Journal of Power Sources 290 (2015) 61–70

Contents lists available at ScienceDirect

Journal of Power Sources

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

A polyaniline-coated mechanochemically synthesized tin oxide/graphene nanocomposite for high-power and high-energy lithium-ion batteries

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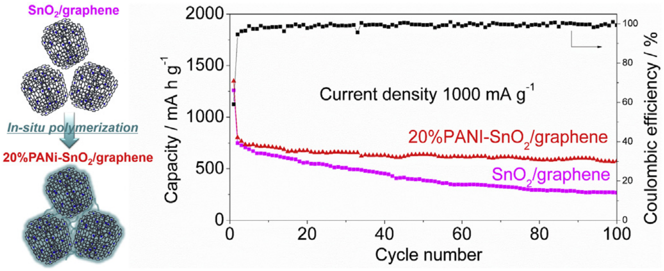
HIGHLIGHTS

- SnO_2/graphene nanocomposite is synthesized by a mechanochemical approach.
- PANI grows on the surface of graphene by *in situ* polymerization.
- PANI nanofibers form conductive bridges between SnO_2/graphene nanoparticles.
- PANI-SnO_2/graphene shows a stable cycling performance at 1000 mA g^{-1}.
- PANI-SnO_2/graphene shows a superior rate performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 December 2014
Received in revised form
23 April 2015
Accepted 4 May 2015
Available online 15 May 2015

Keywords:
Polyaniline
Tin oxide
Graphene
Mechanochemical method
In situ polymerization
Lithium-ion batteries

ABSTRACT

Although intensive efforts have been made during the past decades, development of an anode material with high specific capacity and stable cycling performance for lithium-ion batteries (LIBs) using a cost-effective preparation method still remains challenging. Herein, we report a polyaniline (PANI)-coated mechanochemically synthesized SnO_2/graphene (SG) nanocomposite via *in situ* polymerization. PANI-coated nanocomposites are successfully prepared with different raw material mass ratios (aniline:SG, 0.15:1, 0.2:1, 0.25:1). The nanocomposite with initial aniline:SG mass ratio of 0.2:1 (20%PANI-SG) contains an optimal structure housing genuine PANI nanofibers as conductive bridges and a relatively high surface area of 158.5 m^2 g^{-1}; furthermore, it exhibits a stable cycling performance over 100 cycles at high current density (1000 mA g^{-1}) with a specific capacity of more than twice that of the starting SG electrode at the 100th cycle. Additionally, this material achieved an outstanding cycling rate with current densities changing stepwise from 100 to 3000 mA g^{-1} and back, and exhibited a specific capacity of 467 mA h g^{-1} even at 2000 mA g^{-1}. In terms of the electrochemical stability, rate capability and cost-effective preparation process, the PANI-SG nanocomposite is a viable anode material for next-generation high-power and high-energy LIBs.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the dominant power source for commercial personal electronic devices and are now

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http://dx.doi.org/10.1016/j.jpowsour.2015.05.009

being applied to other technologies including electric/hybrid electric vehicles and energy storage for renewable resources to address the rise in energy usage and environmental issues [1–7]. The very common commercial anode material graphite no longer meets the significantly increasing demands for high electrochemical performance [8–12]. Development of novel electrode materials with high reversible capacity, good rate capability and long-term stability is the key to the next-generation LIBs. The biggest challenge may be finding a material that meets all three desired characteristics: (1) electrochemical stability; (2) high specific capacity; and (3) cost-effective preparation method. For example, lithium titanate, a well-known "zero-strain" anode material for LIBs, could achieve excellent cycling stability and high-rate capability. However, its theoretical capacity is very low at only 175 mA h g^{-1} [13–16], thus limiting its commercial application.

Tin oxide (SnO_2), with a high theoretical capacity of 782 mAh g^{-1}, is a very promising anode material candidate for LIBs [17–19]. However, its large volume variation during the lithium insertion/extraction process [20,21] leads to degradation of the electrode, resulting in poor cycling stability. Many efforts have been carried out to improve the cycling stability of SnO_2, such as synthesis of nanostructures to minimize the strain [22–25] and formation of composites with carbon, metals or oxides to accommodate the volume variation [26–30]. Notably, the synthesis of nanostructured SnO_2 on conductive and flexible graphene forms a composite and has been recognized as an effective approach to achieving a stable cycling performance.

