



Multi-functional separator/interlayer system for high-stable lithium-sulfur batteries: Progress and prospects

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abstract

The development of advanced energy storage systems is of crucial importance to meet the ever-growing demands of electric vehicles, portable devices, and renewable energy harvest. Lithium-sulfur (Li-S) batteries, with the advantages in its high specific energy density, low cost of raw materials, and environmental benignity, are of great potential to serve as next-generation batteries. However, there are many obstacles towards the practical application of Li-S batteries such as the electrical insulating nature of sulfur, the volume expansion during lithium insertion, and the shuttle of soluble polysulfide intermediates that induces severe degradation of the cell performance. In this review, the progresses of multi-functional separators/interlayers in Li-S batteries are highlighted. The introduction of multi-functional separators/interlayers with unexpected multiple functionalities is beneficial for better sulfur utilization, efficient polysulfide diffusion inhibition, and anode protection. Multi-functional separator system with ion selective/electrical conductive polymer, sp^2 and porous carbon, metal oxide modified separators, as well as interlinked free-standing nanocarbon, micro/mesoporous carbon, and other conductive interlayers have been proposed. The biomass derived materials was also included as interlayer for advanced Li-S batteries. These novel Li-S cell configurations with multi-functional separators/interlayers are especially suitable for Li-S batteries with high capacity, high stability, and high-rate performance. The opportunities of high-performance separators/interlayers and their applications in next-generation Li-S batteries were also involved. New insights on the role of working separators/interlayers in practical Li-S cells should be further explored to obtain the principle and process for advanced components for energy storage devices based on multi-electron conversion reactions.

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1. Introduction

The supply and usage of energy at an affordable expense of environment damage is one of the most important challenges for human society. Although fossil energy has been powering the development of the society, the limited reserves of fossil energy and its impact on the pollution motivated the alternative clean energy applications. Energy storage systems are one important component for the usage of these intermittent clean energies. Only with cheap and efficient energy storage system, such as high-performance electrochemical energy storage systems, can clean sustainable energy be widely applied. Meanwhile, advanced energy storage system also draw great attention as one key technical cornerstone for booming demands in electric vehicles and portable devices [1–3]. With the rapid improvement of the performance of the electronic devices, the batteries have become the bottleneck for the overall portable devices. Similarly, the status of high-energy-density battery also limited the driving range of electric vehicles and broad applications of bulk energy storage systems for renewable energy harvest.

Among various battery systems, lithium ion batteries have dominated the market of high-energy-density batteries in portable devices for more than 20 years, and are currently the optimized choice for electric vehicles. However, as the performance of lithium ion batteries is approaching their theoretical limits, there is little room for improvements in its electrochemical performance [4,5]. Meanwhile, the relative high cost and unexpected safety issues of lithium ion batteries also hindered the large scale applications in electric vehicles. The research and development of next generation of batteries with higher energy density and lower cost are urgently needed [6–8].

Lithium-sulfur (Li-S) battery system with ultrahigh theoretical energy density is therefore considered as one of the promising candidates [9,10]. Metallic lithium, as the grail in electrochemical energy storage, has the lowest reduction potential in the electrochemical series and a high specific capacity of 3860 mAh g⁻¹. Sulfur, as one high earth abundant element, is in vogue for promising multi-electron conversion chemistry. When employed as cathode material, it possesses a theoretical specific capacity of 1675 mAh g⁻¹. An ultrahigh theoretical energy density of 2600 Wh kg⁻¹ can be achieved by sulfur cathode against metal lithium anode. Moreover, the low cost of sulfur as a redundant byproduct in petroleum industry ensured the low cost of Li-S batteries. These features make Li-S batteries competitive in next-generation batteries. However, there are huge challenges for their practical applications [11–14].

The research on Li-S system has long been stuck in place due to the complexity of the system. The electrical insulating nature of elemental sulfur makes it difficult to electrochemically utilize sulfur in batteries. With the pioneered work by incorporating mesoporous carbon into the sulfur cathode from Nazar and co-workers, a high performance and rechargeable cathode is fabricated [15]. The recent development in nanotechnology, especially the fabrication of high conducting nanocarbon materials, brings great progress in the design of sulfur cathode [9,11,15–19]. The introduction of robust cathode scaffolds also benefits to endure the volume fluctuation between sulfur and lithium sulfide state

[20]. Besides, the Li-S batteries also suffer from so called “shuttle effect” induced by the complex phase transition [21,22]. The multi-electron electrochemical pathway gives rise to the ultrahigh capacity of sulfur cathode, while also brings complex phase transition during electrochemical cycles. During the multi-electron electrochemical reactions, active sulfur materials turn into soluble polysulfides and solid-state lithium sulfide/disulfide. The shuttle effect was induced by the diffusion of high-order polysulfides into the electrolyte, and their parasitic reactions with metallic lithium anode to form low-order polysulfides without power output. The shuttle effect not only causes the low coulombic efficiency of Li-S cells, but also leads to the loss of active sulfur in anode surface, separator and other dead space in a cell, which is one of the major reasons for the rapid capacity fading in Li-S batteries. Several strategies have been employed to limit the diffusion of polysulfides and their parasitic reactions with Li anode. A family of conductive scaffolds (e.g. micro/meso-porous carbon [23–28], hollow nanostructures [29–32], sp² carbon of carbon nanotubes (CNTs) and graphene [33–35], MXene [36], conductive polymers [37,38], as well as their hybrids [39–41]) were proposed in the cathode. The introduction of polysulfide absorbers are also effective to partially confine the diffusion of polysulfides [42]. Other protective additives like LiNO₃ are also incorporated to avoid the side reactions between lithium metal and polysulfides [43].

The novel battery configuration in Li-S system is another strategy to accommodate the special property induced by the multi-electron reactions [12]. As the polysulfides dissolved in electrolyte, the diffusion of polysulfides towards anode side is inevitable in routine cell configurations [44]. The emerging researches in the field of separators and interlayers contribute to the significant improvement in the electrochemical performance of Li-S system. The capability of modified separators and interlayers to trap/block polysulfides significantly reduces the parasitic reactions, and their ability to reactive dead sulfur also helps to improve the cyclic stability of Li-S cells. In this Review, we present the recent progresses regarding the advanced separator and interlayer system for Li-S batteries. The novel separators with polymer, carbon, and oxide as well as interlayers with a family of novel components were involved. Future challenges and opportunities in this field are also involved.

2. Multi-functional separator system for Li-S battery

Separator is one essential part in an electrochemical cell with the vital role to prevent internal short-circuit and maintain the diffusion pathway for ions [45]. Porous polymer separators are suitable and efficient to meet these requirements in routine lithium ion cells. However, the multi-electron electrochemical reaction generates polysulfides in a Li-S cell. This degrades the performance of a battery by parasitic reactions of polysulfides with anode lithium metal or by irreversible decomposition due to its metastability and forming “dead” sulfur-containing species [46]. In fact, separator is a complete screen between cathode and anode side. The separator is one perfect platform for modification that can introduce novel cell configuration for Li-S batteries.

Recent progresses in advanced separators are aimed at the high-stable Li-S cells by: (i) shielding the diffusion of polysulfide to suppress the shuttle effect; (ii) reactivating the deposited dead sulfur-containing species; and (iii) inhibiting the dendrite growth in the lithium metal surface. Various functional layers, including polymers, carbons, oxides, and their composites, have been applied to controllably modify the separators for better battery performance.

2.1. Polymer-modified multi-functional separators

With the distinct difference in positive and negative charge of lithium cations and polysulfide anions, the use of ion selective separator is a straight idea. It is expected that the ion selective separator can block the diffusion of polysulfides while maintain lithium ion transfer pathway for electrochemical reactions.

A lithiated Nafion ionomer was introduced as functional separator in Li-S cells by Jin et al. [47]. The transference number of lithium ions is calculated to be 0.986, which indicates that polysulfide anions can hardly diffuse through the Nafion ionomer. The coulombic efficiency of the cell with lithiated Nafion ionomer reaches 97% with an electrolyte without LiNO_3 , which also indicates a successful inhibition of shuttle effect. The capacity retention within 50 cycles are 69% and 46% for cells with Nafion ionomer separator and normal porous polypropylene (PP) separator, respectively, corresponding to a cyclic decay rate of 0.62 and 1.08%/cycle. While the Nafion ionomer film are still thick and bring considerably large resistance to the battery system. The lithium ion conductivity in Nafion ionomer is $2.1 \times 10^{-5} \text{ S cm}^{-1}$, about two orders of magnitudes lower than liquid electrolyte. This induces an increased polarization from 0.2 to 0.35 V, which degraded the energy efficiency of the Li-S cell. Recently, a Nafion-enveloped sulfur composite cathode, in which the Nafion layer is formed on the sulfur skin, covering its surface and edge while not restricting the porosity, was proposed by Song and co-workers for enhanced cycling stability of Li-S batteries [48].

Nafion is highly efficient to build an ion selective layer. Therefore, it comes to the idea of using Nafion layer to build composite separator system for a double-layer separator with very high ion selectivity and high lithium ion transfer capability. An efficient polysulfide ion shield by the incorporation of thin Nafion layer onto conventional PP separator was proposed by our group (Fig. 1a) [49]. With a simple coating-drying process, a thin Nafion layer with an areal loading amount of 0.7 mg cm^{-2} was attached onto the PP matrix. The sulfonate-ended perfluoroalkyl ether groups on the functional separators were inter-connected. The $-\text{SO}_3^-$ groups coated channels allow ion hopping of lithium ions but reject the hopping of S_n^{2-} [50]. In this case, lithium ions transfer freely and no significant increase in polarization and electrochemical impedance is detected on the cell with the ion selective separator. Both high coulombic efficiency of over 95% and high cyclic stability of 0.08%/cycle decay rate were achieved within a long test of 500 electrochemical cycles. The self-discharge of the Li-S cell was also retarded since the shuttle constants decreased and spontaneous reactions between polysulfides and Li metal was inhibited [51]. Another important result was also reported by Bauer et al. that Nafion was casted onto Celgard 2500 support very homogeneously to form a functional separator (Fig. 1b) [52]. A low loading amount of 0.25 mg cm^{-2} of lithiated Nafion was achieved for high coulombic efficiency and good rate capabilities. With the lithiation of Nafion thin film, no significant influence on polarization was observed. This work opens up a new route for modified separator in Li-S cells to render double-layer separators with multi-functions by the rational incorporation of components. This film can also be applied in room-temperature Na-S batteries

[53,54]. The lithiated Nafion separator is also applied as a ion selective electrolyte for Li-S cells, which exhibits significantly enhanced cyclability compared to the batteries with the routine organic electrolyte integrated porous membrane [55].

Different polymers with ion selective properties were also adopted in a modified separator system. Jin et al. introduced lithium perfluorinated sulfonyl dicyanomethide (Li-PFSD) with an ion selective function group of $(-\text{SO}_2\text{C}(\text{CN})_2\text{Li})$ as functional ionomer for Li-S cells [56]. Cells with Li-PFSD ionomers exhibit superior performance compared with Li-Nafion ionomer, especially in the high-rate capability, which are mainly resulted from the improved lithium ion conductivity of Li-PFSD ionomer against Li-Nafion ionomer. Ion selective polymer modified separators were also fabricated by the layer-by-layer assembly of poly(allylamine hydrochloride) and poly(acrylic acid) (Fig. 1c) [57]. By the permselectivity of polymer layer and the improved wettability, the coulombic efficiency approaching 100% and a high discharge capacity of 1418 mAh g^{-1} was achieved. Plasma-induced modification for separator was also proposed, which can be applied to alter the surface functional groups or trigger the co-polymerization. By oxygen-plasma treatment, lots of electro-negative oxygenic functional groups such as carbonyl and hydroxyl groups were generated on the surface of PP separator. The oxygen plasma modification played a critical role in improving the wettability of separator and increased the electrical insulating properties, which contributed to a higher stability of Li-S cells [58]. An asymmetric porous separator with polysulfide barrier layer was also designed through a one-step plasma-induced graft of styrene sulfonate onto the surface of PP separator. The presence of sulfonate groups on the surface of PP separator led to a much higher coulombic efficiency of the Li-S cells compare with those obtained with normal separators [59].

