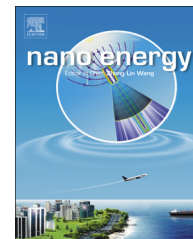




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RAPID COMMUNICATION

Macroporous free-standing nano-sulfur/reduced graphene oxide paper as stable cathode for lithium-sulfur battery



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Abstract

A macroporous free-standing nano-sulfur/graphene (S-rGO) paper is introduced directly as an electrode for lithium-sulfur battery. The S-rGO paper is synthesized through a facile freeze drying route followed by low-temperature heat treatment. The flexible S-rGO paper not only provides a conductive framework for electron transport but also alleviates volume effect during cycling. The as-designed S-rGO paper exhibits excellent rate capability and cyclability. The specific discharge capacity is 800 mAh g⁻¹ after 200 cycles at a current density of 300 mA g⁻¹ and the capacity fading rate is only 0.035% per cycle. Even at a high current density of 1500 mA g⁻¹, it still shows a good performance. We ascribe the high performance of the S-rGO paper to stable macroporous structure and strong interaction between sulfur nanoparticles and graphene.

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Introduction

With increasing demand for electrical energy storage systems, the current lithium-ion batteries (LIBs) with lithium transition-metal oxides or phosphates as cathodes suffer from limited

energy density for some large-scale applications such as smart grid energy stations and electric vehicles [1–3]. LIBs with traditional intercalation cathode materials such as LiCoO₂ and LiMn₂O₄ have a limited gravimetric energy density usually less than 200 Wh kg⁻¹, which is not sufficient to meet the increasing demand of high energy/power density. Exploring new electrode materials or new battery systems with higher capacity is of great importance. In recent years, lithium-sulfur batteries have been paid more and more attention as promising electrochemical devices due to exceptionally high

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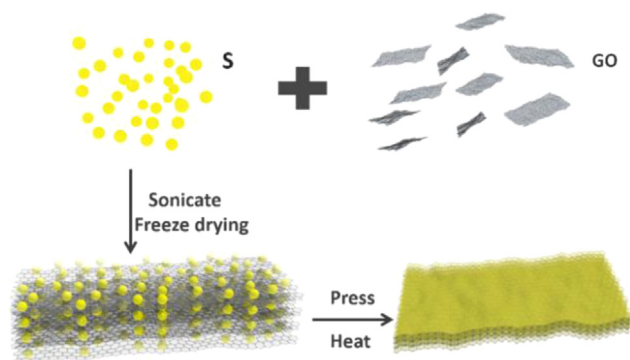


Fig. 1 Schematic illustration of synthesis process and structure of the designed S-rGO paper.

theoretical capacity of 1675 mAh g^{-1} and energy density of 2600 Wh kg^{-1} [4]. In addition, the sulfur is attracted by abundant resource on earth, environmental friendliness and low cost, which makes it more suitable for commercialization [5,6]. The boost of research in Li-S batteries greatly promotes the fast development and practical application into our daily life in a near future.

However, for Li-S batteries, some recognized problems should be solved before commercialization. One is the low electrical conductivity of elemental sulfur ($\sim 5 \times 10^{-30} \text{ S cm}^{-1}$ at room temperature), which makes the direct utilization of sulfur impossible. Another issue is the high solubility of intermediate lithium polysulfides (Li_2S_x , $x > 2$) in organic electrolyte, which not only leads to the loss of active materials from the cathode, but also causes serious “redox shuttle” reactions between polysulfide (PS) anions in the electrolyte and Li metal anode, resulting in low coulombic efficiency, high self-discharge rate and short cycle life. The volume effect of sulfur is also a problem. The volume expansion of sulfur during charge and discharge is about 80%, which will decrease the mechanical integrity and the stability of electrodes over long cycles [7,8].

