

Review

Review on Multi-Functional Separator for Li-S Batteries

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Received: 18 December 2022; Accepted: 06 March 2023; Available online: 13 March 2023

ABSTRACT: Because lithium-ion batteries cannot meet increasing demand for power density, lithium metal batteries are expected as the next generation of rechargeable batteries. As one of lithium metal batteries, lithium-sulfur (Li-S) batteries have attracted extensive attention because of their ultrahigh power density (2600 Wh kg^{-1}) and low cost of sulfur. In order to overcome problems of active material loss, volume expansion and dendritic growth of Li metal in Li-S batteries, researchers have adopted several methods such as adding electrolyte additives, electrode modification and separator modification. Among them, separator modification shows significant advantages in inhibiting the shuttle effect of lithium polysulfides. This paper reviews research progress of inhibiting the shuttle effect of Li-S batteries by the means of the separator modification in recent years, including direct design of new type of separator and physical/chemical modification of separator surface. Through extensive reading and summarizing of the research results of the separator modification of Li-S batteries, we give the possible development direction of Li-S batteries at the end of the paper.

Keywords: Li-S batteries; Functional separator; Shuttle effect



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1. Introduction

With the increasingly prominent energy crisis and more serious environmental problems, people are trying to reduce the proportion of fossil energy (carbon energy) in human energy use structure. In recent years, governments and enterprises all over the world are committed to the development of new energy vehicles, in order to reduce the demand for traditional internal combustion engine vehicles. At present, commercial electric vehicles with lithium-ion batteries as main power sources are developing in the ascendant [1], while difficulties and challenges are constantly emerging in this process. The insufficient energy density of lithium-ion batteries is one of these challenges. Although the commercial lithium-ion batteries are close to the theoretical limit, they still cannot meet the requirements of people of endurance for electric vehicles. Therefore, lithium-sulfur (Li-S) batteries, one of the most potential batteries in the next generation of large capacity batteries, is being widely studied [2,3].

A typical Li-S battery consists of sulfur cathode, lithium metal anode, separator and electrolyte. Lithium metal anode has a capacity density as high as 3860 mAh g^{-1} and an electrode potential as low as -3.04 V vs. SHE (standard hydrogen electrode). Correspondingly, the sulfur cathode has a theoretical capacity density of 1675 mAh g^{-1} and an energy density of 2400 Wh coupled with lithium anode [4]. This is far more than the current commercial lithium-ion batteries. Unfortunately, there are still some unsolved technical problems, such as volume expansion, capacity attenuation, and poor rate performance of sulfur cathode [5,6] as well as dendrite growth of lithium anode [7]. The shuttle effect is one of the biggest difficulties hindering the further development of Li-S batteries [8–10]. When a Li-S battery is running, the electrochemical reaction of sulfur cathode will produce soluble lithium polysulfides (LPS). Some of the LPS will pass through the separator to lithium metal anode surface and be reduced to insoluble Li_2S_2 or Li_2S . Since this part of S is unable to return to S cathode, this phenomenon of LPS migration denoted as the shuttle effect results in severe capacity attenuation. In addition, the shuttle effect will corrode lithium metal anode, promote growth of lithium dendrites, and induce safety risks.

In view of these problems, the academia has launched a long-term and extensive research [4,11–15]. As far as lithium metal anode is concerned, researchers have tried to improve its electrochemical performance by constructing better solid electrolyte interface (SEI) [16,17] or adding electrolyte additives. At the same time, different doping materials were added to prepare composite

sulfur cathode to improve its charge discharge performance [18]. These works have achieved certain results, but they have not yet reached the requirement for commercialization of Li-S batteries. The simple electrode modification cannot effectively inhibit the shuttle effect, so more and more scholars began to study the modification of separators. Well-designed Li-S separator can not only inhibit the shuttle effect, but also guide fast Li^+ transport and regulate Li^+ deposition at the same time. In this review, we have summarized the research progress on the separator modification of Li-S batteries in recent years, including structure design and surface modification. We demonstrate different mechanisms by which different separator modifications solve problems such as volume expansion, low conductivity of S/Li₂S and the shuttle effect. We also highlight multiple pathways of inhibiting the shuttling effect and discuss the perspective for Li-S batteries for the future commercialization and large-scale application.

2. Structure Design

Traditional polyethylene (PE) and polypropylene (PP) separators have been widely used in lithium-ion batteries due to their good mechanical strength, thermal stability and chemical stability. However, in Li-S batteries, the PE and PP separators can no longer meet requirements of stable operation due to the shuttle effect. LPS dissolved from sulfur cathode would shuttle through pores and crevices of the PE/PP separators and react with lithium metal anode, resulting in severe side reactions, capacity decay and dendrite growth. In order to solve such problems, the most direct method is structure design of the separator through a variety of film forming technology using different materials. Polymer materials are widely used in the preparation of newly designed functional separators due to their flexible structural design capabilities. There are two common structural design strategies. (1) One is to prepare separator skeleton with other polymer materials like polyacrylonitrile (PAN) [19] and poly(m-phenylene isophthalamide (PMIA) [20] or inorganic materials like HAP [21]. Then, these skeletons are modified by functional materials like carbon nanotubes, Mn_3O_4 , reduced graphene oxide and MOFs. Specific groups and modification materials on the separator skeleton will have different interactions with LPS to alleviate the shuttle effect. (2) In addition, some researchers chose to directly design the polymer structure at the molecular level, introducing polar functional groups through grafting or cross-linking to achieve the purpose of blocking, capturing and converting LPS. Compared with commercialized PE/PP, these alternative separators provide more options for the construction of advanced Li-S battery separators. Here are some examples:

Rao et al. [21] reported a hydroxyapatite (HAP) nanowire-based separator and coated it with Mn_3O_4 anchored carbon nanotubes (CNT) interlayer by filtration method (Figure 1). This composite separator not only has a good thermal stability which makes it maintain structural integrity at 400 °C with no shrinkage, but also can effectively inhibit the shuttle effect of LPS because of the modification of CNT/ Mn_3O_4 . In addition, due to the good compatibility with electrolyte, this separator can achieve fast Li^+ transport and inhibit the growth of lithium dendrite. The battery with such separator achieves the remaining capacity of 1000 mAh g^{-1} after 150 cycles and the rate performance of 607 mAh g^{-1} at 4 C.