Functional polymer layers on a membrane determine the surface property of a composite separator, which further affect the electrochemical properties of Li-S cells. Kim et al. introduced a mussel-inspired polydopamine (PD) coating layer onto a polyethylene (PE) separator to suppress the Li dendrite growth by uniform Li ionic flux and wet-adhesion (Fig. 1d) [60]. PD layer was uniformly coated onto routine porous separator. The Li^+ flux was uniformed through the enhanced wetting with electrolyte by the uniform PD layer attached to the polymer matrix, which prevented the locally enrichment of lithium ions and the continuous growth of Li dendrites. The wet-adhesion between PD and lithium metal surface also prevented the growth of Li dendrites by the release of surface tension of lithium metal surface. With PD incorporated separator, the morphology of Li metal surface exhibited more round and suppressed morphologies of Li dendrites. PD-modified separator was also reported by Li et al. [61] and Zhang et al. [62], with the coating of PD layer onto routine separator surface by auto-oxidization and self-polymerization of dopamine monomers. The PD-modified separator benefits the electrochemical performance of Li-S cells by turning the surface from conventional hydrophobic surface to hydrophilic one and increasing the electrolyte uptake amount. The cell with PD modified separator presented a discharge capacity of 1217 mAh g^{-1} at initial cycle and 1020 mAh g^{-1} at 30th cycle, corresponding to a cyclic decay rate of 0.53%/cycle within 30 cycles. In comparison, the decay rate of cell with bare separator was around 1.9%/cycle. The hydrophilic surface of separator also reduced the charge-transfer resistance of the Li-S battery, which was helpful to enhance the cell performance, especially the high-rate capacitance.

Very recently, a size- and ion-selective transport can be achieved using microporous separators fabricated from polymers of intrinsic microporosity (less than 1.2–1.7 nm). Such novel separator was proposed by Helms and co-workers [63] to retard the crossover of polysulfide intermediates. There was 500-fold enhancement of polysulfide

blocking ability of the separator with ~ 0.8 nm than the mesoporous Celgard separators with ~ 17 nm pores.

2.2. Carbon-modified multi-functional separators

Carbon materials are widely applied in cathode materials as conductive scaffolds for Li-S batteries [12,18,64–66]. By the facile modification of a separator with carbon, the diffusion of polysulfide species towards the anode side was trapped. Moreover, the conductive and porous carbon layer is helpful to reactivate the dead sulfur species in a separator and facilitate the complex reactions by forming one upper current collector on the top surface of cathode materials.

Manthiram research group have carried out a serial of pioneer researches in this research field. A light-weight SuperP-coated separator was proposed for high-stable Li-S cells, which was

fabricated by the slurry-coating process of commercial conductive carbon black on one side of a commercial PP separator (Fig. 2a) [67]. The SuperP coating is cost-efficient and the casting process only includes isopropyl alcohol solvent, and the related fabrication process is facile and adaptable for scaling up. By the suppression of shuttle effect and facilitate the upper electron transfer, such SuperP modified separator contributes to both dynamic and static cycle stability. Dynamically, the cell presented a high initial discharge capacity of 1400 mAh g^{-1} for pure sulfur cathode and a high reversible capacity of 828 mAh g^{-1} after 200 cycles at 0.2 C, corresponding to a low cyclic decay rate of 0.20%/cycle. The carbon coating layer was also found effective in limiting the self-discharge properties of Li-S cells with 0.19% per day over a 3-month period. Zhang and co-workers [68] also employed the SuperP coated separator for Li-S batteries with high coulombic efficiency of nearly 90% without the addition of LiNO_3 additive. The reasonable

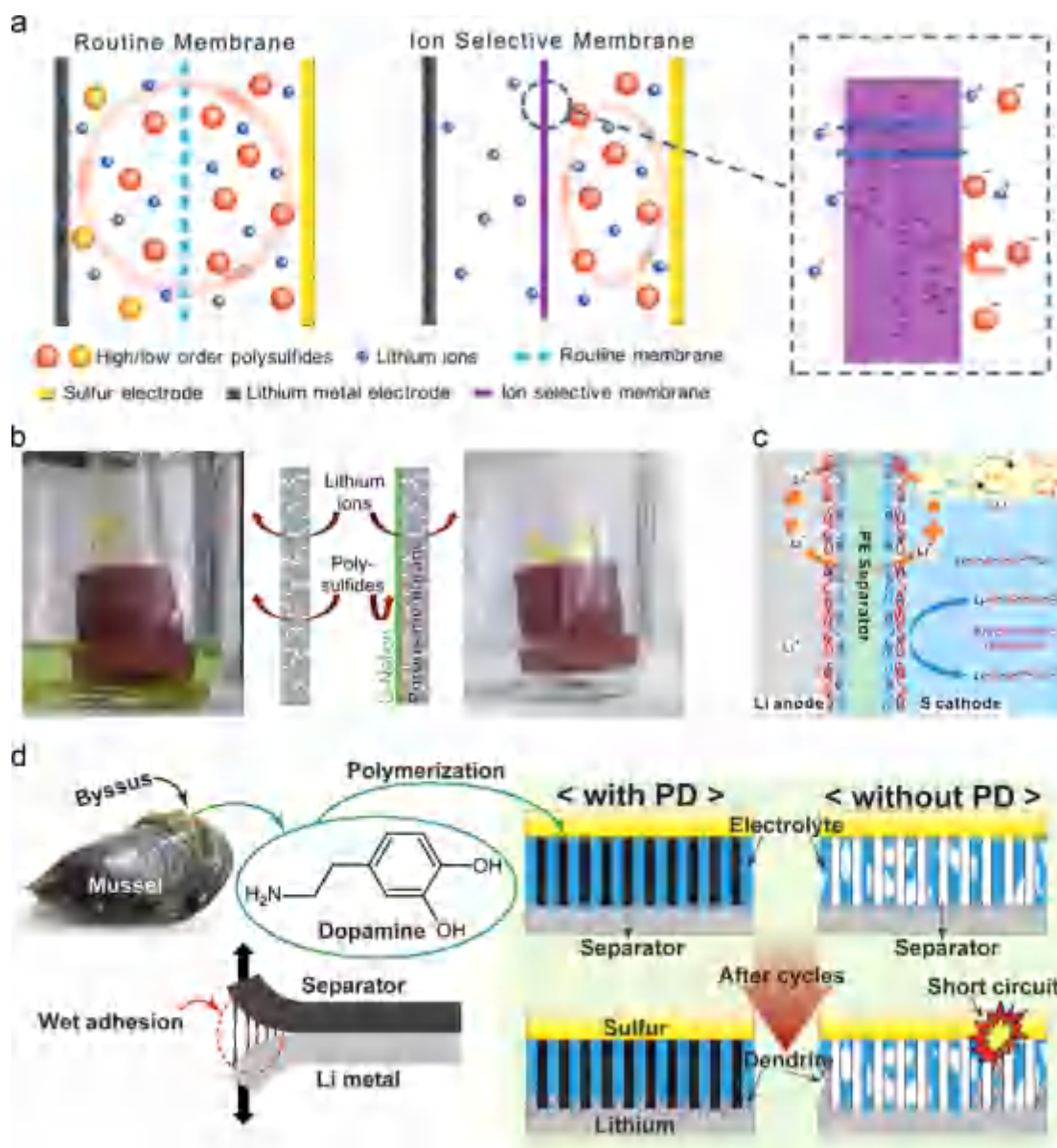


Fig. 1. (a) Scheme of the novel Li-S battery configurations with routine porous polymer separator that allow the polysulfide shuttle and Nafion-coated ion selective separator in which the polysulfide anions are limited to the cathode side [49]. (b) Scheme exhibiting the cross-separator diffusion of polysulfides through routine separator and double-layer separator with lithiated Nafion-coating [52]. (c) Scheme of layer-by-layer assembled poly(allylamine hydrochloride) and poly(acrylic acid) as multilayer separator in a Li-S cell [57]. (d) Scheme of mussel-inspired separator with polydopamine coating to alleviate Li dendrite growth through uniform Li ionic flux and wet-adhesion [60].

selection and arrangement of carbon materials on separators are expected to introduce full cell with much improved sulfur utilization and longer life span.

A multi-walled CNT (MWCNT)-modified separator was also reported by Manthiram's group with MWCNTs as a porous filter on a conventional porous separator [69]. The MWCNT layer consisted of interwoven curved MWCNTs deposited into a dense filter. This structure afforded several enhancements to the Li-S system: the efficient block of the free migration of polysulfide species, the effective reactivation of the trapped active materials, and the valid stabilization of the active sulfur within the cathode electrode. As a result, a high discharge capacity of 1324 mAh g^{-1} was achieved due to the additional conductive pathway constructed by MWCNTs. Capacity decay rate of as low as 0.14% was achieved by the suppression of polysulfide diffusion. Remarkable capacity with elevated current densities at higher current densities of 0.5 and 1.0 C for 1107 and 1073 mAh g^{-1} , respectively, was also achieved in a Li-S cell with MWCNT coating separators. Very recently, a customized separator with an activated carbon nanofiber filters were attached onto a PP membrane by Manthiram and co-workers [70] to filter out the freely migrating polysulfides, which demonstrated an superb boost in high sulfur utilization of 76% and a very small capacity fade rate of 0.13% per cycle after 200 cycles.

During the electrochemical cycles of Li-S batteries, the separator accommodates a large amount of electrolyte and the dissolved polysulfides, which precipitate as inactive sulfur materials. By attaching a conducting layer of carbon black onto the separator, Yao et al. reported a multi-functional separator that prevented the formation of inactive sulfur in a separator and

achieved high specific capacity and cyclic stability for Li-S cells (Fig. 2b) [71]. By precise characterization of the cycled separator, the sulfur-containing species were observed on routine separator even when discharged to 1.7 V, which indicated the difficulties in recycling these dead sulfur materials. While for the carbon-coated separator, the much lighter color after cycling test indicated that much less polysulfides were accommodated in the composite separator. The reactivation of sulfur-containing species contributed to a much enhanced cyclic stability of the cell with carbon-coated separator. Our group also developed a Janus separator of mesoporous cellular graphene (CGF)/PP separator to promote the sulfur utilization in the cell (Fig. 2c) [72]. The CGF layer was coated onto PP separator by filtration of CGF dispersed in N-methyl-2-pyrrolidone solvent in the presence of poly(vinylidene fluoride) binder. In the Janus separator, porous PP layer served as the insulating substrate that prevent short circuit, while CGF with high specific surface area of $2120 \text{ m}^2 \text{ g}^{-1}$, high mesopore volume of $3.1 \text{ cm}^3 \text{ g}^{-1}$, and high conductivity of 100 S cm^{-1} are in close contact with the sulfur cathode to reactivate the sulfur-containing species. The Janus separator improved both the capacity and the electrochemical kinetics of the Li-S battery. Recently, Balach et al. reported a mesoporous carbon layer with a surface area of $843 \text{ m}^2 \text{ g}^{-1}$ and an areal mass loading of 0.5 mg cm^{-2} onto PP separators that affords a physical barrier to localize dissolved polysulfides [73]. A high initial capacity of 1378 mAh g^{-1} at 0.2 C and a low degradation rate of 0.081% per cycle were achieved after 500 cycles at 0.5 C. The application of both micro- and mesoporous carbon onto separators offer new opportunities in the utilization

