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Enhanced electrochemical performance by wrapping graphene on carbon nanotube/sulfur composites for rechargeable lithium–sulfur batteries



Yishan Wu, Chunmei Xu, Jinxin Guo, Qingmei Su, Gaohui Du, Jun Zhang*

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China

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ABSTRACT

A novel graphene-wrapped carbon nanotube/sulfur structure was designed to improve the electrochemical performance of the lithium–sulfur (Li–S) batteries. Owing to the introduction of the reduced graphene oxide (rGO) with the aim to restrain the polysulfide anions diffusion phenomenon, increase the overall electronic conductivity of the electrode and accommodate volume expansion between the delithiated S and lithiated Li_2S phases, the resulted graphene-wrapped carbon nanotube/sulfur (S/CNT@rGO) composite makes the cycling performance of the Li–S batteries better than that without rGO. The S/CNT@rGO composite showed an initial discharge capacity of $\sim 1299 \text{ mA h g}^{-1}$ at 0.2 C rate. After 100 cycles of charge/discharge, the S/CNT@rGO composite retained a high specific capacity of $\sim 670 \text{ mA h g}^{-1}$, much higher than that without rGO ($< 150 \text{ mA h g}^{-1}$). The results show that the graphene-wrapped carbon nanotube/sulfur composite could be a promising cathode material for high-rate performance Li–S batteries.

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1. Introduction

With the advantages of high theoretical specific capacity (1675 mA h g^{-1}), low-cost, abundant resources, high specific energy density (2500 W h kg^{-1}) and nontoxicity, sulfur, a promising cathode material, makes Li–S battery show great potential for the next generation of lithium batteries [1–3]. However, several problems remain in practical applications of Li–S batteries from appearing, including low utilization of active material, poor cycle life, and low system efficiency. The underlying reasons for these issues in Li/S batteries are: (a) the insulating nature of sulfur; (b) the high solubility of lithium polysulfides as intermediate products and (c) the deposition of insoluble and insulating Li_2S_2 and Li_2S on reaction surface [3].

In recent years, the use of conductive carbon nanomaterials, e.g. mesoporous carbon [1,4,5], carbon nanotubes [6], graphene [7], CNT/graphene hybrids [8], carbon hollow spheres [9], and polymers such as polyaniline [10], polypyrrole [11], polyacrylonitrile [12], etc. gives rise to advanced composite cathode with excellent conductivity, robust electron/ion pathway, as well as superior reversible charge–discharge capacity and cycling

performance. Among them, CNT/graphene hybrids are a promising material to improve the electrochemical performance of the sulfur cathodes. Encapsulating sulfur in carbon nanotubes can minimize the shuttle of polysulfides, improving the cycle life of lithium–sulfur batteries. Moreover, graphene, a two-dimensional one-atom-thick conductor, with large surface area, high mechanical strength, and exceptionally high electrical conductivity is beneficial not only to anchor active materials and increase the overall electronic conductivity of the electrode to mitigate the sluggish kinetics, but also to buffer the large volume change between the delithiated S and lithiated Li_2S phases [13]. In this paper, we present a rational design and synthesis of novel CNT/graphene hybrids, incorporating the merits of the CNTs and the graphene, especially using a novel graphene-wrapped structure, to improve the high-rate cycling performance of the Li–S batteries.

2. Experimental

The S/CNT composite was prepared following a melt-diffusion strategy. The mass ratio of CNT and sulfur was 1:4. The powder was ground and heated to $160 \text{ }^\circ\text{C}$ in N_2 atmosphere for 20 h. Then the temperature was increased to and kept at $300 \text{ }^\circ\text{C}$ for 2 h to vaporize the superfluous sulfur on the outer surface of CNTs. Graphene oxide (GO) was synthesized using improved Hummers'

* Corresponding author. Tel.: +86 579 82283897; fax: +86 579 82282234.

E-mail addresses: zhangjun@zjnu.cn, zhangjun1985@gmail.com (J. Zhang).

method[14]. Typically, S/CNT composite was dissolved in ethanol solution, and then dropped in GO (2 mg mL^{-1}) solution under ultrasonication and stirred for 6 h. Finally, hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was added to reduce GO to rGO. After stirring for another 12 h at room temperature, the S/CNT@rGO composite was washed by water and freezing dried.

Sulfur content in the composite was determined using a thermogravimetric/differential thermal analysis (TG/DTA) measurement (Netzsch STA 449C thermal analyzer). The composite was characterized using X-ray diffraction (XRD) on a Philips PW3040/60 X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$), scanning electron microscopy (SEM) on a Hitachi S-4800 microscope and transmission electron microscopy (TEM) on a JEOL 2100F microscope, respectively.

The sulfur-based electrodes were prepared by dispersing the as-prepared S/CNT@rGO composites (75 wt%), acetylene carbon black (15 wt%), SBR glue (8 wt%) and carboxymethyl cellulose binder (2 wt%) in mixture solution of ethanol and deionized water to form a slurry. The slurry was coated on an aluminum foil and vacuum dried at 60°C . The assembling of cells was conducted in an Ar-filled glove box. The electrolyte is 1 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (volume ratio 1:1) with 0.1 M LiNO_3 additive. Batteries tests were performed using a Neware battery tester (Shenzhen Neware Technology Co., Ltd). Cyclic voltammetry and electrochemical impedance were conducted on an electrochemical workstation CHI604D (CHI instrument).

