



Well-dispersed sulfur wrapped in reduced graphene oxide nanoscroll as cathode material for lithium–sulfur battery



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ABSTRACT

For large scale batteries, sulfur is an attractive cathode active material for lithium batteries because of high theoretical capacity of 1675 mA h g⁻¹. However, severe capacity fading and low conductivity of sulfur are significant challenges for its practical application. Here, we report a facile approach to prepare reduced graphene oxide nanoscroll embedded with well-dispersed sulfur (S/GNSC) through a one-pot oxidation of sulfide and reduction of graphene oxide followed by freeze-casting process to generate graphene nanoscroll. The S/GNSC takes the novel shape of reduced graphene oxide sheet spirally wrapped into one-dimensional tubular structure, which enhances electrochemical performance by acting as physical barrier to prevent polysulfide from dissolving and an effective network to promote electron and Li⁺ transport during reaction. Therefore, the S/GNSC composite with high sulfur loading of 76 wt% exhibits high initial capacity of 1295 mA h g⁻¹ and reversible capacity of 744 mA h g⁻¹ after the 100th cycle at 0.2 C when it is used as a cathode material for lithium-sulfur battery, while the capacity of sulfur loaded on reduced graphene oxide sheet (S/rGO) is continuously fading to 510 mA h g⁻¹ after the 100th cycle due to the irreversible loss of polysulfide.

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1. Introduction

Since a variety of portable electronic devices such as laptop computer, digital camera and mobile phone as well as some types of electric vehicles are being developed explosively, market demands for rechargeable batteries with longer lasting and higher power density are ever increasing [1–3]. Lithium-sulfur battery (Li-S) is one of the most attractive alternatives among many kinds of next generation batteries [4,5]. Li-S batteries show great potential due to the fact that both cathode and anode materials can theoretically deliver high capacities (1672 mA h g⁻¹ for sulfur and 3860 mA h g⁻¹ for lithium metal) [6]. Additionally, sulfur is naturally abundant and cost-effective. However, despite these advantages, practical applications of Li-S battery are still prevented by several challenges. First of all, the poor electrical conductivity of elemental sulfur (5×10^{-30} S/cm at 25 °C) hinders it from direct using as an electroactive material. Secondly, part of sulfur is converted into polysulfides (Li₂S₈, Li₂S₆, Li₂S₄ 2.15–2.4 V and Li₂S₂, Li₂S ≤ 2.15 V) and dissolved in organic electrolytes, which cause severe capacity fading during charge/discharge process [7,8].

During the past decade, there are tremendous efforts to resolve these challenges through many new cathode designs to achieve higher

conductivity, polysulfide-trapping capability, and durability. Many kinds of carbon materials, such as porous carbon [9–13], hollow carbon sphere [14,15], carbon nanotube (CNT) [16] and reduced graphene oxide (rGO) [17–23], were employed on electrode materials to improve the electrochemical performances of Li-S batteries. Particularly, rGO based materials have demonstrated huge improvements in electrical conductivity and capability of preventing the dissolution of sulfur into electrolyte. Recently, the development of advanced rGO/sulfur nanocomposite materials has been a very active research topic. For example, Yang et al. [19] developed a one-step approach to encapsulate sulfur uniformly onto graphene sheet layer and obtained a high reversible capacity of 804 mA h g⁻¹ after 80 cycles of charge/discharge at 0.186 C. They suggest that the size of sulfur on graphene strongly influence the electrochemical performances. Wu and coworkers [22] exhibited flexible self-supporting graphene-sulfur paper which was fabricated by vacuum filtration and drying. The graphene-sulfur electrode delivered a reversible capacity of 600 mA h g⁻¹ after 100 cycles of charge/discharge at 0.1 C. Also, Shao et al. [23] prepared an acetylene black/sulfur@graphene nanocomposite with sandwich structure via an in situ sulfur deposition strategy and self-assembly, which remained a stable capacity of 824.6 mA h g⁻¹ after 100 cycles at a current density of 200 mA g⁻¹.

Even though the electrochemical performance of the sulfur cathode was improved to some extent by using rGO, the open structure of two-dimensional rGO sheet was unfavourable to inhibit the dissolution of polysulfides. Recently, reduced graphene oxide nanoscroll (GNSC), graphene sheet spirally wrapped into one-dimensional tubular

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structure, has become one of attractive carbon materials for Li-S batteries [24–27]. Owing to its special structure, volume expansion of electro-active material could be more effectively inhibited in GNSC during charge-discharge process and ion and electron transport could be further promoted by acting as an effective network, accordingly improving the electrochemical kinetics of the sulfur cathode. In this sense, Ko et al. [25] used an ice templated self-assembly approach to converse two dimensional graphene nanosheets into hierarchically porous graphene nanoscroll networks. Yang et al. [28] also prepared a series of GNSC hybrid nanocomposites, which showed superior rate performance due to the effective promotion of ion and electron transport and mitigation of volume expansion by GNSC during the charge-discharge process.

Herein, we integrated the sulfur casting method on rGO [19] and the rGO conformation change process [25] to prepare reduced graphene oxide nanoscroll embedded with well-dispersed nano-sized sulfur (S/GNSC). This nanostructured material was synthesized through the oxidation of sulfide and reduction of graphene oxide at the same time, which was followed by using freeze-casting process to convert graphene nanosheet into graphene nanoscroll. This structure with composed of one-dimensional tubular structure spirally wrapped graphene sheet was assessed as a cathode material of Li-S battery. Due to the well-designed nanostructure, the electrochemical performance of the cathode is significantly improved. The as-prepared S/GNSC composite with high sulfur loading of 76 wt% exhibits high initial capacity of 1295 mA h g⁻¹ and reversible capacity of 744 mA h g⁻¹ after the 100th cycle at 0.2 C when it is used as a cathode material, while the capacity of sulfur loaded on reduced graphene oxide sheet (S/rGO) is continuously fading to 510 mA h g⁻¹ after the 100th cycle due to the irreversible loss of polysulfide. Because our strategy is cost-effective and simple, it has potential for practical application in Li-S battery.