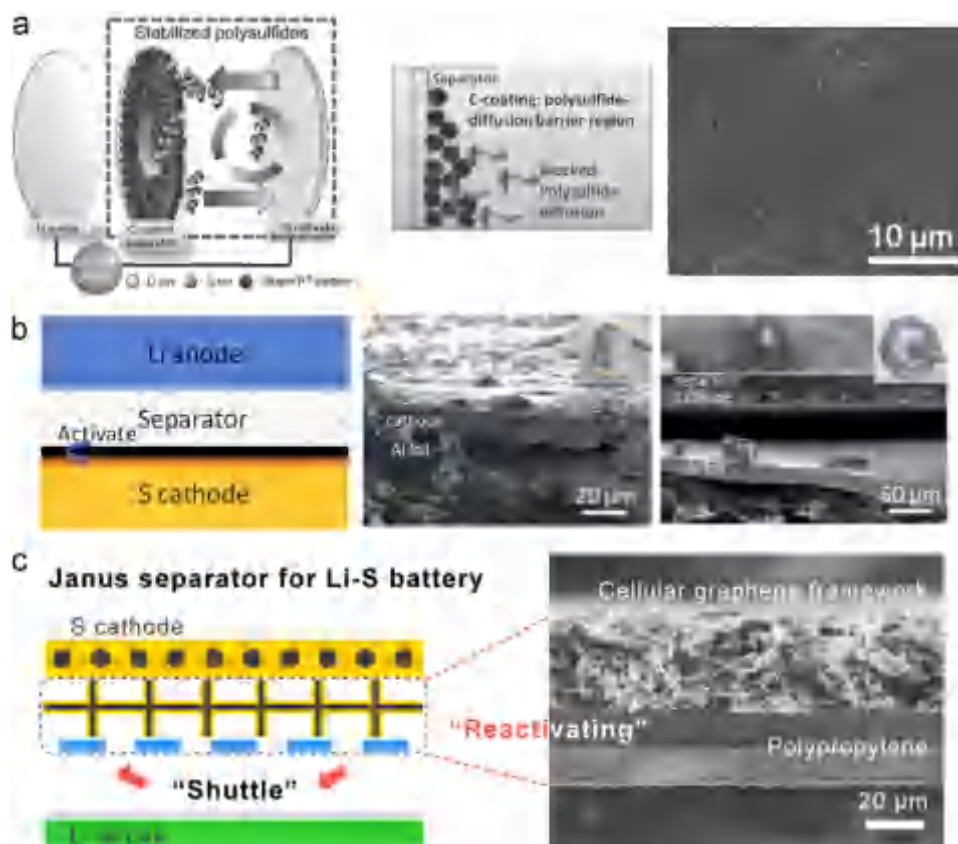


Fig. 2. (a) Schematic configuration of a Li-S cell with the carbon-coated separator, the barrier effect of the diffusion of polysulfides, and the surface morphology of the carbon-coated separator [67]. (b) Scheme of Li-S battery with a separator of conductive surface. The comparison of separator after cycles: separator with conductive surface (middle) and routine separator (right) [71]. (c) Schematic illustration of a Janus separator with a mesoporous cellular graphene layer that prevents the formation of insulating sulfur containing species, and the cross-sectional SEM image of the Janus separator [72].

of active materials, especially for the systems involving complex phase evolution and conversion electrochemistry.

Graphene materials, with typical two-dimensional structures, are also feasible to be assembled into membrane with layered structure. As one of the most attractive macroscopic form of graphene-based materials, graphene oxide (GO) membranes are inherently of good mechanical strength. GO membranes were also reported to allow unimpeded permeation of water and rapid diffusion of small cations [74]. Based on these considerations, our group proposed a permselective separator system based on ultrathin-GO coating (Fig. 3a) [75]. GO layers contain abundant oxygen-containing functional groups. Therefore, GO flake is a polar plane. The carboxyl groups acted as ion hopping sites for positively charged ions (lithium ions) while reject the negatively charged ions (polysulfide anions) by electrostatic interactions. Therefore, the GO-coated separators exhibited high permselectivity to lithium ions and rendered Li-S battery with superior stability (cyclic capacity decay rate reduced to 0.23%) and improved energy efficiency (improved Coulombic efficiency from 60% to over 95% with LiNO_3 -free electrolyte at 0.1 C). As one versatile platform of advanced functional materials, GO membranes are with highly tunable functionalization properties, high mechanical strength, low electric conductivity, and facile fabrication procedure, which makes it promising to form better separator for practical Li-S cells. When the GO was reduced by chemical treatment, reduced GO

(rGO) with few oxygen-containing functional groups were obtained. When the rGO were attached to PP membrane, the rGO coating exhibited 3D porous structure, high electrical conductivity, and abundant functional groups. This can not only increase the conducting interface between membrane and cathode, but also efficiently prevent the polysulfide shuttle through the separator. Consequently, the initial discharge capacity can be as large as 1067 mAh g^{-1} at 0.2 C which can retain 878 mAh g^{-1} after 100 cycles [76], which is a good demonstration of 2D rGO for high-stable Li-S cell.

Zhou et al. proposed a unique exfoliated graphene coating onto separator and provided a comprehensive comparison between different cell configurations including graphene sheet [77]. By replacing Al foil as current collector, or by coating onto the separator, the exfoliated graphene served as graphene current collector (GCC) or graphene coated separators (G-separator) (Fig. 3b). The graphene coated on separator enables good mechanical properties of the barrier layer, which is highly effective in alleviating the shuttle of polysulfides and therefore suppressing the notorious shuttle effect. By replacing the Al foil current collectors with light GCC, the contact impedances between the current collector, active materials, and the electrolyte system are reduced as well. By combining the G-separator and GCC together to form a sandwich structure for sulfur active materials, a high discharge capacity of 1354 mAh g^{-1} was delivered at 0.3 A g^{-1} .

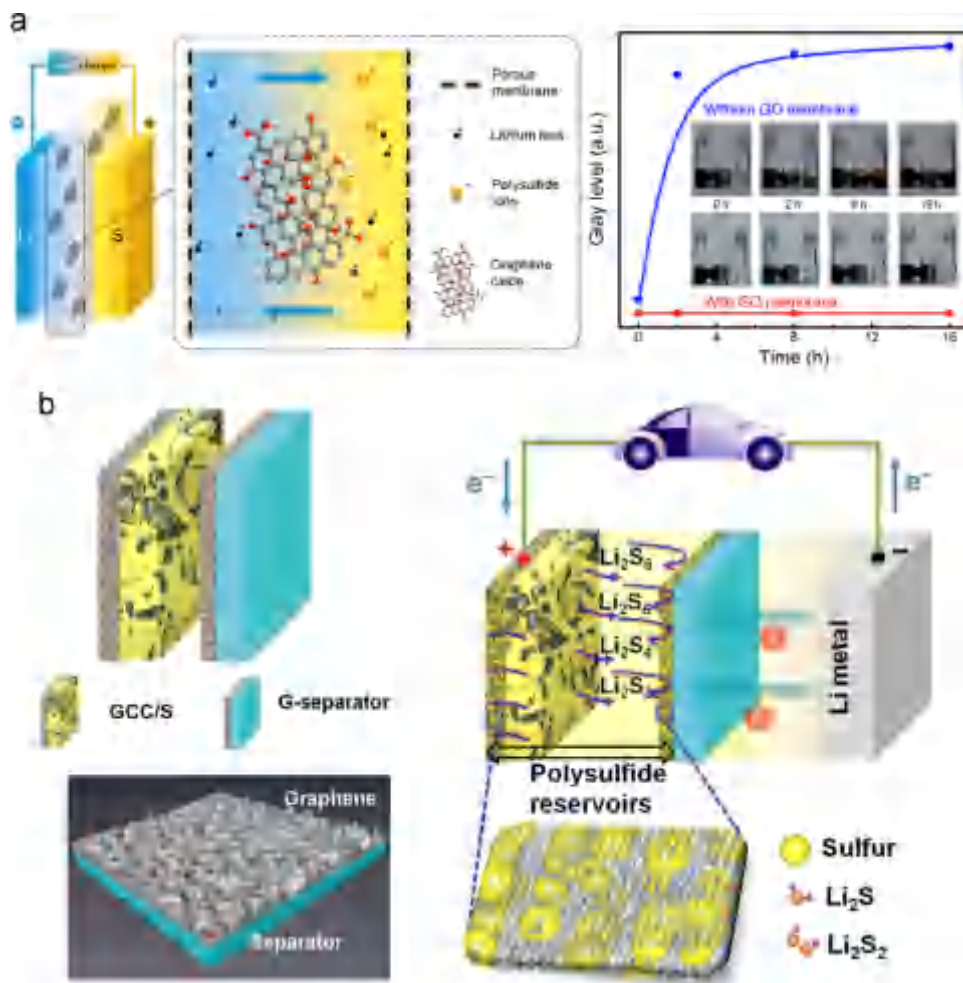


Fig. 3. (a) Scheme of a GO membrane serving as ion selective membrane in Li-S battery, and the permeation properties of polysulfide across GO separator and routine separator [75]. (b) Scheme of a Li-S battery with graphene-coated separator and the graphene current collector, and a 3D reconstructed image of graphene-coated separator [77].

The ultralow capacity decay rate at 0.1%/cycle was also achieved within 300 cycles at 1.5 A g^{-1} . With the three-dimensional (3D) X-ray microtomography (XRM) method, Zhou et al. firstly elaborated how graphene contributes to high performance Li-S batteries. After electrochemical cycles, part of sulfur-containing species was captured by graphene nanosheets in a homogeneous state, which indicated GCC served not only as current collectors, but also entrapped part of the dissolved sulfur. A 3D reconstruction of the G-separator also verified that the layer-by-layer structure retained polysulfide and alleviated their diffusion towards the separator/anode. As the fabrication procedure of light-weight GCC and G-separator are facile and easy to be applied in many laboratories and factories, this route favors the assembly of Li-S batteries with much improved energy densities.

The rational combination of CNT and GO is also a novel route to obtain advanced hierarchical nanostructures with unexpected performance. Zhi and co-workers [78] explored an impressive spray-coating of GO/oxidized CNT mixture to obtain a barrier coating of only 0.3 mg cm^{-2} on PP separators, which has no negative impact on the energy density but significantly enhances the electrochemical performances of the whole battery device.

Various carbon materials were applied in modified separators for Li-S batteries, which led to different functions of the separators. The functional network built up by 1D CNTs and 2D graphene materials are highly conductive, which are helpful for the reutilization of precipitated sulfur species. In comparison, carbon materials with abundant micro/mesopores are likely to absorb the polysulfides. With the assist of different functional groups, electrostatic repulsions effects can be introduced into the carbon modification layer. Generally, the function of modified separator varies with different carbon materials, and a rational design or

wise combination of functional carbon materials may introduce practical separator for advanced Li-S battery.

2.3. Oxide-modified multi-functional separators

Another route for the separator modification is realized by oxide additives. Oxide materials are of very high thermal and mechanical stability compared with routine separators such as PP and PE. By changing the wettability of the surface, oxide modification also alters the properties in electrolyte uptake and influences the polysulfide diffusion properties. With lithium ion conducting oxides, such as V_2O_5 , a high efficient ion selective layer can even be easily built.

A novel Al_2O_3 -coated separator was firstly proposed by Zhang et al. for Li-S batteries by simply coating Al_2O_3 powders onto conventional separators (Fig. 4a) [79]. The powders formed a highly porous structure with inter-connected voids, which served as high efficient lithium ion diffusion channels and localized the polysulfide species diffusion by the tortuous pores in Al_2O_3 layer. Consequently, the Al_2O_3 coating layer alleviated the shuttle of polysulfides and improved the cyclic stability of the Li-S cells. However, the deposition of sulfur-containing species was still observed after 50 cycles, which was the dominate reason for the rapid capacity fading from 967 to 593 mAh g^{-1} within 50 cycles.

