



Enhanced electrochemical performance of sulfur/carbon nanocomposite material prepared via chemical deposition with a vacuum soaking step



Xiaolan Cui^a, Zhongqiang Shan^{a,*}, Lan Cui^b, Jianhua Tian^a

^a School of Chemical Engineering and Technology, Tianjin University, Weijin Road 92#, Tianjin 300072, PR China

^b Analysis Center, Tianjin University, Weijin Road 92#, Tianjin 300072, PR China

ARTICLE INFO

Article history:

Received 23 December 2012

Received in revised form 28 April 2013

Accepted 30 April 2013

Available online 9 May 2013

Keywords:

Lithium–sulfur battery

Sulfur/carbon nanocomposite

Vacuum soaking

ABSTRACT

A sulfur/carbon nanocomposite was prepared by a simple chemical deposition method. A feasible vacuum soaking step was introduced to absorb the sulfur source (Na_2S_x) into the carbon micropores/mesopores. It is confirmed from the scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), galvanostatic discharge–charge, cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) that the S/C composite with vacuum soaking (78 wt% sulfur) leads to more dispersion of sulfur into the carbon micropores/mesopores and displays better electrochemical features, compared to the S/C composite without vacuum soaking, the synthesized sulfur/carbon and pristine sulfur/carbon ball-milled composites. The S/C cathode with vacuum soaking delivers an initial discharge capacity of 1116.1 mAh g^{-1} (based on sulfur weight) and retains 534.2 mAh g^{-1} after 150 cycles with a discharge/charge rate of 0.35 C. The stable capacity retention and sturdy structure of the electrode are attributed to an intimate nanoscale contact established between the smaller sized sulfur and the conductive carbon.

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1. Introduction

Due to high theoretical capacity of 1672 mAh g^{-1} , high theoretical specific energy of 2567 Wh kg^{-1} , natural abundance, extremely low cost and environment friendly, sulfur-containing cathode materials have received considerable attention as prime candidates for high performance energy storage systems [1].

Many important advances have been made recently to prepare composite materials based on sulfur and various kinds of carbon, resulting in enhanced cycling stability of Li–S battery. However, they suffer from some significant drawbacks which inhibit the commercialization of Li–S batteries. Poor charge transfer ability and limited rate performance are derived from the insulating nature of sulfur as $5 \times 10^{-30} \text{ S cm}^{-1}$ and its reduction intermediates Li_2S_n ($3 \leq n \leq 8$)/products ($\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$). Moreover, various soluble Li_2S_n ($3 \leq n \leq 8$) intermediates give rise to shuttle effect and active mass loss, leading to fast capacity degradation. Besides, structure collapse of the cathode during cycling is a troublesome issue as well [1–5].

Several approaches have been pursued to prepare sulfur-containing cathodes in order to address the above problems. These

approaches involve ball milling [6], sulfur melt-infusion approach, solvent exchange method and chemical deposition method. Ball milling is a method of mechanically mixing sulfur and conductive matrix together. Sulfur cannot be filled into the carbon pores leading to weak contact between sulfur and conductive matrix. Sulfur melt-infusion approach is based on capillary adsorption and has attracted significant interest [7,8]. The micropore–mesopore filling mechanism has been accepted by most of the researchers. The adsorption energy increasing with the decreasing pore size determines that the micropores are filled in advance compared to the mesopores [2,9,10]. However, the sulfur melt-infusion approach with harsh condition and high energy consumption results in high manufacturing costs. Solvent exchange method is based on different solubility of sulfur in various solvents in order to prepare small sized sulfur particles, yet the use of toxic solvents is inevitable. Tetrahydrofuran [11], dimethyl sulfoxide [12], o-xylene and CS_2 [13] are used to obtain different sulfur-containing cathode materials. Attention has also been devoted to the scalable chemical deposition method due to its favorable process without extra heat treatment. The conductive matrix is suspended in aqueous solution and then sulfur nucleates on the conductive matrix by chemical reaction. $\text{Na}_2\text{S}_2\text{O}_3$ was used as sulfur source to prepare graphene–sulfur composite [14,15] or carbon–sulfur composite [16]. Particularly, Wang et al. [14] synthesized PEG modified graphene–sulfur composite containing 70 wt% sulfur. The result

* Corresponding author. Tel.: +86 13612032260; fax: +86 022 27890885.

