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A functional carbon layer-coated separator for high performance lithium sulfur batteries

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A composite separator consisting of a functional layer of conductive carbon on the cathode-side of a Celgard separator has been investigated to improve the electrochemical performance of lithium sulfur batteries. The cell with functional carbon layer-coated separator can reach a high initial capacity of 1070 mAh g^{-1} at the rate of 0.5 C, and maintain a high capacity retention ratio with the capacity of 778 mAh g^{-1} after 100th charge/discharge cycle. Besides, the coulombic efficiency of the cell with functional carbon layer-coated separator rises from 80% to nearly 90% without the addition of $LiNO_3$ additive, which indicates the reduction of shuttle effect. The improved cell performance is attributed to the functional carbon-coating layer, which serves as an upper current collector to facilitate electron transport for high active-material utilization and a conductive network for trapping and depositing dissolved sulfur-containing active materials, as confirmed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

1. Introduction

Advanced energy storage systems are highly desired to meet the increasing demands of high energy density batteries [1,2]. Accordingly, lithium sulfur (Li–S) batteries have attract great attention as one of the most promising systems for the next generation high energy density rechargeable lithium batteries because of their high theoretical specific capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}) [3,4]. As a cathode active material, sulfur also has advantages of non-toxicity and abundance in nature [5]. However, the practical applications of Li–S batteries are still hindered by some major basic obstacles. Sulfur and its final discharge products (Li_2S_2, Li_2S) are electrical insulators, which can cause poor electrochemical accessibility, leading to a low utilization of active materials. In addition, polysulfides (Li_2S_n, $4 \le n \le 8$) produced in discharge/charge processes can dissolve into organic electrolyte and be reduced to lower-order polysulfides at the interface of the lithium anode. These reduced products will migrate back to the cathode where they may be reoxidized. This process takes place repeatedly, creating polysulfides shuttle, which can cause loss of active materials and the low coulombic efficiency of Li–S batteries, eventually resulting in rapid capacity fading [6,7].

In order to prevent polysulfides shuttling in organic electrolyte, various approaches have been proposed by research teams over the latest three decades. One of the most effective strategies is to confine sulfur into porous frameworks, such as porous carbon materials [8–10], metal oxide matrix [11], and polymer matrix [12,13]. The porous networks can significantly improve the capacities of the cathodes by limiting the ploysulfide diffusion, while the shuttle effect has not been fully addressed. Another promising approach is the modification of cell configuration, which means building a physical barrier to prevent the migration of polysulfides. The cell modification can be concluded into three aspects, that is, surface coating of the sulfur cathode [14,15], insertion of free-standing interlayer (carbon interlayer [16–18], polypyrrole interlayer [19]), and modification of separator. The first two methods of cell modification have been proven to be effective to enhance the performance of lithium–sulfur batteries, while the study on the separation modification of lithium–sulfur batteries is still at a very early stage.

Separator, the basic component of the lithium–sulfur battery, is a porous membrane (e.g. polypropylene, polyethylene, glass fibers), which serves solely as an electronic insulator and does not influence the transportation of ions through the membranes [20,21]. Polysulfides can diffuse freely through the membranes and react with the anode, which can cause the degradation of the battery. Therefore, the inhibition of the shuttle effect by modification of separator will be an effective method to improve the performance of lithium–sulfur batteries. A nafion coated separator was used as an ion selective membrane to block the diffusion of polysulfide anions across the membrane to the anode side, which greatly suppresses the shuttle effect and improve the cycling performance with an ultralow capacity degradation rate of 0.08% per cycle [22]. Recently, we prepared the Al_2O_3-coated separator and found that the lithium-ion conductive Al_2O_3 layer can block the diffusion of polysulfides and enhance the electrochemical performance of lithium–sulfur batteries [23].

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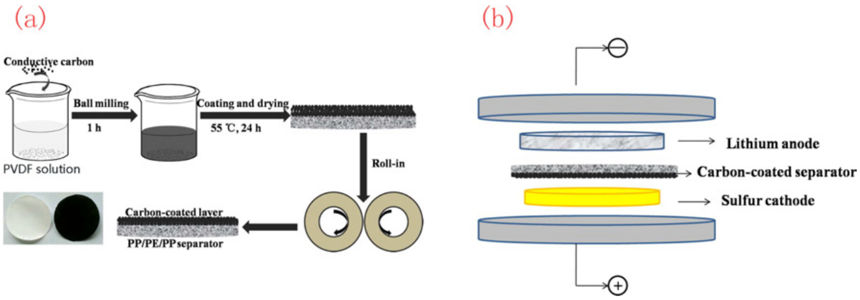

Fig. 1. Schematic illustration of functional carbon layer-coated separator preparation (a), configuration of a Li–S cell with functional carbon layer-coated separator (b).