A coating layers with montmorillonite (MMT) was also reported by Ahn et al. for high performance Li-S cells [80]. In general, well-dispersed MMT in polymer matrix improved the thermal and mechanical stability of the film [81], and hydrophilic MMT enhanced the wettability of the separator in electrolytes. By the Raman spectrum study and zeta potential investigation, it was confirmed that the MMT coating layer prevented the diffusion of

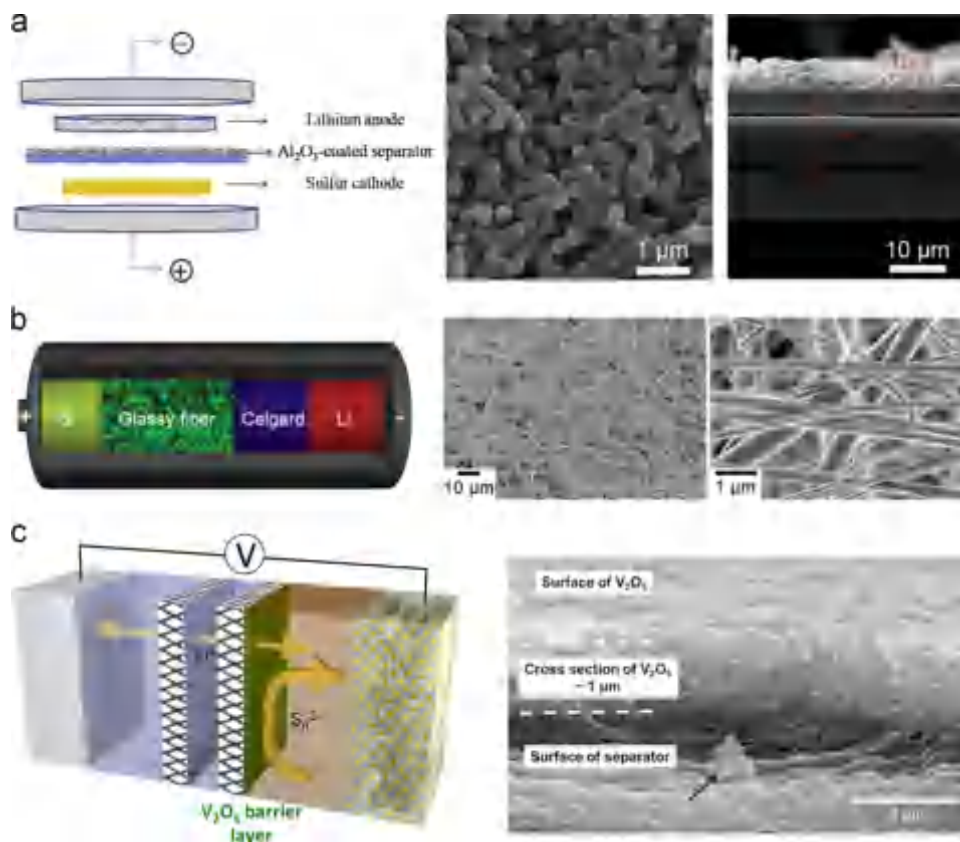


Fig. 4. (a) Configuration of a Li-S cell with Al_2O_3 -coated separator, and the morphology of Al_2O_3 -coated separator [79]. (b) Scheme of the architecture of a Li-S cell composed of glassy fiber, and the SEM image of the porous glassy fiber paper [82]. (c) Scheme of a Li-S battery with V_2O_5 -coated separator, and the SEM image exhibiting the morphology of V_2O_5 -modified separator [83].

polysulfides towards the anode by repulsive force. A high initial capacity of 1382 mAh g^{-1} was therefore delivered with low capacity fading rate of $0.16\%/ \text{cycle}$ within 200 cycles at a current density of 100 mA g^{-1} .

A cost-effective glassy fiber-based hybrid separator was rationally designed by Wang et al. for rechargeable Li-S batteries (Fig. 4b) [82]. The glassy fiber layer are beneficial for Li-S cells in several aspects: (i) the highly porous structure results in the high electrolyte uptake and slows down the diffusion rate of polysulfides towards the anode side as a buffer layer; (ii) the high electrolyte uptake also induces high lithium ion conductivity; and (iii) the high thermal-stability improves the safety of Li-S cells against internal thermal-runaway. This modified separator structure led to high specific capacity of sulfur, high coulombic efficiency, improved cyclic stability, good rate capability, and also suppressed the self-discharge.

V_2O_5 modified separator was proposed by Li et al. with V_2O_5 as the lithium ion conducting layer (Fig. 4c) [83]. V_2O_5 is a good solid state lithium ion conductor, and is widely applied as electrode material in lithium ion batteries. Lithium ions can transfer through the V_2O_5 layer and enable the electrochemical reactions with sulfur cathodes. In contrast, by forming a dense and nonporous V_2O_5 layer on conventional porous separator, the dissolved polysulfide anions are localized within the cathode and therefore the parasitic reactions with lithium anode were prevented. With the

barrier V_2O_5 layer, the severe overcharge phenomenon originated from shuttle effect was eliminated. However, it was noticed that the dense layer introduced into a modified separator had negative influence on the rate capability of Li-S cells. The capacity retention was 62% for cells cycled at 0.67 C against that cycled at 0.067 C .

The addition of oxide layer for composite separator improves the cell performance by the inhibition of polysulfide shuttle, while the extra resistance for lithium ions is inevitable. Therefore, a reasonable balance between the lithium ion flux and polysulfide suppression efficiency is important for composite separator with oxide coating layers.

2.4. Multi-functional separators with multi-component modifications

The routine membranes are altered into multi-functional ones through the rational integration of polymer matrix with functional components in Li-S batteries for the valid suppression of polysulfide diffusion, the outstanding improvement of the cathode conductive network, and even effectively help to stabilize the lithium anode. Multi-component modifications of membranes are therefore important to render the composite separators with multi-functions.

One typical combination of multi-component modification is based on carbon materials and polymers. Chung et al. proposed polyethylene glycol (PEG)-supported mesoporous carbon (MPC)

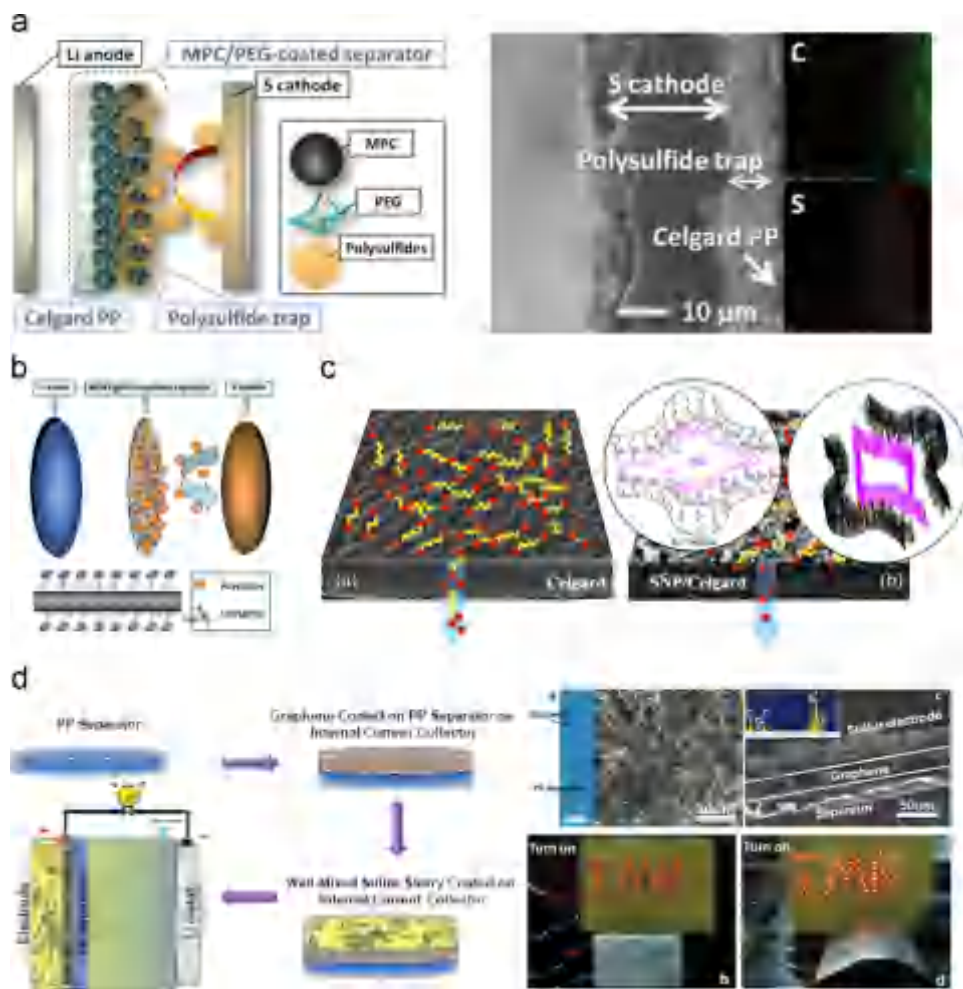


Fig. 5. (a) The schematic illustration of a Li-S cell with a microporous carbon/PEG-coated separator, and the cross-sectional SEM image of the separator with element mapping image [84]. (b) Scheme of a Li-S cell configuration with a MWNT@PEG modified separator [85]. (c) Scheme describing different permeation properties of Celgard and SuperP-Nafion-PEO modified Celgard membranes when charging [86]. (d) Scheme of the integrated electrode structure of sulfur and graphene on PP separator, the surface and cross-sectional morphology of the integrated electrode, and the pouch cell test at flat and bended states [88].

coating onto the Celgard PP separator to form a polysulfide trap (Fig. 5a) [84]. By the combination of MPC/PEG layer, several advantages have been achieved: (i) the coating layer served as upper current collector since the MPC-containing layer are electrical conductive; (ii) the trapping capability of polysulfides was chemically improved by PEG and physically enhanced by MPC; (iii) the PEG served as a binder and significantly reduced the thickness of the coating layer. Therefore, the Li-S battery with MPC/PEG-coated separator exhibited a high discharge capacity of 1307 mAh g^{-1} , a high cyclic stability with $0.11\%/ \text{cycle}$ capacity fading rate within 500 cycles. Similar strategy with MWCNT@PEG-coated separator was also proposed by Wang et al. to restrain the shuttle of polysulfides, which simultaneously contributes to the high cyclic stability and superb rate capability due to the multi-component coating layer (Fig. 5b) [85]. PEO binder structure was also introduced into a Nafion-SuperP-PEO system for the separator modification, which included additional capability of ion selectivity into the functional layer (Fig. 5c) [86]. Another modification of the separator with a polyvinylidene fluoride-carbon (PVDF-C) layer was also reported. The unique PVDF-C exhibited a interlinked glue-like network morphology, which localized the generated polysulfides in the cathode side of Li-S cells [87].

Zhou et al. proposed a superb integrated separator with active sulfur materials and graphene directly coated on a commercial polymer separator (Fig. 5d) [88]. This novel Li-S cell configuration with integrated sulfur and graphene-modified separator brought several advantages, including: (i) high energy density with the replacing of metal current collectors, (ii) inhibition of shuttle of polysulfide intermediates by graphene barrier layer on separator; (iii) lowered interfacial contact resistance between cathode and separator by graphene conductive layer; and (iv) feasibility for scale up and flexible energy storage devices. The integrated S-G@PP separator is also of high mechanical strength, excellent flexibility, high wettability, which contributed to the impressive electrochemical performance. With a high sulfur content of 70% in cathode, this integrated configuration delivered a very high specific capacity of over 1200 mAh g^{-1} at 0.3 A g^{-1} . Excellent cyclic stability with capacity fading rate of $0.064\%/ \text{cycle}$ was achieved during 500-cycle test. The bend test in the pouch cells also indicated its potential in the future application of flexible battery systems.

Xu et al. combined CNTs and Al_2O_3 onto a PP separator, and proposed a CNT/ Al_2O_3 /PP tri-layer separator [89]. The inorganic Al_2O_3 underlayer not only exhibited advantage on thermal stability, but also provided a strong shield for CNT coating layer. The CNT layer with porous structure is effective in trapping polysulfides. Li-S cells with CNT/ Al_2O_3 /PP separator presented improved performance in cyclic performance and rate capability. Modified separator with Mn-silicalite-1 zeolite was also reported, which demonstrated the capability to effectively absorb polysulfides [90]. A ternary layered separator was also proposed by our group with the concept of rational integration. The ternary layered separator are composed by a macroporous PP matrix layer that provided mechanical support, an ultrathin GO barrier layer ($0.0032 \text{ mg cm}^{-2}$) that blocked the macropores of PP matrix, and a dense Nafion retarding layer with an very low areal loading of 0.05 mg cm^{-2} that efficiently served as ion selective layer to suppress the crossover of sulfur-containing species. The wise combination of the three components as the separator renders the Li-S batteries with high Coulombic efficiency and superior cyclic stability. Very recently, an ultra-lightweight polyaniline nanofiber/CNT coating (only 0.01 mg cm^{-2}) on PP separators were applied in Li-S cells to demonstrate the synergistic physical adsorption and chemical immobilization of the intermediates [91]. Very high capacity retention was found in the Li-S batteries with this novel separator after 12 h resting.

The progresses in multi-functional separators open up a new direction towards high-performance Li-S cells. By the facile

modification of separators by electrical conductive materials, it acted as an upper current collector to improve the electrochemical performance of cathode materials. The diffusion of polysulfides are inhibited by either physical confinement (e.g. through tortuous pores) or chemical interactions (e.g. ion selective coating layers) through the composite separator. The multi-functional separator is even effective to prolong the cycle life of the lithium metal anode. The modified separators are expected to contribute more to achieve the Li-S cells or even other battery systems with high-rate performance and long cycle life.

