[14]

To address these challenges, we believe that an ideal matrix for sulphur-containing composites must include the following: 1) a high electrical conductivity, 2) an appropriate structure for loading higher sulphur contents and accommodating polysulphides, 3) a stable framework to sustain the strain generated by the volume changes of the active material during cycling, 4) a liquid electrolyte with access to the active material, and 5) an electrochemical affinity for sulphur.

Previously, organic sulphide, which stores and releases energy by forming or breaking S-S bonds, have numerous reported drawbacks, such as low specific capacities, unstable S-C bonds, no electrochemically active functional group to generate a lower energy density, and others.[15] These issues caused a development bottleneck. However, in the past 5 to 10 years, the interest in lithium-sulphur batteries has gradually increased due to the opportunities provided by modern science for designing new nanostructured architectures, overcoming some of the issues with the bulk material counterparts.

In July 2010, the Sion Power Corporation used Li-S batteries in unmanned aircraft and recorded14 days of continuous flight, making it one of the most successful examples and bringing Li-S batteries back to the forefront.

Based on studies from the past several years, the primary efforts toward improving the electrochemical performance of Li-S batteries have emphasised sulphur composites in recent years. These composites can be divided into three categories: carbon/sulphur, polymer/sulphur and metal oxide/sulphur composites. Carbon/sulphur composites have been the most extensively studied and well-reviewed; different carbon structures have their own advantages and limitations.[16-19] In comparison, the soft polymers in polymer/sulphur composites are more flexible and may accommodate more strain. [20, 21] Metal oxide/sulphur composites have been rarely studied due to their heavy weight and poor electronic conductivity. [22, 23] Moreover, polymer/sulphur composites have not been reviewed.

In this account, recent published work focused on polymer/sulphur composites will be discussed. The various polymer/sulphur composites and their impact on the overall electrochemical performance will also be discussed. Meanwhile, the synthetic approaches toward the various polymer/sulphur composites are summarised. Finally, future research with polymer/sulphur composites is proposed.

Polymer/sulphur composites

Polymers are commonly used in electrochemical applications, such as supercapacitors and lithium ion batteries (cathode materials and electrolyte), due to their diversity, functional groups, chemical stability, and abundance.[24-30] A recent boom in polymer-related energy research has been triggered by the emerging focus on Li-S batteries. The merits of employing polymers include the following. 1) Polymers have good mechanical resilience, solving issues associated with volumetric expansion and material pulverisation.[20, 31] 2) Unlike carbon structures, polymers are usually synthesised using chemical oxidation at lower relative temperatures. These processes did not require complicated templates or high-temperature carbonisation (>600 °C).[32, 33] Therefore, different structures of polymer/sulphur composites could be easily realised. 3) Unique polymer backbones with inter- and/or intra-chains could provide strong physical and chemical confinement for elemental sulphur and polysulphides.[34, 35]

Next, the discussion would be given into three categories, classified by conductive mechanism of the polymers, including conductive polymer/sulphur composite, sulphurised polyacrylonitrile and other polymer/sulphur composite.

Conductive polymer/sulphur composites

To support the sulphur effectively, the matrix must contain the sulphur without significantly diminishing the overall practical, properties of the cell, particularly the gravimetric/volumetric energy density. The optimal material must be lightweight, conductive, and able to encapsulate the insulating sulphur completely. Due to their more extensive conjugation, conductive polymers demonstrate excellent electronic conductivity after doping, which decreases the energy gap. Moreover, the formation of a complex conductive network and a unique soft and porous structure in the conductive polymer/sulphur composite could enhance the conductivity of the active material and the absorption of the polysulphide. Obviously, conductive polymers were a superior host material to all but some carbon materials.

In general, conductive polymers, such as polyaniline (PANi), polypyrrole (PPy), polythiophene (PTh) and their derivatives, are extensive studied in sulphur-modified materials.

Polyaniline PANi has been widely used in lithium second batteries due to its availability as a raw material, easy preparation, good stability, reversible redox reactions and high-density charge storage.[36]

Ma and co-workers reported the first use of polyaniline as a host material for sulphur through an in-situ chemical oxidative polymerisation.[37] Consequently, aniline is preferentially polymerised on the surface of the sulphur, forming a layer of polyaniline.

Polyaniline is effective as an electronic conduit to enable redox accessibility toward the sulphur while acting as a framework that encapsulates the redox products. The specific capacity of the first and 30th discharge improved significantly compared to the material containing the bare sulphur. Therefore, the polyaniline/sulphur composite exhibit better electrochemical properties. When using hydrochloric acid as an acidic dopant to generate a polyaniline/sulphur$_{HCl}$ composite, a superior electrochemical behaviour relative to the polyaniline/sulphur$_{HClO4}$ composite.[38]

Another report with polyaniline/sulphur composites utilised PVSM as a template to obtain water-soluble polyaniline, and the electrochemical properties of a material containing this polyaniline as a coating with different thicknesses on sulphur particles was investigated by Xiong *et al*.[39] The conductivity of the positive sulphur electrodes was remarkably ameliorated when using the water-soluble polyaniline coating. This coating layer also confines the soluble polysulphide, improving the cycle life. The best electrochemical properties were observed when 5.8 wt% (PANi) was used. The initial discharge was 1356 mA h g^{-1} with a reversible capacity of 1000 mA h g^{-1} after 50 cycles.

In addition to the common chemical oxidative polymerisation, Zhang *et al*. constructed a barrier layer at one end of the sulphur cathode by electrodepositing PANi.[40] PANi nanowires covering layer with acceptable electronic conductivity provided conductive media for the charge transfer while inhibiting the dissolution of the polysulphides and providing space for conventional sulphur species. The thickness of the coating is an important factor that influences the electrochemical performance of the as-fabricated electrode. An electrodeposition time of 5 min generated PANI-5, which displays the best charge-discharge performance. The novel electrodeposition approach provided an effective and convenient method for improving the electrochemical properties by directly building cathode for Li-S batteries.