In this paper, we were motivated to prepare a functional carbon layer coated separator via a simple and cheap slurry-coating technique. All the raw materials of the slurry are commonly used in laboratory and commercially available, for instance, super P carbon and PVDF. The electrochemical performance of lithium sulfur batteries with functional carbon layer-coated separator can be greatly improved, with a specific capacity of 778 mAh g^{-1} after 100 cycles at 0.5 C, which is higher than that of lithium sulfur batteries with routine separator. These results indicate that the functional carbon layer-coated separator is more suitable in lithium sulfur battery applications.

2. Experimental

2.1. Preparation and characterization of a functional carbon layer-coated separator

Commercial conductive carbon powder (Super P Timcal) was added to 8 wt% polyvinylidene fluoride (PVDF 6020 Solef) solution with N-methyl-2-pyrrolidinone solution (NMP) as solvent where a ratio of SP/PVDF was fixed at 75/25 (wt%/wt%). And the slurry was dispersed by ball milling for 1 h. This slurry was coated on the cathode side of a

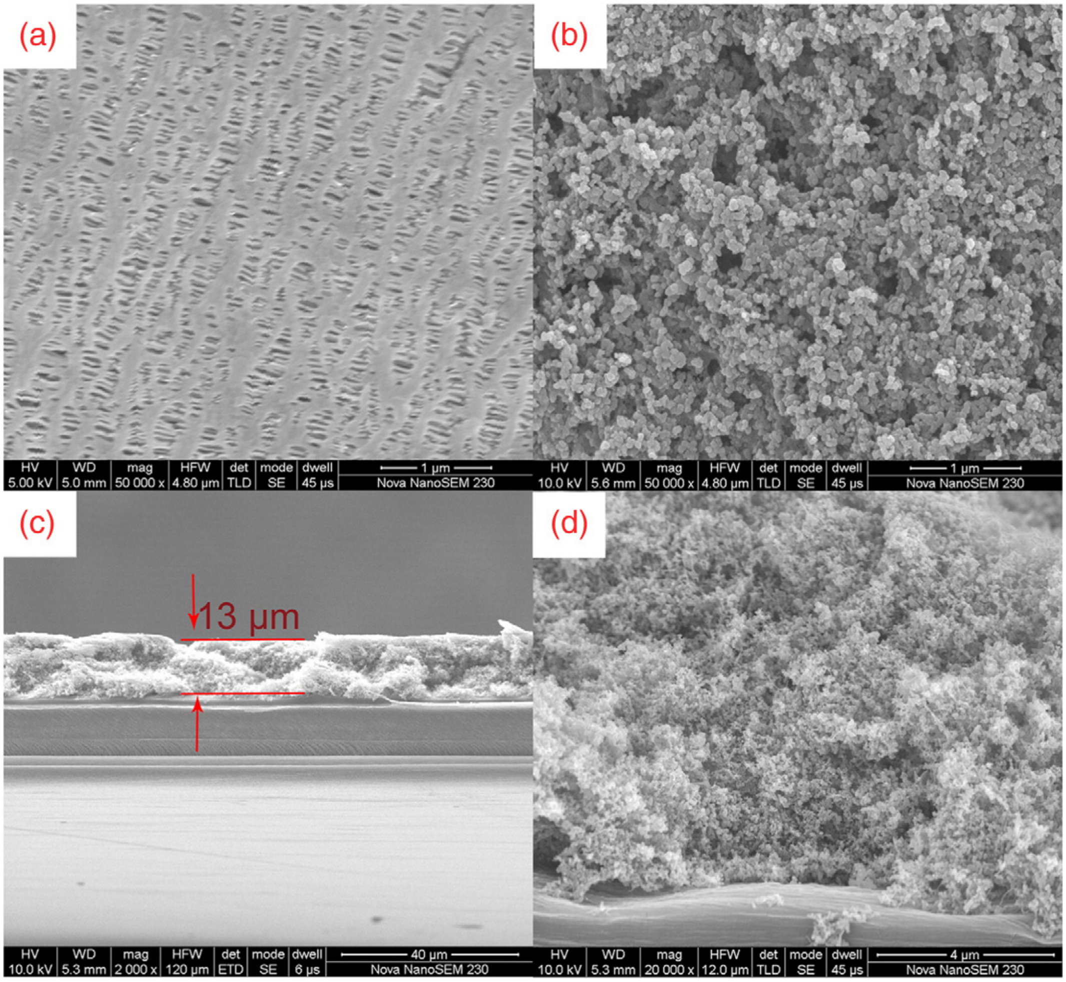

Fig. 2. SEM photographs of (a) routine PP/PE/PP separator (surface); (b) carbon-coated PP/PE/PP separator (surface); (c) carbon-coated PP/PE/PP separator (cross-section); and (d) carbon coating layer at high magnification (cross-section).