E-mail address: shanzhongqiang1957@yahoo.cn (Z. Shan).

showed a specific capacity up to about 600 mAh g⁻¹ over more than 100 cycles at 0.2 C. Another chemical precipitation method involving Na₂S and S has also been reported. A graphene-enveloped sulfur composite [17] with 87% sulfur loading synthesized by Nazar et al. delivered the initial capacity of 705 mAh g⁻¹ and 50th capacity of 500 mAh g⁻¹ at 0.2 C. A nano-carbon/sulfur composite [18] and carbon nanofiber–sulfur composite [19] were prepared by Rao et al. showing an initial capacity as 1200 mAh g⁻¹ and 1313 mAh g⁻¹, respectively and retaining 668 mAh g⁻¹ after 50th cycles, 586 mAh g⁻¹ after 60th cycles at 0.05 C, respectively. Long-term stable cyclability is an important indicator for Li–S battery. However, further cycling data haven't been presented in these articles.

Herein, we report a feasible and low-cost chemical deposition method to synthesize carbon supporting sulfur cathode material. A vacuum soaking step was employed for the sulfur source absorption, facilitating sulfur to deposit into the carbon pores. The carbon micropores/mesopores act as microreaction chambers for sulfur precipitation. Subsequently, the electrochemical reaction constrained in the carbon pores would be a critical factor for cycling enhancement. The immediate polysulfides can be retarded to diffuse out of the electrodes during cycling. The morphology, X-ray diffraction, nitrogen adsorption and desorption, galvanostatic cycling performance, cyclic voltammograms, and electrochemical impedance spectroscopy were used to characterize the sulfur/carbon composites. The improved cycling stability would be attributed to the reduced dimension of sulfur and the enhanced electric contact provided by the increased confinement of sulfur in the carbon matrix.

2. Experimental

2.1. Synthesis of sulfur/carbon composite

S (AR, Aladdin, China) and Na₂S·9H₂O (AR, Tianjin Guangfu, China) according to a weight ratio of 1:2 were dissolved into 10% NaOH to obtain a deep orange solution. 0.1 g carbon (Black Pearls 2000, Cabot Corporation) was dispersed in the obtained solution under bath sonication for 1 h. The suspension was placed under vacuum condition of -0.08 MPa for 1.5 h. 5% HCl was dropwisely added to acidity within 1 hr in order to precipitate the sulfur onto the surface or into the pores of the nano-carbon particles. Magnetic stirring was maintained for 2.5 h subsequently. The obtained product was filtered and washed several times with water, followed by drying at 50 °C for 12 h.

Elemental sulfur sample was synthesized through a same procedure without carbon. For comparison, S/C composite sample was prepared by the above-mentioned procedure without vacuum soaking step. The pristine sulfur/carbon composite and synthesized sulfur/carbon composite with the same sulfur content were also prepared by planetary ball milling for 6 h. The samples with or without vacuum soaking step are marked as S/C-VS and S/C, respectively. The other two ball-milled samples with the pristine sulfur and synthesized sulfur are denoted as PS/C and SS/C, respectively. The S/C-VS-38 composite with 38 wt% sulfur and S/C-35 composite with 35 wt% sulfur were obtained by reducing the amount of sulfur for reaction.