However, the conductivity of PANi is not sufficient for inducing charge transfers with the sulphur. Most of the recent strategies have focused on improving the electrochemical performance. Li *et al*. used commercial conductive carbon black as a conductive matrix to prepare sulphur/carbon (S/C) composites through ball-milling and a subsequent heat treatment.[41] A conductive polyaniline (PANI) layer was coated onto the surface of the S/C composites through an in-situ chemical oxidative-polymerisation method. The PANI@S/C composite containing 43.7 wt% sulphur exhibited the optimal electrochemical performance. This performance was attributed to the synergistic effects of the conductive carbon black and polyaniline coating. In addition, a maximum discharge capacity of 635.5 mA h g^{-1} was retained for the PANI@S/C composite after activation, even at an ultrahigh rate (10 C). Unfortunately, the weight fraction of sulphur in the composite was only 43.7 wt%. Similarly, Wu *et al*. obtained a PANi-S/MWCNT composite with 70 wt% sulphur and obtained promising results: the initial discharge capacity was 1333.4 mA h g^{-1} for the PANi-S/MWCNT electrode, and the capacity was 932.4 mA h g^{-1} after 80 cycles.[42]

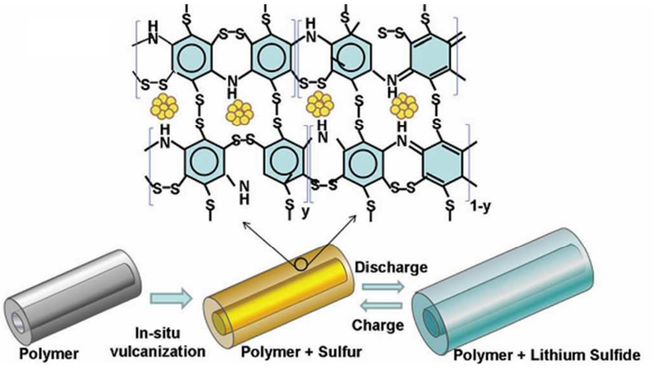

Fig. 1 Schematic illustration of the construction and discharge/charge process of the SPANI-NT/S composite.[35] Reproduced from ref. 35. Copyright 2012 Wiley-VCH.

The advantages of the polyaniline/sulphur composite were highlighted by Xiao and co-workers.[35] Three-dimensional,cross-linked, structurally stable sulphur-polyaniline nanotubes were synthesised through an in-situ vulcanisation process by heating a mixture of PANI-NT and sulphur at 280 °C. During the vulcanisation process, a small amount of elemental sulphur reacts with polyaniline to form a cross-linked stereo SPANI network with both inter- and/or intra-chain disulphide bonds; therefore, sulphur is both physically and chemically confined within the nanotubes at a molecular level, as is shown Figure 1. Moreover, the SEM data strongly suggest that the soft polymer nanotubes can support and accommodate reversible charge/discharge reactions. Interestingly, an initial capacity of 755 mA h g^{-1} at 0.1 C was achieved, but the capacity increased over the next few cycles before decreasing slightly to 837 mA h g^{-1} after 100 cycles. The increase may have occurred because the electrolyte had not completely infiltrated the internal surfaces of the polymers due to the low surface area of the composite. When generating the soluble polysulphide during cycling, the additional porosity enables the better accessibility and capacity. With its special structure, the electrode manifested very stable cycling capacity up to 500 cycles, even at a high discharge rate of 1 C, and retained a capacity of 432 mA h g^{-1} after 500 cycles, which corresponds to capacity retention of 76% after 400 cycles.

After cycling, the structures of the PANi/sulphur composites were a concern in the context of volumetric variation. Zhou *et al*. prepared S-PANi core-shell composites through a chemical oxidative polymerisation method on the surface of sulphur nanospheres, and yolk-shell nanocomposites with a buffer void were prepared after the subsequent a heat treatment, as shown Figure 2a.[43] Compared to the sulphur-polyaniline core-shell species, the yolk-shell nanostructures exhibited better cyclability due to the void inside the polymer shell, which accommodates the volumetric expansion of the sulphur during lithiation. Figure 2b shows that most of the polyaniline shells on the core-shell composite were cracked after five cycles, but the buffer space in the yolk-shell structures accommodated the volumetric expansion. The cycling performance of the right side also revealed a relatively slow decrease in capacity due to its unique morphology.

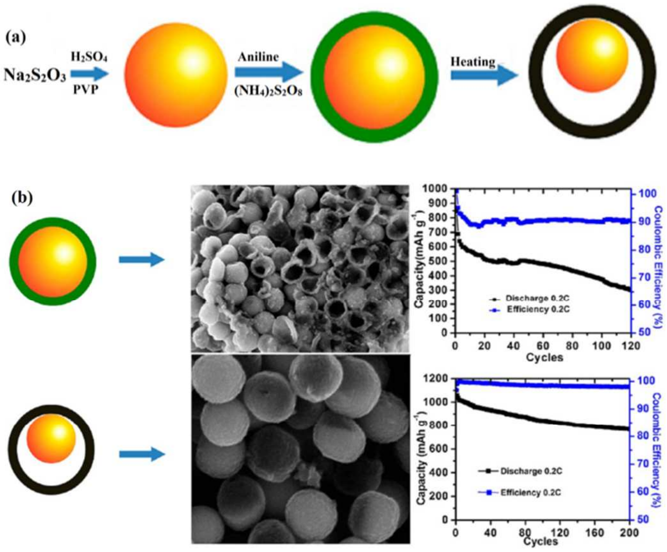

Fig. 2 (a) A two-step synthetic route for a S-PANi composite and (b) Schematic comparison of the S-PANi core-shell and yolk-shell SEM images using the data collected after running five cycles in cells and the long-term cycling performance.[43] Reproduced from ref. 43. Copyright 2013 American Chemical Society.

In addition, an impressive multi-core/shell with conductive network structured CPANI/S@PANI composite was synthesised by Wang *et al*. [44] Surprisingly, the sulphur content reached 87 wt% .When the sulphur loading of the cathode exceeded 6 mg cm^{-2}, the composite cathode with a well-designed structure delivered higher specific capacity and excellent cycling stability, retaining a reversible discharge capacity of 835 mA h g^{-1} after 100 cycles.

