



A simply effective double-coating cathode with MnO₂ nanosheets/graphene as functionalized interlayer for high performance lithium-sulfur batteries



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ABSTRACT

Herein, we report a facile and effective adsorption strategy to improve the performance of Lithium-Sulfur (Li-S) batteries. MnO₂ nanosheets grown on the surface of highly conductive graphene resulted in a coupled composite bilayer electrode when coated onto a sulfur cathode. In this way, a high initial specific capacity of 1395 mA h g⁻¹ at a rate of 0.5C, a coulombic efficiency approaching 100% and steady cyclic efficiency with a fade rate of 0.3% per cycle from 10 to 100 cycles has been achieved. This hybrid electrode not only shows enhanced electrochemical performance but can also be easily controlled and scaled thereby aiding future commercialization of high-performance Li-S batteries.

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1. Introduction

Advanced lithium-sulfur (Li-S) batteries are an attractive option for the development of low-cost, environmentally-friendly energy storage technologies for use in high power applications such as electric vehicles as well as other mobile devices. This is particularly due to their high theoretical capacity (1675 mA h g⁻¹) and high energy density (2500 kW kg⁻¹) especially in multi-electron systems [1–3], which exceeds traditional Li-ion battery several fold [4]. However, there are several challenges in realizing the commercialization of Li-S battery technology. This includes the insulating nature of S and its discharge products Li₂S or Li₂S₂ and also the huge volume expansion of sulfur during the cycling process which can lead to low S utilization capacity and degradation [5,6]. Furthermore the notorious reaction between the out-diffusing soluble polysulfide (PS) and the anode results in a

rapid decrease in cycle performance and capacity, namely the “shuttle effect”, which is highly problematic [7,8].

Recently, the application of carbon materials (such as mesoporous carbon [9,10], carbon microspheres [11], carbon nanotubes [12], graphene [13–16] and carbon nanofibers [17]) has been shown to enhance the electrochemical performance of Li-S batteries in numerous ways due to their high electrical conductivity and large specific surface area [18,19]. However, the presence of nonpolar carbon can decrease its ability to capture and immobilize PS, which cannot be ignored [20]. It has been reported that polar metal oxides (TiO₂ [21,22], La₂O₃ [23], V₂O₅ [24], Ti₄O₇ [25,26], ZrO₂ [27], MoO₂ [28], ITO [29] and MnO₂ [30]) can make up for the shortages of carbon materials as they yield stronger chemical reactions with PS and can form a pore structure conducive for ion-shuttling thereby significantly reducing the influence of the “shuttle effect”. Unfortunately these oxides inevitably decrease the utilization of sulfur resulting from their low electrical conductivity [28,31].

In spite of the great contributions of these above-mentioned approaches on improvements of capacity, cycle life and discharge/charge plateau of Li-S batteries, there are several additional problems which arise when considering commercialization relating to the options for modification of the sulfur cathode rather than

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the materials self-deficiency. These include complex manufacturing techniques and rigorous preparation conditions etc., all of which result in increased costs [32,33]. In 2015, Huang et al. [33] reported a simple two-step coating technique for Li-S batteries which was a major development in improving electrochemical performance. In addition, Zhang et al. [32] demonstrated a similar design, in which an ultralight interlayer of Super P was fabricated onto the cathode, resulting in a steady cyclability despite its low initial capacity.

Therefore, in this paper, we outline a strategy leading to improved battery capacity and cycling stability by utilising a cathode which is composed of a modified double-coating and functionalized layer which acts as a barrier layer. This was achieved through in-situ growth of MnO₂ onto graphene (MnO₂@GP). This design greatly improves the electrical conductivity of MnO₂ and address the insulating nature of the S cathode, as well as the polarity of the system. Furthermore the adsorption of the soluble PS and transportation of Li-ions is enhanced. Therefore, it is believed that this new cost-effective and easily applied technique can considerably advance the development of future Li-S batteries.

2. Experimental

2.1. Synthesis of the MnO₂@GP composites

In-situ growth of MnO₂ nanosheets onto GP was achieved through a one-step simple redox reaction between the permanganic acid radical and GP. First of all, a measured amount of commercialized GP (Ningbo Morsh Technology Co., Ltd.) was dispersed into a 2 M sulfuric acid solution under ultrasound at 80 °C. After 2 h granules of potassium permanganate were dissolved into the turbid liquid and stirred at a middle mixing-speed for 5 h at 100 °C. The obtained mixture of MnO₂@GP underwent vacuum filtration, and was then washed several times with deionized water and alcohol. Afterwards the powders were dried at 80 °C overnight to obtain the MnO₂@GP composite. By changing the mass ratio between potassium permanganate and GP different contents of MnO₂@GP could be achieved.

