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Review article

A review on separators for lithium–sulfur battery: Progress and prospects

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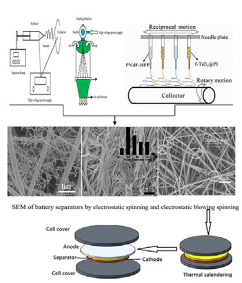
HIGHLIGHTS

- Review the current trends and developments of lithium-sulfur separators.
- Some modified functional and novel separators were presented.
- Discuss different separators affecting battery performances.
- Recommend approaches to better prepare the separators functionality.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-sulfur battery is considered as one of high performance batteries of the new generation owing to its extremely high theoretical capacity, energy density, good environmental protection and low cost. These features make it of great significance to serve as the next-generation battery especially in electric vehicles and portable devices. However, the practical application of lithium-sulfur battery is still hindered due to some obstacles including the low electrical and ionic conductivity of elemental sulfur, the discharge product Li_2S and the "shuttle effect" caused by the dissolved polysulfide species. In this review, the current trends, fundamental studies and developments for lithium-sulfur battery separators including some modified functional and novel battery separators with the customized structure designs are presented and reviewed. The effects of different selections and the resulting properties of the separators affecting the overall lithium-sulfur battery performances are discussed as well. The current research directions and challenges associated with the use of battery separator and the future perspectives for this class of the battery separator are concluded as well.

1. Introduction

The fossil energies are limited and their applications inevitably bring environmental harms, so there is a need to develop alternate, sustainable and clean energy technologies. So, solar and wind energy can be applied to avoid environmental crises. But these energies have certain limitations owing to their intermittent and

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uncontrollable characteristics. Batteries have become the major energy sources for all electric and portable devices due to the rapid modification and improvement in these devices. The lithium-ion batteries have been utilized over the past decades. As the electrochemical performances of the batteries are approaching to the theoretical limits, there is no space for development of lithium-ion battery. Accordingly, new batteries are being intensively explored and researched. Lithium-sulfur battery is widely concerned because of its high theoretical specific capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}), which has many other advantages of rich raw materials, good environmental protection and low cost [1,2].

Although lithium-sulfur battery has a very high specific capacity and energy density theoretically, but the battery capacity attenuation is extremely quick in the cycling process. This aspect makes lithium-sulfur battery far from the practical commercial application. Many aspects are contributing in capacity attenuation *i.e.* low electrical and ionic conductivity of elemental sulfur and the discharge product Li_2S, the "shuttle effect" (caused by the dissolved polysulfide species), the lithium anode deterioration due to surface passivation, solid-electrolyte interphase and the huge volume change in the conversion reaction. Because of these limitations and intricate challenges, further researches and efforts are needed to enhance the electrochemical performances of the battery [3–5]. The "shuttle effect" of the dissolved polysulfide species not only causes the low columbic efficiency of lithium-sulfur batteries but also leads to the loss of active materials, which is one of the main reasons of the rapid capacity fading in lithium-sulfur batteries. The definition of polysulfide's shuttle phenomenon is that "a variety of polysulfide anions can freely migrate between the cathode and anode in the charge-discharge process" [6]. The formed intermediate redox product (Li_2S_x ($6 < x \leq 8$)) is easily soluble in most of the liquid electrolyte. The soluble polysulfide ions with high valence state migrate towards the anode end of the battery and react with the lithium metal. This migration greatly reduces the amount of active material leading to lowering the Columbic efficiency. The battery experiencing "shuttle effect" keep an infinite recharging and low charge efficiency. The capacity degradation mechanism including the "shuttle effect" is shown in Fig. S1 [7].