3. Multi-functional interlayer system for Li-S battery

Advanced separator systems are beneficial for the performance of Li-S batteries. However, the medication on the separator is not sufficient to fully address the global challenges originated from polysulfide diffusion in both cathode and anode. Due to the existed concentration gradient during cycling, the diffusion of polysulfides outwards the cathode conductive scaffolds is inevitable. Although the polysulfide anions are blocked by multi-functional separators, the decomposition of metastable polysulfides in a porous separator induces the irreversible loss of active sulfur materials and the continuous degradation of cell performance. To slow down the diffusion of polysulfides and prevent the loss of sulfur species in a cell, a polysulfide trap that alleviates the diffusion of polysulfides and has the capability to re-utilize precipitated sulfur is essential for Li-S cell with long cycle life and high sulfur utilization. Manthiram research group firstly proposed this important concept of “interlayer” in 2012. Afterwards, extensive researches on interlayer materials include various carbon-based interlayers and polymer-based interlayers have greatly improved the electrochemical performance of Li-S cells.

3.1. Carbon-based interlayers

Carbon materials are suitable to serve as an interlayer between cathode and separator in a Li-S cell for several reasons, including the high electrical conductivity, the feasibility to form stable films, and the tunable pore structure and surface properties. Extensive progresses have been achieved in the utilization of carbon-based interlayers in Li-S batteries.

3.1.1. Interlinked freestanding carbon interlayers

In a Li-S cell, the deposition of low-conductive sulfur-species in conductive scaffolds and the simultaneously volume fluctuation requires a high efficient upper current collector with highly flexible character. Interlinked free-standing carbon interlayer formed by MWCNTs, carbon nanofibers, and other sp^2 carbon provided a highly adaptive interlayer to fulfill these demands.

Manthiram group reported the fabrication of MWCNT interlayer by facile dispersion and vacuum filtration (Fig. 6a) [92]. The free-standing MWCNT interlayer served as a pseudo-upper current collector, which was bifunctional in lowering the charge transfer resistance of the sulfur cathode and trapping of polysulfides in the cathode. The intrinsic flexibility of MWCNT interlayer also ensured the high efficient contact that endured the volume change during the cycling test. These features afforded an improved electrochemical performance of the cells in both high specific capacity and excellent stability. A high initial discharge capacity of 1446 mAh g^{-1} was delivered, with a 962 mAh g^{-1} capacity after 50 cycles at 0.2 C . This work indicates that the new cell configuration with interlayer can significantly improve the cell performance without complex synthesis and surface modifications, and opened up a new research field for Li-S batteries. Progress of interlayer based on SWCNT interlayers was also recently reported

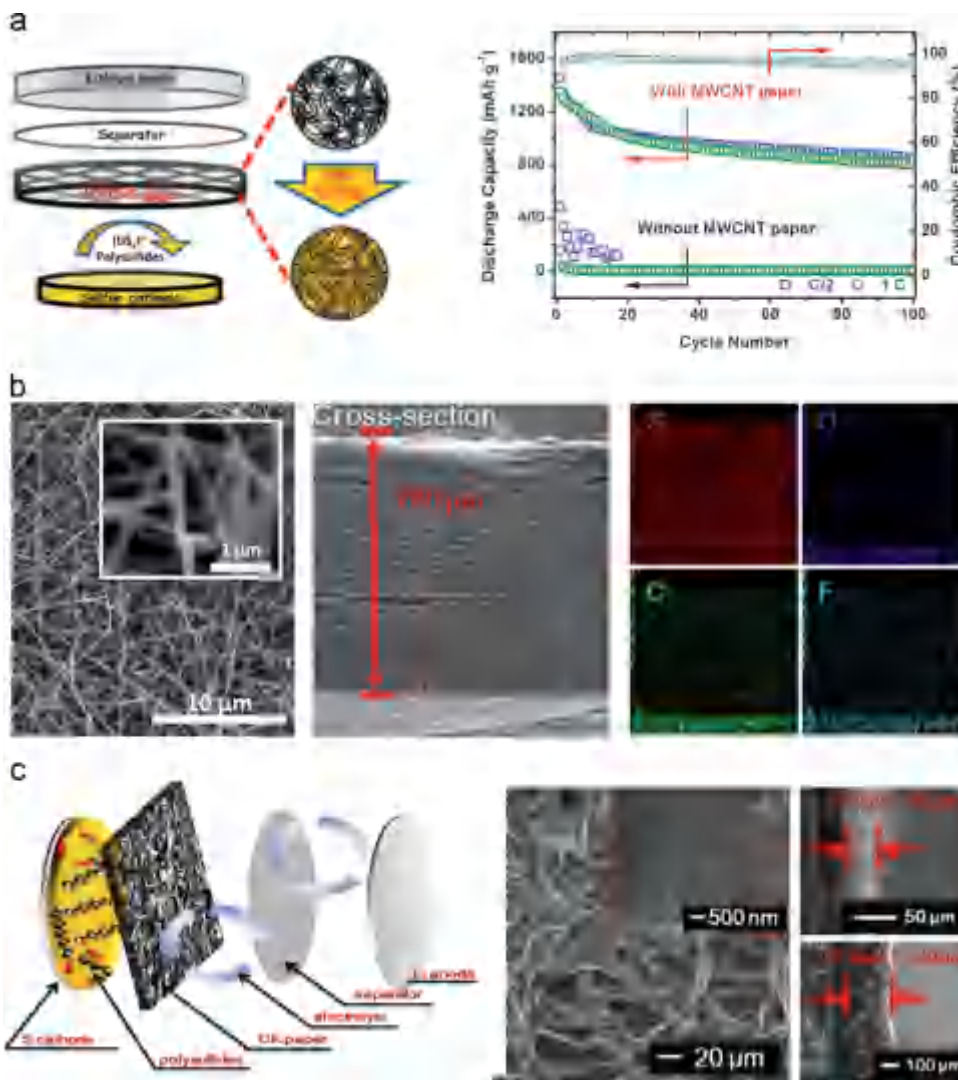


Fig. 6. (a) A schematic cell configuration of rechargeable Li-S batteries with MWCNT interlayer, and corresponding high-rate cycle performance and Coulombic efficiency [92]. (b) SEM of the surface and cross-section morphology of activated carbonized nanofiber interlayer, and corresponding element mapping [94]. (c) A schematic model of the cells with carbonized Kimwipes interlayer, and the surface/cross-section morphology of the carbonized Kimwipes interlayer [98].

by Kaiser et al. in a systematic investigation based on the combination of high performance cathode and interlayers [93].

Carbon fiber-based film is another type of interlayers, which are composed of fibers with the diameter of over one hundred nanometer, and commonly with an activation process to increase the amount of micropores in the flexible interlayer. Singhal et al. explored CO₂ activated carbonized PAN nanofiber paper and carbonized PAN-Nafion nanofiber paper for Li-S batteries (Fig. 6b) [94]. The carbon nanofiber interlayer not only reduced the electrochemical resistance, but also localized the diffusion of polysulfides. The sulfur-containing species are trapped on the nanofibers after cycling test. With the optimization of interlayer thickness and pore structures, a high initial discharge capacity of 1549 mAh g⁻¹ was delivered. Wang et al. reported a similar structure with a flexible activated carbon nanofiber interlayer derived from electro-spun process [95]. The 3D structure of the interwoven networks with abundant porous structure created by the chemical activation is considered a key for the high capacity and stability of a Li-S cell. Based on carbon fiber cloth, the facile chemical modifications also render additional functions when serving as interlayers for Li-S batteries.

An interlayer structure based on Fe₃C-carbon fiber web structure was recently reported by Kim and co-workers [96]. This composite interlayer provided macropores for ion transportation, nitrogen-containing functional groups for polysulfide entrapment, and enhanced electric conductivity for improved electron/ion transfer. Li-S cells with Fe₃C carbon fiber interlayer delivered an initial discharge capacity of 1177 mAh g⁻¹, which a capacity fading rate of 0.24%/cycle within 100 cycles.

An interlayer based on atomic layer deposition (ALD) of Al₂O₃ in nanoporous carbon cloth was reported by Han et al. [97]. A 0.5 nm thick Al₂O₃ layer was conformally coated onto the carbon cloth interlayer, which maintained the high surface area and electrical conductivity of the carbon cloth. Meanwhile, the Al₂O₃ layer reduced the pore size and facilitated the polysulfide adsorption by the altered surface property. Therefore, the interlayer was highly efficient in polysulfide trapping and in reactivating the sulfur-containing species. Compared with interlayer without ALD process, the Al₂O₃ layer contributed to a significant increased capacity of 1136 mAh g⁻¹ with 25% enhancement, and capacity retention of 67% against 39% was achieved. The combination of an ALD coating and porous carbon substrate present a

new and important strategy to improve the performance of Li-S batteries.

The direct carbonization of commercial papers is another very important strategy for highly controllable carbon interlayer structure. Chung et al. presented a low-cost interlayer based on the carbonized Kimwipes interlayer (Fig. 6c) [98]. Kimwipes paper is a common lab supply with long fiber in it to afford high mechanical strength and prevent the dust loss. The interlinked fiber network was preserved during the carbonization process. The carbonized fibers became electrically conductive to serve as interlayer materials. Such interlayer structure is beneficial to alleviate of the polysulfide diffusion, provide extra electron transfer pathways, and maintain the electrolyte channels. The utilization of carbonized Kimwipes also affords a facile but efficient way to precisely control the thickness of interlayer by stacking different number of interlayers. Zhang et al. [99] reported another interlayer structure based on the carbonization of a filter paper into flexible carbon interlayer with porous structure, which are beneficial for high capacity, high stability, and high rate capability for Li-S cells. The introduction of other scaffolds (e.g. glass fiber paper, carbon fiber cloth) is also a facile route to obtain free-standing composite layer for Li-S batteries. For instance, Lee and Kim [100] fabricated a CNT-loaded GF composite interlayer, in which the GF paper offers large electrolyte uptake and the CNT scaffolds afford a rapid electron pathway for insulating the active materials. Such free-standing carbon interlayers are beneficial for high sulfur utilization and good cycling life. A very thin interlayer with a low areal mass loading is always expected in a practical Li-S cell.

3.1.2. Carbon interlayers with micro/mesopores

Although the diffusion of polysulfides can be partially slowed down by the tortuous macropores in carbon paper, extra polysulfide-interlayer interactions are highly required towards highly efficient absorption and effectively retarding for polysulfides. The interlayer with abundant micro/mesopores played outstanding role in reducing the migration of polysulfides.

Manthiram group have successfully developed a microporous carbon paper (MCP) as interlayer for Li-S cells (Fig. 7a) [101]. Conducting MCP interlayer decreased the surface resistance of the cathode, and the abundant micropores in the interlayer significantly facilitated the capability for polysulfide adsorption. Moreover, the absorbed sulfur-containing species are reutilized, which process significantly improved the cyclic stability of Li-S cells. The cell cycled at 1.0 C exhibited a capacity of over 1000 mAh g⁻¹ after 100 cycles with capacity retention of 85%. The chain length was estimated to be less than 2 nm, therefore, both micropores and small mesopore structures were more likely for the high efficient confinement of polysulfides due to the size effect. The performance of mesopores was also tested as the interlayer materials for Li-S cells, which was not as good as microporous carbon corresponding to the weak polysulfide accommodation capability.

The application of mesoporous-carbon-based interlayer was comprehensively investigated by Balach et al. for Li-S cells (Fig. 7b) [102]. A mesoporous carbon with pore size around 12 nm and tuned the pore volume of the mesoporous carbon from 1.1 to 3.2 cm³ g⁻¹ was obtained by a facile silica-templated casting process. The intrinsic mesoporosity of the interlayer effectively entrapped the polysulfides. Rather than the specific surface area, the higher pore volume was more crucial for the high-efficiency in trapping the polysulfide intermediates.

The construction of acetylene black mesh interlayer was explored by Jeong et al. [103], in which the particle sizes of acetylene blacks were around 0.1 μm and formed abundant macropores ranging from a few hundred nanometers to a few micrometers. By the insertion of this acetylene black mesh that is effective in capturing polysulfides,

enhanced capacity of 1491 mAh g⁻¹ was achieved, together with improved cyclability and rate capability. Compared with the fabrication of mesoporous and microporous carbon, this cheap and facile method is more potentially feasible for practical applications.

By the rational integration of carbon materials with different pores sizes into the cells, Su et al. proposed an interlayer containing bimodal meso-/micropores for rapid and reversible sulfur/polysulfide redox couple (Fig. 7c) [104]. The microporous structure in the bimodal interlayer system served for the storage of long-chain polysulfides, and the mesopore structures not only accommodate the polysulfides, but also hold electrolytes for rapid Li⁺ transfer and enable high-rate capability for electrochemical reactions. A full capacity of the S/polysulfide redox (S₈ to S₄²⁻) of over 400 mAh g⁻¹ was achieved at 5.0 C on a Li-S cell with a bimodal interlayer. A high capacity of over 250 mAh g⁻¹ can still be achieved for over 250 cycles at 10–15 C.

