Full paper

Ultra-small self-discharge and stable lithium-sulfur batteries achieved by synergetic effects of multicomponent sandwich-type composite interlayer

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A B S T R A C T

The severe lithium polysulfide (LiPS) shuttling and self-discharge behavior of lithium-sulfur (Li-S) batteries remarkably hinder their practical application. The construction of interlayer is an effective strategy to obstruct the diffusion of LiPS. However, the simplex physical block or chemical absorption of monotonous interlayer is difficult to reuse sulfur species, reduce impedance and restrain self-discharge of the Li-S battery simultaneously. In this study, a multicomponent sandwich-type interlayer was integrated by vanadium disulfide and carbon nanotubes composite (VS_2/CNT), carbon nanofibers (CNF) substrate and graphene coating layer. The VS_2/CNT presented strong affinity towards LiPS and effectively restrained the self-discharge of Li-S batteries. The CNF substrate as supporting framework increased the wettability of electrolyte and reduced the diffusion impedance of lithium ion. The graphene coating layer acting as the second collector effectively recovered the inactivated sulfur species. The multiple components of VS_2/CNT adsorbent, CNF substrate and graphene coating layer exhibited favorable synergetic effects to suppress the LiPS shuttling and self-discharge of Li-S batteries. Besides, this interlayer endowed Li-S batteries with boosted redox kinetics and outstanding rate performance. The specific capacities at 0.1, 1 and 10 C were 1525, 834 and 621 mAh g^{-1}, respectively. More importantly, the Li-S batteries with this multicomponent interlayer performed a high residual capacity of 605 mAh g^{-1} after 1145 cycles at 1 C. Even at a high sulfur loading of 5.6 mg cm^{-2}, the cell still had high capacity of 1150 mAh g^{-1} and 750 mAh g^{-1} at 0.1 C and 0.3 C, respectively. The synergetic effects of multicomponent sandwich-type composite interlayer provided a new strategy for ultra-small self-discharge and stable of Li-S batteries.

1. Introduction

Lithium sulfur (Li-S) batteries have attracted great interest for researchers due to its properties such as high theoretical specific capacity (1675 mAh g^{-1}), high energy density (2600 Wh Kg^{-1}), low cost and environmental friendliness [1,2]. Whereas, their fata drawbacks such as LiPS shuttling, insulation of sulfur and discharged products (Li_2S/Li_2S_2), and severe self-discharge during cycling have greatly limited the commercialization of Li-S batteries [3–8]. An amount of efforts have been put in to settle the mentioned problems by designing novel structures. A series of carbon materials such as hierarchical meso/microporous carbon [9–11], graphene [12–17], self-closure graphene aerogels [18], novel composite of porous carbon and graphene [19] have been widely used in the structure design of Li-S batteries. These materials could increase the initial specific capacity significantly through improving the electronic conductivity and raising the initial utilization of sulfur [20]. Unfortunately, the cycle stability was still not satisfactory due to the weak physical binding between polar LiPS and non-polar carbon materials. Therefore, some polar metal compounds, for instance, TiO_2 [21,22], MnO_2 [23], CeO_2 [24] were introduced into cathode to suppress the shuttling effect owing to their strong chemical binding towards LiPS. Whereas, this strategy would lead to low specific capacity because of the poor electrical conductivity of these compounds. In addition, metal embedded porous carbon materials were synthesized to be applied as sulfur hosts [25]. Because of its limited adsorption ability to polysulfide, the capacity still faded rapidly yet. Transition metal sulfides such as CoS_2 [26], MoS_2 [27], WS_2 [28], Co_3S_4 [29] and TiS_2 [30] present good conductivity and strong chemical affinity to LiPS, which have been used in the structure design of cathode in Li-S batteries. Excitedly, transition metal sulfides also have catalytic effect on the process of LiPS redox reaction. However, the introduction of substantial inactive substance would offset the superiority of high
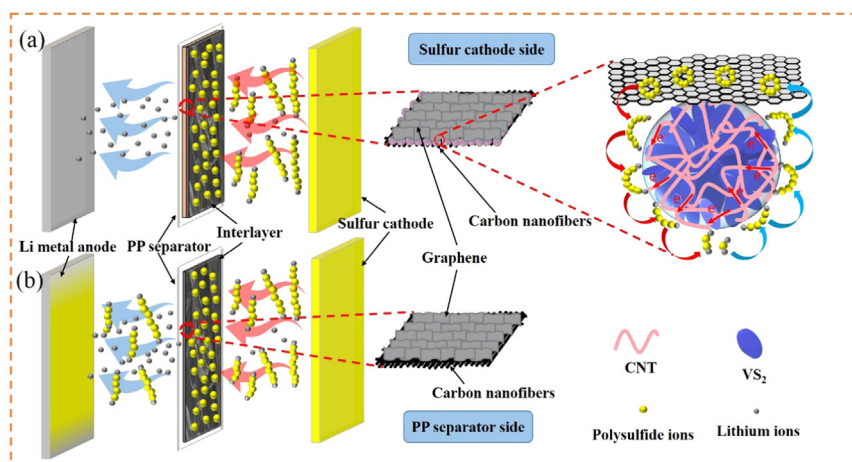
Fig. 1. The schematic diagrams of the role of (a) CNF@VS$_2$/CNT@GN and (b) CNF@CNT@GN interlayers in Li-S batteries.

energy density of Li-S batteries.

