Electrochimica Acta 154 (2015) 321–328

Contents lists available at ScienceDirect

Electrochimica Acta

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

One-step synthesis of continuous free-standing Carbon Nanotubes-Titanium oxide composite films as anodes for lithium-ion batteries

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ARTICLE INFO

Article history:
Received 2 September 2014
Received in revised form 23 November 2014
Accepted 11 December 2014
Available online 15 December 2014

Keywords:
carbon nanotubes
Titanium oxide
free-standing
continuous film
flexible electrode

ABSTRACT

Continuous free-standing Carbon Nanotubes (CNTs)/Titanium oxide (TiO_2) composite films were fabricated in a vertical CVD gas flow reactor with water sealing by the One-Step Chemical Vapor Deposition (CVD) approach. The composite films consist of multiple layers of conductive carbon nanotube networks with titanium oxide nanoparticles decorating on carbon nanotube surface. The as-synthesized flexible and transferrable composite films show excellent electrochemical properties, when the content of tetrabutyl titanate is 19.0 wt.%, which can be promising as binder-free anodes for Lithium-Ion Battery (LIB) applications. It demonstrates remarkably high rate capacity of 150 mAh g^{-1}, as well as excellent high rate cyclic stability over 500 cycles (current density of 3000 mA g^{-1}). Such observations can be attributed to the relatively larger surface area and pore volume comparing with pristine CNT films. Great potentials of CNTs/TiO_2 composite films for large-scale production and application in energy devices were shown.

1. Introduction

Lithium-ion batteries (LIBs) are key components determining the efficiency as well as working sustainability of portable mobile devices [1,2]. Development of electrodes materials for LIBs [3,4] has been greatly motivated by the increasing enthusiasm for flexible, lightweight energy storage devices. In terms of negative electrodes (anodes), carbon nanotubes (CNTs) possess outstanding advantages due to their unique structure and attractive properties among various candidates [5–7], and special attentions have been focused on the binder-free and bendable free-standing CNTs electrodes [7–9]. Mainly four methods were proposed for the synthesis of free-standing CNTs electrodes including: filtration method [8], rod coating method [9], LBL method [10] and chemical vapor deposition (CVD) method [11,12]. Comparing to the other methods, CVD method provides relatively precise control of the mass as well as the overall morphology of CNT films. Production of large quantities of CNTs at relatively low cost can be quite promising using the CVD method. However, practical application of CNT anodes is restrained by their high irreversible lithium-ion (Li^+) capacity (C_{irr}) and limited reversible capacity (C_{rev}). Generally upon the first discharge and charge, species of lithium ions inserted into the carbon nanotubes prevail the quantities of lithium ions being moved out from the nanotubes [5,6]. Further development of CNT anodes also requires higher capacity and cyclic performance [1,2]. TiO_2 receives wide interests as one of the most promising anode materials for lithium-ion batteries due to its relatively high capacity (335 mAh g^{-1}), and low volume expansion during lithium intercalation/deintercalation [13–16]. As reported in literature, TiO_2 nanoparticles can be decorated on the surface of other anode materials to improve the electrochemical performance as composite because of their high ionic conductivity and other unique chemical properties. Huang et al. prepared a nanocomposite of TiO_2/CNTs by mechanically blending, which demonstrated that the TiO_2/CNTs nanocomposite exhibited an improved cycling stability and higher reversible capacity than pure CNTs [14]. Gao et al. shows that coating graphite with a layer of nano-TiO_2 particles can greatly suppress the decomposition of propylene carbonate and exfoliation of graphite [16]. In this work, we propose a facile way to fabricate continuous CNTs/TiO_2 composite films by a one-step chemical vapor deposition (CVD) method. Good correlations between improved electrochemical

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http://dx.doi.org/10.1016/j.electacta.2014.12.068
0013-4686/

performance, combination of chemically stable TiO_2 and transferrable CNTs were observed.

2. Experimental

The scroll of CNTs/TiO_2 film was obtained in a vertical CVD system [11] without water-densification. Tetrabutyl titanate and ethanol were used as the titanium oxide precursor and the carbon source, respectively. Firstly, tetrabutyl titanate was dispersed in ethanol at weight percentages of 12.6 wt.%, 19.0 wt.% and 30.2 wt.%. The as-prepared CNTs/TiO_2 films are termed as 12.6 wt.%-CNTs/TiO_2, 19.0 wt.%-CNTs/TiO_2 and 30.2 wt.%-CNTs/TiO_2, correspondingly. Subsequently, ferrocene as the catalyst precursor and thiophene as promoter were dissolved in the above solution with the ferrocene, thiophene and ethanol at same weight ratio of 15:8:787. All the chemicals were obtained from Tianjin Guangfu. The liquid precursors were injected into the tube furnace under a H_2 flow (400–800 sccm) with an injection rate of 6 ml h^{-1} when the temperature reaches 1100–1130 °C, and being instantly vaporized at the pipe orifice. Tetrabutyl titanate vapor dispersed in the tube was decomposed to TiO_2 at high-temperature zone while carbon atoms from the decomposition of ethanol grew into suspending CNTs simultaneously. The sock-like assemblies travelled downstream, and then were drawn onto a spindle in the reactor. The synthesis process and condition of pristine CNTs films is identical with that of the CNTs/TiO_2, and the content of the precursor liquid is ethanol (97.2 wt.%), ferrocene (1.9 wt.%) and thiophene (0.9 wt.%). To investigate the effect of temperature on the CNTs/TiO_2 films, the 19.0 wt.%-CNTs/TiO_2 composites were synthesized under different temperatures (<1100 °C and >1130 °C).