Polypyrrole PPy has been the most popular conductive polymer in recent years when coupled to sulphur in a Li/S battery. The first sulphur-polypyrrole composite was constructed by Wang *et al*. to reduce the inert weight of the carbon black while maintaining the conductivity of the electrode. The conductive polypyrrole played multiple roles in the composite when incorporated in a lithium cell, acting as a conducting additive, an active material, and an adsorbent.[45]

Afterwards, different polymerisation processes using oxidising agent, surfactant, doping acid, *etc*. were investigated to form polypyrrole with various morphologies: nanowires,[46] granules,[47] tubules,[47] networks,[48] branches,[49] and hollow spheres.[50] The polypyrrole/sulphur composites were synthesised through chemical deposition or thermal treatment.

Arumugam Manthiram and co-workers contributed a notable development.[32, 51-53] In 2012, they reported a facile approach for synthesising well-shaped bipyramidal sulphur in an aqueous solution in the presence of a cationic surfactant (DeTAB), which can be coated in situ using a layer of stacked conductive polypyrrole nanospheres to form a conductive nanolayer. An SEM image is shown in Figure 3a. After applying a uniform coating of polypyrrole, the sulphur-polypyrrole composite cathode shows better electrochemical behaviour than the material using pristine sulphur because the polypyrrole coating acts as a conductive matrix for electron transfer while prohibiting the dissolution of the lithium polysulphide. In another reports, *p*-toluenesulphonic acid (*p*TSA) was used as an anionic surfactant that provided protons while forming micelles that acted as nucleation sites for sulphur, producing sulphur particles with a uniform spherical shape. These particles were added to an aqueous solution containing (DeTAB) to synthesise nanosized spherical polypyrrole in the same way. The morphology of this material is displayed in Figure 3b. A sulphur-polypyrrole composite cathode with a core-shell structure exhibited an excellent rate capability with good cyclability. The polypyrrole/sulphur composite was also produced by using polypyrrole directly as a surfactant. Although the above-mentioned work demonstrates an effective approach for improving the performance of sulphur cathodes, its poor conductivity still limited the cycle performance. To improve the ion and electron transport of conductive matrix, PAAMPSA, which has a proton conductivity of as high as 1 S cm^{-1} in water, was added to form water dispersible, 3D, mixed ionic-electronic conductor (MIEC). With its uniform dispersion, the PAAMPSA-doped polypyrrole acted as a conductive matrix for sulphur, facilitating ion and electron transfers and capturing intermediate polysulphides within the electrodes to improve the electrochemical performance. Nevertheless, several important factors, including bulk sulphur particles, low sulphur contents, excess conductive agent and a lack of rigidity limited the improvements to the cycling stability of the sulphur composites.

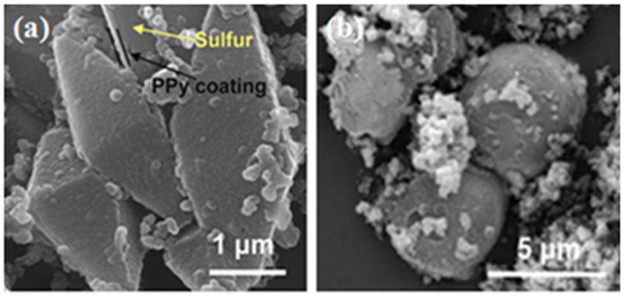

Fig. 3 (a) SEM image of bipyramidal sulphur particles coated with a layer of conductive polymer nanospheres.[51] Reprinted from ref. 51. Copyright 2012 American Chemical Society. (b) SEM image of a few core-shell structured S-PPy composite particles.[52] Reproduced from ref. 52. Copyright 2013 American Chemical Society.

Another approach to improve the electrochemical performance of polypyrrole/sulphur composites involves conductive frameworks such as multi-walled carbon nanotubes (MWCNT). Liang *et al.* proposed a core/shell polypyrrole and MWCNT composite. The MWCNT provides a high electronic conductive network.[54] Meanwhile, the PPy has high surface area, ensuring a uniform dispersion of sulphur. Consequently, the S/PPy-MWCNT composite containing 25 wt% PPy shows the best cycling performance with a discharge capacity of 725.8 mA h g^{-1}.

Last year, a novel dual core-shell structured sulphur composite with multiwalled carbon nanotubes and polypyrrole, which was

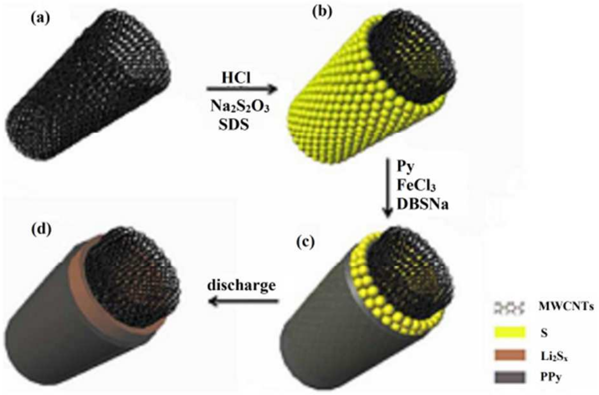

Fig. 4 Schematic illustration of the synthesis and discharge process for a dual core-shell structured MWCNTs@S@PPy composite.[55] Reproduced from ref. 55. Copyright 2013 Royal Society of Chemistry.

called MWCNTs@S@PPy, was introduced as cathode by Wang *et al*. through a facile one-pot method, and the synthesis and discharge process for the ternary composites are shown in Figure 4.[55] A combination of MWCNTs and PPy provided access for the Li^+ ingress and egress necessary for reactions with sulphur while inhibiting the diffusion of polysulphide out of the cathode, reducing the capacity decay. These composites could cycle these MWCNTs@S@PPy electrodes at 200 mA g^{-1} with an initial discharge capacity up to 1517 mA h g^{-1} while maintaining a high and relatively stable discharge capacity of 917 mA h g^{-1} at the 100th cycle.

