Electrochimica Acta 155 (2015) 54–60

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Interface polymerization synthesis of conductive polymer/graphite oxide@sulfur composites for high-rate lithium-sulfur batteries

Xiwen Wang, Zhian Zhang *, Xiaolin Yan, Yaohui Qu, Yanqing Lai, Jie Li

School of Metallurgy and Environment, Central South University, Changsha, 410083, China

ARTICLE INFO

Article history:
Received 16 September 2014
Received in revised form 22 December 2014
Accepted 23 December 2014
Available online 26 December 2014

ABSTRACT

The novel ternary composites, conductive polymers (CPs)/graphene oxide (GO)@sulfur composites were successfully synthesized via a facile one-pot route and used as cathode materials for Li-S batteries The poly(3,4-ethylenedioxythiophene) (PEDOT)/GO and polyaniline (PANI)/GO composites were prepared by interface polymerization of monomers on the surface of GO sheets. Then sulfur was *in-situ* deposited on the CPs/GO composites in same solution. The component and structure of the composites were characterized by XPS, TGA, FTIR, SEM, TEM and electrochemical measurements. In this structure, the CPs nanostructures are believed to serve as a conductive matrix and an adsorbing agent, while the highly conductive GO will physically and chemically confine the sulfur and polysulfide within cathode. The PEDOT/GO@S composites with the sulfur content of 66.2 wt% exhibit a reversible discharge capacity of 800.2 mAh g^{-1} after 200 cycles at 0.5 C, which is much higher than that of PANI/GO@S composites (599.1 mAh g^{-1}) and PANI@S (407.2 mAh g^{-1}). Even at a high rate of 4 C, the PEDOT/GO@S composites still retain a high specific capacity of 632.4 mAh g^{-1}.

1. Introduction

Recently, with increasing demand of green and renewable energy, great efforts have been devoted to develop advanced secondary battery systems with high energy density and high power density. Among them, lithium-sulfur (Li-S) batteries is one of most attractive candidates due to its high theoretical capacity of 1675 mAh g^{-1}, high theoretical energy density of 2600 Wh kg^{-1}, low cost and natural abundance of sulfur [1–3]. However, the practical application of Li-S batteries is still limited because of the insulating nature of sulfur, the solubility of polysulfide as well as large volume expansion during discharge [4]. Therefore, a novel material design strategy is essential to address the above issues, especially for the dissolution of polysulfide.

Tremendous attentions have been focused on the porous carbon materials with different structure and morphology, which could improve electrical conductivity of electrode, buffer volume expansion during discharge and inhibit the dissolution of polysulfide [5]. Conducting polymers such as polyacrylonitrile (PAN) [6–8], polyaniline (PANI) [9–11], polypyrole (PPY) [12–14], polythiophene (PTH) [15], poly(3, 4-ethylenedioxythiophene) (PEDOT) [16,17] have also been widely explored as a coating layer or a conductive matrix in sulfur composites, based on their controllable morphologies, good electrochemical stabilities and good compatibility with sulfur. Cui also found that the effect of the different conductive polymers on improving the long cycling stability and high-rate performance of sulfur cathode decreased in the order of PEDOT > PPY > PANI [18]. However, the CP@S composites still exhibit relative poor conductivity and limited rate capacities. Therefore, incorporating carbon with CP@S composites would be an optimized strategy to enhance the electrochemical performance. This ternary nanostructure not only serves as highly conductive matrix to load abundant active sulfur, but also displays co-adsorption with polysulfide [19]. It is also noted that muti-composites integrated sulfur with both carbon and conductive polymers, such as sulfur/graphene/PPy [19] or PAN [20], sulfur/carbon nanotubes/PANI [21] or PPy [22] and sulfur/carbon black/Nafion [23] have proved to be effective on improving the cycle stability and high-rate capability of the sulfur cathode.

Graphene nanosheets as an emerging two-dimensional carbon nanomaterial with high surface area of 2630 $m^2 g^{-1}$, excellent intrinsic electric conductivity, superior mechanical flexibility and chemical stability, have been considered as an ideal matrix or coating layer for the cathode in advanced lithium-sulfur batteries [24–26]. Graphene oxide (GO) has been explored as a good matrix to anchor sulfur due to the abundant oxygenate functional groups on its surface that absorbs the polysulfides via chemical interaction [27–29]. GO could both physically and chemically suppress the dissolution and diffusion of the polysulfides anions in liquid

---

* Corresponding author.

http://dx.doi.org/10.1016/j.electacta.2014.12.142
0013-4686/

electrolyte. Moreover, the highly functionalized graphite oxide will form stable dispersions in water, which make it possible to prepare hybridized materials with controllable morphology and size [30] or modified by some functionalized polymers [31].

Herein, we report a simple one-pot synthesis of CP/GO@S ternary composites with a hierarchical nanostructure via interface polymerization of CPs nanostructures onto GO, and the subsequent deposition of sulfur nanoparticles to CP/GO binary composites in aqueous solution, as illustrated in Fig. 1. It is found that this ternary composites can afford a large reversible capacity with high Coulombic efficiency, excellent cyclic and rate performance, highlighting the importance of a multiplex fixing strategy of sulfur using graphite oxide and conductive polymer for maximum utilization of active sulfur in Li-S cells. Moreover, the PEDOT/GO@S composites have been proven to be the better option that can achieve a long cycle life and high-rate capability for Li-S cells in many CP/GO@S ternary composites.