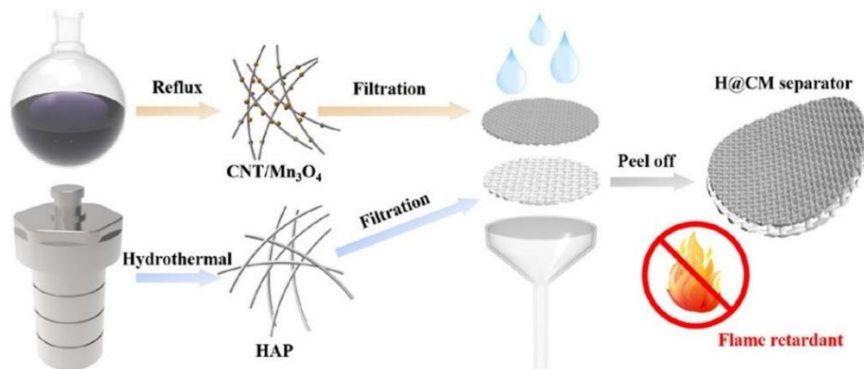


Figure 1. Schematic illustration of the fabrication procedure of the H@CM separator [21].

Different polymer frameworks could confer different properties on functional separators like better mechanical strength, excellent thermal stability, and significant flame retardancy. As a material widely used in other fields, polyacrylonitrile (PAN) nanofiber membrane synthesized through electrospinning is utilized by Zhou et al. [19] to prepare functional separator of Li-S batteries. As shown in Figure 2, this separator is a double-layered composite membrane constructed by metal organic frameworks (MOF), reduced graphene oxide (rGO) and PAN. In addition to good mechanical property and thermal stability, the PAN network can adequately absorb electrolyte profiting from its excellent electrolyte wettability and abundant pores. MOF particles perform as LPS trapper to confine the shuttle effect and meanwhile the rGO-PAN layer is responsible for guiding diffusion of Li^+ .

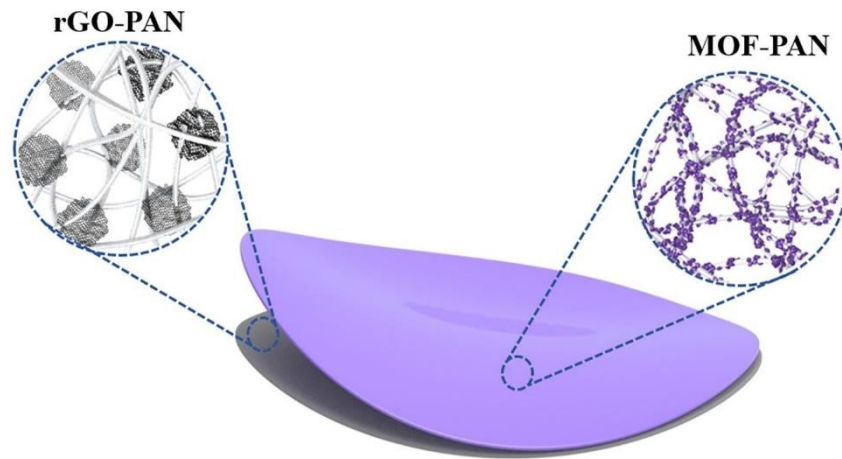


Figure 2. Schematic of the multifunctional electrospun MOF-PAN/rGO-PAN separator and PP separator for Li-S batteries [19].

In addition to simply blocking LPS, it is a good idea to add materials that can catalyze LPS. CeO_2 is a good choice for constructing composite Li-S separator with catalyzing effect. Zhang et al. [22] reported an asymmetric bilayer PAN/CNF- CeO_2 separator in which the PAN nanofiber mat performed as a support framework with unique thermal stability and electrolyte wettability and the CeO_2 nanocrystals spatially besieged by carbon nanofiber (CNF) were introduced to simultaneously restrain LPS as well as electrocatalytically accelerating LPS reducing. Deng et al. [20] proposed a MOF nanoparticles and F co-doped composite separator by one-step electrospinning. The preparation process is shown in Figure 3. The obtained separator has a relatively high porosity, small aperture and prominent electrolyte wettability and excellent ionic conductivity benefited from slight fiber diameter caused by F-doping. The MOFs were introduced in order to chemically absorb LPS and perform as catalyzer to accelerate the redox reaction at the same time. It is proved that F-MOFs-co-doped poly(m-phenylene isophthalamide) (PMIA) separator displays significant electrolyte wettability, exceptional electrolyte storage, distinctive thermal stability, strong catalytic conversion and effective confinement for LPS shuttling.

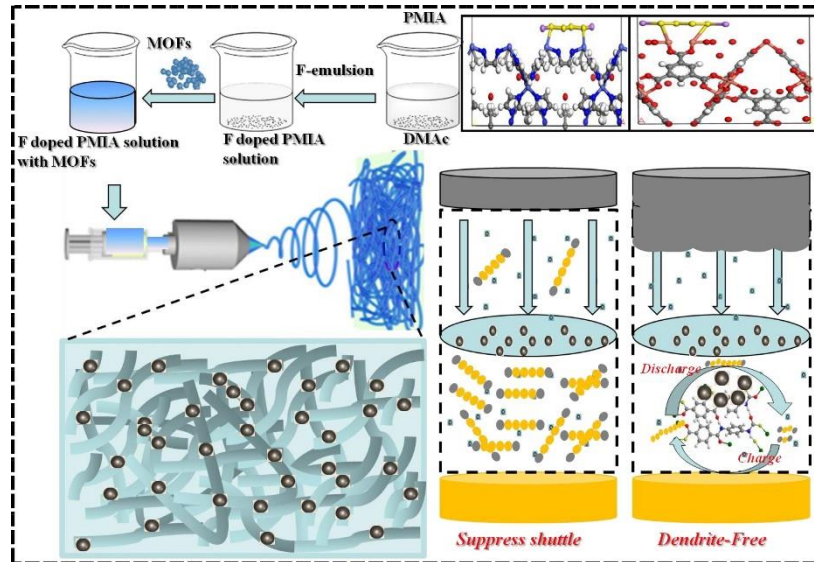


Figure 3. The schematic illustration of the as-obtained multifunctional MOFs nanoparticles (ZIF-67 and Cu-BTC (HKUST-1))-modified PMIA membrane on the preparation process, catalytic conversion, “shuttle effect” of lithium polysulfides suppression and anode protection in working Li-S battery [20].

