Reduced graphene oxide-hollow carbon sphere nanostructure cathode material with ultra-high sulfur content for high performance lithium-sulfur batteries

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ABSTRACT

Lithium-sulfur (Li-S) batteries have been regarded as promising next generation rechargeable energy storage system, due to the high theoretical specific capacity and energy density. However, the low sulfur content in the cathode electrode greatly decrease the practical energy density of the Li-S batteries. Herein, we report a reduced graphene oxide-hollow carbon sphere (rGO-HCS) composite to encapsulate sulfur with high sulfur contents from 70 to 90 wt% as sulfur cathode. The rGO-HCS/S composite loading 90 wt% sulfur delivers the highest energy density of 1281 Wh kg^{-1} based on the mass of the whole cathode, even at a high sulfur areal density of 3 mg cm^{-2}, it could still reach a high discharge capacity of 860 mA h g^{-1} (corresponding to 1300 Wh kg^{-1} based on mass of the whole cathode) and obtain a high capacity retention of 77% after 78 cycles.These results indicate the great potential of the rGO-HCS nanostructure as promising sulfur host loading high content of sulfur with high gravimetric and volumetric energy density.

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1. Introduction

Lithium-sulfur (Li-S) batteries have been regarded as one of the most promising rechargeable energy storage systems for next generation electric and plug-in hybrid vehicles, due to the high theoretical specific capacity of 1672 mAhg^{-1} and high energy density of 2600 wh kg^{-1} of sulfur [1–4]. Additionally, element sulfur is naturally abundant with low cost and environmentally benign. However, the practical application of Li-S batteries is facing some challenges regarding sulfur cathode: (1) the insulating characteristic of sulfur (5×10^{-30} S cm^{-1} at 25 °C) induces the low capacity and poor rate performance, which usually needs a large amount of conductive materials to improve; (2) the dissolution and shuttle effect of long chain polysulfides in electrolyte lead to loss of active materials and deteriorate the cycling performance [5,6]; (3) the large volume changes during charge-discharge process result in structural pulverization of electrode and poor cycling performance [7].

In the past decade, great efforts have been paid to address these issues by encapsulating sulfur into conductive materials, such as porous carbon [8–11], hollow carbon spheres [12–16], carbon nanotubes [17–20], graphene [21–30], and conductive polymers [31,32]. These conductive matrixes with high electrical conductivity, large specific surface area and abundant porosity greatly improve the reversible capacity, cycling performance and rate capability of the sulfur cathodes. However, in most cases, the sulfur content of the cathode composites is usually less than 80 wt% [8–19,22–24,30,31] and rarely reaches 90 wt% [20,26]. Moreover, additional carbon agents and binders are introduced during the electrode fabrication process, which further decrease the sulfur content in the whole electrode. The large amounts of these conductive materials and binders are usually electrochemical inactive in sulfur cathode and inevitably reduce the energy density both in mass and volume of the whole electrode. Generally, the higher sulfur content, the poorer electrochemical performance of the cathode materials based on sulfur, probably due to the poor electronic conductivity and large volume expansion during cycling of the electrodes. Increasing the sulfur content/loading in the cathode electrode as many as possible while keep good electrochemical performance is essential to improve both the gravimetric and volumetric energy density of the Li-S batteries.

Some recent work have made efficient attempts to encapsulate large amounts of sulfur from 80% to 90% into Ketjen Black [33,34], CNTs [20], graphene [25,26], and hollow carbon spheres [16] to improve energy density of the Li-S batteries. Wang et al. [33]

reported a multi-core/shell C-PANI/S@PANI composite with sulfur content of 87 wt% and it delivered a high discharge capacity of 835 mAhg^{-1} after 100 cycles at 0.2C rate. Cheng et al. [20] mixed 90 wt% sulfur with alighed CNTs by ball milling and the obtained CNTs/sulfur composite offered a low discharge capacity of 611 mAhg^{-1} at 0.1C rate. Liu et al. [26] prepared a S-nanosphere@G composite with high sulfur content of 91 wt%, however, a low discharge capacity of 430 mAhg^{-1} was retained after 100 cycles at 0.2C rate. It is still a big chanllenge to obtain good electrochemical performance with high sulfur content.

Herein, we encapsulted sulfur into a reduced graphene oxide-hollow carbon sphere (rGO-HCS) composite with high sulfur content from 70 to 90 wt% by a simple melt-diffusion method. Sulfur was infiltrated into and distributed homogeneously among the rGO-HCS composite without aggregation even when the sulfur content is up to 90 wt%. The rGO-HCS/S composite loading 90 wt% sulfur delivers the highest discharge capacity of 610 mAh g^{-1} (with energy density of 1281 Wh kg^{-1}) based on the mass of the whole cathode, much higher than that of the composites loading 70 wt% and 80 wt% sulfur. Moreover, even when the sulfur areal density increases to 3 mg cm^{-2}, the rGO-HCS/S composite loading 90 wt% sulfur could still reach a high energy density of 1300 Wh kg^{-1} at a power density of 240 W kg^{-1} and obtain a good capacity retention of 77% after 78 cycles. The ultrahigh content of sulfur in the rGO-HCS composite renders remarkable increase of both gravimetric and volumetric energy density, which was probably ascribed to the 3D conductive graphene networks, hierarchical porous structure with large pore volume, homegeneous distribution and efficient confinement of sulfur in the rGO-HCS nanostructure.

