Materials Chemistry and Physics 153 (2015) 155–160

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Synthesis and optimization of tin dioxide/functionalized multi-walled carbon nanotube composites as anode in lithium-ion battery

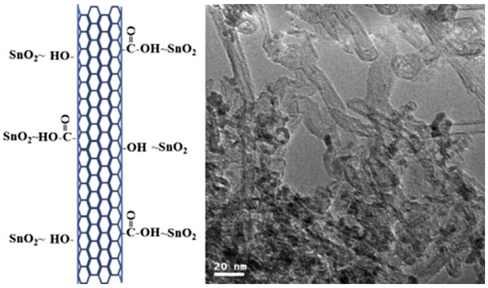
Xiao-Bing Xu, Hong-Zhang Geng*, Yan Meng, Er-Xiong Ding, Yan Wang, Ze-Chen Zhang, Wen-Yi Wang

State Key Laboratory of Hollow Fiber Membrane Materials & Membrane Processing, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China

HIGHLIGHTS

- SnO_2/MWCNT nanocomposites were prepared using chemical deposition method.
- SnO_2 nanoparticles presented a uniformly dispersion on the surfaces of MWCNTs.
- SnO_2/MWCNT composite anode exhibited high reversible capacity for rechargeable Li-ion battery.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 May 2014
Received in revised form
28 November 2014
Accepted 27 December 2014
Available online 31 December 2014

Keywords:
Nanostructures
Precipitation
Chemical techniques
Electrochemical properties

ABSTRACT

In this paper, nanocomposite electrodes for rechargeable Lithium-ion battery composed of tin dioxide (SnO_2) and multi-walled carbon nanotubes (MWCNTs) were prepared using the chemical deposition method with a subsequent sintering process. The as-prepared hybrids were characterized by thermal gravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction and transmission electron microscopy. The results showed that the size of pure SnO_2 particles was ~5 nm and hybrids presented a uniform dispersion of SnO_2 nanoparticles on the surfaces of the MWCNTs. The electrochemical properties of the composites were researched through a cyclic voltammetry and a galvanostatic charge–discharge test. It was found that the electrochemical performance of the composite was strongly dependent on the content of MWCNTs in the composites. The SnO_2/MWCNT composite with 18.40 wt% MWCNTs gave the best performance, exhibiting a relatively higher reversible capacity of 475 mAh g^{-1} and an extended capacity retention of 65% even after 30 cycles at a current density of 78.2 mA g^{-1}.

1. Introduction

With the development of hybrid electric vehicles and portable electric devices, high energy and high power rechargeable Lithium-ion (Li-ion) batteries and battery related technologies have aroused an increasing concern. It is well known that the rechargeable batteries are commonly used by comsumers in hybrid of electric vehicles and portable electronic devices due to their high specific energy and long cycling life, and importantly, they do not suffer from memory effects. Li-ion batteries are consisted of three parts: anode, cathode, and electrolyte [1]. During charging and discharging, Li^+ ions move between the anode and cathode via the electrolyte using lithium salt such as lithium iron phosphate or

---

* Corresponding author.
E-mail address: genghz@tjpu.edu.cn (H.-Z. Geng).

http://dx.doi.org/10.1016/j.matchemphys.2014.12.047
0254-0584/

lithium hexafluorophosphate ($LiPF_6$) [2]. The typical electrolyte contents 1 M $LiPF_6$ dissolved in the mixed organic solution with a volume ratio of 1:1:1 of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC).

Anode materials in many commercial lithium-ion batteries are composed of graphite [3]. The discharge–charge reactions [Eqs. (1) and (2)] of the graphitic carbon anode and the discharge–charge reactions [Eqs. (3)–(5)] of SnO_2 are as follows. In fact, theoretical capacities of SnO_2 are far greater than that of graphite because lithium-ion can not be stored through the intercalation mechanism, but graphite can [4]. However, it mainly formed an alloy with tin atom. Obviously, whereas it takes 6 carbons in graphite to insert one lithium-ion, one tin atom can often alloy itself with 2–4.4 lithium atoms [5,6]. This results in a much higher theoretical specific capacity (782 mAh g^{-1}), which is higher than that of graphitic carbon (372 mAh g^{-1}). But it also leads to a large initial irreversible capacity with the formation of Li_2O since it is assumed to be electrochemically inert after the first introduction of Li^+, and poor capacity retention due to the volume expansion/contraction of Sn during alloying/dealloying reactions with Li^+ [7–9].

$$\text{Discharge: } 6C + xLi^+ + xe^- \rightarrow Li_xC_6 \tag{1}$$

$$\text{Charge: } Li_xC_6 \rightarrow 6C + xLi^+ + xe^- \tag{2}$$

$$\text{Discharge: } SnO_2 + 4Li^+ + 4e^- \rightarrow 2Li_2O + Sn \tag{3}$$

$$Sn + xLi^+ + xe^- \rightarrow Li_xSn\ (0 \le x \le 4.4) \tag{4}$$

$$\text{Charge: } Li_xSn \rightarrow Sn + xLi^+ + xe^-\ (0 \le x \le 4.4) \tag{5}$$

Recently, much research has gone into nano-architectures to increase the specific capacity and improve the cycling ability of the lithium-ion cell. MWCNTs as an allotrope of graphite have been revealed as one of the foremost anode materials for lithium-ion cell owing to their unique structure and peculiar properties such as high conductivity and high tensile strength [10]. MWCNTs not only have a higher capacity than graphite, but also can be used as a support matrix forming novel metal/MWCNT composites which can take advantage of the higher capacity of metals and prevent the problem of pulverization [11].