The above work proves that the preparation of composite separator by doping functional materials in polymer skeleton can significantly improve the related properties and help batteries to run better. Besides, direct copolymerization, crosslinking and grafting of polymer frameworks is also an effective method. Hu et al. [23] proposed an ammoniated polyacrylonitrile nanofiber separator which is denoted as APANF. This separator can inhibit formation of lithium dendrite and shuttling effect of LPS by polyethyleneimine (PEI) groups which were connected to PAN nanofiber via chemical grafting. The Li^+ flux can be well regulated and the LPS can be blocked. The preparation process is shown in Figure 4a. Assembled with APANF, the battery exhibited a coulombic efficiency of 98.8% and an overpotential of 15 mV. The remarkably uniform three dimensional (3D) spherical Li deposition pattern was synthesized as shown in Figure 4b,c.

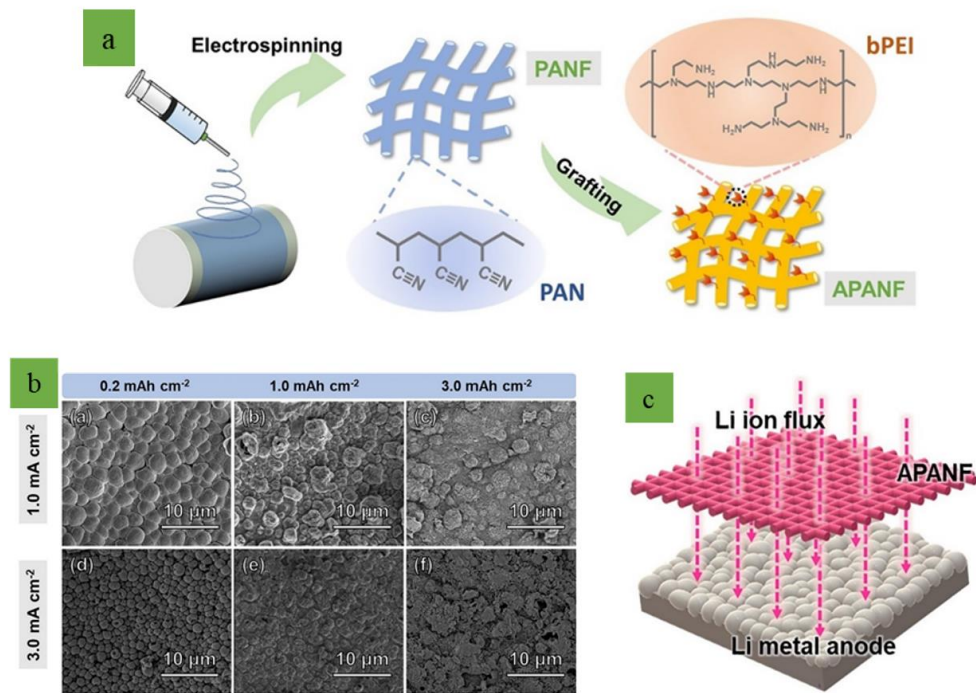


Figure 4. (a) A schematic of preparation of APANF. (b) SEM images of lithium deposits with APANF separator under current densities of 1.0 and 3.0 mA cm⁻² for total capacity of 0.2, 1.0 and 3.0 mAh cm⁻². (c) The illustration of APANF for regulating Li ion flux and uniform Li metal anode [23].

Polyimide, one of the most suitable polymer materials to be utilized as Li-S separator matrix with excellent thermal stability, good insulation performance and significant chemical stability, was also used in preparing separator by Luo et al. [24]. Electrospinning technique was employed by them to fabricate fluorinated polyimide (F/PI) nanofiber separator in which the F/PI was synthesized from polycondensation of a diamine (FTPAP) and a dianhydride (PMDA). The -CF₃ polar groups which are uniformly distributed on the separator help create an electronegative climate so that the diffusion of positively charged Li⁺ is promoted and the shuttle effect of LPS is suppressed. In addition, a remarkable advantage of such separator is its prominent thermal stability and flame retardancy, which was also addressed by Li et al. [25] The battery can achieve initial capacity of 1512 mAh g⁻¹ at 0.1 C, rate performance of 532 mAh g⁻¹ at 5 C and capacity retention of 95.6% after 500 cycles at 1 C. Li et al. [26] reported a polypyrrole (PPy) separator prepared by in situ template-sacrificing approach. This kind of PPy separator has three-dimensional networks with remarkable electrical conductivity.

The key parameters of the above research are summarized in Table 1. To sum up, the structure design of Li-S separator by replacing skeleton materials is an effective strategy to inhibit the shuttle effect of LPS. Suitable polymer materials give the separator better mechanical strength, thermal/chemical stability and electrolyte wettability. Grafting special polar groups or doping functional materials can help achieve better LPS capture. All the above studies show that an ideal Li-S battery separator should have not only excellent physical properties, but also well-designed macroscopic structure like “double layered structure”, “reticular structure” or “framework structure” to prevent the shuttle effect of LPS. In terms of microstructure design at molecular level, through appropriate functional materials or polar groups modification, the LPS dissolved from the S cathode can be blocked, captured and converted, so as to improve the cycle stability of Li-S battery, mitigate capacity degradation and potential safety hazards.

Table 1. Electrochemical performance of separators in terms of structure design.

Structural Composition	Thickness (μm)	Capacity after Cycles (mAh g ⁻¹)	Year
PEI/SiO ₂ /PVP/acetylene black	80	650 (after 200 cycles, 0.2 C)	2021 [27]
Hydroxyapatite framework/Mn ₃ O ₄ /carbon nanotube	90	1000 (after 150 cycles, 0.1 C)	2020 [21]
MOF-PAN/rGO-PAN	135	925 (after 100 cycles, 1 C)	2020 [19]
PAN/CNF-CeO ₂	55	802 (after 200 cycles, 1 C)	2020 [22]
ZIF-67/HKUST-1/F-doped poly-m-phenyleneisophthalamide	37	752 (after 500 cycles, 0.5 C)	2020 [20]
Ammoniated polyacrylonitrile (PAN) nanofiber separator	60	510 (after 500 cycles, 2 C)	2020 [23]
Fluorinated polyimide nanofiber separator	30	487 (after 500 cycles, 1 C)	2020 [24]
Polyimide/MoO ₃ nanoparticles/MWCNTs-COOH	94	800 (after 100 cycles, 0.2 C)	2020 [25]

3. Surface Modification

The design and manufacture of a Li-S separator from scratch is often accompanied by complex preparation process, high cost and harsh technological conditions. The synthesis of specific polymer structures makes it expensive to prepare a composite separator, which is not conducive to large-scale commercial application. It is a simpler and more practical way to make functional surface modification directly on the mature PE and PP separator. Currently, a variety of materials such as carbon-based materials (graphene (GE), carbon nanotubes (CNT), carbon black (CB), ketjen black (KB) and etc), metal oxides, metal sulfides, metal nitrides and MOFs have been widely used to modify commercial PP/PE separators to gain excellent performance. Carbon-based materials are the earliest used to modify the Li-S separator. In 2012, the method of inserting a free-standing multiwalled carbon nanotube (MWCNT) paper between the cathode and the separator was firstly reported by Yu-Sheng Su and Arumugam Manthiram [28]. In 2020, Zhu et al. [29] reported a N-doping carbon aerogel interlayer in coral-like structure (NHCA) to modify the separator. Besides, they also explored influences of specific surface area of interlayer. Rana et al. [30] proposed a Nafion/KB (KBN) composite coating which possessed abundant SO_3^- groups and electronically conductive porous framework. Since there have already been many summaries about carbon-based materials modified separator, this paper will mainly focus on other materials.

