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Electrostatic-spraying an ultrathin, multifunctional and compact coating onto a cathode for a long-life and high-rate lithium-sulfur battery

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ABSTRACT

Serious shuttle effect of polysulfides is the main obstacle preventing the practical application of lithium sulfur batteries. Herein, we report an ultrathin yet multifunctional polysulfide blocking layer (MPBL) coated on the cathode to effectively restrain the polysulfides shuttling. This MPBL, which was prepared by a simple, one-step electrostatic spray deposition (ESD) technique, was fully and compactly coated on the electrode with controllable thickness, realizing the full protection of the whole cathode. It is noted that the MPBL can be very thin that guarantees the fast ion diffusion but still keeps a high efficiency of blocking polysulfides due to a combination of physical (from carbon) and chemical confinement (from conductive polymer). In addition, the MPBL with good conductivity can act as the upper current collector to reuse the captured polysulfides, and thus improve the sulfur utilization during cycling. With such multifunctional design, the MPBL-coated carbon-sulfur cathode exhibits long cyclic stability and high rate capability, which has only 0.042% capacity decay per cycle at 1C for 1000 cycles and a capacity of 615 mA h g^{-1} even at a high rate of 3C.

1. Introduction

The lithium sulfur (Li-S) battery is one of the most promising next-generation rechargeable batteries due to its much higher theoretical energy density (2600 Wh kg^{-1}) and lower cost than current commercial Li-ion batteries [1–5]. However, the practical application of the Li-S battery is still confronted by many challenges. On the one hand, the inferior electronic and ionic conductivities of sulfur and the discharge products (Li_2S/Li_2S_2) result in the low utilization of sulfur and a poor cycle life. On the other hand, the polysulfides easily dissolve into the electrolyte and then diffuse to the anode to react with the Li metal, resulting in an irreversible loss of sulfur and low Coulombic efficiency [6–10]. Thus, it is well accepted that both improving the conductivity of the sulfur cathode and well as retaining the soluble polysulfides in the cathode are crucial to make the best use of sulfur and have an ideal performance.

Encapsulating sulfur in conductive and porous carbon materials has been widely used [11–18], where the carbon frameworks provide the two above-mentioned functions, improving the conductivity of the sulfur cathode and restraining the shuttling of the polysulfides, thus enhancing the cycle life and Coulombic efficiency of the cathode. However, during discharge/charge, the polysulfides still gradually dissolve in the electrolyte and subsequently pass through the separator to the lithium anode because the direct contact of sulfur in the cathode with the bulk electrolyte outside cannot be totally prevented due to the open surface pores in the carbons. Recently, additional interlayers or separator coatings as secondary barrier layers (SBLs) have been designed to be placed between the cathode and the separator to retard the diffusion of polysulfides and suppress their shuttling [19,20]. These show great potential to improve the capacity and cycle stability of the Li-S battery. Microporous carbon paper [21], mesoporous carbon [22], carbon nanotubes [23], porous carbon fibers [24,25], graphene [26,27]

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and metal oxides [28,29] have been used to form these SBLs. SBLs effectively act as barriers to prevent polysulfides shuttling to the anode system, while unexpectedly blocking Li ion diffusion because of their large thickness. This does not help achieve long cyclic stability and high power capability, and it also adds to the volume and weight of the device [30]. Also, the use of only carbon or an oxide still falls far short of being an ideal SBL. For example, nonpolar carbon acts only as a physical barrier to polysulfide migration due to its weak interaction with them, while oxides including TiO_2 [31], MnO_2 [32], and MoO_2 [33] may capture the polysulfides more effectively because of a chemical interaction, but their low electrical conductivity hinders the reuse of these captured sulfur species. Thus, an ideal protection layer should satisfy the following criteria. First, but most important, the SBLs should cut down the direct contact of sulfur with the bulk electrolyte and effectively block the diffusion of the polysulfides, so a compact coating on the cathode, confining polysulfides inside it, is ideal for this purpose. Second, the SBLs should be thin enough to guarantee fast ion diffusion through it, and therefore a well manipulated approach is needed for preparation of the ultra-thin coating. Third, but easily overlooked, the SBLs must be robust and conductive so that it can act as an upper current collector, where the captured polysulfides inside SBLs can be reused effectively. Therefore, a composite membrane integrating all the above functions should serve as an ideal SBL.