In this work, we applied chemical deposition method with a subsequent sintering process to fabricate SnO_2/MWCNT nanocomposites. SnO_2 nanoparticles can be deposited on the outside and inner surfaces of the MWCNTs, and then these particles are able to form an alloy with Li^+ without impeding the insertion/desertion of Li^+ in the MWCNTs. Many papers have reported the functionalized MWCNTs as the buffering agent to suppress the mechanical degradation of SnO_2 based negative electrode and the conducting medium to facilitate electron transport and lithium ion diffusion [12–14]. The pristine MWCNTs can not combine with SnO_2 nanoparticles to form well distributed SnO_2/MWCNT nanocomposites to improve the performance of lithium-ion batteries. We demonstrated that polar functional groups (–COOH, –OH) were grafted on the surface of MWCNTs and the content of MWCNTs in the nanocomposite electrodes indeed played a dominant role in improving the reversible capacity and cycling stability of lithium-ion batteries [15].

2. Experimental

2.1. The functionalization of MWCNTs

Four grams pristine MWCNTs (OD < 8 nm, length 10–30 nm) were treated with concentrated sulphuric and nitric acid mixture (3:1vol.%) by sonicating at 40 °C for 3 h and the mixture was then refluxed with magnetic stirring at 60 °C for 6 h [16,17]. Then, the resulting mixture was filtered and the residual substance was repeatedly washed with deionized water to neutral PH. Finally, the sample was dried overnight at 80 °C in vacuum and the functionalized MWCNTs with carboxylic acid and hydroxyl groups were obtained, which were called MWCNT–COOH, and the amount of carboxylic acid and hydroxyl groups on the MWCNTs was around 2.90% deduced from TGA and X-ray photoelectron spectroscopy [18].

2.2. Preparation of SnO_2/MWCNT nanocomposite samples

$SnCl_4 \cdot 5H_2O$ and MWCNT-COOH at a mole ratio of 1:1, 1:1.6, 1:3.3, 1:6.6 and 1:10 were dissolved in 40 mL deionized water with 0.5 wt% sodium dodecyl benzene sulfonate (SDBS) as surfactant and then were dispersed using a probe sonicator for 30 min. Then, 12.5 M NaOH was slowly added as precipitator under magnetic stirring at 80 °C until sediment was absolutely formed. The mixture was then centrifuged at 10,000 rpm for 20 min. The upper solution was carefully decanted and the sediment was collected. Finally, the resulting sediment was washed with deionized water to neutral PH. The residual substance was dried overnight at 80 °C and then heated under air atmosphere at 300 °C for 2 h and 450 °C for 1 h to obtain SnO_2/MWCNT nanocomposites [19]. Pure SnO_2 nanopowders were prepared by the same method in the absence of MWCNTs and SDBS. A schematic diagram of this synthesis process as mentioned above is shown in Fig. 1.

2.3. The preparation of electrode and battery assembly

SnO_2/MWCNT composites as an active material, acetylene black as a conductive agent, and polyvinylidene fluoride (PVDF) as a binder at a weight ratio of 8:1:1 were dissolved in N-methyl-2-pyrrolidone (NMP) [20,21] and stirred until a good slurry was achieved. The slurry was uniformly coated onto the surface of Cu foil. Such prepared electrode sheets were cutted into wafers with diameter of 13 mm and then dried overnight at 110 °C in vacuum to remove the solvent of water and NMP.

The above electrode pieces were used as the working electrode in a CR-2430 coin cell with Li foil as both the counter electrode and reference electrode [22,23]. Microporous multi-layered polypropylene (PP) membrane and 1 M $LiPF_6$ in a 1:1:1 volume ratio mixed solution of EC, EMC and DMC were elected as the separator

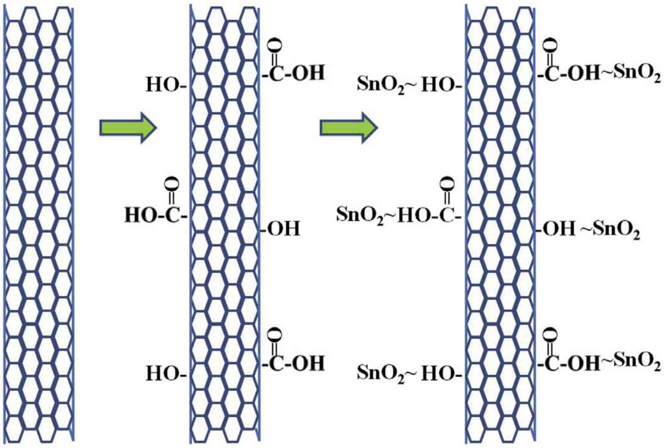


Fig. 1. Schematic illustration of the synthesis process for SnO_2/MWCNT nanocomposites.