In recent years, by utilizing the novel materials and modifications *i.e.* the introduction and adoption of polysulfide absorbers or additives such as high conductive nanocarbon/sulfur, the design of electrodes and innovation in cell configuration to alleviate the "shuttle effect" etc has attracted wide interest. Rechargeable lithium-sulfur batteries have been achieved much significant progress. Separator is also an important part of the battery, which affects the electrochemical performances and safety of battery. Separators mainly have two roles: a) Separator which has a microporous functional polymeric membrane plays a significant job to separate the positive and negative ends avoiding the chance of short circuit occurrence. b) They need have ability to inhibit polysulfide migration and protect them from being destroyed or malfunctioning. Therefore, separators must have the excellent strength, flexibility, bending, shrinkage, ionic conductivity, proper porosity and wettability for proper functioning. The traditional separators are mainly referred to polyolefin separators *i.e.* polypropylene microporous membrane, polyethylene microporous membrane and their multi-layer composite membrane. Besides some advantages of lithium-sulfur batteries separators such as low cost, proper mechanical strength, chemical stability, electrochemical stability and controlled porosity, there are some disadvantages as well. Conventional separators which may cause some shortcomings can't be neglected: 1) The charge-discharge performance is extremely poor when the battery environment is at high temperature or high voltage, leading to the short circuit and safety hazard; 2) It is not suitable to restrain intermediate polysulfide diffusion in the lithium-sulfur batteries. Therefore, higher quality and functional separators have significant importance in improving the performances of lithium-sulfur battery *i.e.* significantly trapping/blocking the polysulfide and reducing the parasitic reactions.

Zhang' group [8] has introduced the research work on various modified functional separators based on polyolefin separators and the modification methods which was performed before 2015. In the current review, the research work about the most recently developed separators based on nonpolyolefin polymers, ceramics, nanofibers and modification technologies on conventional separators was fully addressed and presented, including organic polymers such as Nafion polymer, polyacrylonitrile (PAN), poly (acrylic acid) (PAA), polyvinylidene Fluoride (PVDF), polyethylene oxide (PEO), poly(methyl methacrylate) (PMMA), polyetherimide (PEI) and their gel polymer electrolytes. The effects of different separator choices and the influence from different separator on the overall performances of lithium-sulfur battery were described in this review. Future challenges and opportunities in this field were also discussed [9–13].

2. Modified separators

The porous polymer separators are suitable and efficient to meet the requirements *i.e.* preventing the internal short-circuit and maintaining the diffusion pathway for the routine lithium-sulfur cells [14]. However, the parasitic reactions of polysulfide with anode (lithium metal) and the irreversible decomposition due to its metastability and forming "dead" sulfur-containing species inevitably bring about extremely quick decline in the battery capacity after the cycling process. Recent progress in advanced separators is aimed to achieve the high stable and performance lithium-sulfur battery by implying some modified functional separators in lithium-sulfur battery. Fig. S2 shows the schematic design of lithium-sulfur battery with modified separators. The modified functional separators possessing flexibility and outstanding mechanical strength are regarded as the polysulfide trapper, the upper current collector to intercept the migrating active material and an efficient utilization of active material during the battery cycle [15,16]. Meanwhile, the modified way of applying carbon material is usually through the slurry coating technology, the vacuum filtration process, magnetron sputtering, screen-printing or the combinations to form thin layer coating on the commercial separator. Hence, these modified functional separators mainly limit the diffusion of polysulfide from nanocomposites or trap the migrating polysulfides and provide convenient transportation of lithium ion.

2.1. *Carbon materials modified separator*

Carbon materials possess the excellent conductivity and thermostability, so they can be utilized in separator of lithium-sulfur battery. These carbon materials mainly include conductive carbon powder (Super P, Ketjen Black, Acetylene Black and so on), carbon nanowire, graphene, carbon nanotubes, carbon sphere and their hybrid. In addition, porous carbons (mesoporous, microporous or hierarchically porous carbon) also attracted researchers' concern and attention for the modified separator. The preparation method of conductive carbon powder by coating is simple and the cost is cheap, these features make it of wide interest and attracted a large number of researchers' focus. Zhang et al. [17] made the commercial conductive carbon powder (Super P Timcal) by forming the slurry to coat on one side of the routine polyolefin separator (Celgard 2320). Fig. 1a shows the schematic illustration of functional carbon layer-coated separator preparation. When compared with some routine separators, the carbon-coated separators (Fig. 1b) had