2.2. Cell assembly

To prepare the working electrode, the obtained composite material was mixed with Super P carbon and PTFE in a weight ratio of 70:20:10 and suspended into ethanol. The foam nickel was punched into small circular disk of φ 11 mm with a round hollow punch and pressed on a stainless steel stamp after coating the slurry. The film

disk was dried in a vacuum oven at 50 °C for 12 h before assembling the testing cells. The electrode typically had an active material content about 2 mg cm⁻². The coin-type cells of 2032 were assembled in a glove box filled with argon. Lithium metal was used as the counter and reference electrode, and a microporous polypropylene film (Celgard 2000) was used as separator. The electrolyte consists of 0.1 M anhydrous lithium nitrate and 1 M LiN(CF₃SO₂)₂ (LiTFSI) in a mixed solvent of 1,3-dioxolane (DOL) and dimethyl ether (DME) at a volume ratio of 1:1 (AR, Guotai-Huarong New Materials, China).

2.3. Characterization and electrochemical evaluation

Thermal gravimetric analysis (Q500, TA Instrument, USA) were conducted to assess the sulfur content of the S/C-VS and S/C composites with a heating rate of 10 °C min⁻¹ under flowing N₂ (10 mg for testing). The morphology of the carbon matrix, the pristine sulfur, the synthesized sulfur and four sulfur/carbon composites were examined by FESEM (Hitachi S-4800, accelerating voltage as 15 kV, Japan), TEM (Hitachi JEM-2100F, Japan) and EELS (Tecnai G2 F20, Netherlands). Nitrogen adsorption and desorption isotherms were obtained using a BEL mini-instrument (Netherlands). BP2000 carbon was degassed at 150 °C on a vacuum line following a standard protocol before measurement. Before measurement of S/C-VS and S/C composites, only room temperature degassing was used for 12 h owing to the possibility of sulfur sublimation. The X-ray powder diffraction patterns of four samples were recorded using Cu K α radiation at 40 kV and 20 mA in the region of $2\theta = 10\text{--}80^\circ$ (Bruker AXS, Germany).

To evaluate the electrochemical capacity and cycle stability of the electrodes, galvanostatic charge/discharge tests were carried out in the voltage range of 1.5–3.0 V (versus Li⁺/Li) at 0.35 C (585 mA g⁻¹), 0.5 C (836 mA g⁻¹) and 1 C (1672 mA g⁻¹) (LAND-CT2001A, Wuhan Jinnuo, China). Cyclic voltammetry (CV) measurements were conducted at a scan rate of 0.1 mV s⁻¹ (LK3200 electrochemical workstation, Lanlike, China). Furthermore, electrochemical impedance spectroscopies (EIS) were also measured in the frequency range of 100 kHz–10 mHz at a disturbance amplitude of ± 5 mV (Zahner IM6e electrochemical workstation, Germany).

3. Results and discussion

The TG curve of the S/C and S/C-VS composite is presented in Fig. 1. As shown in Fig. 1(a), sulfur melts at 115 °C and the weight of the composite materials decreases continuously as the temperature increases from 150 to over 380 °C. The sulfur loading in two chemical deposition composites and the cathodes are 78 wt% and 54.6 wt%, respectively. Meanwhile, the sulfur content of the PS/C and SS/C composite is designed for 78 wt% as well. The evaporation rate depends on the location and the content of sulfur within the carbon matrix. It can be supporting evidence to evaluate the interaction between carbon and sulfur. The DTG curve of the S/C-VS composite has slightly positive shift of 6 °C distinguishable compared to that of the S/C composite, implying that sulfur evaporation process for the S/C-VS composite may overcome higher adsorption energy than the S/C composite under the same testing condition due to stronger interaction between carbon matrix and sulfur [20,21]. For further illustration, the DTG result of the S/C-VS-38 composite with 38 wt% sulfur content and the S/C-35 composite with 35 wt% sulfur content is compared in Fig. 1(b). The temperature of maximum peaks for S/C-35 composite and S/C-VS-38 composite are recognized as 298 °C and 315 °C, respectively. The shoulder peak around 358 °C in S/C-VS-38 composite suggests a proportion of sulfur is located in smaller pores. Therefore, it is indicated that sulfur in S/C-VS nanocomposite penetrate deeper

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