2. Experimental section

2.1. Synthesis of rGO-HCS composite

The rGO-HCS composite was synthesized by a hydrothermal self-assembly method [35] followed by high temperature annealing and HF etching, which was reported previously by our group [36]. Briefly, the RF@SiO$_2$ nanospheres were prepared by a stober method [37] and the GO was synthesized by an improved Hummers method [38]. Then, 1.5 g RF@SiO$_2$ nanoparticles were sonicated in 60 ml water for 3 h, then 30 ml well dispersed GO aqueous solution (10.0 mg ml^{-1}) and 30 ml ascorbic acid solution was added and stirred for 1 h, finnally,the mixed solution was heated for 12 h at 180°C in a sealed autoclave to form a 3D GO-RF@SiO$_2$ gel.The gel was freeze dried and then annealed at 900°C for 2 h under N$_2$ protection, after that, the obtained powders were finely ground and etched in 10wt% HF solution to obtain the rGO-HCS composite.

2.2. Synthesis of rGO-HCS/Scomposites

The rGO-HCS/S composites were prepared by a facile melt-diffusion method. Breifly, the rGO-HCS composite was mixed with sulfur powder in the expect ratio by finely grinding and then heated to 155 °C for 8 h under N$_2$ atmosphere. The obtained rGO-HCS/S composites were named as rGO-HCS-0.7S, rGO-HCS-0.8S, and rGO-HCS-0.9S according to the designed sulfur contents in the composites.

2.3. Material characterization

The structure of the rGO-HCS/sulfur composites were measured by XRD (SIEMENS D-500) using Cu Ka radiation, ranging from 10° to 60° at a step of 8° min^{-1}. The micro morphologies of the obtained composites were studied using a field emission scanning electron microscope (HITACHI S4800, Japan). The nitrogen adsorption-desorption analysis was carried out at 77.3 K on a V-Sorb 2800 equipment. The thermogravimetric analysis (TGA) was performed with a TGA-600 with a heating rate of 10 °C min^{-1} under a N$_2$ atmosphere to confirm the sulfur contents in the composite.The tap density of the composites was determined by dividing the mass of the composite into its tap volume.
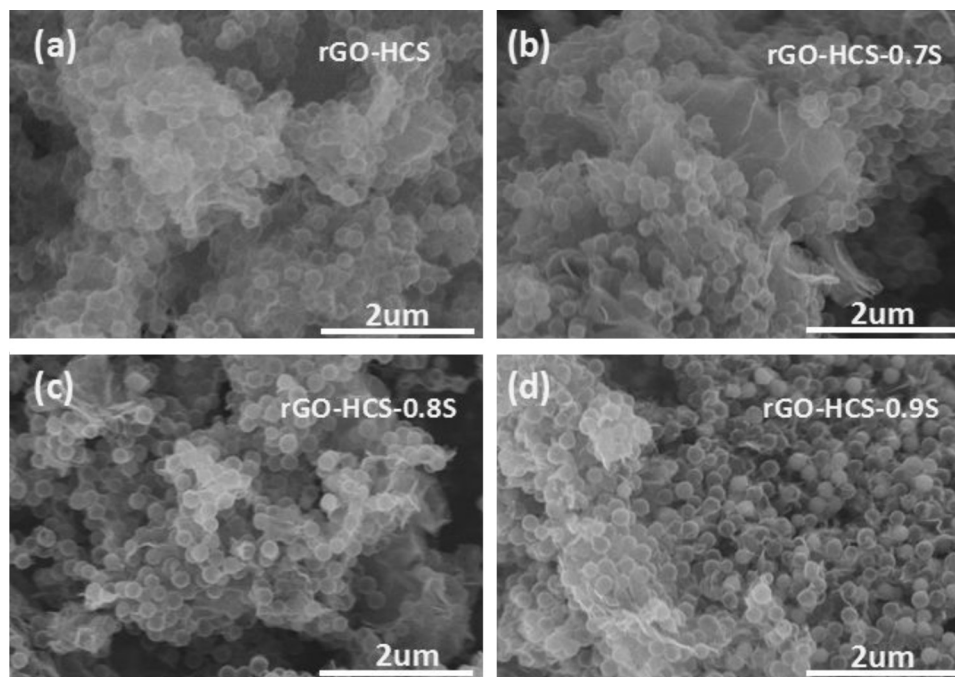

Fig. 1. SEM images of (a) the rGO-HCS composite, (b) the rGO-HCS-0.7S composite, (c) the rGO-HCS-0.8S composite and (d) the rGO-HCS-0.9S composite.