3.1. Metal Oxides

Metal oxides have been widely used in separator modification because of their lower price and stronger polarity which have been proved to effectively adsorb LPS in many studies. In Cheng et al.'s work [31], spontaneously polarized bismuth ferrite BiFeO_3 (BFO) particles were firstly used in separator modification of Li-S battery. Combining with graphene oxide (GO) and acetylene black (AB), they fabricated a functional BFO/GO/AB@PP separator. The spontaneous polarization of BiFeO_3 is regarded as the key factor which achieves effective LPS anchoring. In 2020, Wang et al. [32] proposed to use FeOOH and $\text{C}_3\text{N}_4/\text{KB}$ to build a self-assembled bifunctional separator. Different from the physical adhesion method used in previous studies, they were the first to chemically synthesize a layer of FeOOH to capture LPS by floating commercial PP separator onto acidic K_2FeO_4 solution, and then coated a layer of $\text{C}_3\text{N}_4/\text{KB}$ on this basis to improve the conductivity and promote Li^+ diffusion. Benefiting from this bifunctional separator, the battery displays rate capacities of 1000, 901, and 802 mAh g^{-1} at 0.5, 1, and 2 C as well as long cycle discharge capacity of 444 mAh g^{-1} after 900 cycles at 1 C. In addition, MoO_2 was also used in construction of Li-S separator. Choi et al. [33] reported a $\text{MoO}_2@\text{CNT}$ nanocomposite and applied it to the surface modification of separator. Such $\text{MoO}_2@\text{CNT}$ nanocomposite was prepared through a customized electrical wire-explosion process conducted at room temperature using Mo wires and CNTs. The CNTs scaffold served as a physical barrier for lithium polysulfides and a current collector for Li^+ transport as well as lithium polysulfides conversion. At the same time, MoO_2 was supposed to chemically anchor the polysulfides. Benefited from a number of voids and mesopores, the as-prepared $\text{MoO}_2@\text{CNT}$ nanocomposite can also alleviate the volume change of cathode and provide additional active sites. The Li-S batteries introduced with $\text{MoO}_2@\text{CNT}$ -modified separator exhibited a significant cycle performance of 1067 mAh g^{-1} at 0.2 C and achieved a coulombic efficiency of more than 96% after the first ten cycles as well as quite low-capacity decay of only 0.066% per cycle. As displayed in Figure 5, Zuo et al. [34] used acrylic cloth carbon (ACC) decorated with MnO_2 to modify the separator. On the one hand, MnO_2 has been proved to be effective in capturing LPS. On the other hand, acrylic cloth carbon (ACC) was reported to be more reactive and conductive than graphite nitrogen, rGO, dopamine and CNT because of sufficient pyridine and pyrrolic nitrogen generated during the carbonation. The ACC/ MnO_2 hybrids coating significantly improved the stability of the obtained Li-S battery.

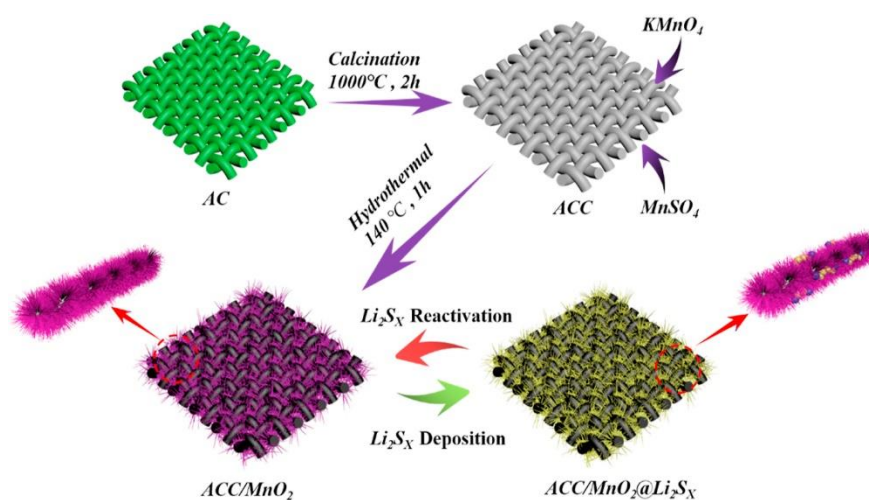


Figure 5. Schematic illustration of the fabricated ACC/ MnO_2 hybrids [34].

Wan et al. [35] developed a Titanium-based nanorods/Ketjen Black (KB) modified separator named as KTO-2/PP, and applied it to a typical Li-S battery which showed wonderful electrochemical capability. The KTO-2 was fabricated by a simple one-pot hydrothermal method using Ketjen black as well as tetrabutyl titanate and then vacuum-filtered through Celgard PP separators to prepare KTO-2/PP. The results of A.C. impedance test showed that the separator coated with KTO-2 presented a lower charge transfer resistance (25.7Ω) than that of either KB/PP (39.9Ω) or PP (102.3Ω). In other words, the KTO-2 can really improve the conductivity of the coating and its lithium-ion transport capacity. Besides, the great physical and chemical LPS adsorption properties owned respectively by Ketjen black and Titanium-based nanorods are also proved which both relieve the shuttle effect of such Li-S battery. After 200 cycles, the battery equipped with KTO-2/PP displays a reversible capacity of 754 mAh g^{-1} under the rate of 1 C. Huang et al. [36] developed a Sodium-containing Titanium oxides nanowires/nanosheets (denoted as STO-W/S) composite coating by one-pot method. Instead of simply physically mixing, the reaction condition controlling is more helpful for structure fabrication of STO-W and STO-S. The STO-W/S is able to enhance Li^+ conductivity as well as suppressing shuttle effect. The battery assembled with this functional separator can achieve an initial capacity of up to 813 mAh g^{-1} at 1 C and remain the capacity of 541 mAh g^{-1} after 500 cycles.

