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

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A B S T R A C T

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], sp^2 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 $LiNO_3$ 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.