3.1.3. Carbon interlayers with surface functional groups

The functional groups attached on the carbon surface are employed to trap polysulfide anions in a working Li-S cell. The heteroatoms and functional groups introduce polarization to the framework of carbon and exhibit strong absorption to polysulfides [105–107]. By introducing functionalized materials in an interlayer system, an improved performance in the confinement of polysulfides is achieved for better Li-S cells.

Zu et al. presented an functionalized interlayer based on Toray carbon papers (Fig. 8a) [108]. By the alcohol-alkaline/thermal treatment, the hydrophobic pristine carbon fibers and smooth surface turned into hydrophilic through controllable oxidation of surface. The hydroxyl functional groups on the surface of carbon interlayers built a chemical gradient that chemically inhibited the diffusion of polysulfides. Meanwhile, the porous surface structures in the interlayer structure physically absorbed polysulfides. These two effects contributed to a strong polysulfide trap. The sulfur-containing species were enriched in the interlayer near the cathode side. With the treatment, a reduced electrochemical charge transfer resistance was also achieved with treated carbon paper. These features of the alcohol-alkaline/thermal treated Toray carbon paper interlayer led to much improved sulfur utilization and contributed to an initial discharge capacity of 1651 mAh g⁻¹ at 0.2 C and 900 mAh g⁻¹ after 50 cycles.

Based on GO as a highly tunable raw material with abundant functional groups, Wang et al. reported an interlayer film composed of reduced GO (rGO) and carbon black particles [109]. The remaining polar epoxy and carboxyl groups on the surface of the rGO sheets are helpful to localize the generated polysulfides, while the interlayer composed of pure rGO suffered from severe mass transfer problem. A long activation process was observed for the permeation of electrolyte into tightly stacked rGO sheets. With the incorporation of carbon black particles dispersed within rGO sheets, a loose architecture was obtained with electrolyte channels to ensure a rapid electrochemical kinetics. With the combination of functional groups and rational ion pathway design, a high initial discharge capacity of 1260 mAh g⁻¹ was delivered by the cell with a composite interlayer. With an interlayer composed of fluoro-functionalized rGO, Vizintin et al. developed a interlayer material with hydrophobic surface properties (Fig. 8b) [110]. Owing to the hydrophobicity of rGO-F or rGO-CF₃ interlayer, the precipitation of the solid electrochemical reaction products was more homogeneous throughout the entire electrode. This feature of fluoro-functionalized rGO interlayer led to an improved cyclic stability of Li-S cells. Very recently, Wang and co-workers [111] proposed electroactive GO interlayers between cathode and separator for polysulfide trapping and lithium storage. The residual sp² carbon domains in weakly oxidized GO donate electrons to improve polysulfide absorption and the enriched oxygen-containing

functional groups react with lithium ion for higher cathode capacity, which afforded the important insights on the role of oxygen atoms in the carbon interlayers for high capacity cell.

The use of carbon based composite is another route to turn the surface of interlayers. For instance, an integrated interlayer is proposed by Yang, Huang, and co-workers [112] to mitigate shuttle of

polysulfides by attaching the surface of a carbon/sulfur composite cathode with a graphene/TiO₂ film that accounted for 7.8 wt% of the cathode. The porous graphene afforded 3D conductive framework and physically trapped polysulfides, as well as the TiO₂ chemically suppressed the dissolution of polysulfides and alleviated the undesirable crossover. Therefore, the as-obtained Li-S cell exhibited a very

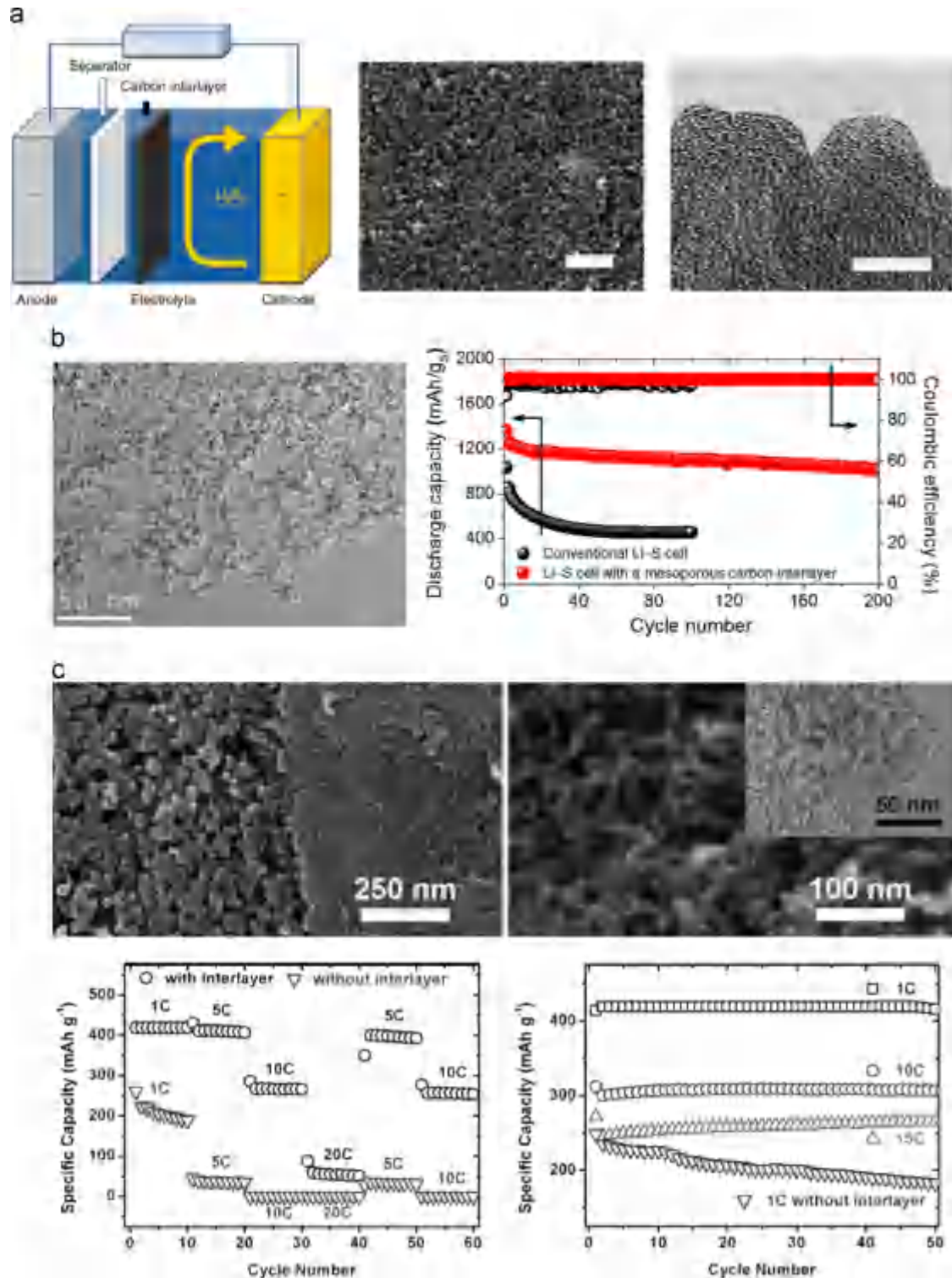


Fig. 7. (a) Schematic illustration of a Li-S cell with a bifunctional microporous carbon interlayer between sulfur cathode and separator, SEM of the microporous carbon interlayer and TEM image of the microporous carbon particles [101]. (b) TEM image of the mesoporous carbon for the interlayer, and the comparison of electrochemical performance of cell with and without a mesoporous carbon interlayer [102]. (c) SEM and TEM image of bimodal meso-/microporous carbon, and the electrochemical performance of Li-S cell with and without bimodal meso-/microporous carbon interlayer [104].

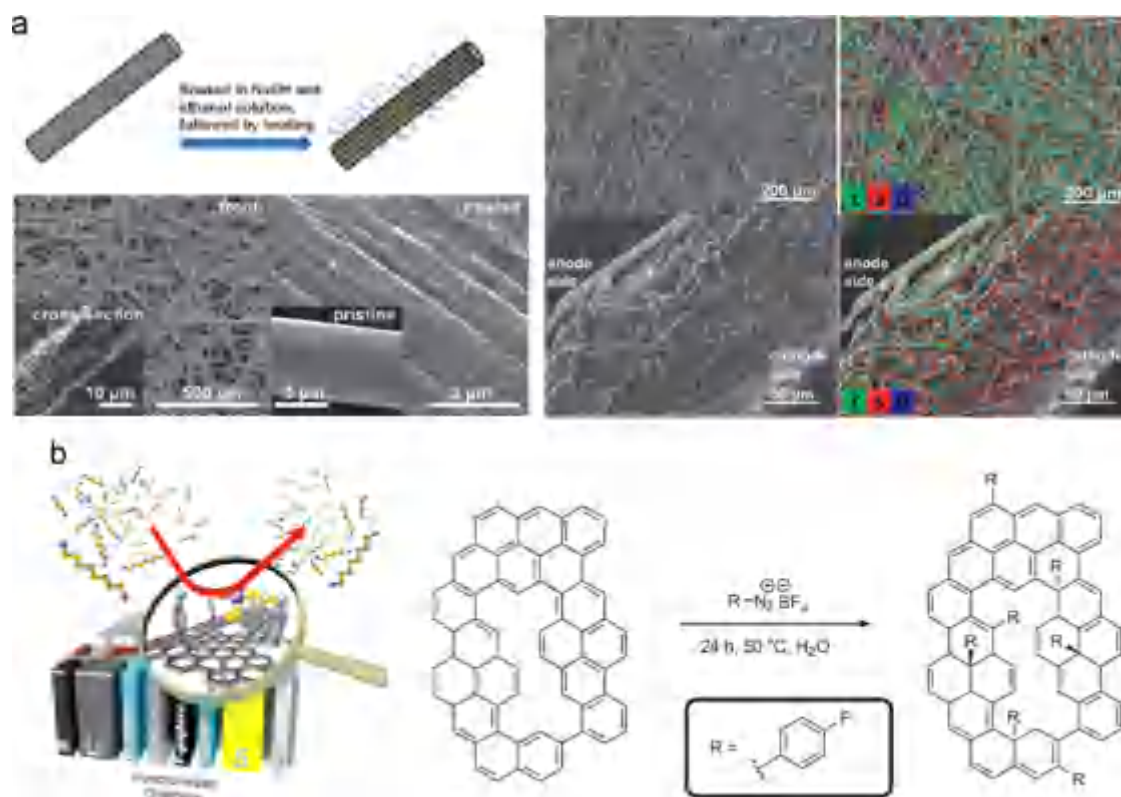


Fig. 8. (a) Schematic illustration of the treatment of the carbon paper and the SEM image of the treated carbon paper, SEM image and element mapping of the treated carbon paper interlayer after electrochemical cycles [108]. (b) Scheme of Li-S battery with a hydrophobic interlayer on the separator by using fluoro-functionalized rGO, and the corresponding reaction for the chemical modification of rGO with fluorobenzene [110].

high reversible specific capacity and extraordinarily excellent cycling stability. The use of other inorganic compounds (e.g. oxide, nitride, carbide, and sulfides) is also expected to anchor the polysulfides in a working Li-S cell.

3.1.4. Biomass derived carbon interlayers

The functional groups and the porosity of the interlayer materials are closely related to its capability to retard polysulfides and to facilitate the sulfur utilization. Natural biomass is of abundant functional structures to meet the requirements for the biochemical functions of the lives. By the structure imitation or direct transfer of the biomass materials, various types of new structures and functions have been realized when serving as interlayer materials for Li-S batteries.