Recently, a Ni/SiO₂/Graphene coated separator was reported by Chen et al. [37] in order to make an improvement in such typical Li-S battery. As shown in Figure 6, the coating consists of Ni/SiO₂ hollow sphere with mesoporous structure as well as graphene and a great number of silica nanosheets and Ni nanoparticles are evenly distributed on the Ni/SiO₂ hollow sphere. The function of silica nanosheets and Ni nanoparticles is to anchor polysulfides and catalyze to quicken their transformation. Meanwhile, the introduction of graphene aims to fabricate conductive network as well as hampering polysulfides to shuttle from cathode to anode. Moreover, the rapid Li^+ transportation is achieved by outstanding electrolyte infiltration and retention benefited from mesopores structure. Because of these advantages mentioned above, the battery equipped with Ni/SiO₂/Graphene exhibits a significant cycle performance of 922 mAh g^{-1} after 100 cycles at 0.2 C as well as 772 mAh g^{-1} after 300 cycles at 1 C and rate capability of 1463 mAh g^{-1} at 0.1 C and 782 mAh g^{-1} at 2 C.

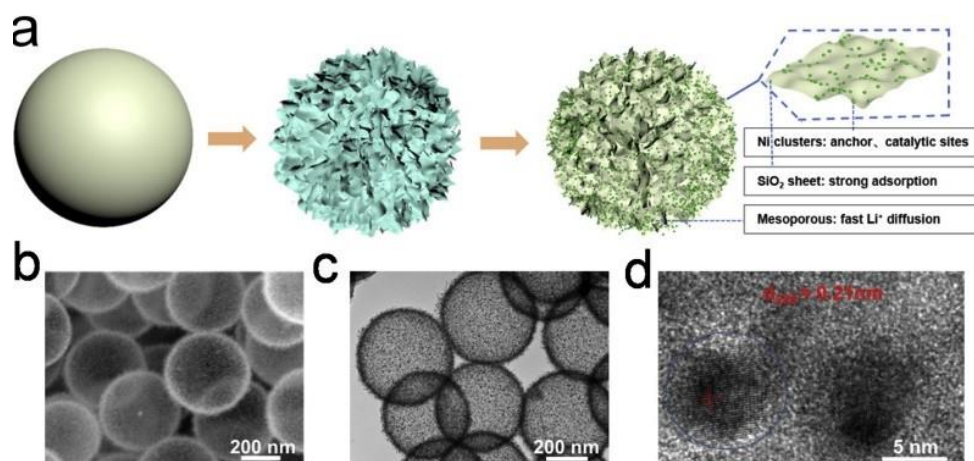


Figure 6. (a) Schematic illustration of the synthesis route of Ni/SiO₂. (b) SEM image of the 700Ni/SiO₂. (c,d) TEM and HRTEM images of 700Ni/SiO₂ [37].

Li et al. [38] proposed a CNTs-COOH@Fe₃O₄ coating made up of Fe₃O₄ nanoparticles along with carboxylate carbon nanotubes (CNTs) and put it on a commercial separator so as to form a functional Li-S separator. The introduction of CNTs-COOH is to fabricate a physical barrier and network structure, effectively catching polysulfides. At the same time, ultrasmall Fe₃O₄ nanoparticles help trap the polysulfides. Furthermore, the coating with CNTs-COOH and Fe₃O₄ possesses a superior conductivity so that it can be considered as the second current collector to promote the conversion and reutilization of insulated polysulfides. As a result, the Li-S battery equipped with CNTs-COOH@Fe₃O₄ achieved a prominent cycle stability of 0.023% capacity decay per cycle at 1 C over 2000 cycles. Wu et al. [39] developed a carbon black/LiMn₂O₄-modified separator in which the LiMn₂O₄ (LMO) nanoparticles could chemically adsorb LPS and serve as a fast channel for Li^+ transportation. Wang et al. [40] firstly used binary transition metal oxide manganese ferrite MnFe₂O₄ prepared by coprecipitation as well as conductive acetylene black to modify the separator. Zhu et al. [41] used magnetic mesoporous Fe₃O₄ mixed with Ketjen Black to modify the glass fiber separator. Angulakshmi et al. [42] reported a bi-functional permselective separator prepared by using Li₇La₃Zr₂O₁₂ as well as activated carbon. They proved that Li₇La₃Zr₂O₁₂ is helpful for Li^+ transport and hindering LPS shuttling. Cho et al. [43] developed a composite separator which consisted of the poly(vinylidene fluoride-co-hexafluoropropylene) and anodic aluminum oxide. The above works prove that metal oxides have great application potential as the separator modification materials.

3.2. Metal Sulfides

Metal sulfides and metal oxides have similar properties in many respects, but metal sulfides have better chemical adsorption of LPS. For example, Yan et al. [44] used TiS_2 sheets prepared by fast solid-phase synthesis method to modify the separator. TiS_2 has strong chemisorption and electrocatalysis towards LPS, which can capture LPS and promote its catalytic conversion and recycling. The authors also proved that vacuum filtration for separator modification is a more advanced process than slurry coating due to the formation of the more densely packed film in a fast solvent removal process. Mao et al. [45] developed a ZENs/G/Celgard separator in which the ZENs refers to $\text{ZnS}(\text{en})_{0.5}$ prepared by microwave-assist exfoliation method and G refers to graphene. The ZENs mixed with graphene can facilitate the Li^+ diffusion as well as hindering the polysulfides shuttling so that the battery induced with such separator displayed as low as 0.036% capacity decay per cycle during 1000 cycles at 0.5 C. Li et al. [46] proposed to embed ZnS into a nitrogen-doped carbon nanosheet skeleton and then use it to modify the separator, thereby fabricating a dual-function ZnS-modified separator. SnS was researched to modify the Li-S separator by Li et al. for the first time [47]. The specific preparation process is shown in the Figure 7. They used NaCl and Na_2SiO_3 as double templates in order to prepare extremely thin porous carbon nanosheet skeletons (PCNS). The hexadecyl trimethyl ammonium bromide was employed as the surfactant and then the SnS_2 was loaded onto PCNS by the hydrothermal method. After heated to 600 °C, the SnS was synthesized from SnS_2 decomposition and therefore the as-prepared material was named as SnS/PCNS. The function of SnS/PCNS is to facilitate the adsorption and reduction of polysulfides as well as enhancing the rapid nucleation and uniform deposition of Li_2S , effectively inhibiting the shuttle effect. The electrochemical performance was tested to be significant with an initial capacity of 1270 mAh g^{-1} at 0.5 C and a low capacity decay of 0.039% per cycle at 1 C. $\text{NiCo}_2\text{S}_4@\text{C}$ composites was used to fabricate interlayer by Li et al. [48] to improve the performance of Li-S battery. The NiCo_2S_4 was derived from MOF, so it has significant three-dimensional structure with nanopores. The utilization of carbon materials is to offer electron transport pathway. NiCo_2S_4 is helpful for Li^+ transport and LPS intercepting.

