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Enhanced performance of lithium-sulfur batteries with an ultrathin and lightweight MoS_2/carbon nanotube interlayer

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HIGHLIGHTS

- MoS_2/CNT interlayer serves as both physical and chemical barrier for polysulfides.
- CNT film provides the electrodes with excellent conductivity.
- MoS_2 nanosheets form effective chemical interactions with the polysulfides.
- Li-S battery with the MoS_2/CNT interlayer displays enhanced cycling and rate performances.

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ABSTRACT

Ultrathin and lightweight MoS_2/carbon nanotube (CNT) interlayers are developed to effectively trap polysulfides in high-performance lithium–sulfur (Li–S) batteries. The MoS_2/CNT interlayer is constructed by loading MoS_2 nanosheets onto a cross-stacked CNT film. The CNT film with excellent conductivity and superior mechanical properties provides the Li–S batteries with a uniform conductive network, a supporting skeleton for the MoS_2 nanosheets, as well as a physical barrier for the polysulfides. Moreover, chemical interactions and bonding between the MoS_2 nanosheets and the polysulfides are evident. The electrode with the MoS_2/CNT interlayer delivers an attractive specific capacity of 784 mA h g^{-1} at a high capacity rate of 10 C. In addition, the electrode demonstrates a high initial capacity of 1237 mA h g^{-1} and a capacity fade as low as -0.061% per cycle over 500 charge/discharge cycles at 0.2 C. The problem of self-discharge can also be suppressed with the introduction of the MoS_2/CNT interlayer. The simple fabrication procedure, which is suitable for commercialization, and the outstanding electrochemical performance of the cells with the MoS_2/CNT interlayer demonstrate a great potential for the development of high-performance Li–S batteries.

1. Introduction

Nowadays, lithium-ion (Li-ion) batteries are widely used in portable electronic devices, electrical vehicles, and power grids. As these applications have developed over time, the energy requirements have increased. Batteries with high energy, power density, and specific capacity are in great demand [1]. Li–S batteries, with a theoretical capacity of 1672 mA h g^{-1} and specific energy density of 2600 W h kg^{-1}, have received extensive attention from many researchers. Sulfur cathodes display numerous advantages, such as high abundance of the raw material, relatively low cost, and environmental benignity. However, the application of Li–S batteries is hindered by the following challenges. First, both the active material (sulfur) and the discharge products (Li_2S_2/Li_2S) are electrically insulating. Second, the volume expansion during cycling reaches up to 80%. Last, and most important, the intermediate polysulfides (Li_2S_n, $4 \le n \le 8$) are highly dissolvable in the electrolyte and the shuttling of them between the electrodes results in a fast loss of capacity, i.e., the shuttle effect [2,3]. All these issues lead to a low utilization of sulfur, fast capacity fading, poor rate capability, and significant self-discharge behavior [4–6]. To overcome these difficulties, various approaches have been proposed for the design of sulfur composite cathodes. For example, various carbon matrices such as

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carbon nanotubes [7–9], carbon nanofibers [10,11], graphene [12], and porous carbon [13,14] have been designed to provide cathodes with high electrical conductivity and a porous structure to enhance the electrical conductivity of the cathodes and suppress the shuttle effect. Conductive polymers [15–17] and metal oxides [18,19] have also been used to make composite sulfur cathodes. All these modifications can promote the electrochemical properties, accommodate the volume expansion, and restrain the diffusion of polysulfides to some extent. Nonetheless, the rapid capacity fading and severe self-discharge induced by the shuttle effect have not been fully addressed.

Separators, as an essential part of batteries, play an important role in blocking polysulfides at the cathode side and preventing them from shuttling to the anode to react with the lithium metal. Various separators and functional interlayers have been developed to suppress the diffusion of the polysulfides in Li–S batteries. For example, Manthiram's group revealed that a porous carbon interlayer between the sulfur cathode and the separator could effectively inhibit the shuttle effect of polysulfides, resulting in improved cycling performances of the electrode [20]. Kim and his co-workers reported that the dissolved polysulfides could be captured by introducing an acetylene black mesh; the electrodes demonstrated an enhanced rate and cycling results [21]. In fact, all these improvements can mainly be attributed to the excellent conductivity of the interlayer. The physical confinement of the polysulfides was not significant owing to the weak interaction between the highly polar polysulfides and the nonpolar carbon interlayer. Therefore, chemical interactions between the polysulfides and the separator or interlayer were necessary. Considering this, researchers have been investigating materials that can establish chemical bonding with polysulfides. For example, Nazar's group reported that ultrathin MnO_2 nanosheets formed surface-bound intermediates after reacting with polysulfides [22]. TiO_2 was applied as a highly effective polysulfide absorbent to improve the cycling performance by forming a Ti–S bond to suppress the dissolution of polysulfide [23]. Moreover, metal oxides/carbon and hydroxides/carbon interlayers such as ZnO nanowires/carbon nanofiber mat, magnesium borate hydroxide (MBOH)/CNT membrane, and NiFe layered double hydroxide (LDH) nanoplates/graphene layer, were designed to take advantages of both carbon matrix and metal oxides/hydroxides in improving the performance of Li-S batteries [24–26]. Compared with metal oxides, metal sulfides with metal–S bonds can bind polysulfides through the stronger S–S interaction and dipolar interaction of metal–sulfur bonds on the polarized surface. It has been reported in the literature that MoS_2 could effectively trap the polysulfides owing to the strong chemical interaction between MoS_2 and polysulfides [27–29]. However, it is still challenging to introduce MoS_2 into the Li–S system to effectively suppress the shuttle effect and improve the cell performance.

