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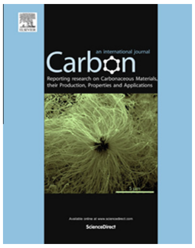

Carbon coated porous tin peroxide/carbon composite electrode for lithium-ion batteries with excellent electrochemical properties

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ABSTRACT

A porous tin peroxide/carbon (SnO_2/C) composite electrode coated with an amorphous carbon layer is prepared using a facile method. In this electrode, spherical graphite particles act as supporter of electrode framework, and the interspace among particles is filled with porous amorphous carbon derived from decomposition of polyvinylidene fluoride and polyacrylonitrile. SnO_2 nanoparticles are uniformly embedded in the porous amorphous carbon matrix. The pores in amorphous carbon matrix are able to buffer the huge volume expansion of SnO_2 during charge/discharge cycling, and the carbon framework can prevent the SnO_2 particles from pulverization and re-aggregation. The carbon coating layer on the outermost surface of electrode can further prevent porous SnO_2/C electrode from contacting with electrolyte directly. As a result, the repeated formation of solid electrolyte interface is avoided and the cycling stability of electrode is improved. The obtained SnO_2/C electrode presents an initial coulombic efficiency of 77.3% and a reversible capacity of 742 mA h g^{-1} after 130 cycles at a current density of 100 mA g^{-1}. Furthermore, a reversible capacity of 679 mA h g^{-1} is obtained at 1 A g^{-1}.

1. Introduction

Li-ion batteries (LIBs) have attracted intensive research because of their wide applications in portable electronic devices such as mobile phones and lap-top computers [1–3]. LIBs are also considered as one of the most promising power sources for electric vehicles (EVs). Whereas, the energy density of current LIBs still need to be improved to satisfy the demands of EVs. The prevailing commercial graphite anode material is far from meeting the requirements for high energy/power density because of its low theoretical capacity (372 mA h g^{-1}). Much effort has been done to develop the anode material with large energy capacity and stable cycling performance [4–6].

Tin peroxide (SnO_2) is one of the most promising anode materials for its abundance, suitable lithiation potential and

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high theoretical capacity (782 mA h g^{-1}) [7,8]. During lithiation, SnO_2 is firstly transformed to Sn metal which then reacts with lithium atoms to form $Li_{4.4}Sn$ alloy. However, during the cycle of charge/discharge with lithiation/delithiation, SnO_2 suffers from pulverization behavior caused by the huge volume change. This results in the formation of thick solid electrolyte interface (SEI) film and the loss of electronic contact with conductive additives, which consequently contribute to a rapid capacity decay in the cycling process [9–11].

Two strategies have been applied to improve the cycling stability of SnO_2 electrode [12]. One is to control particle size and the other to incorporate SnO_2 particles into carbon matrix to form SnO_2/C composites. The activated carbon, carbon nanotube, graphene and graphene oxide have been employed as carbon matrix to support the SnO_2 nanoparticles [13–15]. However, the SnO_2/C composites usually present too low initial coulombic efficiency (CE) to be used in battery industry. Paek et al. developed a SnO_2/graphene nano-porous electrode with a three-dimensional delaminated flexible structure with an initial coulombic efficiency less than 50% [14]. Tang and co-workers [16] fabricated meso-porous graphene-based TiO_2/SnO_2 hybrid nano-sheets, which had a stable capacity of 600 mA h g^{-1} after 300 cycles at a current density of 160 mA g^{-1}. The high cycling stability is due to the two-dimensional nano-sheet structure with large specific surface area, excellent charge carrier mobility and extraordinary mechanical properties. Whereas, the initial CE was only 49%, which was far from industrial demand.