Manthiram group reported a unique interlayer structure based on a carbonized leaf (Fig. 9a) [113]. The inherent structure of a leaf contains hierarchical pore structures composed of epidermis and parenchyma cells for their biological functions. Especially, the upper epidermis and palisade mesophyll cells are densely packed to form water-locking film, while the spongy mesophyll and the lower epidermis acts as a reservoir. After the carbonization of leaf, a pore size gradient was generated: the macroporous side composed pores and stomata that can serve as a reservoir and a dense layer with micro/mesopores that served as a locking layer. When integrated into a Li-S cell (locking layer close to the sulfur cathode), the locking layer can intercept the migration of polysulfide, and the reservoir layer can facilitate the ion pathways and enable the accommodation of electrolyte. Li-S cells with the carbonized leaf interlayer contributed to a high discharge capacity of 1320 mAh g⁻¹, and high Coulombic efficiency of over 98%, and a superior cyclic stability of 80% retention after 100 cycles. The effect of the polysulfide locking layer and the electrolyte reservoir was

also confirmed by using a carbonized leaf interlayer with the reservoir side attached to the sulfur cathode. In this situation, the polysulfides freely diffused out from the cathode and degraded the performance of the Li-S cell. The extraordinary structure derived from natural leaf brings novel concept on the applications of biomass structure as functional interlayer in Li-S batteries.

By the utilization of the hierarchical porous structure, Chung et al. also proposed an inhibitor interlayer based on free-standing carbonized sucrose-coated eggshell membrane (CSEM) (Fig. 9b) [114]. The CSEMs are composed of coalescing fibers and conducting coating layers onto it, which possessed macroporous channels and micropores on the membrane as well. When applied in a Li-S cell, CSEM served as an inhibitor interlayer for the migration of polysulfides, in which the micropores contributed to the absorption of polysulfides and the macropores acted as electrolyte pathways for the multi-electron electrochemical reaction. The conducting coating layer also provided high electrical conductivity and a continuous 3D electron pathway, which is beneficial for the high sulfur utilization. By applying the CSEMs as the current collect of the sulfur active materials, a high sulfur loading of 3.2 mg cm⁻², a high discharge capacity of 1327 mAh g⁻¹, and a long-term cycle stability over 100 cycles with a capacity retention of 75% were achieved. Moreover, the CSEMs were also applied in sulfur cathode and acted as polysulfide absorbent for high-stable Li-S batteries [115].

With biomass raw materials, other interlayer structures were also created to trap the polysulfides by porous structure for high-stable Li-S batteries. Huang et al. proposed a 3D carbonized bacterial cellulose membrane as interlayer, which are composed of interconnected nanofibers with excellent electrical conductivity and mechanical stability [116]. The interlayer adsorbs migrating polysulfides and provides an extra conductive framework for the sulfur cathode. A conductive interwoven bamboo carbon fiber

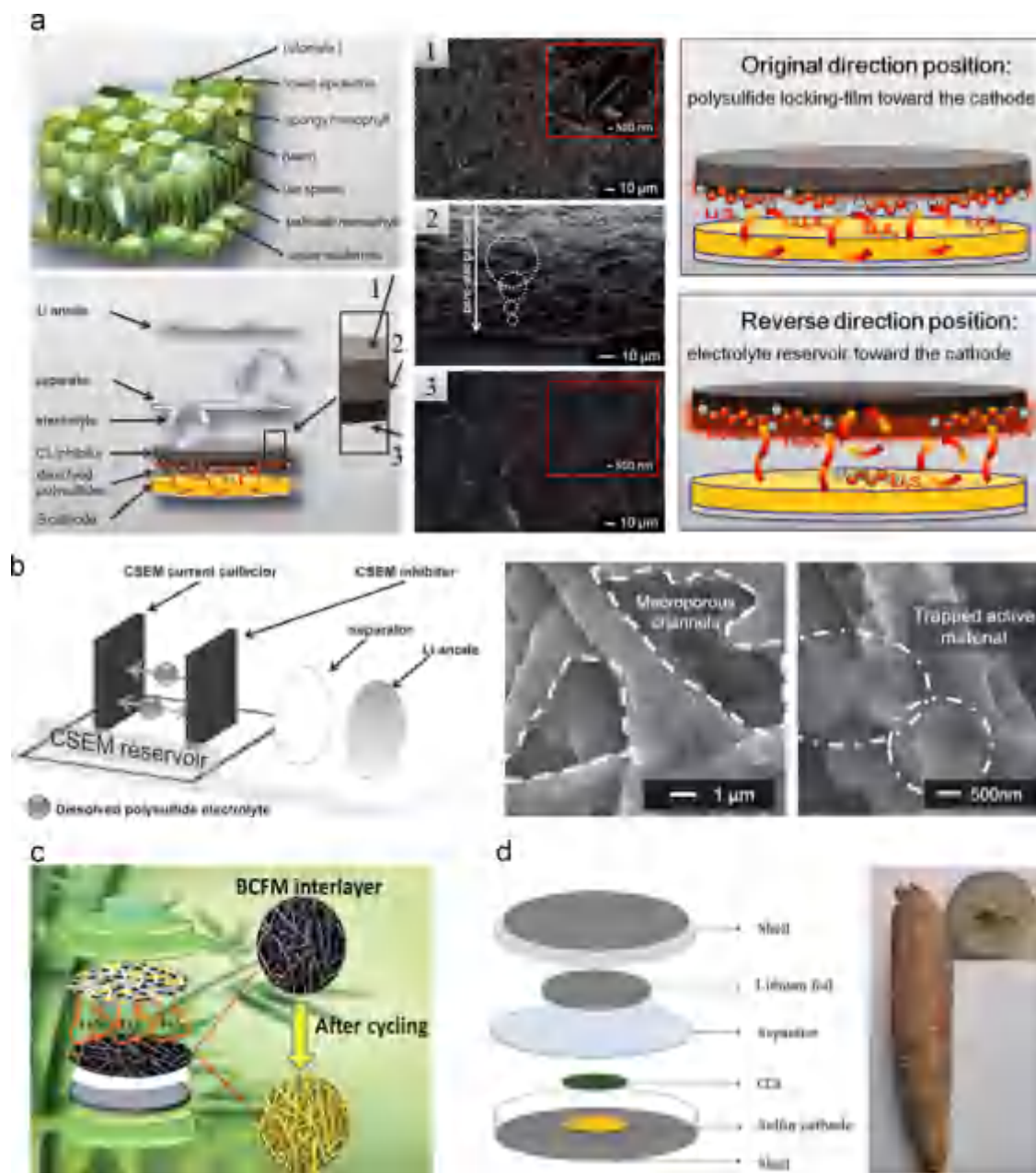


Fig. 9. (a) Schematics of the leaf structure and the carbonized leaf interlayer as polysulfide diffusion inhibitor, SEM showing the pore distribution gradient in carbonized leaf, and the schematic showing the influence of the pore gradient on its effect as interlayer [113]. (b) Scheme of the battery configuration with the carbonized sucrose-coated eggshell membranes (CSEM) interlayer, and the SEM image showing the pore structure of CSEM and the trapping of polysulfide after electrochemical cycles [114]. (c) Scheme of the Li-S cell with a conductive interwoven bamboo carbon fiber membrane as interlayer [117]. (d) Scheme of the cell configuration with a cassava-derived carbon sheet as interlayer, and the photo of raw cassava [118].

membrane (Fig. 9c) [117], and a cassava-derived high conductive carbon sheet with macroporous structure (Fig. 9d) [118], and were also applied as interlayer materials for high stable Li-S cells. Except for the unique porosity structures derived from biomass materials, non-carbon functional group can also be introduced into the carbon matrix by the direct carbonization of the biomass that normally contains nitrogen and phosphorus elements. Zhang et al. reported a carbon-fiber monolith prepared by the carbonization of filamentous fungi, which led to a conductive and porous structure doped by nitrogen and oxygen [119]. The applications of the carbon monolith as conductive interlayer contributed to an enhanced performance of Li-S battery especially in the cyclic stability.

Except for the above-mentioned carbon interlayers in the cathode side, interlayer in the anode part also contributes to better Li-S cells. One pioneering work was conducted by Liu's group with a graphite interlayer in the anode side in the new configuration of a hybrid anode structure [120]. With a hybrid anode of electric connected graphite film and lithium metal anode, and a separator between them, the lithiated graphite interlayer was generated during the electrochemical charge/discharge of a Li-S cell and laid between cathode and lithium metal anode. This lithiated graphite film as an artificial solid-state electrolyte interface decouples the Li ion extraction/reinsertion and the parasitic reaction between polysulfide and lithium metal surface. As polysulfides cannot

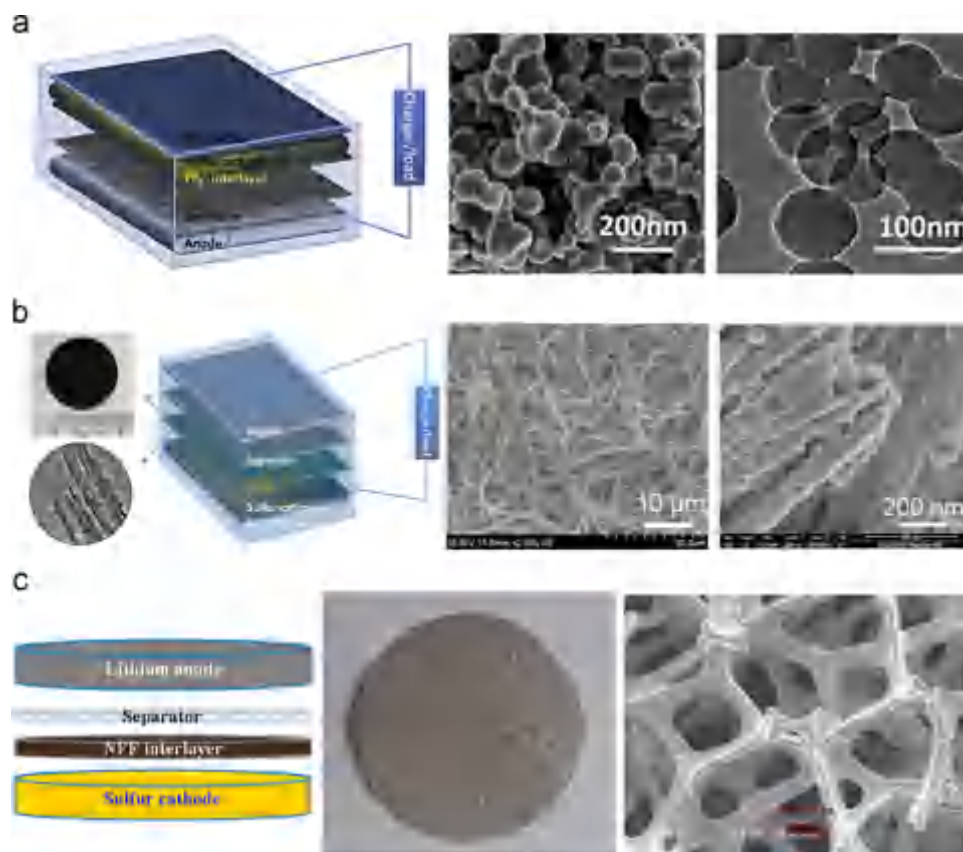


Fig. 10. (a) Schematic illustration of the functional interlayer in Li-S battery, and the SEM/TEM images of polypyrrole nano-particles [121]. (b) Schematic cell configuration of Li-S batteries with polypyrrole nanotube film interlayer, the SEM/TEM image of polypyrrole nanotube film [124]. (c) A schematic cell configuration of Li-S batteries with nickel foam foil interlayer, photo of the rolled nickel foam interlayer, and the SEM image of the surface of the raw nickel foam [126].

insert into or diffuse through the graphite film, the harmful parasitic reactions on the surface of lithium metal anode were prevented. The reduced irreversible loss of sulfur active materials on the Li metal anode and the physical barrier effect provided by the lithiated graphite film layer led to an exceptional electrochemical performance of Li-S batteries. Future exploration in the application of interlayers in anode side is required, which favor the performance of Li-S battery by both the inhibition of polysulfide diffusion and improvement of the lithium anode lifespan.