3. Results and discussion

The XRD patterns of elemental sulfur, S/CNT and S/CNT@rGO composite are shown in Fig. 1a. The XRD pattern of the sulfur

shows an Fdd orthorhombic structure (JCPDS: 08-0247). The characteristic peaks in the XRD pattern of the S/CNT composite remain the same, denoting the S/CNT composite did not bring any structure change of sulfur. However, the diffraction intensity of peaks of sulfur in the S/CNT composite are weaker than those of the elemental sulfur powder, which is probably due to the infiltration of sulfur into the channels of the CNTs. No obvious characteristic peaks can be observed for S/CNT@rGO composite, indicating that sulfur is amorphous in the composite. Moreover, only a broad peak representing the carbon content around 26° appears in the XRD of the S/CNT@rGO, which is attributed to graphene, suggesting GO is reduced completely by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. From the TG curves shown in Fig. 1b, it is found that sulfur evaporates completely at 350°C , revealing a sulfur content of 75 wt%. Electron dispersion X-ray spectroscopy (EDS) elemental mapping was used to evaluate the distribution uniformity of carbon and sulfur in the composite. As shown in Fig. 1c, it is clearly evidenced that sulfur distributes homogeneously in the composite.

Fig. 2a–c shows SEM images of S/CNT and S/CNT@rGO, respectively. It can be seen that no large bulk sulfur particles exist, suggesting the sulfur coating is uniform. A thin film can be clearly observed outside the S/CNT composites, indicating the S/CNT is perfectly wrapped by rGO. TEM is also applied to analyze the morphology and structure of the S/CNT@rGO. As shown in Fig. 2d, no single bare CNTs can be observed, suggesting S/CNT is mainly wrapped by rGO, which is consistent with the results of the SEM images. It should be noted that the obtained structure has enough space to accommodate volumetric expansion of sulfur during charge–discharge process.

In order to comprehensively investigate the electrochemical mechanisms of the as-prepared Li–S cells, cyclic voltammograms (CVs) are carried out. As shown in Fig. 3a, the reduction peak at

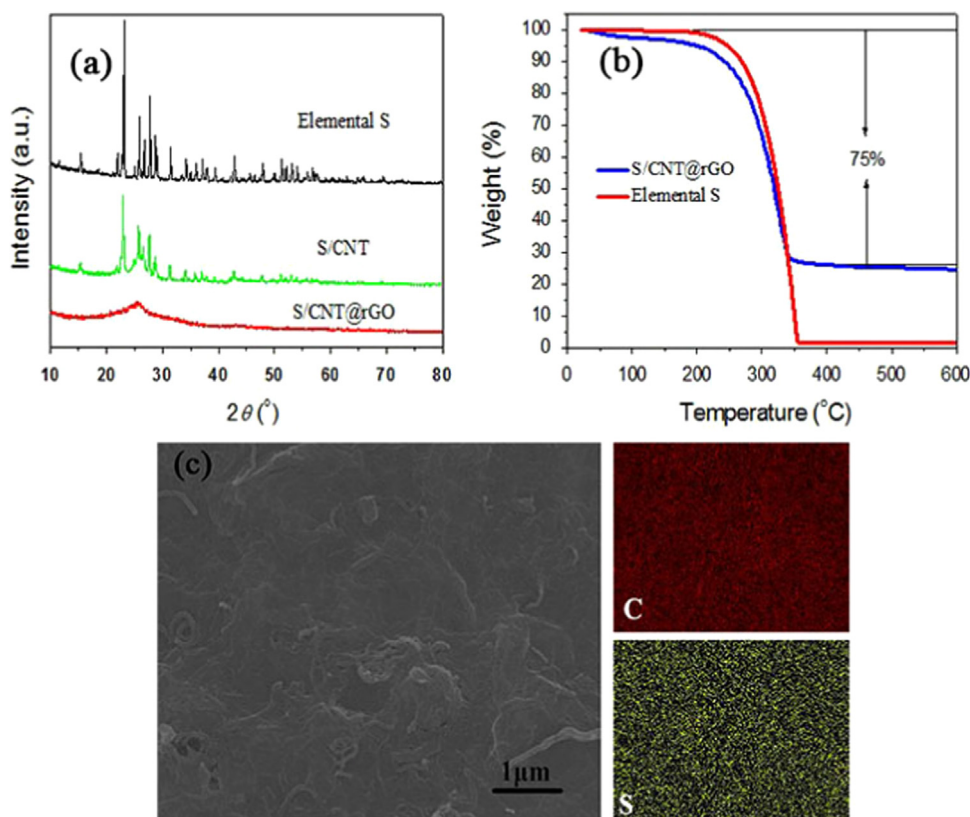


Fig. 1. (a) XRD patterns of elemental S S/CNT composite and S/CNT@rGO; (b) thermogravimetric curve of the elemental S and S/CNT@rGO composite; (c) SEM image of the S/CNT@rGO and EDS for the region.

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