A thermogravimetric method was used to analyse the samples named here as 40% MnO₂@GP, 52% MnO₂@GP and 61% MnO₂@GP, where the percentage given is the weight of MnO₂ in the composite. Mixtures consisting of an appropriate amount of super-p and MnO₂@GP were blended with N-methyl-2-pyrrolidone (NMP) and polyvinylidene fluoride (PVDF) (weight 5%) and mixed to form a slurry. Blank GP slurries were also prepared with same compositions for comparison.

2.2. Synthesis of the double-layer cathode

The cathode was made up of two parts, including an active S/C layer and a functionalized interlayer. The S cathode was prepared by mixing elemental S, carbon black (Super P) and PVDF binder (70:20:10 by weight) in NMP which was then coated onto an aluminum foil and then dried in a vacuum oven at 50 °C for 24 h. The MnO₂@GP composite slurry was coated onto the dried S cathode as the interlayer to thus fabricating a MnO₂@GP/S double-coating cathode. Meanwhile, the MnO₂@GP without S cathode and the GP with or without S cathodes were separately prepared in the same way. In order to acquire more precise experimental data during the experiments, all components were adequately mixed as far as possible. The S content of the electrode was determined by average of the electrode plates from the same sample and calculated by area density acquired before the process of the coating of interlayer.

2.3. Electrochemical Characterization

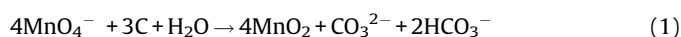
The CR2025-type coin cells were placed in an argon-filled glove box to avoid contamination by moisture and oxygen. 1.0 M lithium bis(trifluoromethanesulfonyl)imide with 0.4 M LiNO₃ was dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 by volume) forming the electrolyte. Porous polypropylene Celgard 2400 was pre-pressed for 24 h as a separator to isolate electrons and lithium metal. The discharge/charge performance of cells was tested with a CT2001A battery test system (LAND Electronic Co.) over a voltage interval ranging from 1.5 V to 2.8 V. Different current densities were chosen to test the rate performance in the same voltage range. The cyclic voltammetry (CV) experiments were conducted with a CHI660D electro-chemical workstation between 1.6 and 2.8 V vs. Li⁺/Li at a scanning rate of 0.1 mV s⁻¹. All electrochemical measurements were tested at room temperature.

2.4. Structure Characterization

The crystal structure of the samples was determined by X-ray powder diffraction (XRD, Rigaku Ultima IV, Cu Kα radiation, 40 kV, 40 mA). Diffraction patterns were taken at room temperature in the range from 10° to 80° at intervals of 0.02°. Thermal gravimetric analysis (TGA) was measured with a thermo gravimetric analyser in air from room temperature to 900 °C under a heating rate of 10 °C min⁻¹. The morphologies were obtained using scanning electron microscopy (SEM, Quanta FEG 250) and transmission electron microscopy (TEM, JEOL JEM-2100 F). Samples for TEM were prepared by dispersing the materials in alcohol by ultrasonic treatment for several minutes before observation. The Brunauer–Emmett–Teller (BET) specific surface area and the adsorption-desorption properties of the samples were measured using an Autosorb-IQ2-MP-C system. Raman spectra (Renishaw in Via Raman Microscope) were recorded using 532 nm diode laser excitation. The samples mixed with KBr pellets and were analysed with a FT-IR Spectrometer, while the obtained spectra were normalized using OMNIC spectra software. X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ultrahigh vacuum setup, equipped with a monochromatic detector, and the binding energies were calibrated by referencing the C 1s peak (284.6 eV).

3. Results and discussion

To produce functional groups (such as carbonyl (-CO) and hydroxyl (-OH) species), 2 M sulfuric acid was used to acidify the surface of the pre-ultrasonicated GP. Under heating, the addition of potassium permanganate triggers the redox reaction between KMnO₄ and carbon as follows (Eq. (1)) [34]:



The assembled ultrathin MnO₂ nanosheets are a direct result of this in-situ synthesis process and a uniform covering on the surface of GP is obtained due to the electrostatic absorption of Mn²⁺ with the oxygen-containing groups [35]. From this a novel cathode can be obtained by using the MnO₂@GP composite to overlay the S cathode as a interlayer with a coverage of ~0.8 mg cm⁻² as determined by calculation of the average (Fig. 1), as discussed below.

TGA analysis confirmed that the MnO₂ species accounts for 40%, 52% and 61% in the respective MnO₂@GP composites (Fig. 2a). Approximately 10% of water was also noted within the GP [31]. The weight loss of GP in the composites over the temperature range of 400 ~ 600 °C is notably lower than that observed for pure GP. It was

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