3.2. Non-carbon-based interlayers

Except for the carbon-based interlayer materials, polymer and metal interlayers were also reported for Li-S batteries. The polymer interlayer was firstly reported by Ma et al. with a polypyrrole functional layer (Fig. 10a) [121]. Polypyrrole is one typical conductive polymers, which have been applied as cathode scaffolds to host sulfur materials, in which the interactions between sulfur molecules and the polymer chains through hydrogen bonds are able to stabilize polysulfides and enhance the performance of Li-S cells [122,123]. By forming the polypyrrole interlayer between the cathode and the separator, it benefits the Li-S cells in several aspects: (i) the conductive polypyrrole interlayer can improve the electron and ion transfer on cathode surface; (ii) the high surface area polypyrrole particles can trap polysulfides through hydrogen bonds; and (iii) the flexibility of interlayer can buffer the volume change of the cathode materials. Later, Ma et al. further proposed a polypyrrole nanotube film as a functional interlayer for Li-S batteries (Fig. 10b) [124]. Compared with interlayer formed by polypyrrole particles, the interlayer composed of polypyrrole

nanotubes exhibited much higher specific surface area and larger amount of pores. Therefore, polypyrrole nanotubes film as a functional interlayer not only reduced the polarization of the cell, but also exhibited advantages in the suppression of shuttle effect. Furthermore, the addition of this interlayer significantly prevented the Li anode from corrosion reactions due to the efficient inhabitation of polysulfide migration. Recently, a nano-Li⁺-channel interlayer was proposed and fabricated by Zhang and co-workers for Li-S batteries aiming to separate the polysulfide particles through a size exclusion [125]. The poly(vinylidene fluoride) is selected as the interlayer backbone, and the Li⁺ channels were built by swelling the poly(vinylidene fluoride) dense membrane with organic electrolyte to obtain the inter-connected ions transport pathways among the 3D molecular chains. Consequently, the Li-S battery assembled with the Li⁺-channel interlayer delivered very lower polysulfide permeability and better Li ion storage performance than the cell without the interlayer.

Metal interlayer was also reported by Zhang et al. with a nickel foam foil interlayer for Li-S batteries (Fig. 10c) [126]. The interlayer provided the sulfur cathode with a good conductive network to enhance the utilization of sulfur cathode. In addition, the nickel foam interlayer also served as an extraordinary matrix to retain and accommodate the stress during the electrochemical process. These features guarantee a Li-S cell containing interlayers with much improved cycling stability.

With the specific electrochemical process of Li-S batteries, the introduction of interlayer concept brings a new suitable configuration for high-performance Li-S batteries. Generally, interlayers of porous, conductive, and flexible structures bring several benefits to the battery system. The porous interlayers absorbed the polysul-

vides generated during the electrochemical process and therefore mitigated the shuttle effect with parasitic side reactions, which also alleviated the corrosion of lithium anode and contributed to the higher stability of cells. The conductive property of interlayer afforded a reduced surface charge transfer resistance since the interlayer acted as an upper current collector to facilitate the sulfur utilization. The conductive network in interlayers also reactivated the precipitated sulfur species and contributed to a higher capacity with better cyclic stability. The flexibility of interlayer also ensured the robust mechanical property, which accommodated the volume change of the sulfur materials and preserved structural stability of sulfur cathode. With the further development of interlayers, the facile manufacture and utilization of interlayer bring a breakthrough for high-performance Li-S batteries.

4. Concluding remarks and perspective

The introduction of multi-functional separator/interlayer has been widely explored towards advanced Li-S batteries with high sulfur utilization, large coulombic efficiency, and superior cycling stability through alleviating the polysulfide shuttle effect, facilitating the sulfur utilization, and protecting the lithium anode. Multi-functional separator system with ion selective/electrical conductive polymer, sp^2 and porous carbon, metal oxide modified separators, as well as interlinked free-standing carbon, micro/mesoporous carbon, and other conductive interlayers have been proposed. The addition of ultralight separator/interlayer is an effective routine to achieve Li-S batteries with expected properties. The rational design of the separator/interlayer structures in proper combination of micro/meso/macropores and functional groups also contributes to better performance of battery cells.

Despite the progresses achieved, there is enough open space for the exploration of the new component in Li-S batteries and great challenges together with opportunities lies before the practical applications.

4.1. Towards high-performance separator

Up to now, the functions of modified separator system for Li-S batteries mainly focused on the block of polysulfide shuttling, the maintaining of lithium ion transfer pathway, and the protection of lithium anode.

The modified separator for the block of polysulfides is highly efficient to improve the coulombic efficiency and the cyclic stability of the Li-S cells. Most of the modified separator realized the confinement of polysulfides in the cathode chamber by the porous structure and/or the functional groups on the modified layers. Towards higher performance in polysulfide inhibition, integrated structures that bring together the effect of pores and functional groups are highly promising. For instance, if ion selective polymers are grafted onto one end of the long tortuous pores, a high selectivity of lithium ion can be expected together with an ultralow loading amount of the functional layer. Based on the current development, future efforts on the composite and hybrid modification of separator are highly demanded.

Secondly, compared with interlayer system, the modified separators are commonly aiming at higher performance in blocking polysulfide anions, which inevitably introduced extra high resistance to the transfer of lithium ions. There are always compromises between the flux of lithium ion and the selectivity of lithium ion transfer against polysulfide transfer. Therefore, the future development of modified separator for polysulfide inhibition will introduce the customized structure based on the requirement of the Li-S cells. For Li-S cells working at low current densities, modified separator of low lithium ion flux and high polysulfide blocking effect can be

applied, which are able to offer high cyclic stability. In contrast, a modified separator with moderate polysulfide inhibition property is more suitable for working cells at a very high current density to achieve superb high-rate capability.

Based on modified separator system, the lithium anode can also be protected both by the positive effect of polysulfide inhibition and the direct contact between anode and the separator. By the polydopamine modification of the separator in the anode side, the suppression of Li dendrite growth was reported [60]. Inspired by this pioneered work, the modifications of separator in the anode side are promising to further improve the performance of Li-S cells. Currently, the rapid pulverization of lithium metal anode cause severe problems in Li-S batteries [127,128], including the rapid capacity degradation of anode, the consumption of large amount of electrolyte, and also the safety issue in Li-S batteries. With the modification of proper polymer layers, a wet adhesion between polymer layer and the anode surface can be established for a uniform ionic flux and lead to a smooth dissolution/precipitation of lithium metals. The modifications of stiff metal oxide are promising to prevent the dendrite penetration, which render advanced Li-S batteries with high safety. As a component that divides the cell into cathode and anode, the dual-modification in anode and cathode side for both polysulfide inhibition and anode protection are of great importance in the future.

4.2. Towards the high-performance interlayers

The current functions of reported interlayer in Li-S batteries lies in the polysulfide inhibitor, current collectors, and structure stabilizer of the sulfur cathode.

For a higher efficiency in the polysulfide inhibition, rational designs of porous structure and the surface properties of the interlayer are highly required. Given that the micropores are mainly responsible for the trapping of polysulfide diffusion and the macro/mesopores mainly serve as electrolyte pathways, there should be a balanced amount of different pores. One ideal micro-meso-macroporous structure of the interlayer is: long and tortuous micropores penetrate across the interlayer for electrolyte permeation and provide the lithium ion pathway; a large amount of mesopores locates around the macroporous channels to form a branch-like structures to extend the electrolyte that can be taken in the interlayer; and numerous micropores dispersed in the branched structure for the selective absorption of polysulfides. A hierarchical pore structure is reasonable to achieve the function of polysulfide trapping, gradient or layered structures are also promising to slow down the polysulfide permeation process through the interlayer. Moreover, by the introduction of functional groups that exhibit extra interactions with the polysulfides, an interlayer with high affinity with polysulfides can be achieved. The previously reported carbon additives with functional groups (such as GO based interlayer) and interlayer derived from nitrogen-containing biomass showed good performance in polysulfide trapping [35,67,114,117,118,129]. Nitrogen-containing groups are of high affinities with polysulfides and can be easily grafted onto the common carbon substrates [24,31,99,130,131], which is a highly promising route towards interlayer with high trapping efficiency for polysulfides.

For a superb performance in lowering the charge transfer resistance for the sulfur cathode, an interlayer with higher conductivity and better contact with the cathode are strongly considered. Metal foam interlayers are of highest conductivity in the reported interlayers, while the contact with sulfur cathode and the interaction with polysulfides are doubtful as the high stiffness of nickel and the few micro/mesopores existed in metal frameworks. On the other hand, the interlayer structure composed with solely carbon all suffered from relatively low electrical conductivity due to the large contact resistance between the nanosized building

blocks. In this case, a hybrid structure with combined advantages can render much improved performance. For example, by combining the metal framework with the carbon nanomaterials, a hybrid with metal framework and carbon nanomaterials decorated on the surface of metal framework will be achieved. This hybrid structure provides long-range conducting network with metal framework, and local conducting network with carbon nanomaterials, which also ensures the intimate contact with sulfur cathode and introduces porous structures in the interlayer system.

For the accommodation of structure change during the cycle, self-woven structures composed with interlinked structures are favorable rather than the interlayers formed with powders through binders. The entire metal foam structure and flexible membranes constructed by long CNTs and carbon nanofibers are of high structural stability, which can endure the structural change due to the volume change of the cathode/anode. In contrast, the nano/micro-powders bonded together with the polymer binders suffer from polymer swelling and are possible to crack after long-term cycling, which results in the degradation of the interlayer. A high-stable, self-woven, and self-standing skeleton is suitable for the design of future high-performance interlayer.

The wise combination between highly conducting framework with high mechanical stability, and a rational design of pore structure together with proper surface modification will introduce the next-generation of high-performance interlayer system for Li-S batteries

4.3. Towards the applications of advanced separator/interlayer system

In addition to the development of advanced interlayer and separator system, the feasibility of the new component in Li-S batteries should also be considered, including their effects in overall energy densities, the possibilities for mass production and application, etc.

The key advantage of Li-S batteries lies in its ultrahigh theoretical specific energy density compared with routine battery systems such as lithium ion batteries. However, considering the inactive component in Li-S batteries such as large amount of solvent in electrolyte, excessive lithium metal anodes, etc., the advantage in energy density has been weakened. Interlayer and separator system, although helpful for the performance of Li-S batteries, are inert overweight, which need to be lightened as much as possible. Meanwhile, the extra coating layer or interlayer in the system inevitably increases the electrolyte uptake, which also impacts the energy density of the Li-S cells. Therefore, the wise design of separator/interlayer is crucial towards the practical applications of the new configurations. Especially for interlayer system, the areal density of interlayers are commonly higher for coating layers on separators as they need to stand by themselves rather than attach onto polymer supports. The development of effective but lightweight interlayers is very important. As there is always compromise between the thickness of functional layer and effect, a thin but less effective functional separator/interlayer is more compatible with cathodes of low sulfur areal loadings to avoid severe loss in energy density. A thicker and more effective separator/interlayer is preferred in case of cathode with high sulfur areal loading amount.

Meanwhile, the applications of multi-functional separators/interlayers also require easy fabrication process that is compatible with the cell assembly process. Currently, the fabrications of the multi-functional separator/interlayer are either through the slurry coating process or the filtration process to form a film structure. Generally, the coating process is of better compatibility with traditional battery fabrication process. In comparison, the filtration process commonly requires building blocks with special structures, which is currently difficult in the mass production and requires future technology

improvement for large scale applications. Recently, development based on the direct coating of carbon layers and sulfur cathode layer onto the separator introduced a new idea of cathode-separator integration, which are highly compatible with and even simplified the traditional battery assembly process.

To achieve these research goals, fundamental understanding on the working Li-S systems should be further improved. For instance, the dynamics role of separator/interlayer is not well understood yet, the structural evolution of separators/interlayers during long-time durable cell is not tracked, and the relationship between the structure and working performance is not exactly determined yet. These basic scientific understanding strongly hinders the rational design and delicate fabrication of advanced separators/interlayers. The operando characterization of working cells is a direct strategy to explore the real roles but few researches has been carried out. A practical cell with very high areal sulfur loading ($> 6.0 \text{ mg cm}^{-2}$) and small electrolyte amount (electrolyte/sulfur ratio is less than 3.0) should be employed to further evaluate the performance of the advanced separators/interlayers. The engineering to combine the advanced materials processing of separators/interlayers with current battery production should be further explored wisely to achieve practical Li-S batteries with high energy density and reproducibility. A multidisciplinary strategy from the viewpoint of polymer, electrochemistry, advanced materials, physical chemistry, chemical engineering, mechanical engineering, and automation science, is highly required for the exploration of Li-S system with advanced separators/interlayers.

The concept of Li-S batteries has been proposed more than 40 years ago, and great achievements have been made with the combination of energy nanomaterials and modern materials chemistry within the recent 6 years. These innovations in the fabrication of new-generation separator/interlayer systems are expected to enhance the performance of practical Li-S cells. These new insights from the Li-S batteries is also applied to other multi-electron conversion reactions based energy storage systems (e.g. Li-air batteries, Zn-air batteries, fuel cells, Mg-S batteries) for sustainable society.

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