2. Experiment

2.1. Materials

Graphite powder (<20 μm, synthetic), phosphorus pentoxide (P₂O₅, 97%), potassium permanganate (KMnO₄, 99.3%), sulfuric acid (H₂SO₄, 95–98%) and sodium sulfide nonahydrate (Na₂S·9H₂O, 98%) from Aldrich and sodium sulfite (Na₂SO₃, 97%) hydrochloric acid (HCl, 35.0–37.0%), hydrogen peroxide (H₂O₂, 30%), ammonia solution (28%) from SAMCHUN were purchased, respectively. All reagents were used without further purification. Water Purification System produced 18.2 M Ω deionized water was used throughout the experiments.

2.2. Synthesis of graphene oxides

Graphene oxide was prepared using a modified Hummers method [29]. In a typical synthesis, 3 g of graphite was added to a mixture of 2.5 g of K₂S₂O₈ and 2.5 g of P₂O₅ in 80 ml of concentrated H₂SO₄ solution. The mixture was heated to 95 °C for 5 h under vigorous stirring. After 5 h, it was cooled down to room temperature and DI water was added to 250 ml for dilution. Then, it was filtered and washed with DI water for several times until neutral pH. After drying in an oven at 60 °C, the pre-oxidized graphite was added to 120 ml of concentrated H₂SO₄ solution in an ice bath. Keeping the temperature of the mixture below 20 °C, 15 g of KMnO₄ was slowly added to the solution and stirred for 4 h. After that, it was stirred again at 80 °C for 4 h. The mixture was diluted using DI water and 10 ml of H₂O₂ (30%) was added to the mixture, which results in the color change to yellow with violent bubbles. This mixture was centrifuged several times with 10% HCl solution to remove residual salts, and subjected to dialysis to adjust the acidity. The resulting solution was frozen and freeze dried overnight. Finally, the resultant was re-dispersed in certain amount of DI water by sonication to obtain GO solution with specific concentration.

2.3. Synthesis of sulfur/reduced graphene oxide composite

Sulfur/reduced graphene oxide composite was synthesized by previously reported method without modification [19]. Typically, 60 ml of the as prepared GO solution (1 mg ml⁻¹) was mixed with 0.44 g of Na₂SO₃ and 1.44 g of Na₂S·9H₂O to functionalize the surface of GO with thiol groups. After stirring for 30 min, 10 ml of H₂SO₄ solution (1 mol L⁻¹) was added dropwise over a period of 1 h to oxidize sulfide to sulfur and reduce GO to rGO. The solution was further stirred vigorously for 12 h. Then, the as-prepared product was collected by centrifugation and washed three times with DI water to remove any remaining Na₂SO₃ and Na₂S. Finally, the product was subjected to freeze drying to obtain a dry substance in powder form.

2.4. Synthesis of sulfur/reduced graphene oxide nanoscroll composite

Typically, the sulfur/reduced graphene oxide composite solution (1 mg ml⁻¹) mentioned above was adjusted to pH 10 using ammonia solution (28%) to deprotonation of carboxylic groups of rGO edge. After that, the dispersion was frozen using liquid nitrogen and freeze dried overnight. Finally, the composite was achieved after lyophilisation for 3 days [25].

2.5. Structural and morphological characterizations

The surface composition of the as-prepared product was characterized via X-ray photoelectron spectroscopy (XPS, AXIS-His spectrometer-KRATOS). The morphologies of the samples were investigated by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800). High resolution transmission electron microscopy (HR-TEM) images were obtained using a JEM-2010 microscope at an acceleration voltage of 200 kV. TEM equipped with an energy-dispersive X-ray spectrometer (EDX) was used to obtain elemental distribution images. Nitrogen adsorption/desorption isotherms at 77 K were obtained using a Micromeritics Tristar 3000 instrument. The specific surface area and pore volume were calculated by the Brunauer–Emmett–Teller (BET) method and the average pore diameter was calculated by the Barrett–Joyner–Halenda (BJH) method. X-ray diffraction (XRD) peaks were obtained using a Bruker D8 ADVANCE X-ray diffractometer with CuKα radiation (λ = 1.5418 Å, rated as 1.6 kW) with a scan range between 10 and 70° with a step of 2° min⁻¹. Sulfur content in the samples was revealed by thermogravimetric analysis (TGA) measurements, with a TA Instruments Q-5000 IR model at 20–700 °C and a heating rate of 10 °C min⁻¹ in N₂ flux.

2.6. Electrochemical characterizations

For electrochemical evaluation, a mixture composed of S/GNSC, Super P (MTI Korea) and polyvinylidene fluoride with a weight ratio of 70:20:10 were dissolved in *N*-methyl-2-pyrrolidinone to form a slurry. The slurry was coated onto aluminum foil current collector with 0.82 mg cm⁻² mass loading of active material. Coin-type half cells (2016 type) were assembled using lithium foil as counter electrodes in an Argon-filled glove box. 1.0 M bis(trifluoromethane)sulfonamide lithium salt (LiTFSI) and 0.3 M LiNO₃ in a 1:1 volume mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) was employed as an electrolyte and Celgard 2400 was used as a separator. Each cell was filled with 30 μm of electrolyte using a micropipette. For Galvanostatic charge/discharge measurements of the cell were carried out using a WBCS3000s cycler (WonATech, Korea) in a voltage window of 1.7 and 2.8 V vs. Li/Li⁺. All electrochemical characteristics were performed at 25 °C.

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