The combination of conductive materials is an efficient way to improve the conductivity of sulfur. Various combination methods have been employed. Very common conductive additives are conductive polymers, [9-11] graphene materials (GO, rGO, doped GO etc.), [12-14] carbon nanotubes, and other carbon-based materials [15,16]. As for the dissolution of PS, some novel structures are desirable to impregnate sulfur and trap the dissolved PS during cycling. In this regard, we hope that the design can enhance the conductivity and tolerate the volume change at the same time. It has been demonstrated that using porous carbon, porous graphene or three dimensional graphene etc. has these multifunctional effects and shows good performance [12,14,15,17]. Here, it should be mentioned that most of decent capacities reported previously were obtained with low sulfur contents. In many cases, the total sulfur content in the cathode is no more than 60 wt.%, i.e., by considering the mass of alumina foil, the sulfur content may be lower than 30 wt.% [18,19].

In this work, we try to develop a binder free and free-standing electrode, which can increase the sulfur content in the whole electrode, and avoid the complicated traditional electrode making process. Herein, we report a nano-sulfur/reduced graphene oxide paper (S-rGO paper) material which can serve directly as an electrode for Li-S battery. In a typical procedure, we use sulfur nanoparticles and graphene

oxide as raw materials. Sulfur nanoparticles can be easily bought from some companies at cheap price. The graphene oxide is synthesized from expanded graphite, resulting in large size pieces. The flexible self-supporting graphene paper has already been used in Li-ion batteries. It has high mechanical strength, superior electrical conductivity and large surface area [20]. In our case, it acts as both conducting agent and current collector. In S-rGO paper, there are many adhesion points and continuous physical barriers to trap the polysulfides formed during cycling, so the cathode reaction can be confined within the electrode. In addition, the flexible nature can relieve volumetric expansion of sulfur during charge and discharge, and hence improve the stability of the electrode. More interestingly, a mesoporous structure is formed in the graphene paper during synthesis without any template and additive. The structure is illustrated in Fig. 1. It can provide a structural stability for Li-ion insertion and extraction, and hence is expected to exhibit a good electrochemical performance during cycling.

Experiment section

Materials synthesis

GO gel was prepared from expanded graphite using the same method in our previous study [12]. Sulfur nanoparticles were bought commercially from Shanghai Huzheng Nano Technology Co., Ltd. The synthesis procedure is shown in Fig. 1. The original GO aqueous suspension was diluted to 3 mg ml^{-1} , and sonicated for 1 h to form a uniformly dark brown suspension. Sulfur nanoparticles were washed for three times with deionized water before use, and then put into water to form a white suspension with a concentration of 75 mg ml^{-1} after being sonicated for 1 h. Afterward, 19 ml GO suspension and 1 ml sulfur suspension were mixed together and sonicated for 1 h. A uniform gray S-rGO precursor was formed. The pictures of the three suspensions are displayed in Fig. 2a. The as-formed S-rGO precursor was then transferred into a Petri dish with diameter of 6 cm, and frozen at -80°C for 2 h. A S-GO aerogel was achieved by freeze-drying of the ice solid under vacuum for 48 h. The S-GO aerogel was converted into S-rGO aerogel by directly heating at 200°C for 5 h (ramp rate = $10^\circ\text{C min}^{-1}$) in 5% H_2/Ar atmosphere. S-GO paper was obtained by pressing the graphene aerogel in a compression machine. The photos of the S-GO aerogel and the S-rGO paper are shown in Fig. 2b,c. As shown in Fig. 2d, the S-rGO paper was punched into circular disks with diameter of 12 mm, which is flexible and reversible in deformation. For comparison, a reference S-rGO composite was synthesized through the same precipitation route in our pervious study [12]. rGO was synthesized by reducing GO in hydrazine at 80°C for 2 h. Then it was dispersed into water and sonicated for 1 h. Sulfur was generated from $\text{Na}_2\text{S}_2\text{O}_3$ and HCl. $\text{Na}_2\text{S}_2\text{O}_3$ was added into the rGO solution and then diluted HCl was added dropwise. The final S-rGO composite was collected by vacuum filtration.

Materials characterization

The phases of S-GO paper, S-rGO paper and sulfur nanoparticles were checked by X-ray diffraction (XRD) on a Rigaku

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