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APSUSC-27636; No. of Pages 5
ARTICLE IN PRESS
Applied Surface Science xxx (2014) xxx–xxx
Contents lists available at ScienceDirect
Applied Surface Science
journal homepage: www.elsevier.com/locate/apsusc

Multiwalled carbon nanotubes-sulfur composites with enhanced electrochemical performance for lithium/sulfur batteries

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ARTICLE INFO

Article history:
Received 26 February 2014
Received in revised form 3 April 2014
Accepted 4 April 2014
Available online xxx

Keywords:
Multiwalled carbon nanotubes-sulfur composites
Cathode materials
Lithium–sulfur batteries

ABSTRACT

Multiwalled carbon nanotubes-sulfur (MWCNTs-S) composites were synthesized by chemical activation of MWCNTs and capillarity between sulfur and MWCNTs. The MWCNTs activated by potassium hydroxide (denoted as K-MWCNTs) were used as conductive additive. The as-prepared K-MWCNTs-S composites can display excellent cycle stability and rate capability with the initial discharge capacity of 741 mAh g^{-1} and capacity retention of 80% after 50 cycles compared to pure S. The improvement in the electrochemical performance for K-MWCNTs-S composites is attributed to the interstitial structure of the MWCNTs resulted from the strong chemical etching, which can facilitate the insertion and extraction of Li ions and more better percolation of the electrolyte, and also ascribed to enhanced electronic conductivity of K-MWCNTs-S composites. It is indicated that the K-MWCNTs-S composites can be used as the cathode materials for lithium–sulfur batteries.

1. Introduction

Rechargeable lithium ion batteries (LIBs) have been used widely in mobile phones, laptop computers, digital cameras, electrical vehicles and hybrid electrical vehicles [1–4]. In rechargeable LIBs, the cathode material is a key component mainly relating to the performance of the batteries. The elemental sulfur is an attractive cathode active material due to low cost, low equivalent weight, no toxicity, high theoretical specific capacity of 1675 mAh g^{-1} and high energy density of 2600 Wh kg^{-1} [5], assuming the complete reaction of lithium with sulfur to Li_2S. However, both its electronic and ionic insulting nature leads to poor capacity retention upon cycling and limits the practical applications [6]. In the meantime, the elemental sulfur is reduced into intermediate lithium polysulfides Li_2S_n ($n > 2$) which are highly soluble in common organic electrolytes. Nevertheless, some of the highly soluble polysulfides are reduced into insoluble Li_2S when contacting with lithium and leads to poor capacity retention. The current method to resolve poor cycling performance is adding conductive additives, restricting the movement of intermediate polysulfides and coating $LiFePO_4$ onto the surface of sulfur [7–10].

Carbon nanotubes (CNTs) have been widely used in LIBs due to their many unusually mechanical, electronic, magnetic, physical and electrochemical properties, as introduced as follows. Jin et al. [11] demonstrated that the added MWCNTs not only increased the electronic conductivity and lithium-ion diffusion coefficient but also decreased crystallite size and charge transfer resistance of $LiFePO_4$-MWCNTs composite. Yuan et al. [12] prepared a novel sulfur-coated MWCNTs composites material with a reversible capacity of 670 mAh g^{-1} after 60 cycles. Yin et al. [13] synthesized a novel PAN-S@MWCNTs core-shell composite *via in situ* polymerization of acrylonitrile on the surface of MWCNTs, mixing with sulfur and final pyrolysis, and indicated that the homogeneous dispersion and integration of MWCNTs in the composite created an electronically conductive network and reinforced the structural stability, leading to the outstanding electrochemical performance as a cathode material for rechargeable lithium–sulfur batteries.

In this study, multiwalled carbon nanotubes-sulfur (MWCNTs-S) composites were synthesized by chemical activation of MWCNTs and capillarity between sulfur and MWCNTs [14]. The MWCNTs activated by potassium hydroxide (denoted as K-MWCNTs) were used to open the end, shorten the tube length and create more nanopores on the wall [15]. This provided more channels and cavities for the free migration of Li ions and more better percolation of the electrolyte during the discharge/charge process, leading to the improved electrochemical properties. The structural and morphological performance of K-MWCNTs-S composites was investigated

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http://dx.doi.org/10.1016/j.apsusc.2014.04.036
0169-4332/

Please cite this article in press as: X.Z. Ma, et al., Multiwalled carbon nanotubes-sulfur composites with enhanced electrochemical performance for lithium/sulfur batteries, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.04.036

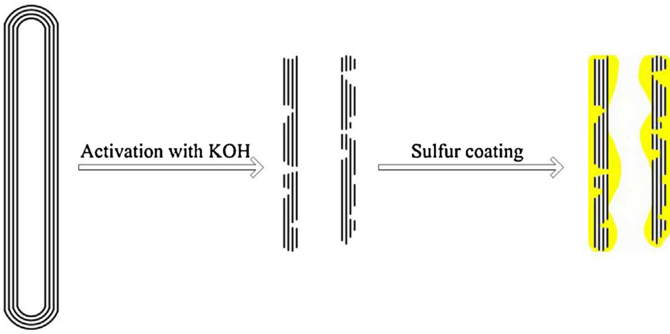

Fig. 1. The synthesis schematic diagram of K-MWCNTs-S. The black lines represent the MWCNTs and the yellow area on the MWCNTs surface is sulfur. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