Much effort has been devoted to improving the initial coulombic efficiency of carbon-based SnO_2 composite electrode [17–20], where the fabrication of composites with a three-dimensional structure of less SEI formation area is an effective strategy. Yu's group encapsulated Sn nanoparticles in porous multichannel carbon micro-tubes by electro-spinning technique [21]. Their fabricated composite anode had a reversible capacity of 648 mA h g^{-1} after 140 cycles, as high as about 70% of initial CE. Most recently [22], Sn nanoparticles were embedded in N-doped porous carbon network by carbonizing divalent Sn complex, which achieved a current density of 722 mA h g^{-1} after 200 cycle at 0.2 A g^{-1}, with an initial CE of 75%. The high electrochemical performance was attributed to the uniform distribution of ultra-small Sn nanoparticles in the integrated porous network. The embedment of Sn nanoparticles in carbon network to form Sn/C composite with larger particles size may have relatively less SEI area to result in a larger CE of electrode. In addition, the carbon network can prevent the embedded Sn nanoparticles from contacting with electrolyte solution to improve their cyclic stability [23]. However, the reports on three-dimensional SnO_2/C composite electrode with high cyclic stability and CE remain rare.

Herein, we report a quite facile and suitable large-scale method to prepare a porous SnO_2/C electrode coated with a carbon layer derived from PAN. The prepared electrodes are shown to present high initial CE and excellent cycling stability. Specifically, the spherical graphite particles are used to serve as framework supporter of electrode. The interspace among graphite particles is filled with porous amorphous carbon matrix derived from PVDF and PAN, and embedded uniformly with SnO_2 particles. The carbonized products of PAN and PVDF, together with the spherical graphite and super-P, generate a dense and entire electrode with a porous carbon network interconnecting the SnO_2 particles in interior and having an integral carbon coating layer on the electrode surface. The designed electrode presents high conductivity and excellent restriction on the expansion of $SnO_{2,}$ to contribute to a stable cyclic performance.

2. Experimental

2.1. Synthesis of SnO_2 nanoparticles and preparation of electrode

The SnO_2 nanoparticles were synthesized using a simple hydrothermal method in an ethanol–H_2O mixed solvent. Typically, $SnCl_2{\cdot}H_2O$ (9.026 g) was added into an ethanol–H_2O mixture with 30% ethanol to obtain a solution with $SnCl_2$ concentration of 0.2 mol L^{-1}. The solution was stirred for 30 min and then transferred into a 100 ml Teflon-lined stainless steel autoclave and maintained at 180 °C for 24 h. The obtained faint-yellow product was washed by filtration with water and ethanol, which was subjected further to ultrasonic treatment in ethanol for 2 h and was dried at 80 °C for 8 h to obtain SnO_2 nanoparticles.

A slurry consisting of 48 wt% SnO_2 nanoparticles, 16 wt% spherical graphite, 16 wt% PAN, 10 wt% super-P and 10 wt% PVDF were prepared as followed. The PVDF was added in N-methyl-2-pyrrolidone (NMP) solvent under stirring for 2 h, and then PAN and super-P were added into the above solution, which was stirred for 2 h. Here, super-P was used as an electric conductivity enhancer. The SnO_2 nano-particles were dispersed in the obtained solution by ultrasonic treatment for 1 h and further stirring 2 h. At last, the spherical graphite was added and followed ultrasound for 1 h and stirring 2 h to obtain the slurry of electrode. The slurry was coated on Cu foil and dried in a vacuum oven at 80 °C for 8 h to obtain SnO_2 electrode. The SnO_2 electrode was treated at 250 °C for 2 h and then calcined at 500 °C for 5 h (with a heating-up rate of 5 °C/min from 250 °C) in argon atmosphere to form the porous SnO_2/C electrode. Besides, the outer surface of SnO_2 electrode was coated by dimethyl formamide (DMF) solution with 8 wt% PAN and then the electrode was dried at 80 °C for 8 h. The dried electrode was treated and calcined using above similar method to obtain the porous SnO_2/C electrode coated with a carbon layer. The schematic diagram of preparation procedure for porous SnO_2/C electrode coated with a carbon layer is indicated in Fig. 1.

2.2. Characterization of SnO_2 powders and electrode

The phase structure of the SnO_2 powders were characterized by X-ray diffraction measurement (XRD, Rigaku D/max 2500/PC using CuKα radiation with $\lambda = 1.5418$ Å). The morphologies of SnO_2 powders and electrodes were examined on a field emission scanning electron microscope (FE-SEM, HITACH S4800) at 10 kV and a field emission transmission electron microscope (FE-TEM, JEOL 2010F) at an accelerating voltage of 200 kV. Nitrogen adsorption/desorption isotherms were obtained at 77 K using an automated adsorption apparatus (Micromerit-ics ASAP 2020). The surface area was calculated