Graphene has also been employed as another conductive material for its other advantageous properties, such as its large surface area and the ability to tune the hydrophobicity or hydrophilicity through surface functionalisation. Therefore a strategy to combine the in-situ polymerisation of polypyrrole on the surface of graphene and molten sulphur were reported by Wang *et al*. and Zhang *et al*. during the same year.[56, 57] Through capillary action and adhesion, the ternary composites gain advantageous properties, such as a uniform sulphur dispersion, a highly conductive network, and an effective coating layer, improving the cycle performance and rate capabilities significantly.

Lithium sulphide is also a promising cathode material for high-energy lithium ion batteries due to the safety concerns associated with the high reactivity of lithium toward conventional electrolytes.[58] Because Li_2S has both low electronic conductivity and poor ionic diffusivity，Seh *et al*. synthesised a Li_2S-polypyrrole (PPy) composite structure through an *in-situ* polymerisation of pyrrole on Li_2S particles.[59] PPy can be strongly connected to Li_2S to constrain the intermediate Li_2S_n species during cycling due the presence of N in the PPy. The Li_2S-PPy composites exhibit a high discharge capacity of 785 mA h g^{-1} for Li_2S (~1126 mA h g^{-1} of S), which was achieved with stable cycling over 400 charge/discharge cycles to demonstrate the effectiveness of the architecture for the homogeneously encapsulation of Li_2S with a conductive polymer.

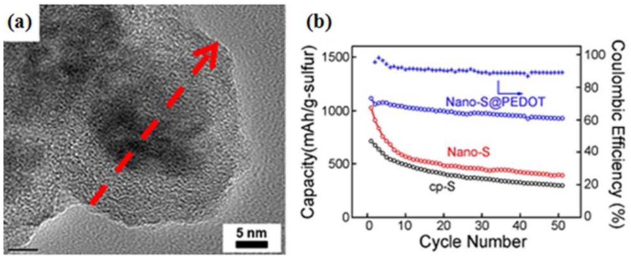

Fig. 5 Schematic illustration of the preparation of S/PEDOT core/shell nanoparticles and their application as cathode materials for Li/S batteries.[60] Reproduced from ref.60. Copyright 2013 Natural Publishing Group.

Polythiophene and its derivatives Although it lacks the simple and scalable preparation of PANi and PPy, PTh has also been used in Li-S batteries due to its good conductivity.

Wu *et al*. circumvented the use of a support for sulphur by simply coating sulphur particles with a conductive polymer, specifically polythiophene, to form core/shell composites.[33] At high magnification, the surface of the S-PTh composite has a flake-like morphology with highly developed porous structures, which significantly enhanced the electrical conductivity of the composite and distributed the electrolyte throughout the electrode. Therefore, when using PTh as a conductive coating, the initial discharge capacity of the S-PTh electrode was 1119 mA h g^{-1}, and the remaining capacity was 830 mA h g^{-1}, delivering better cyclability.

Polythiophene without substituents have led to process difficulties because it is insoluble and infusible; however, its conductivity and stability decrease with increased alkyl substitutions. Therefore, one of its derivatives-poly (3, 4-ethylenedioxythiophene) (PEDOT) became the focus of research.

Chen *et al*. synthesised ultrafine sulphur nanoparticles 10-20 nm in diameter through a membrane-assisted precipitation technique; afterwards, the as-prepared sulphur nanoparticles were incorporated in a polymerisation of PEDOT at room temperature with varying thicknesses. A TEM image of the S/PEDOT core-shell nanoparticles is shown in Figure 5a.[60] The great potential of the nanosizing effect could benefit the electrical conduction and improve the utilisation of sulphur. Moreover, the PEDOT encapsulation restricts the polysulphides diffusion and alleviates the shuttle effect while improving the charge/discharge performance and cycling stability. Figure 5b reveals that the best overall results were obtained for the composites containing 72 wt% sulphur. These materials retained 83% of their capacity, totalling ~930 mA h g^{-1} after 50 cycles at 400 mA g^{-1}, and its cycling performance exceeded that of the pure nano-S particles and cp-S particles.

Li *et al*. disclosed a room temperature, one-step, bottom-up approach toward fabricating monodisperse polymer (polyvinylpyrrolidone)-encapsulated hollow sulphur nanospheres for sulphur cathodes.[21] In addition, modifying the sulphur nanospheres with a surface layer of PEDOT enables high-rate capabilities. Notably, their unique structural characteristics led to impressive cycling stability over 1000 cycles with capacity decay as low as ~0.46 mA h g^{-1} per cycle.

PEDOT was insoluble; therefore, a solution called PEDOT:PSS was prepared by doping with PSS, which is a type of soluble polymer electrolyte. Yang *et al*. obtained a PEDOT:PSS-coated CMK-3/S composite by using a PEDOT:PSS solution with sonication for 1 h.[20] With the PEDOT:PSS coating, the polysulphides could be trapped, minimising their dissolution and the loss of active mass in the cathodes, to significantly improve the performance. The initial discharge capacity reached 1140 mA h g^{-1}, which is 10% higher than that of the bare material, and the discharge capacity stabilised at approximately 600 mA h g^{-1} after 150 cycles.

In general, tremendous progress in conductive polymer/sulphur composites has been achieved in recent years, and many conductive polymer/sulphur composites were summarised, as shown in Table 2. However, improvements to conductive polymers/sulphur composites through direct combination methods was limited due to several problems, such as the poorer conductivity of sulphur relative to carbon, low sulphur contents, insufficient rigidity, *etc*. Three major strategies were explored as follows: 1) structural stabilisation through chemical interactions, 2) adding carbon materials as conductive frameworks, and 3) preparing special morphologies with conductive polymers/sulphur composites. Therefore, optimised morphologies and structures, different combined methods, and interactions between sulphur and conductive polymers remain the primary focus of further investigations.