2. Experimental

2.1. Preparation of CP/GO@S composites

GO was prepared from natural graphite powder by a modified Hummers method [32]. The GO was dispersed into distilled water by ultrasonic agitation for 2 h. The transparent orange-yellow sodium polysulfide (Na_2S_x) solution was prepared by dissolution of stoichiometric quantity sulfur into Na_2S solution [27].

Firstly, PEDOT/GO hybrids were synthesized via the interfacial polymerization method. Typically, 5 mL $FeCl_3$ (1 M) aqueous solution as an oxidant was added into 5 mL GO dispersion (1 mg mL^{-1}). Subsequently, the above solution was added slowly into 10 mL of EDOT solution in $CHCl_3$ (0.2 M). The above mixture was kept at 60 °C under static conditions. The dark green products were produced on the interface and gradually dispersed into aqueous solution. Finally, the organic solvent at the bottom was removed and the Na_2S_x solution was added drop-wise. Upon the addition of Na_2S_x solution, the yellow sulfur precipitates were immediately formed due to the acidic and oxidative property of $FeCl_3$ solution. After stirred for 12 h, the precipitate was filtered and washed with ethanol and distilled water several times. The obtained products were dried at 50 °C in oven for 24 h. For the preparation of PANI/GO@S composites, the polymer monomer was changed. 0.2 mL aniline monomer was firstly added into $CHCl_3$ solution and followed by the unchanged procedures of PEDOT/GO@S composites. PANI@S composite were fabricated without the addition of GO.

2.2. Materials characterization

The morphology was characterized by scanning electron microscope (SEM, Nova NanoSEM 230) and transmission electron microscope (TEM, JEOL JEM-2100F). The Fourier transform infrared spectra (FT -IR) were recorded on a Nicolet560 spectroscopy with KBr pellet technique. Raman spectra were test with Dior LABRAM-1B instrument. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher ESCALAB250xi XPS system. The XPS curve-fittings were performed using the XPS Peak 41 program with Gaussiane-Lorentzian functions after subtraction of a Shirley background. The fitting errors of XPS test results using this method are within ±1%. The sulfur content of the composites was determined by thermogravimetric (TGA) analysis (SDTQ600).

2.3. Cell assembly and electrochemical measurements

The sulfur containing composites powder was mixed with Super-P carbon black (Timcal) and Poly(acrylic acid) binder (Aldrich), with mass ratio of 70: 20: 10, in suitable amount of distilled water to produce electrode slurry. The slurry was coated onto aluminum foil current collector (20 μm thickness) by a doctor blade and dried in vacuum oven at 50 °C for 12 h. The typical mass loading of active sulfur was ~1.5 mg cm^{-2}. The electrochemical characterization was performed using a CR-2025 type coin cell using Celgard 2400 separator and filled with 30 μL liquid electrolyte. These cells are assembled in an argon-filled glove box (Universal 2440/750) in which oxygen and water contents were less than 1 ppm. 1 M bis (trifluoromethane) sulfonamide lithium salt (LiTFSI, Sigma Aldrich) and 0.1 M $LiNO_3$ in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v, 1:1) was used as the electrolyte.

Galvanostatic measurements were carried out using a LAND CT2001A charge-discharge system. The cells were first discharged to 1.5 V and then the cycle numbers was counted. Electrochemical impedance spectroscopy (EIS) measurement were conducted with PARSTAT 2273 electrochemical measurement system in the frequency range of 100 kHz to 0.01 Hz with an AC amplitude of 5 mV. All the electrochemical tests were conducted at room temperature.

3. Results and discussion

The morphology and microstructure of PANI PANI/GO@S and PEDOT/GO@S composite were investigated by SEM, and shown in Fig. 2. In Fig. 2a, some large sulfur crystallites in size of 1~2 μm

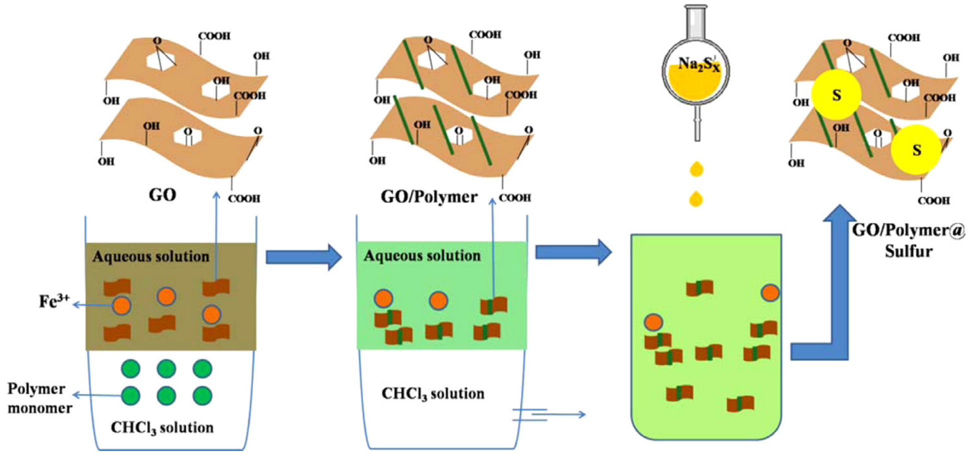

Fig. 1. Schematic illustration of synthesis process of the CPs/GO@S composites.