Electrochimica Acta 149 (2014) 136–143

Contents lists available at ScienceDirect

Electrochimica Acta

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

Wet ball-milling synthesis of high performance sulfur-based composite cathodes: The influences of solvents and ball-milling speed

Ge Liu [a,b], Zhong Su [b], Deqing He [b], Chao Lai [b,*]

[a] Department of Chemistry, Chifeng University, Chifeng 024000, China
[b] School of Chemistry and Chemical Engineering, and Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou, Jiangsu 221116, China

ARTICLE INFO

Article history:
Received 30 July 2014
Received in revised form 30 September 2014
Accepted 10 October 2014
Available online 14 October 2014

Keywords:
Wet ball-milling
Sulfur
Carbon nanotubes
Lithium-sulfur batteries
Solvent

ABSTRACT

Wet ball-milling route is employed to prepare sulfur-carbon nanotubes composites. The influences of solvents, including ethanol and chloroform, on the structure and electrochemical performance of the composites are firstly investigated. As compared to the conventional dry-milling process, high loose structure and uniform distribution of sulfur can be obtained by adding ethanol during the ball-milling process, and significant enhancement of electrochemical performance is presented. At the current density of 800 mA g^{-1}, the discharge capacity can be stably retained at 861.6 mAh g^{-1} after 150 cycles for the composite prepared by adding ethanol, showing obvious advantages over the dry-milling sample and the composite prepared by adding chloroform. When the current density increase to 1600 mA g^{-1}, it can still demonstrate a high reversible capacity of 640.9 mAh g^{-1} after 200 cycles. Furthermore, the influence of ball-milling speed is also investigated, but a low utilization of sulfur active materials is obtained after high-energy ball milling process.

1. Introduction

Lithium-sulfur (Li-S) batteries has been the hot topic during the last decade according to its almost highest theoretical capacity of 1675 mAh g^{-1} and resulting in potential applications in EV, HEV and large-scale storage [1,2]. However, the commercial applications of Li-S batteries are still seriously hindered by its low sulfur utilization and poor cycle life, which has been known to arise from the insulating nature of sulfur ($5 \times 10^{-30}\ \Omega^{-1}\ cm^{-1}$ at 25 °C) and dissolution of polysulfides. To address these problems, various strategies have been developed, for example, surface coating, sulfur/nanoporous carbon composite and electrolyte optimization [1–3]. Significant improvement of discharge and cycle performance has been obtained for such modifications [1–8]. Till now, the reversible capacity of sulfur-based composite cathode can easily reach more than 1000 mAh g^{-1} (calculated by sulfur), corresponding to a higher energy density than that of commercial cathodes [4–8]. Thus, for further practical application of high-performance sulfur-based cathodes, the synthesis route will become equally important as its electrochemical performance. Developing facile and large-scale synthetic routes to prepare homogeneous sulfur-based cathodes will assume immense importance to realize commercial lithium-sulfur batteries in subsequent research.

Ball-mill technology is widely used for grinding materials in industrial applications. For its application in the synthesis of electrode materials, the advantages can be described as follow: (1) it is an easy process to realize large scale synthesis of homogeneous electrode materials, which is important for battery consistency; (2) reliable operation can ensure reproducible results; (3) it is favorable to obtain high tap density due to violent treatment; (4) it is suitable for various synthesis systems, due to its economy and easy replicability [7,9]. However, for Li-S batteries, the ball-milling method was just employed to mixing sulfur and carbon in previous reports, and further thermal treatment, surface coating or special treatment of carbon materials are necessary to obtain high performance sulfur-based cathodes [9,13–15]. Till now, there is no reports on effects of ball-milling conditions on the structures and following electrochemical performance of sulfur-based composite. Accordingly, in this work, different solvents have been added to prepare sulfur-carbon nanotubes composites during the ball-milling process, and the very high ball-milling speed is also investigated. The choosing of carbon nanotubes as the conductive additives is because that it can offer a three-dimensional conductive net work during ball-milling process to prevent the agglomeration of sulfur. Surprisingly, obvious improvement of

---

* Corresponding author. Tel.: +86 13775975658.
E-mail address: laichao@jsnu.edu.cn (C. Lai).

http://dx.doi.org/10.1016/j.electacta.2014.10.033
0013-4686/

electrochemical performance can be obtained just by simple wet ball-milling process.

2. Experimental

2.1. Preparation and characterization

To prepare the precursor sulfur/carbon nanotubes composite, sulfur (2 g, analytical) and Multi-walled carbon nanotubes (2 g, diameter: 10–20 nm, length: 5–15 μm, ≥95%) were added in the agate tank (250 mL) and then mixed well by ball-milling. The ball-milling was performed in a planetary ball mill (QM-3SP04, Nanjing) under ambient conditions at a speed of 300 rpm for 3 h. To investigate the influence of solvent, sulfur/carbon nanotubes composite are also prepared via same procedure by adding ethanol (10 mL, analytical) and chloroform (10 mL, analytical), respectively. For comparison, blank sample is also prepared via the same process without adding element sulfur.

The influence of ball-milling speed is also investigated. The detailed experimental procedure was as follow: the mixture of sulfur and carbon nanotubes with a ratio of 1:1 was treated with high-energy ball mill in a hardened steel vial with zirconia balls in ethanol, using a *01-HD/HDDM Lab Attritor* at 1500 rpm for 30 minutes. The total ball-milling time was also set as 3 h.

