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Titanium-dioxide-grafted carbon paper with immobilized sulfur as a flexible free-standing cathode for superior lithium–sulfur batteries

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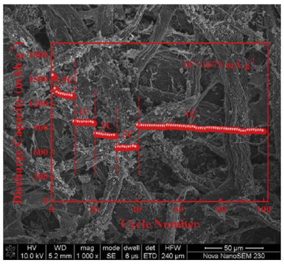
HIGHLIGHTS

- A free-standing electrode based on carbonized filter paper for Li–S batteries.
- Carbon paper and TiO_2 synergistically construct electronic/ionic conduction pathways.
- The CP@TiO_2 membrane owns the ability of physically/chemically trapped polysulfides.
- CP@TiO_2 membrane owns potential suitability for other high-performance batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

Titanium-dioxide-grafted carbon paper (CP@TiO_2) has been synthesized by pyrolysis of tetrabutyltitanate-treated filter paper, which is a simple, large-scale, and green method, while the product is a superior material for immobilising sulfur as a flexible free-standing electrode for lithium–sulfur (Li–S) batteries. The as-synthesised CP@TiO_2 membrane is constructed of interlaced circuitous carbon fibers and TiO_2 nanoparticles distributed on/in the void among the carbon fibers. The CP@TiO_2–S membrane retains the robust and flexible structure of the CP membrane after infiltrating the sulfur, and the sulfur particles are homogeneously distributed within the CP@TiO_2. As a free-standing cathode, the CP@TiO_2–S membrane exhibits superior electrochemical performance than the CP-S membrane, displaying a reversible discharge capacity of 850 mAh g^{-1} after 200 cycles at 0.5C and a specific capacity of 660 mAh g^{-1} at 5C. The superior electrochemical performance of the CP@TiO_2–S membrane is ascribed to the synergetic effect between the interlaced carbon fibers of the CP membrane, which provides electronic conduction pathways and works as mechanical support, and the TiO_2 nanoparticles with relatively high surface area and pore volume, which could physically/chemically trap polysulfides. The results indicate that the CP@TiO_2 membrane owns potential suitability for efficient, free-standing, and high-performance batteries.

1. Introduction

The requirements of emerging energy storage applications in electric vehicles necessitate the development of new materials and higher energy density beyond that of most advanced lithium secondary batteries [1]. The lithium–sulfur (Li–S) system is one of the most promising candidates for high energy density applications, due to its environmental friendliness, low cost, and high theory capacity of 1675 mAh g^{-1} and energy density of 2500 Wh kg^{-1} [2].

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Nevertheless, the commerical application of Li–S system has been hindered by several issues [1–3]. The most critical issues are the dissolution and shuttle effect of polysulfides in the organic electrolyte, which bring about loss of active materials, formation of passivation films on the electrodes, and rapid capacity degradation and depressed Coulombic efficiency [4]. Other issues include poor electric conductivity of sulfur and the reduced products Li_2S_2/Li_2S, which may deposite on the surfaces of cathode and lithium anode, leading to reduced capacity utilization and lower rate capability of the sulfur active material [5]. Moreover, the big volume changes in sulfur cathode can result in pulverization of the sulfur cathode and poor cell reversibility [6].

In order to solve the above-mentioned issues, various strategies have been developed to date, such as optimizing the electrolyte [7], synthesizing composite electrodes of carbon–sulfur [8–10], polymer-sulfur [11,12], and metal oxide-sulfur [13], and optimizing the electrode configuration [14–16]. Among these approaches, the strategy of combining conductive carbon and a metal oxide with sulfur has been demonstrated as one of the most effective approaches to increase the sulfur utilization rate, cycling stability, and rate capability of sulfur cathodes [17,18]. On the one hand, carbon materials in the composite cathode could physically confine sulfur, accommodate volume expansion and enhance the electric conductivity of the cathode. On the other hand, metal oxide can serve as absorbent in the sulfur cathode to trap polysulfides and further maintain high Coulombic efficiency. Until now, metal oxides, including Al_2O_3 [19], $Mg_{0.6}Ni_{0.4}O$ [20], $Mg_{0.8}Cu_{0.2}O$ [21], La_2O_3 [22], and TiO_2 [13,23–27], have been successfully explored as absorbents or host materials to confine sulfur. Among them, TiO_2 is a specially promising host to immobilize sulfur for Li–S batteries due to its good physical and chemical absorption capability towards sulfur and polysulfides [23–27]. Specially, Cui's group successfully fabricated sulfur-TiO_2 yolk-shell nanoarchitecture, exhibiting excellent electrochemical performance. The TiO_2 shell effectively confines the dissolution of polysulfides, however, the low electrical conductivity of TiO_2 limits its greater promotion in Li–S batteries [13].