Table 2 Summary of various polymer/sulphur composites

Classification	Polymerisation	Method	Sulphur content (by weight)	Current density	Discharge Capacity (mA h g^{-1}-S)		References
					Initial	After *n*th cycle	
PANi							
SPAn	CO(HCl)	(Na_2S+S+DMF+PANi) 120-130 °C 24h		0.2 mA cm^{-2}	980	403(20th)	34
PANi-5	Electrodeposition	Common sulphur electrode then electrodeposited PANi		320mA g^{-1}	~1300	725(100th)	40
PANi@S/C	CO(HCl)	Polymerisation on the surface of C-S composite	43.7%	10C		635.5(200th)	41
PANi-S/MWCNT	Situ CO(HCl)	Rapid polymerisation on the surface of S/MWCNT	70%	100mA g^{-1}	1334.4	932.4(80th)	42
SPANI-NT/S	CO(DL-tartaric acid)	(S+PANi-NT) Solvent evaporation+ Sulphur melt +vulcanisation	62%	0.1C	755	837(100th)	35
SPC		PANi-C+ 155 °C Sulphur melt +280 °C	58%	0.2C	1150	732(100th)	61
C-PANi-S@PANi	CO(HCl)	(C-PANi+$Na_2S_2O_3$+ HCl) then polymerisation	87%	0.2C	1101	835(100th)	44
PPy							
S-PPy	Situ CO	Situ CO after ($Na_2S_2O_3$+DeTAB+ HCl)	63.3%	0.2C	864	634(50th)	51
S-PPy	CO	$Na_2S_2O_3$+ PPy+ HCl	64%	0.5C	820	~600(50th)	32
S-PPy	CO	Situ CO after ($Na_2S_2O_3$+*p*TSA + HCl)	65%	0.2C	961	~600(50th)	52
S-MEIC	CO(PAAMPSA)	$Na_2S_2O_3$+ MIEC+ HCl	75%	0.1C	968	>700(50th)	53
S/T-PPy	self-degraded template	Sulphur melt	30%	0.1mA cm^{-2}	1151	650(80th)	31
S-PPy	CO(CTAB as template)	Sulphur melt	66.7%	0.1mA cm^{-2}	1222	570(20th)	46
S@H-PPy	CO(SiO_2 as template)	Sulphur melt	48%	0.1C	1426	620(100th)	50
S-CNT-PPy	Situ CO	Polymerisation after (CNT+TX-100+ $Na_2S_2O_3$+oxalic acid)	60.3%	50 mA g^{-1}	~1250	600(40th)	62

S/PPy-MWCNT	CO	Polymerisation on the surface of MWCNT + Sulphur melt	70%	0.1mA cm^{-2}	1303	725(100th)	[54]
S/PPy/MWNT	CO	Polymerisation on the surface of MWCNT + Sulphur melt	52.6%	0.1C	~1500	960(40th)	[63]
MWCNTs@S@PPy	CO	Polymerisation after deposition on the surface of MWCNT	68.3%	200 mA g^{-1}	1517	917(60th)	[55]
nano-S/PPy/GNS	CO	Polymerisation on the surface of GNS+ sulphur melt	52%	0.1C	1415.7	641(40th)	[57]
S-PPy/graphene	CO	Polymerisation on the surface of Graphene+ Sulphur melt	50%	160 mA g^{-1}	831.8	600(60th)	[56]
PTh							
S-PTh	CO	polymerisation on the surface of sulphur	71.90%	100	1119.3	830(80th)	[33]
PEDOT							
Nano-S@PEDOT	CO	polymerisation on the surface of sulphur after solvent evaporation	72%	400	1117	930(50th)	[60]
PEDOT:PSS-coated CMK-S		CMK-S bath sonicated in PEDOT:PSS solution	<50%	0.2C	1140	600(150th)	[20]

(CO represents chemical oxidation, and the bracketed information represents the acidic dopant)

Sulphurised polyacrylonitrile

The above-mentioned polymers have conductive properties because they are sufficiently conjugated; therefore, plain polyacrylonitrile could not transport electrons because it lacks conjugation. Nevertheless, polyacrylonitrile could form conductively conjugated polypyridinopyrdine through pyrolysis at 200-300 °C, inducing nitrile cyclisation, dehydrogenation, conjugation, crosslinking, *etc*., as shown in Figure 6. After the low temperature pyrolysis, polyacrylonitrile became a viable support for composite electrode materials.[64]

In 2002, elemental sulphur was dehydrogenised and vulcanised at 300 °C with a polyacrylonitrile precursor under nitrogen.[65] At the appropriate temperature, the sulphur reacted with the PAN to form a heterocyclic polymer matrix with S-S or S-H bonds in the side-chain, while the C-C bonds of polyacrylonitrile become C=C bonds and the nitriles cyclise. A possible thermal reaction and the molecular structure of the resultant oligomer are shown in Figure 7a, while the lithium storage mechanism is shown in Figure 7b. However, the operating voltage was approximately 1.75 V, as shown in Figure 7C. The discharge potential hysteresis should have been related to the amount of energy necessary to dissociate the sulphur from the

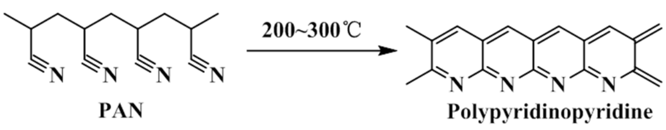

Fig. 6 The molecular structure of low temperature pyrolysis product.[64]