Another strategy is constructing an interlayer between the cathode and separator to impede the diffusion of LiPS towards lithium anode. A group of materials such as mesoporous carbon [31], highly porous carbon [32,33], two-dimensional porous carbon [34], graphene [35,36], and metal compounds [37–39] have been applied to modify the separator to suppress the LiPS shuttling. Whereas, these dense adsorption layers coated on separator directly was detrimental to the infiltration of electrolyte into the interior of adsorption layer, leading to impeded ions transmission, low capacity and poor rate performance. Carbon nanofiber layer modified with metal compound has been also used as the free-standing interlayer in Li-S batteries [40–42]. This method improved the electrolyte wettability effectively, while large internal space between single carbon nanofiber would cause the LiPS through the adsorption layers.

Herein, a multicomponent sandwich-type composite interlayer was proposed for ultra-small self-discharge and stable lithium-sulfur batteries (Fig. 1a), in which the vanadium disulfide and carbon nanotubes compounds (VS$_2$/CNT) were supported by carbon nanofiber (CNF) membrane and covered with graphene layer. The CNF substrate with sufficient interspace acted as a supporting framework, and made the electrolyte contact with VS$_2$/CNT adequately, promoting its absorption towards polysulfide by the polar V–S groups in VS$_2$. The high efficient three-dimensional conductive network formed by CNT, CNF and graphene was conducive to the reaction of LiPS and reuse of inactivated sulfur. The electrochemical catalytic effects and high conductivity of VS$_2$/CNT boosted the redox reaction of LiPS. Moreover, the suitable high potential of VS$_2$ restrained the self-discharge behavior of Li-S batteries and alleviated the continuous dissolution of LiPS. Benefiting from the synergetic effects of each unit in multicomponent sandwich-type composite interlayer, the specific capacities of Li-S batteries at 0.1, 1 and 10 C were 1525, 834 and 621 mAh g^{-1}, respectively. More importantly, it performed an excellent cycling stability, that was 605 mAh g^{-1} after 1145 cycles at 1 C. Even at a high sulfur loading of 5.6 mg cm^{-2}, the cell still had high capacities of 1150 mAh g^{-1} and 750 mAh g^{-1} at 0.1 C and 0.3 C, separately. Furthermore, the open-circuit voltage (OCV) retention of Li-S batteries with multicomponent interlayer after 7 days storage was as high as 95%, presenting ultra-small self-discharge property. The synergetic effects of each unit in the multicomponent sandwich-type composite interlayer provided a new strategy for ultra-small self-discharge and stable of Li-S batteries.

2. Experimental section

2.1. Preparation of the multicomponent sandwich-type composite interlayer

The CNF membrane was fabricated as showed in Fig. S1. First, the polyacrylanitrile (PAN) nanofibrous membrane was prepared by an electrospinning equipment (Beijing Ucalery Co., Ltd.). 1.5 g PAN (Mw = 150000) powder was dissolved in 20 mL N, N-dimethylformamide (DMF) by continuous stirring at 60 °C for 5 h, after that, the light yellow solution with 10 wt% PAN was obtained. Sequentially, the PAN solution was electrospun onto the target rotating collector with a flow rate of 1.0 mL h^{-1} for 8 h and the operating voltage was 20 kV. The obtained PAN electrospun fiber membrane was heated at 280 °C for 90 min in air with a heating rate of 2 °C min^{-1} and carbonized at 1000 °C for 2 h in argon atmosphere with the same heating rate. Then the CNF membrane with the weight of approximately 1.4 mg cm^{-2} was obtained. A piece of CNF membrane (4 cm × 2 cm) and 50 mL 68 wt% nitric acid were transferred into a Teflon-lined stainless-steel autoclave, which was sealed and maintained at 100 °C for 1 h. Afterward, the acidified membrane was taken out and rinsed in deionized water with several times, and dried at 60 °C overnight under vacuum to obtain activated CNF membrane.

The CNF@VS$_2$/CNT@GN was prepared as follows: 0.15 g hydroxylated carbon nanotubes were added to 40 mL deionized water, then ultrasonic treated for 2 h. Spherical VS$_2$/CNT compound was loaded on the CNF membrane by a hydrothermal process (Fig. S1). Briefly, 0.351 g ammonium vanadate was added into the CNT solution and stirred at 60 °C, and then added to 1 mL 1 mol L^{-1} ammonia solution, making sure that the ammonium vanadate was completely dissolved. After that, 1.125 g thioacetamide (TAA) was added to the above solution and stirred for 10 min. Finally, 1.65 g polyvinylpyrrolidone was added and was continually stirred to dissolve completely. Then above solution and acidified CNF membrane were transferred into a Teflon-lined stainless-steel autoclave and maintained at 180 °C for 20 h to obtain CNF@VS$_2$/CNT. The mass loading of VS$_2$/CNT compound on CNF was about 0.5 mg cm^{-2} approximately. When there was no sulfur and vanadium source in the hydrothermal process, the obtained sample was recorded as CNF@CNT. 60 mg graphene nanosheets were added to 200 mL anhydrous ethanol, and then sonicated for 2 h. 10 mL of this graphene ethanol dispersion solution was filtered on CNF@VS$_2$/CNT and CNF@CNT membranes by vacuum filtration (Fig. S1). Finally, the sandwich-type interlayer (CNF@VS$_2$/CNT@GN) and CNF@CNT@GN were obtained. In order to increase the crystallinity of VS$_2$, the CNF@VS$_2$/CNT@GN membrane was heated at 350 °C for 2 h in argon atmosphere.