The CNTs/TiO_2 films were characterized by field emission scanning electron microscope (FE-SEM, JEOL, JSM-6700F), transmission electron microscope (TEM, FEI, Tecnai G2F20), and X-ray diffraction (XRD, RIGAKU D Max 2500 V Pc). Raman spectroscopy was conducted with a diode laser of 632.8 nm wavelength (Renishaw Lab RAM HR800). Nitrogen isotherm adsorption-desorption measurements were carried out at 77 k (Quantachrome, NOVA2000). Thermogravimetric analysis (TGA/DSC, NETZSCH, STA 499 C) was performed at a heating rate of 10 °C/min up to 1000 °C in air.

The obtained free-standing CNTs/TiO_2 films were tested as a working electrode without further addition of carbon or binder. The composite films were pressed under a pressure of 3 MPa, and then dried in a vacuum oven at 120 °C for 12 h. The binder-free circular model electrodes were punched out from the as-prepared free-standing CNTs/TiO_2 films with a diameter of 12 mm, and assembled into coin-type cells (CR 2032) in argon filled glove box (Microuna, China). Lithium foil was used as the counter electrode, and a porous polypropylene film (Celgard) worked as separator. 1 mol L^{-1} $LiPF_6$ dissolved in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 in volume) was used as the electrolyte solution. The electrode loadings were between 1 and 2 mg cm^{-2}. Galvanostatic tests were performed with a voltage range of 0.005–3 V using a battery tester (Neware, CT 3008 W). The cyclic voltammetry (CV) experiments were carried out using a scan rate of 1 mV s^{-1} on an electrochemical workstation (CH, CHI 660D). Electrochemical impedance spectroscopy (EIS) measurements were conducted using 5 mV AC amplitude over 100 kHz–0.01 Hz at the identical electrochemical workstation.

3. Results and discussion

3.1. Fabrication of continuous CNTs/TiO_2 films

Fig. 1a presents a semi-transparent sock-like assembly of plentiful CNTs with dispersed TiO_2 nanoparticles, which travels downstream with gas flow and transforms into narrow thin film by mechanical drawing from the spindle in the reactor (Fig. 1b). The thin films were rolled on the spindle by a spiral type winding with velocities ranging from 2–15 m min^{-1}, and then being formed into multiple layers films. Depending on the winding velocity, the rate of film being yielded is between 60 and 180 mg h^{-1}. Fig. 1c shows an as-prepared unfolded multiple-layer film with a size about 12.8 cm × 4.8 cm and the inset exhibits an as-prepared circular electrode for electrochemical measurements.

3.2. Morphology and structure

The phase and microstructure of the 19.0 wt.%-CNTs/TiO_2 film was identified using XRD, SEM and TEM, respectively. Fig. 2a shows

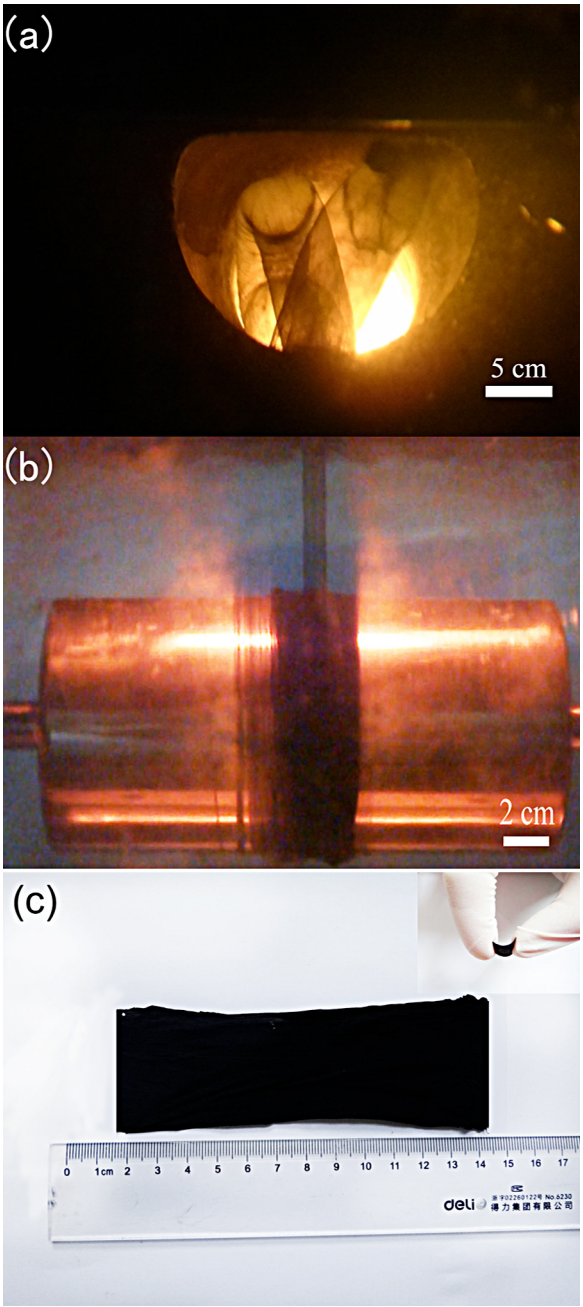

Fig. 1. (a) CNTs/TiO_2 socks travel towards the spindle with gas flow; (b) drawing and spooling of the layered sock into composite film to the rotator in the CVD process (the photograph was taken at typical stages of the spooling process); (c) robust film recovered from the spindle; inset shows a flexible free-standing circular electrode for electrochemical measurements.