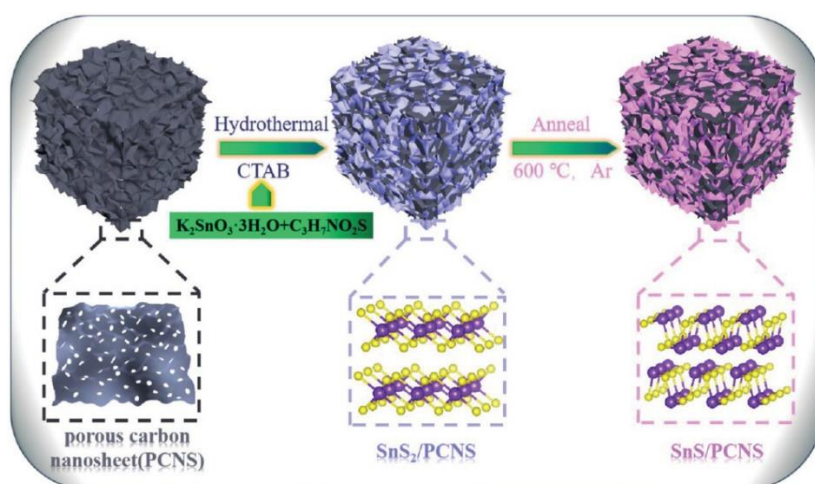


Figure 7. Schematic illustration of the synthesis process of SnS/PCNS [47].

3.3. Metal Carbides/Nitrides

In addition to metal oxides and metal sulfides, some metal carbon/nitrides with good catalytic effects are also used to modify Li-S separators. Zhang et al. [49] modified the separator with bimetallic carbide electrocatalyst $\text{Co}_3\text{Mo}_3\text{C}$ in 2020. The test results showed that the electrochemical performance was significantly improved due to the addition of $\text{Co}_3\text{Mo}_3\text{C}$. In their report, effects of other bimetallic carbides with similar catalytic effects on Li-S batteries were also demonstrated, which reflected the potential of this material family for further application. Shen et al. [50] reported a TiN/Nitrogen-doped Graphene (TiN/NG) nanocomposite synthesized by one-step carbonization method using g- C_3N_4 generated from the decomposition of dicyandiamide as a self-sacrificed template and nitrogen source. The mixture of dicyandiamide, glucose and titanium potassium oxalate were heated to 900 °C under nitrogen (N_2) atmosphere and then the TiN/NG was made after cooling. The obtained slurry was coated on a commercial glass microfiber separator. Graphene nanosheets can help TiN Nanoparticles avoid aggregating and tiny TiN grain with crystal defects is beneficial to the adsorption of polysulfides. The TiN/NG has total pore volume of $2.7 \text{ cm}^3 \text{ g}^{-1}$ and BET surface area of $328.1 \text{ m}^2 \text{ g}^{-1}$ which can effectively enhance the adsorption of polysulfides. Besides, the high electronic conductivity of TiN/NG can also induce the polysulfides to be transformed. Such separator modified with TiN/NG applied in Li-S battery shows an initial discharge capacity of 1005 mAh g^{-1} at 1 C and retains 718 mAh g^{-1} after 300 cycles.

3.4. Framework Materials

A large specific surface area is a key factor in achieving LPS blocking or capture. Various kinds of frameworks materials like metal organic frameworks (MOFs) with abundant polar active sites become ideal materials for separator functional modification. The adjustable pore size of MOF is beneficial for the suppression of LPS shuttle effect. Qi et al. [51] developed a multi-functional separator by coating homogeneous MIL-125(Ti) layer on a conventional PP/PE membrane. Because of the pore size of ~ 1.5 nm, the separator can not only regulate Li^+ transportation but also hinder the shuttle effect by Lewis base–acid interaction between MIL-125(Ti) and Li_2S_n . Wang et al. [52] proposed an ion-permselective LiX@Celgard separator composed of LiX zeolite membrane and commercial Celgard separator. The NaX zeolite was firstly synthesized over commercial Celgard separator and then it was immersed into a 0.3 M LiCl aqueous solution and heated to reflux at 95 °C for 2 h to form LiX zeolite membrane. The thickness of LiX zeolite layer is found to be about 6 μm and the morphology of LiX zeolite layer is pretty continuous and compact through SEM images. As shown in Figure 8, the porous structure of LiX zeolite can physically obstruct the shuttle effect of polysulfides and effectively improve the electrolyte wettability of Celgard separator. Benefited from above excellent properties of LiX@Celgard separator, the electrochemical test showed a specific capacity of 1083 mAh g^{-1} and a capacity retainment of 70% after 400 cycles at 0.2 C.

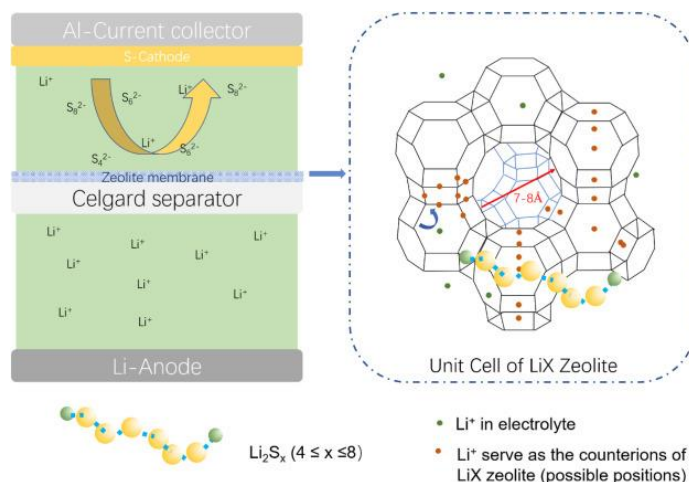


Figure 8. Design principle of Li–S battery employing LiX zeolite membrane-coated Celgard as separator [52].