To date, various methods, including the hydrothermal method [31–33], the microwave-assisted method [34], atomic layer deposition (ALD) [35] and the reflux method [36], have been developed to obtain SnO_2/graphene nanocomposites. However, these methods often involve complicated processes, uncommon conditions or additional chemicals, which limit the broad commercial application of these advanced SnO_2/graphene nanocomposites as anodes for LIBs. Recently, we successfully prepared an outstanding composite anode with ~4 nm SnO_2 nanocrystals on graphene via a facile mechanochemical synthesis using 3–30 μm metallic Sn and graphite oxide as the raw materials [37]. The process could easily be employed for large-scale applications, and the optimal composite as an electrode for LIBs exhibited a stable cycling performance with a specific capacity of 891 mAh g^{-1} after 50 cycles at a current density of 100 mA g^{-1}. Although a high specific capacity and cost-effective preparation process were demonstrated for this nanocomposite, the cycling stability at a current density of 100 mA g^{-1} is still not attractive to commercial application for LIBs. Conducting polymers have attracted increasing attention for improving the electrochemical performance of electrode materials for LIBs because they are conductive, low cost, lightweight and mechanically flexible materials. As a conductive semi-flexible rod polymer, polyaniline (PANI) is easily prepared from aniline monomers by oxidizing and doping [38–43]. Additionally, the PANI-coating layer could also accommodate the large volume variation of SnO_2 during the charge/discharge process. For example, He et al. [42] synthesized a SnO_2/PANI composite by coating PANI on spherical SnO_2 nanoparticles using the polymerization reaction. The composites exhibited a specific capacity of 609.3 mAh g^{-1} after 80 cycles at a current density of 70 mA g^{-1} in the voltage range of 0.01–3 V. Liang et al. [43] prepared a composite with SnO_2 loading on the surface of PANI-reduced-graphene-oxide using a hydrothermal synthesis method. As an anode of LIBs, the hybrid structure showed a high specific capacity of 573.6 mAh g^{-1} after 50 cycles at a current density of 156 mA g^{-1} between 0.01 and 3 V. However, the electrochemical performances of the above composites were tested at low current densities, and the graphene-based composite was synthesized by liquid hydrothermal synthesis limiting the commercial application of these composites.

Herein, mechanochemically synthesized SnO_2/graphene (SG) nanocomposites are further studied for their application as a faster lithium storage material fabricated via an *in situ* polymerization. The SG and PANI-coated SG nanocomposites were investigated as electrodes for LIBs at a high current density of 1000 mA g^{-1}. Different initial aniline amounts were explored, and a PANI-coated SG nanocomposite with an initial mass ratio of 0.2:1 aniline to SG (named 20%PANI-SG) demonstrated an optimal structure with a PANI layer on the surface and PANI nanofiber conductive bridges connecting the SG particles. The 20%PANI-SG nanocomposite exhibited a stable cycling stability through 100 cycles at 1000 mA g^{-1} and an excellent charge–discharge rate capability, indicating that it is a significantly promising anode material capable of replacing the commercial graphite anode for LIBs in state-of-the-art applications.

2. Experiment section

2.1. Preparation of polyaniline-coated SnO_2/graphene composite (PANI-SG)

A nano-SnO_2/graphene composite (SG) was first prepared by a facile mechanochemical method, which was reported recently by our group [37]. Briefly, graphite oxide (GO) from a modified Hummers method and coarse metallic Sn with mass ratio of 1:1 were ground in Ar via ball-milling at a rotational speed of 400 rpm for net grinding times of 8 h 20 min to obtain the nanocomposite, and then it was further calcined at 300 °C for 1 h under Ar atmosphere.

PANI-SG composites were synthesized by *in situ* polymerization of aniline on SG samples with different mass ratios of aniline:SG (0.15:1, 0.2:1 and 0.25:1) and were named 15%PANI-SG, 20%PANI-SG and 25%PANI-SG, respectively. As per the typical synthesis process, SG samples and aniline were added to a 1 M HCl solution and were stirred for 1 h. Then, an HCl solution with ammonium persulfate (mass ratio of ammonium persulfate to aniline, 1.5:1) as an oxidant was added to the above suspension, and it was kept at 0–5 °C for 6 h. After the polymerization reaction, the as-prepared samples were washed by deionized water and ethanol several times, assisted by centrifugation, and then were dried for 12 h under vacuum. Pure PANI was also synthesized in the same process without the addition of SG.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out to study the compositions and phase structures of the samples on a Bruker D8 Advance diffractometer with Cu Kα radiation. Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was used for the observation of the morphology and microstructure of the samples. Transmission electron microscopy (TEM) and bright-field STEM images were acquired using an FEI Tecnai G2T20 electron microscope operating at 200 kV, and corresponding EDX mappings were obtained by an FEI Tecnai G2F30 S-TWIN field emission transmission electron microscope equipped with EDAX energy-dispersive X-ray spectroscopy operating at 300 kV. Fourier transform infrared (FT-IR) spectra and Raman spectra were recorded using a Nicolet 380 FT-IR Spectrometer (Thermo Scientific, USA) and a HR800 UV Raman microspectrometer (JOBIN YVON, France), respectively. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI5000 VersaProbe spectrometer equipped with an Al Kα X-ray source. The nitrogen adsorption-desorption isotherms were acquired using a BELSORP II instrument at the boiling point of liquid nitrogen. The Brunauer–Emmett–Teller (BET) method and