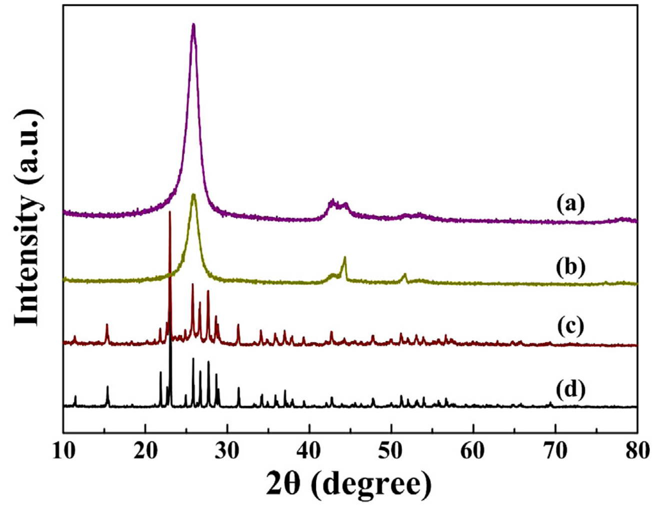

Fig. 2. XRD patterns of (a) MWCNTs, (b) K-MWCNTs, (c) K-MWCNTs-S and (d) pure S.

by X-ray diffraction, high-resolution transmission electron microscope, scanning electron microscopy and field emission scanning electron microscope, and the electrochemical properties were analyzed by cyclic voltammograms and galvanostatic discharge/charge tests.

2. Experimental

2.1. Chemical and synthesis

Multi-walled carbon nanotubes (MWCNTs, Nanjing XFNANO Materials Technology Co., Ltd.) with length of 10–20 μm and diameter of 30–50 nm were activated with potassium hydroxide (KOH), as reported elsewhere [15]. Firstly, 0.5 g MWCNTs and 3.5 g KOH were stirred for 1 h in a 20 ml aqueous solution at room temperature and then dried in a vacuum oven at 100 °C for 24 h. Next, the mixture was heated at 700 °C for 2 h in a tubular furnace under the protection of nitrogen. The heat-treated MWCNTs were washed with deionized water several times to eliminate K_2O, K_2CO_3 and residual KOH, and then dried at 60 °C. The achieved black powder was denoted as K-MWCNTs.

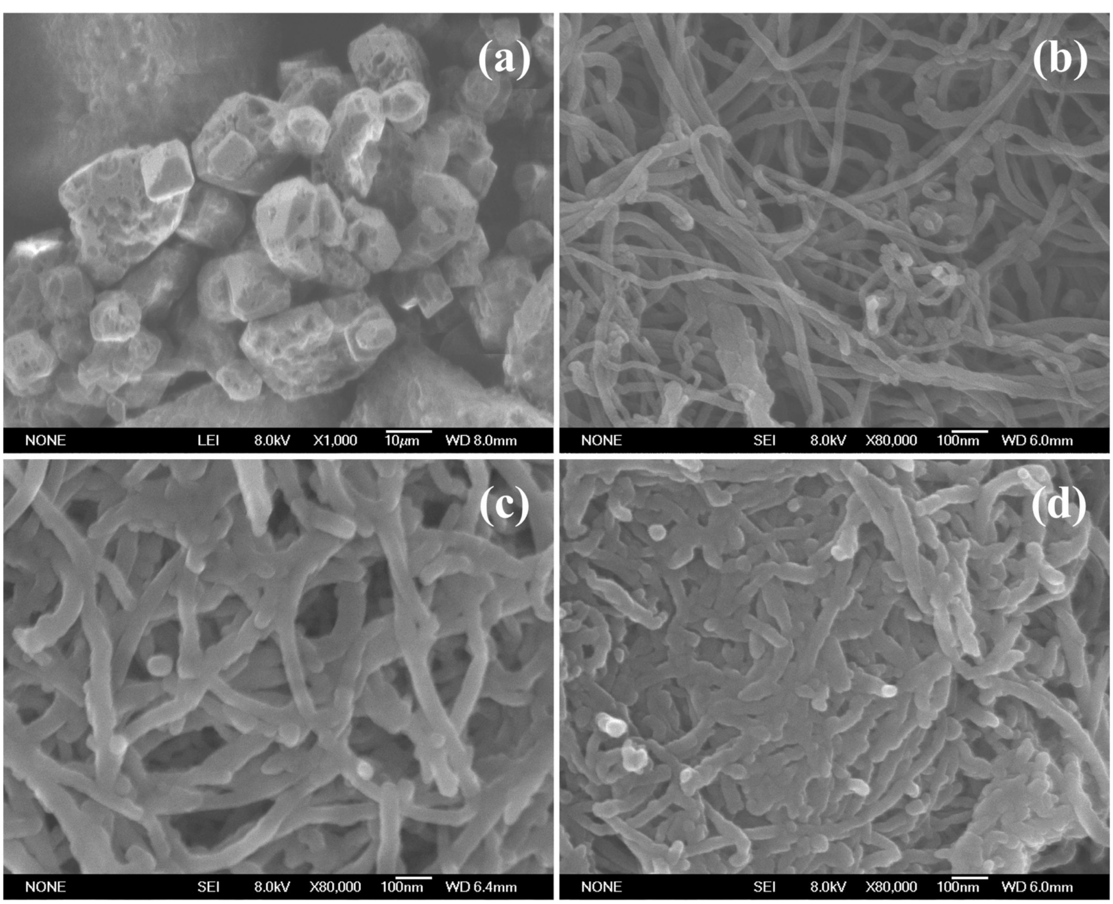

Fig. 3. SEM image of (a) pure S and FESEM images of (b) MWCNTs, (c) K-MWCNTs and (d) K-MWCNTs-S.