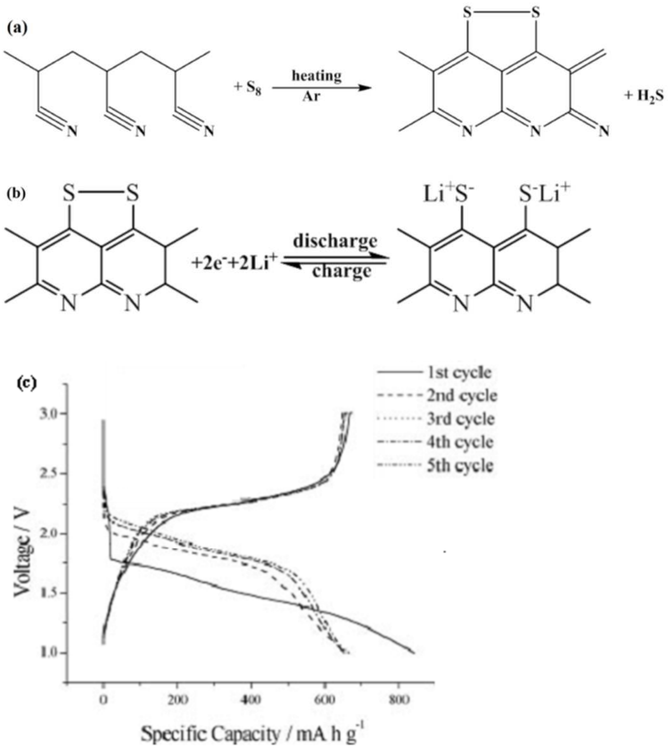

Fig. 7 a) The reaction mechanism for sulphurising the polyacrylonitrile. b) Lithium storage mechanism for the sulphurised polyacrylonitrile. c) Discharge-charge curves for the PAN/sulphur composites.[65]

complex bond. However, the composite, when used as a cathode material, showed good electrochemical performances with an initial discharge capacity of 850 mA h g^{-1} (calculated as the whole electrode), sulphur utilisation as high as 90%, and a reversible capacity of 600 mA h g^{-1} after 50 cycles. Due to its unique molecular structure, the composite could suppress the dissolution of polysulphides in the electrolyte, preventing the deterioration of the electrode during cycling and increasing the utilisation of sulphur. Concurrently, the polymer framework could enhance conductivity of the sulphur electrode. Moreover, the volume changes and self-discharge during discharge/charge were distinctly decreased to prolong cycle life of the cathode materials.

The charge and discharge characteristics of lithium batteries with sulphur composite cathodes were investigated by He *et al*. in 2007.[66] The obtained differential capacities revealed that the discharge process showed voltage plateaus at 2.10 V and 1.88 V, while the charge process also presented voltage plateaus at 2.22 V and 2.36 V. Moreover, the composite imparted intrinsic safety against overcharging in lithium batteries. Even when discharged to 0 V, this material still demonstrated highly reversible capacity.

To improve the conductivity and stability of the materials, ternary composites were prepared by adding higher carbon materials such as MWCNT and graphene, respectively.[67, 68] A novel *p*PAN-S@MWCNT core-shell composite material was obtained, as shown in Figure 8.[67] The establishment of an effective electronically conductive network and unique core-shell structure in the composite significantly improved the cycle and rate performances of the sulphur-based electrodes. After 50 cycles, approximately 85% of the initial reversible discharge capacity of 697 mA h g^{-1} could be retained, which was a ~250 mA h g^{-1} higher capacity than the composite without MWCNT.

Later, graphite oxides (GO) were introduced as a conductive network by Wang *et al*. [68] The acrylonitrile was polymerised on the surface of the as-fabricated graphite oxides (GO) before adding sulphur and undertaking the final pyrolysis to form pPAN-S/GNS composites. The homogenous dispersion and integration of GNS in the composite creates a three-dimensional (3-D) nanoscale current collector while reinforcing the structural stability, leading to the outstanding electrochemical performances when incorporated as a cathode material for rechargeable lithium/sulphur batteries. The pPAN-S/GNS nanocomposite with ~4 wt% GNS and 47 wt% sulphur exhibited a reversible capacity of 1500 mA h g^{-1}-S; specifically, the sulphur use ratio reached 90%.

Another novel approach toward improving the electrochemical performance of S/PAN binary composites was reported by Zhang *et al*.[69] Particles of $Mg_{0.6}Ni_{0.4}O$ were used as additives, generating a sulphur/polyacrylonitrile/$Mg_{0.6}Ni_{0.4}O$ (S/PAN/$Mg_{0.6}Ni_{0.4}O$) composite through wet ball-milling. After discharge-charge cycling, a significant reduction in charge transfer impedance was observed and attributed to the $Mg_{0.6}Ni_{0.4}O$ additive, leading to high sulphur utilisation and excellent reversibility. During the second cycle, the cell had a capacity of 1223 mA h g^{-1}-S and retained approximately 100% of this value over 100 cycles at 0.1 C, maintaining a coulombic efficiency of approximately 100%.

PAN/sulphur composites exhibited good stability and overcharging tolerance. However, various factors affect the total energy density, such as low sulphur contents, poor conductivity, low tap density, and low discharge plateaus. Therefore, many attempts have been made to prepare new nanostructured ternary PAN/sulphur composites using new methods and optimised conditions.

Other polymers

Other polymers, such as poly-ethylene glycol and polydopamine have been applied in sulphur containing composites to achieve good dispersion, adhesion, and affinity, in addition to the two types of polymers, conductive polymers and polyacrylonitrile, which conducted directly or indirectly, mentioned above.

Polyethylene glycol In recent years, polyethylene-glycol (PEG) played a significant role in rechargeable Li-S batteries as an additional coating on the surface of carbon/sulphur composites and as a source during liquid deposition, generating p- AB@S[70], CMK-3/S[71], SWCNT@S[72], Graphene/S[73] composites and others.