As reported in Wang's works [53], cobalt-based zeolitic imidazolate framework-67 (ZIF-67), a crucial member of MOFs, has also been applied in modification of Li-S battery separator. The ZIF-67 was synthesized by mixing 2-methylimidazole and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in deionized water and then the prepared ZIF-67 was mixed with polyvinylidene difluoride (PVDF) and NMP to form slurry, which needed to be uniformly coated on the surface of the pristine polypropylene film.

Figure 9a showed that the ZIF-67 which was synthesized by such route was relatively pure through x-rays diffraction (XRD) and Figure 9b nicely showed the cubic structure morphology with a diameter of 80–100 nm of ZIF-67 through SEM. Benefited from strong chemical adsorption for polysulfides, the ZIF-67 could effectively inhibit the shuttle effect. Furthermore, electrochemical tests exhibited that the Li-S battery equipped with ZIF-67/PP separator showed a high specific discharging capacity of 1365 mAh g^{-1} at 0.1 C and 816 mAh g^{-1} after 300 cycles at 2 C.

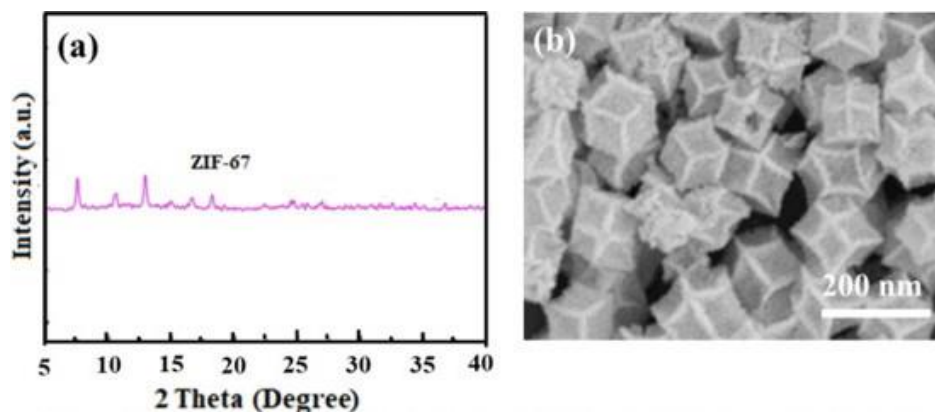


Figure 9. (a) XRD pattern and (b) SEM image of metal organic framework ZIF-67 [53].

3.5. Other Materials

In addition to the above chemicals, a few natural clay minerals were also researched, such as illite and smectite [32]. Wang and co-workers proposed an ISC/C@Celgard separator which was fabricated by coating natural clay mineral (illite/smectite, ISC) and carbon black (C) onto a commercial Celgard separator. The ISC/C@Celgard separator can nicely infiltrate electrolyte and keep its structure stable during the cycling process. It is worth mentioning that the polysulfides anchoring function of such separator is realized by formation of Li-O and Li-S bonds between LPS and OH groups as well as S element which are uniformly distributed on the separator surface. The ISC/C layer also has nanopores which are beneficial for physically inhibiting the shuttle effect. The Li-S battery equipped with ISC/C@Celgard separator displayed an initial capacity of 1322 mAh g⁻¹ at 0.1 C and wonderful cycle stability with low-capacity decay of 0.054% per cycle during 500 cycles at 1.0 C. In recent years, transition metal compounds have caught researchers' attention. As one of the representative transition metal selenides, MoSe₂ has been widely used in many fields such as catalysis, energy storage and optoelectronics due to the crystal structure and thermodynamic properties. It has been found that MoSe₂ has a great improvement in inhibiting the shuttling effect of lithium polysulfide [54]. You et al. developed a MoSe₂@rGO coating which is constructed by two-dimensional MoSe₂ and reduced graphene oxide (rGO), and placed it on the cathode side. The coating is made up of MoSe₂ and rGO in a ratio of nearly 1 to 1. The polar MoSe₂ provides the capacity for chemically absorbing polysulfides and catalyzing the reduction reaction and the rGO serves as a conductive network for its wonderful electric conductivity, capable flexibility, and enormous specific surface area. Therefore, the above-mentioned features of MoSe₂@rGO contribute to as low as 0.03% capacity decay per cycle at 1 C after 1000 cycles. Ferrocene (Fc), an organic transition metal compound with aromatic properties, was also studied by Zeng et al. [55]. In their works, the Fc was mixed with graphene oxide (GO) under the operation of ultrasonication. And then the GO/Fc-modified separator (PP-GO/Fc) was constructed through vacuum filtration. The Fc and GO do have a synergistic effect to suppress the polysulfides shuttling and help them to deposit and carry out catalytic conversion so that the battery exhibit a high reversible capacity of 409 mAh g⁻¹ after 500 cycles at 0.2 C. Additionally, cobalt is also widely developed due to its unique physical and chemical properties, which can effectively block polysulfides shuttling when applied in Li-S batteries. Lu et al. [56] developed a functional separator prepared via in-situ growth of hollow CoSO₄ hydrate arrays on pristine polypropylene membrane. Liu et al. [57] utilized waste LiCoO₂ to modify the separator of Li-S batteries so as to effectively inhibit the shuttle effect and facilitate the conversion reactions of LPS and environmentally friendly recycle of LiCoO₂.

Besides, intermetallic nickel-iron with prospective electrocatalysis of effective polysulfide conversion was also utilized in separator modification in Li-S batteries. Zhang et al. [58] synthesized the above-mentioned nickel-iron intermetallics by urea-assisted precipitation method and the combustion in nitrogen atmosphere.

Figure 10 shows the illustration of operation principle of batteries assembled with different separator. Because of the insert of extraneous iron atoms into the nickel phase, the resulting distorted lattice of Ni₃Fe intermetallic became prominently catalytically active for accelerating the redox kinetics of LPS. Therefore, outstanding rate capability with a capacity of 598 mAh g⁻¹ at 4 C and long cycle life of 1000 cycles at 1 C with a capacity decay rate of down to 0.034% per cycle were achieved.