Here, we present a novel SBL meeting all the above requirements, and this is an ultrathin yet multifunctional polysulfide blocking layer (MPBL) tightly wrapping the cathode, different from the normal SBLs that are isolated from the cathode. Such a MPBL is bi-component coating, comprising of a nanosized carbon black with large surface area and a conductive polymer, which is prepared by a simple, one-step electrostatic spray deposition (ESD) technique. The ESD process helps realize an integrated and compact multi-component layer fully and tightly wrapping the whole electrode surface. The layer thickness can be changed by simply controlling the spray time and, as a result, the obtained layer can be very thin, thus guaranteeing fast ion diffusion while having a high efficiency of blocking polysulfides because of a combination of physical adsorption (from carbon,Fig. S1) and chemical confinement (from conductive polymer), as shown in Fig. 1b. The chemical confinement is derived from the strong chemical binding of poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) with the polysulfides. In addition, such a MPBL, with good conductivity derived from a combination of high conductivity carbon black and a conductive polymer, can act as the upper current collector to make the captured polysulfides reusable, and thus improve the utilization of active materials during cycling. Finally, working with such a novel MPBL for the cathode, we use a nitrogen-doped porous carbon sheet (NPCS) as the carbon host to store the sulfur, where the carbon sheets further lower both the electron and ion diffusion resistance. Generally, the tight contact of the MPBL protects the whole electrode, retains the dissolved polysulfides, and provides close contact with the carbon host in the cathode. At the same time, by acting as an upper current collector to reuse the captured polysulfides, the MPBL improves the utilization of sulfur during cycling. For comparison, in a conventional uncoated NPCS-S electrode (Fig. 1a) during the charge-discharge process, the polysulfides easily dissolve in the bulk electrolyte and are then unimpeded in their diffusion to the Li anode, where they react with the Li to form Li_2S_2/Li_2S, resulting in fast and irreversible capacity decay. With its multifunctional and easy manipulated design, the MPBL-coated cathode exhibits good long cyclic stability with only 0.042% capacity decay per cycle at 1C for 1000 cycles and an excellent rate performance, showing a high capacity of 615 mA h g^{-1} at 3C.

2. Experimental section

2.1. Preparation of nitrogen-doped porous carbon sheet (NPCS) and NPCS-S hybrid

The NPCS was prepared according to our previous report [34] and a typical procedure is as follows. Briefly, 160 mg graphene oxide (GO, 2 mg mL^{-1}), 7.2 g glucose and 4 mL pyrrole were subjected to hydrothermal treatment at 180 °C for 12 h. The product was collected by filtration and washed after drying at 80 °C overnight. The dried product was then mixed with KOH (weight ratio of 1:4) and was thermal treated at 900 °C for 1 h under nitrogen atmosphere protection. The obtained product was washed with 10% hydrochloric acid and distilled water, followed by drying at 100 °C for 24 h to obtain the NPCS. The carbon-sulfur hybrid was prepared using a heat melt-diffusion method. In a typical procedure, as-prepared NPCS and sublimed sulfur were homogeneously mixed and heated at 155 °C for 12 h in a sealed vessel filled with argon protection. After cooling to room temperature, the NPCS-S hybrid was obtained.

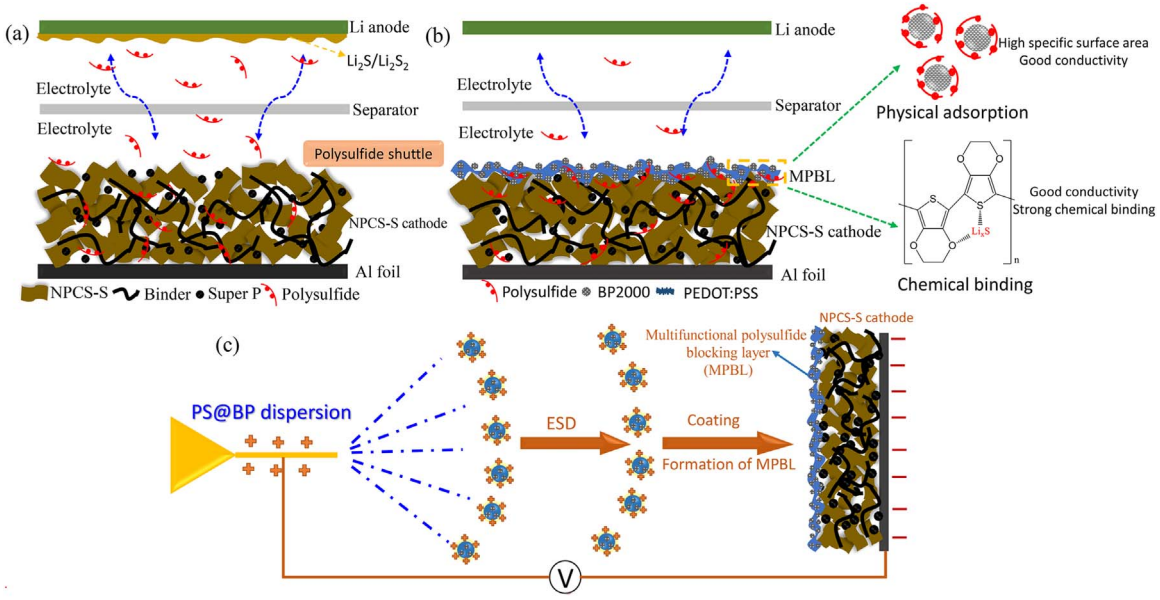

Fig. 1. Schematics of the electrode configurations for (a) a conventional uncoated cathode and (b) a MPBL-coated cathode for Li-S battery. (c) Schematic of the procedure for fabricating a MPBL-coated electrode.