One different strategy for preparing PEG/sulphur composites used PEG as a cationic dopant for polypyrrole, as reported by Wu *et al*. PPy/PEG was polymerised in situ through chemical oxidation on the surface of S/A-CNT (aligned carbon nanotubes), which underwent a thermal treatment after ball milling, as shown in Figure 8.[74] In this case, PEG played two different roles to improve the performance of the sulphur-based electrodes. On the one hand, PEG trapped the polysulphide species by providing a highly hydrophilic surface with a chemical gradient, preferentially solubilising the polysulphides instead of the electrolyte. On the other hand, PEG also acted as a cationic dopant in PPy that stabilised the structure of the PPy

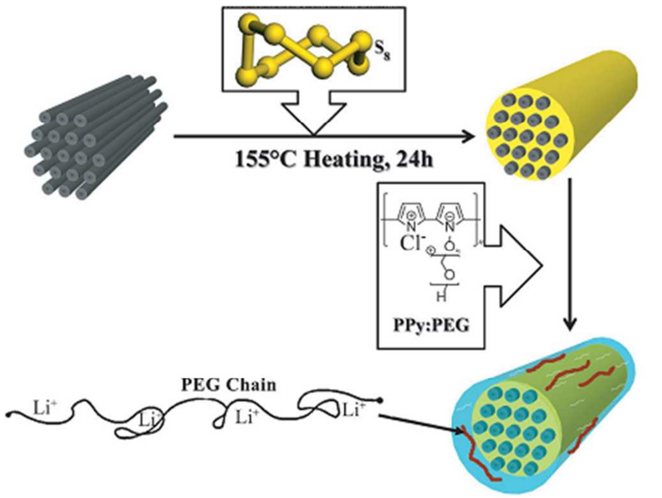

Fig. 8 Synthesis of the PPy/PEG-modified composites.[74] Reproduced from ref. 74. Copyright 2013 Wiley-VCH.

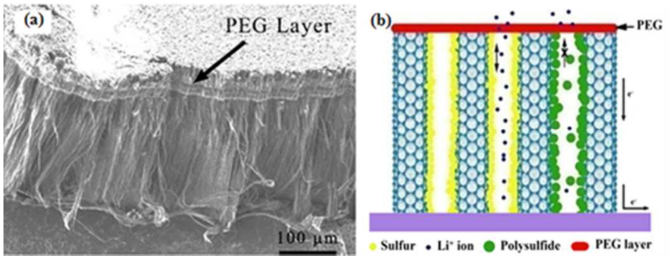

Fig. 9 (a) SEM image of the sulphur-coated CNT cathode with a PEG barrier. (b) A schematic representation of the aligned sulphur-coated CNT electrode with a PEG barrier layer used for highly efficient sulphur cathodes.[75] Reproduced from ref. 75. Copyright 2013 Elsevier.

polymer chain, which had a high surface area. The electrochemical performance of the PPy/PEG-S/A-CNT composite exceeded that of the unmodified S/A-CNTs. The cathode exhibited a high initial specific capacity of 1355 mA h g^{-1} and, after 100 cycles, obtained a reversible capacity of 924 mA h g^{-1}. This cathode could also work at a very high current density (8 A g^{-1}) with the retention rate of 88% after 100 cycles.

Another interesting example by Huang *et al*. revealed that highly efficient sulphur cathode materials constructed by combining aligned sulphur-coated carbon nanotubes (CNTs) with a polyethylene glycol (PEG) barrier at one end (Figure 9).[75] The authors attributed the excellent electrochemical behaviour to two factors: first, the aligned CNT framework provided conductive pathways for electronic and ionic transport, enabling rapid reaction kinetics. Second, the exposed area of sulphur was reduced, and the dissolution of the polysulphides into the electrolyte was greatly attenuated after coating with the PEG barrier layer. Therefore, the PEG-coated cathode showed high cycle stability due to its special structure. In the $LiNO_3$-free electrolytes, a low degradation of 0.38% per cycle over 100 cycles at 0.1 C was obtained.

Polydopamine Polydopamine, due to its strong adhesive properties, has become popular for use in binder and carbon-coating materials in Li-ion batteries.[76-80] This material was also employed in cathode materials for rechargeable Li-S cells.

Polydopamine (PD)-coated S nanosheets (NSs) were used as active materials, while carboxylic acid functionalised multiwall carbon nanotube (MWCNT-COOH) were used as conductive additives; in addition, poly(acrylic acid) (PAA) was used as a binder, forming stronger covalent bonds through amide bond cross-linkages between PD/MWCNT-COOH and PD/PAA, as shown in Figure 10.[81] Therefore, all of the individual components in the electrode were firmly integrated to stabilise the entire structure. Consequently, the discharge capacity retention rate after 500 cycles reached 89.5% at 1 A g^{-1} with a 3% volume expansion.

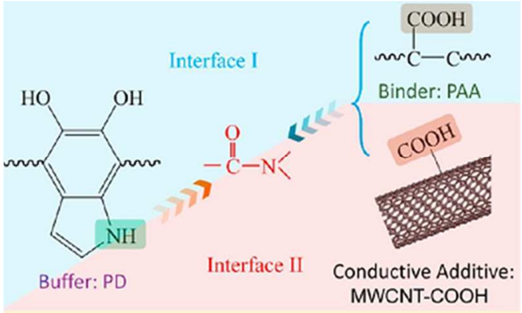

Fig. 10 Schematic for the formation of an amide bond between PD and PAA (denoted interface I) and PD and MWCNT-COOH (denoted interface II).[81] Reproduced from ref. 81. Copyright 2013 American Chemical Society.

Polymer/sulphur Composites Synthesised through Various Methods

Currently, various methods have been proposed for nanostructured sulphur cathodes, and the developments can be divided into two categories based on the sulphur source: 1) a physical method using elemental sulphur, such as mechano-fusion, thermal, and solvent evaporation methods. 2) An oxidative or reductive sulphidation in raw materials in other valence states, such as Na_2S_x、SO_2、$Na_2S_2O_3$, *etc.*, could be performed while adding acid to form elemental sulphur through oxidation or reduction. The details are shown in Table 3.

Moreover, polymers were often polymerised using monomer in solution under relatively facile condition. Compared to carbon/sulphur materials and metal oxide/sulphur materials, the one-step methods used to fabricate polymer/sulphur composites are easier.