The as-prepared samples were characterized by X-ray diffraction (XRD, Model LabX-6000, Shimadzu, Japan), X-ray Photoelectron Spectroscopy (XPS, Thermo ESCALAB 250XI) measurement, Scanning Electron Microscopy (SEM, JSM-7001F), and Transmission Electron Microscopy (TEM, FEI Tecnai F20). The sulfur content in the composite was determined by the Thermal Gravimetric Analysis(TGA, SDT Q600) with a heating rate of 10 K min^{-1} in Argon. N_2 adsorption-desorption data was measured using a Micromeritics (3Flex) instrument, and the pore size distributions are calculated by the Barret, Joyner and Halenda (BJH) methods.

2.2. Electrochemical measurements

The working electrodes were prepared by compressing a mixture of active materials, acetylene black, and binder (polytetrafluoroethylene, PTFE) in a weight ratio of 70:20:10. Lithium metal was used as the counter and reference electrode. The electrolyte was Lithium bis(trifluoromethanesulfonyl) imide (2.8 M) dissolved in a mixture of dimethoxyethane (DME) and dioxolane (DOL) in a volume ratio of 1:1. Half-cell with a pouch type is used to test the electrochemical properties of active materials. The copper collector, composite working electrode, polypropylene separator, lithium counter electrode and copper collector were sandwiched in stainless-steel battery holders with an inner diameter of 16 mm, which were fitted with a polytetrafluoroethylene ferrule. The LAND-CT2001A galvanostatic testers were employed to measure the electrochemical capacity and the cycle life of working electrodes at a current density of 800 and 1600 mA g^{-1} at room temperature. The cut-off potentials for charge and discharge were set at 3.0 and 1.5 V (vs. Li$^+$/Li), respectively.

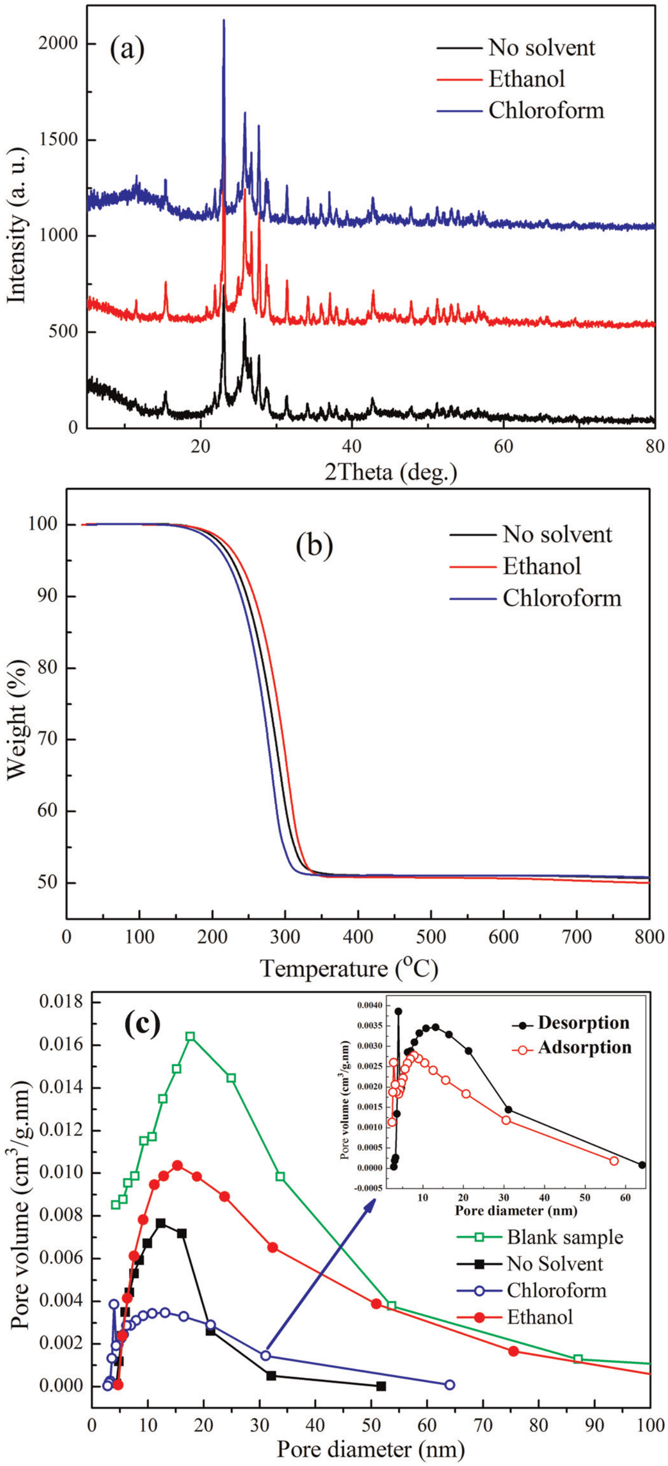

Fig. 1. XRD patterns, TGA curves (argon) and pore size distribution of the blank sample and composites prepared by adding different solvents.

3. Results and discussion

To illustrate the crystalline structure of the composites, XRD tests are performed. As shown in Fig. 1a, all the peaks can be indexed as the characteristic peaks of orthorhombic sulfur [7,9,10], and no difference between the composites prepared by different solvent. Different from previous thermal-treatment route [9,16,17], there is no phase transformation of sulfur during the ball-milling process, even after adding chloroform, and the sulfur particles may be coated on the surface of carbon nanotubes. The content of sulfur in the composites is determined by the TGA, and the weight loss curves are presented in Fig. 1b. For the three composites, similar curves can be observed, and sulfur lose its weight between 150 and 330 °C. The sulfur content is around 50%, in agreement with the original adding amount. Fig. 1c is the pore size distribution of the ball-milling carbon nanotubes and composite. The pore size distribution of the blank sample and composites prepared with and without adding ethanol is similar with a predominant mesopores between 10–20 nm. However, for the composite