Most of the sulfur composites reported as cathodes, however, have required the use of carbon black additives and polymer binders adhered on an aluminum current collector to assure the mechanical stability and electrical conductivity of the whole system. The introduction of conductive carbon (10–50 wt%), binder (8–20 wt%), and Al foil (the density of aluminum is 2.7 g cm^{-3}) to the electrode will definitely neutralize the advantage of the battery with high energy density [28]. To construct better Li–S batteries with high energy density, the most effective strategy is to design flexible, free-standing, and binder-free electrodes, in which all the materials could participate in lithium storage. Recently, flexible and free-standing carbon-S composites, including carbon nanotube-S [29–31], carbon nanofiber-S [32–34], porous carbon-S [35–37], graphene-S [38–41], grapheme/carbon nanotube-S [42], graphene/porous carbon-S [43] and carbon nanotube/carbon-S [44], have been reported for Li–S batteries. Recently, Zhang's group fabricated a flexible electrode by incorporation of CNTs and carbon nanocages via high-temperature chemical vapour deposition (CVD), which can achieve high sulfur loading and deliver a high specific capacity and rate performance in Li–S batteries [44]. Although these free-standing cathodes can deliver excellent electrochemical performance, most of them are synthesized by means of some special methods, equipment, or templates, which results in complexity related with design and preparation process and decreases the feasibility. Therefore, it is essential to develop a more effective and convenient preparation method for the free-standing carbon membrane to immobilize sulfur for high performance Li–S batteries. Filter paper, an inexpensive and very common used material in the laboratory, is monolithic and can turned out carbon paper via a simple pyrolysis without any template.

Therefore, the combination of the above-mentioned two types of materials, metal oxide and filter paper, is ideal for designing a flexible and free-standing carbon membrane with metal oxide for S accommodation that can relieve the dissolution of polysulfides while keeping the overall electrode highly conductive, as well as improving the energy density of the full battery. Herein, we report on the design and fabrication of a flexible free-standing Li–S battery cathode based on immobilizing sulfur on TiO_2-grafted carbon paper via a simple pyrolysis of the tetrabutyl-titanate-treated filter paper and a sulfur-infiltration method. As a free-standing cathode for lithium sulfur batteries without any conductive carbon additives, binder or Al foil, the CP@TiO_2–S membrane exhibits superior electrochemical performance than the CP-S membrane, and delivers a reversible discharge capacity of 850 mAh g^{-1} after 200 cycles at the current rate of 0.5C and a high specific capacity of 660 mAh g^{-1} at 5C. The superior electrochemical performance of the CP@TiO_2–S membrane is attributed to the synergetic effect between interlaced carbon fibers of the CP membrane, which provides electronic conduction pathways and works as mechanical support, and the TiO_2 nanoparticles with relatively high surface area and pore volume, which could physically/chemically trap polysulfides and provide lithium ion conductive pathways.

2. Experimental section

2.1. Preparation of titanium-dioxide-grafted carbon paper (CP@TiO_2) membrane

Firstly, pristine filter papers (Hangzhou Special Paper Co., LTD.) were punched out in circular disks 1.5 cm in diameter, and then the filter paper disks were soaked in a solution of 100 mL ethyl alcohol with 2 mL tetrabutyl titanate (TBOT, Aladdin) at room temperature. After infiltrating for 2 h, the TBOT-treated filter papers were taken out and dried at 60 °C for 1 h to remove the ethyl alcohol. Secondly, the dried TBOT-treated filter papers were soaked in distilled water. After reacting for 0.5 h, the treated filter papers were taken out and dried at 80 °C for 5 h to remove the water. Thirdly, pristine filter papers and the treated filter papers were pyrolyzed at 800 °C with a heating rate of 5 °C/min at Ar to generate black and porous carbon paper (CP) membrane and titanium-dioxide-grafted carbon paper (CP@TiO_2) membrane. After pyrolysis, the obtained CP and CP@TiO_2 membranes ~1.2 cm in diameter and ~90 μm in thickness were used as containers for loading the sulfur active material.

2.2. Preparation of CP@TiO_2-sulfur membrane

To obtain the CP-S and CP@TiO_2–S membranes, a two-step strategy including liquid phase impregnation and heat-treatment was implemented. Sulfur powder (99.98%, Sigma–Aldrich), and the CP and CP@TiO_2 membranes were initially dried in vacuum at 60 °C before further processing. First, 0.5 g sulfur was dissolved in 10 mL CS_2 solution (99.8%, anhydrous, Sigma–Aldrich). Then, the sulfur-containing CS_2 solution was infused into the membranes by drop casting and dried at 60 °C for 2 h to remove the CS_2. Finally, the prepared membranes were heat-treated at 155 °C for 12 h with a heating rate of 5 °C min^{-1} under argon atmosphere. After cooling down to ambient temperature, the CP-S and CP@TiO_2–S membranes were obtained. These as-prepared membranes were directly used as cathodes without the addition of any electrically conductive agent, polymeric binder, or current collector.

2.3. Materials characterizations

The morphologies and elemental distributions on the surfaces of