Table 3 Various Methods for producing sulphur containing composites

Method	Process	Bind	Characteristic	References
Mixing	Mixing materials by magnetic stirring	Weak		82
Ball milling	Mechanical ball milling	Medium	High-energy ball-milling	14
Thermal treatment	One step heating：155 °C	Strong	Suitable for mesoporous material	71 83
	Two step heating：150-200 °C；200-300 °C	Strong	Removed superficial sulphur on the surface	84 85
	Sulphur vaporisation	Very strong	Molecular infiltration	86
Solvent exchange	Adding sulphur containing saturated solution into another solution	Strong	At room temperature	87

Solvent evaporation	S dissolved in CS_2 and removed CS_2 by heating	Strong		88 35
Liquid deposition	$S_x^{2-} + 2H^+ \rightarrow (x-1)\ S + H_2S$	Strong	Producing hazardous H_2S gas	89 90
	$SO_2+2S^{2-}+4H^+=3S\downarrow+2H_2O$	Strong		91
	$S_2O_3^{2-}+2H^+=S\downarrow+SO_2+H_2O$	Strong	The fewest chemicals	92 73
	$SO_3^{2-}+2S^{2-}+6H^+=3S\downarrow+3H_2O$	Strong		93
Chemical reaction-deposition then thermal treatment	$S_x^{2-} + 2H^+ \rightarrow (x-1)\ S + H_2S$ followed by thermal treatment：160 °C	Very strong	Existence of C-S and O-S bond	19, 94

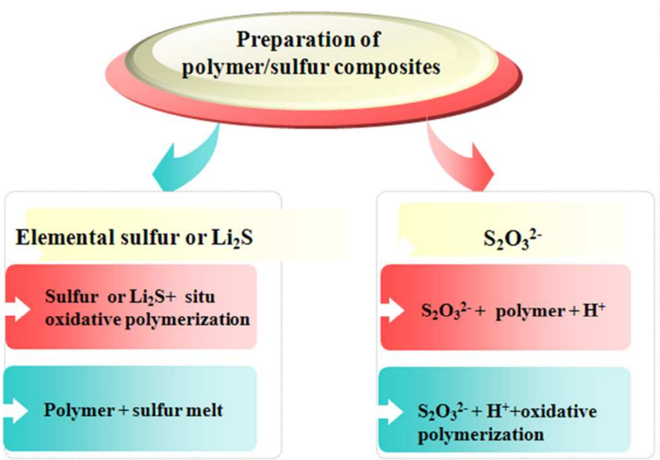

Fig. 11 Summary of various methods used for producing polymer-sulphur composites.
($S_2O_3^{2-}$ was an example using oxidative or reductive sulphidations)

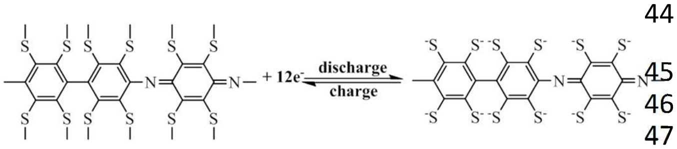

Fig. 12 The possible configuration and reaction of the SPAn.[34]

In addition, the methods used to produce polymers/sulphur composites are plentiful; the production of polymers/sulphur composites is exhibited in Figure 11. Typically, no chemical interactions occur between the sulphur and the modified materials. However, due to the varieties of functional groups and diverse methods, all types of surfactants could be added. Therefore, inter and/or intra-chain bonding could chemically confine sulphur further.

Zhang *et al*. prepared polyaniline (CPAn) by doping HCl during a classical chemical oxidation.[34] After the mixture of Na_2S, sublimed sulphur and DMF were refluxed at 100 °C under nitrogen, CPAn was added to the mixture with magnetic stirring at 120-130 °C. The final product was named SPAn; this material had a polyaniline main chain with 2 four-member rings containing S–S bonds on the side chains of the aniline, according to the characterisation data for the polymer. A possible reaction of the electrode material is shown in Figure 12.

In addition, the SPANi-NT/S composites also contained some S-S bonds linking the polyaniline molecules.[35] These bonds helped immobilise the sulphur atoms to improve the utilisation of the active materials and chemical trapping of polysulphides. These merits offer exciting opportunities for designing sulphur cathodes through chemical interactions.

Conclusions and outlook

The major obstacles hindering the use of elemental sulphur as a cathode material include poor conductivity, polysulphide shuttling and volumetric expansion, which restrict commercialisation. Recently, considerable progress has been made toward viable polymer/sulphur composites. Compared to other mainstream materials such as carbon materials and metal oxides, polymers played a significant role in composites for the following reasons:

1) A 3D conductive network was formed to maintain intimate contact between the particles and to increase the conductivity of the active materials.
2) The soft and porous structures could trap the polysulphides.
3) The abundant functional groups facilitated the impregnation of the electrolyte.
4) The outside coating layer could maintain good physical confinement.
5) Chemical interactions may have occurred, stabilising the sulphur atoms.
6) The observed affinity and adhesion could integrate the entire electrode.

In addition, simple and diverse approaches can be used to obtain various polymers. Therefore, polymers are promising candidates for hosts during the design of lithium–sulphur battery cathodes. However, several drawbacks remain, such as poor conductivity relative to carbon materials and insufficient rigidity. In addition, several fundamental factors are suggested for rationally designing advanced polymer/sulphur composites: 1) reducing the size of the sulphur particles as soon as possible to generate a uniform dispersion across the entire composite and 2) increasing the sulphur content in the cathode while maintaining good conductivity.

Further investigations should focus on the following:

1) Search for polymers with higher electrical conductivities.
2) Choose polymers or co-polymers with suitable pore volumes and frameworks to maximise the sulphur loading and strongly confine the polysulphides.
3) Utilise special functional group or good affinities to enhance the stability of the cathode materials during cycling.
4) Optimise the morphology and structure of the polymer/sulphur composite to improve the electrochemical behaviour. Sometimes, adding small amounts of carbon materials can help maintain the flexible or rigid carbon scaffold and improved conductivity. Notably，novel methods for combining sulphur and polymers should be further employed at nanosize levels.
5) Investigate the mechanism of the interaction between the sulphur and the polymers, and assess the long-term stability of polymers in organic electrolytes.

Finally, we acknowledge that innovations at the negative electrode to reduce dendritic growth are also critical; however, with the above-mentioned considerations in mind, sulphur is unquestionably a viable cathode material after continued studies using good preparation technologies and suitable electrolyte. Li-S energy storage systems with high energy densities, excellent efficiencies and long cycle lives should be provided in the near future.

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