Herein, we report a simple and feasible strategy to develop MoS_2/CNT interlayers by uniformly loading MoS_2 nanosheets on a cross-stacked CNT film and taking advantage of the properties of both MoS_2 and CNTs. The MoS_2/CNT interlayer was ultrathin (2 μm) and lightweight (0.25 mg cm^{-2}). The CNT film provided excellent electrical conductivity for the sulfur electrode and a support skeleton for the dispersion of MoS_2, as well as a physical barrier for the diffusion of the polysulfide. The MoS_2 nanosheets further suppressed the shuttling effect through their chemical interactions with the polysulfides. The sulfur electrode with the MoS_2/CNT interlayer possessed an initial capacity of 1237 mA h g^{-1} at 0.5 C and demonstrated a superior cycling stability with a decay of only 0.061% per cycle for 500 cycles at 0.2 C. Furthermore, it also delivered an impressive rate capacity of 784 mA h g^{-1} at 10 C. The fabrication process of the MoS_2/CNT interlayer can be easily scaled up, and the method presents significant potential for the development of high-performance Li–S batteries.

2. Experimental section

2.1. Fabrication of CNT arrays and a MoS_2/CNT functional interlayer

CNT arrays with a tube diameter of 10–20 nm and a height of 300 μm were synthesized on silicon wafers in a chemical vapor deposition system with iron as the catalyst and acetylene as the precursor. The details of the synthesis have been reported in previous publications [30–32]. Continuous CNT films were directly drawn from the CNT arrays by an end-to-end joining mechanism [30,31,33]. MoS_2 powder (50 mg) (Sigma-Aldrich, USA) was dispersed in 200 mL N-methyl-2-pyrrolidinone (NMP) by sonication. After centrifugation, the supernatant containing the MoS_2 nanosheets was diluted with 30 mL alcohol to form the MoS_2 suspension by sonication. The polypropylene film (Celgard 2400) was fixed on a piece of flat glass and then covered with a 2-layer cross-stacked CNT film. The MoS_2 suspension was deposited uniformly onto the CNT film and a thin MoS_2/CNT layer was obtained after the evaporation of the alcohol. This procedure was repeated to obtain the sandwich-structured MoS_2/CNT interlayer with a 20-layer CNT film. Finally, the separators covered with the MoS_2/CNT interlayer were punched into circular shapes with a diameter of 19 mm. Separators covered with a 20-layer CNT film were also prepared as a control sample.

2.2. Preparation of the S cathode

Sulfur powder (Beijing Dk Nano Technology Co., Ltd), carbon black powder (50 nm in diameter, Timcal Ltd., Switzerland), N-methyl-2-pyrrolidinone (NMP), and polyvinylidene difluoride (PVDF) were used as the active material, conducting agent, dispersant, and binder, respectively. The sulfur slurry was prepared by thoroughly mixing sulfur powder, Super P, and PVDF at a weight ratio of 5:4:1 in an NMP solution. They were ground in a mortar for approximately 30 min. The resulting slurry was uniformly spread on an aluminum foil (20 μm in thickness). After drying at 50 °C for approximately 30 min, the electrode sheets were punched into circular discs with a diameter of 10 mm. Before assembly of the cells, all the electrodes were dried again in a vacuum oven overnight at 35 °C. The loading weight of sulfur was about 1.4 mg cm^{-2}, counting for 50 wt% of the electrode.

2.3. Material analysis

The microstructure and morphology of the MoS_2/CNT interlayer were examined by a scanning electron microscope (Sirion 200, FEI) and a transmission electron microscope (Tecnai G2F20, FEI). X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI Quantera II surface analysis equipment. The XPS spectra were deconvoluted into Gaussian-Lorentzian-type peaks after applying a Shirley background. The binding energy values were all calibrated using the C 1s peak at 284.8 eV [8,34,35].

2.4. Electrochemical measurement

All electrochemical characterizations were performed using CR2016 coin-type cells. The cell assembly was carried out in an Ar-filled glove box (M. Braun Inert Gas Systems Co. Ltd.) with both moisture and oxygen levels below 0.1 ppm. The S cathodes were the working electrodes, and the lithium foils were used as the counter electrodes for all measurements. The MoS_2/CNT interlayer and CNT interlayer covered with polypropylene film (Celgard 2400) were used as separators, in which the side covered by the MoS_2/CNT or CNT interlayer was towards the S cathode. 1 M LiTFSI solution in dioxolane (DOL) and dimethoxyethane (DME) mixed at a volume ratio of 1:1 with the addition of 0.2 M $LiNO_3$ was used as the electrolyte. The ratio of electrolyte and sulfur was 25 μL mg^{-1} in the cells with the MoS_2/CNT modified separator, CNT modified separator, and the pristine separator. The visual