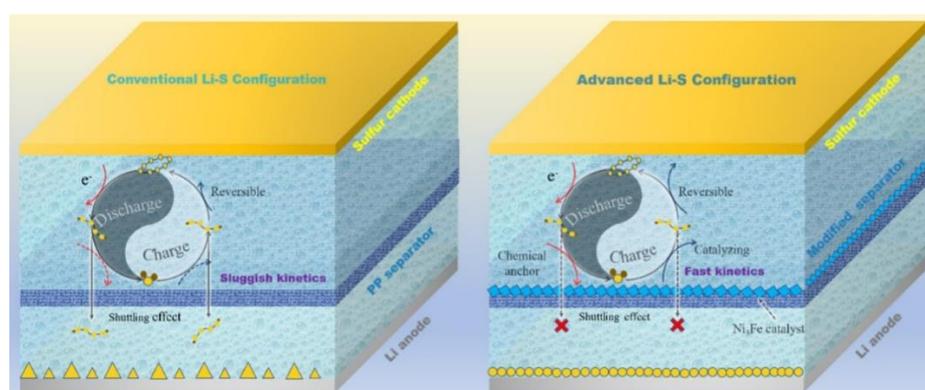


Figure 10. Illustration of the operation principle of the Li-S batteries with the PP separator and the Ni₃Fe@NCNT-based catalytic separator [58].

Studies have shown that polymers can also play a role in inhibiting the shuttle effect. Recently, Ma et al. [59] proposed a dual-engineered separator by coating ammonium alcohol polyvinyl phosphate/carbon black (AAPP/CB) and Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (LAGP) on two different surfaces of a commercial PP using blade coating method, which is denoted as AAPP/CB@PP@LAGP. Because of conductive CB frameworks and plentiful hydroxyl groups/phosphate radical in AAPP, the AAPP/CB layer performs as a “polysulfides stockroom” as well as a physical barrier to guarantee the instantaneous polysulfides absorption and conversion. At the same time, the LAGP layer filled with three-dimensional Li⁺ migration pathways exhibits great Li⁺ transmission ability. Thus, the Li-S batteries equipped with AAPP/CB@PP@LAGP separator achieves superior rate performance of 758 mAh g⁻¹ at 4 C, excellent cycle stability of capacity fade rate of 0.065% per cycle at 1 C over 500 cycles and high reversible capacities of 976.5 and 611.5 mAh g⁻¹ after 150 cycles. It is because of good inhibition for the shuttle effect of polysulfides and the growth of lithium dendrites. In addition, Polyetherimide was used to modify the PE separator by Liu et al. [60] and the battery with such separator

showed an initial specific capacity of 1265 mAh g⁻¹ at 0.2 C. Mathew et al. [61] developed a permselective separator by coating triazine-phenylenediamine-porous organic polymer (TP-POP) onto a commercial Celgard (2320) membrane. The secondary amine groups of POP are beneficial for the separator to facilitate Li⁺ diffusion as well as confining LPS shuttling both chemically and physically. Specially, Zhou et al. [62] proposed a functionalized separator prepared by single-sided chemical tailoring in the oxidative solution and grafting in the organosiloxane vapor. The functional groups on separator formed by organosiloxane fumigation grafting can well suppress LPS diffusion and the channel structure formed by chemical tailoring can well retain the dissolved LPS. Attapulgitte, a kind of natural multi-metal oxide nanorods consisting of Al, Mg, Fe, Si and O ions, was applied as multifunctional ionic sieve to capture LPS between separator and cathode by Sun et al. [63] Furthermore, they find that Fe ions in attapulgitte can catalyze LPS converting, faster and relative amount of polysulfide adsorbent and the conductive agent plays an important role in the performance of Li-S batteries.

The key parameters of more relevant studies are summarized in Table 2. As remarked above, because of the simple preparation process and abundant alternative modification materials, method of Li-S separator modification has shown great potential for inhibiting the shuttle effect of LPS, reducing capacity attenuation of both cathode and anode and improving stability of lithium metal anode.

Table 2. Electrochemical performance of separators in terms of surface modification on PP/PE.

Structural Composition	Separator Thickness (μm)	Capacity after Cycles (mAh g ⁻¹)	Year
FeOOH-PP	\	720.2 (500 cycles, 1 C)	2022 [64]
COF-C16/PE	9	580 (100 cycles, 0.2 C)	2022 [65]
SnS ₂ @CS/PP	13 (coating)	868 (300 cycles, 0.5 C)	2022 [66]
PP/PE/PP@ nitrogen doped hollow carbon nanospheres	11 (coating)	921 (100 cycles, 0.2 C)	2022 [67]
Zr _{0.30} Ni _{2.70} C/C nanosheets/PP	\	705.6 (1100 cycles, 1 C)	2022 [68]
MoS ₂ /nitrogen doped rGO/PP	~40	1040.3 (100 cycles, 0.2 C)	2022 [69]
Ti ₃ C ₂ T _x -PP	\	780 (200 cycles, 0.2 C)	2022 [70]
Mesoporous alumina/graphene /PP	\	695 (300 cycles, 1 C)	2022 [71]
Co@N-CNTs/N-Mo _x C@PP	23 (coating)	610 (500 cycles, 1 C)	2022 [72]
CoMoO ₄ /PP	38	745 (200 cycles, 0.2 C)	2022 [73]
Mn-TaS ₃ @rGO/PP	20 (coating)	683 (1000 cycles, 0.3 C)	2022 [74]
MoS ₂ -MoO ₃ /CS/PP	19.8 (coating)	1408 (600 cycles, 1 C)	2021 [75]
NG@Fe ₃ C/Fe/PP	\	601 (500 cycles, 1 C)	2021 [76]
Titanium nanotube arrays/carbon/PP	\	1050 (300 cycles, 0.5 C)	2021 [77]

4. Conclusions

In this review, based on the shortcomings of Li-S batteries, we summarized the recent advances in separator of Li-S batteries, including structure design and surface modification. The structural design focuses on the synthesis of new polymers to produce separator, while the surface modification is based on the commercial PE/PP separator by coating functional materials, including metal oxides, metal sulfides and metal Carbides/Nitrides, etc. A large number of studies have demonstrated that separator plays an important role in batteries, and the preparation of functional separators can effectively inhibit the shuttle effect of LPS and improve battery performance.

Acknowledgements

We would like to thank all relevant personnel who have provided support for this work.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

Funding

This work was supported by the National Key Research and Development Program (2019YFA0705701); National Natural Science Foundation of China (22179149, 22075329, 22008267, 51573215, and 21978332); Guangdong Basic and Applied Basic Research Foundation (Grant No. 2021A0505030022, 2019A1515010803, 2020A1515011445); Guangzhou Scientific and Technological Planning Project (Grant No. 201804020025, 201904010271).

Declaration of Competing Interest

The authors declare no conflict of interest.

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