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Antimony-Carbon-Graphene Fibrous Composite as Freestanding Anode Materials for Sodium-ion Batteries

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ABSTRACT

Antimony-carbon-graphene fibrous composites were prepared by the electrospinning/spray process as freestanding anodes for sodium-ion batteries. Antimony nanoparticles distribute in conductive carbonized polymer fibers and graphene flakes. The unique structure prevents the aggregation of the antimony nanoparticles and buffers the mechanical stress from volume change of antimony during repeated alloying/de-alloying process. The composites demonstrated an excellent electrochemical performance as anode material for sodium-ion batteries, with a reversible capacity of 274 mAh/g after 100 charge-discharge cycles at a current density of 100 mA/g.

1. Introduction

Sodium-ion batteries are attractive for large-scale energy storage and conversion, owing to the abundance of natural reserve of sodium. Sodium has been applied in sodium-sulphur batteries and ZEBRA battery systems for decades. These high temperature sodium battery systems achieved great success and demonstrated their advantages in the field of stationary energy storage [1–3]. Sodium-ion batteries, which have similar reaction mechanisms (intercalation) with lithium-ion batteries, are considered as near-term substitutes of lithium-ion batteries. Sodium-ion batteries and lithium-ion batteries share the same architecture of battery design. One of the major challenges for sodium-ion batteries is to discover suitable electrode materials with high and stable sodium storage capabilities. The large ionic radius of sodium makes the insertion of the sodium-ions into host materials very difficult. Therefore, the capacity and rate capability of electrode materials for sodium-ion batteries are far from satisfactory. Recent literature proposed a strategy to improve the sodium storage capability of graphitic materials. By increasing the interlayer spacing, the expanded graphite anode showed a massively improved storage capability of sodium-ions with the reversible intercalation process [4]. Alloy anode materials, such as tin, phosphorus, and antimony-based alloys have attracted considerable interest, owing to their high theoretical specific capacities for sodium-ion batteries [5–11]. In order to utilize the high energy storage capabilities of alloy anodes and achieve stable cycling performance, the sizes of active materials need to be made as small as possible to allow the electrode to buffer the large stress from volume change in the repeated alloying/de-alloying process. Many research groups have demonstrated that antimony based composite anode materials can deliver high capacity for sodium storage as well as stable cycle performance through alloy-based reaction in sodium-ion batteries [12–14]. Electrospun Nitrogen-doped carbon fibers, CNT enhanced lithium titanate-carbon fibers composite and antimony-carbon fibers composite were also investigated as freestanding high performance anode materials for sodium-ion batteries [15–18]. Electrospinning and electrospray methods have been widely used in the synthesis of functional materials on polymer fabricated networks of a freestanding nature, which can provide flexibility for the convenience of electrode fabrication [19–22]. Graphene is a frequently used agent in the synthesis of composite electrode materials for sodium-ion batteries [14,23–26]. The strategy of introducing graphene into composite creates a simple and effective path to enhance the electrochemical performance of electrode materials, since the graphene is highly conductive and it is an electrochemical active anode material for sodium-ion batteries [27]. In this paper, we report an antimony-carbon-graphene fibrous composite synthesized by an electrospinning/spray

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method as flexible freestanding anodes for sodium-ion batteries. With homogeneously embedded antimony particles in one-dimensional pyrolyzed fibers and reduced graphene-oxide flakes as a stabilizing additive, the flexible freestanding composite electrodes demonstrate relatively high capacity and excellent cycle stability.

2. Experimental

2.1. Material Preparation

The graphene-oxide flakes were prepared using a modified Hummer's method [28]. First, graphite powders (0.1 g, Sigma–Aldrich) were added to concentrated hydrosulfuric acid (H_2SO_4, 5 ml) together with potassium permanganate ($KMnO_4$, 0.3 g, Sigma–Aldrich) and sodium nitrate ($NaNO_3$, 0.3 g, Sigma–Aldrich). The mixture was kept at 20 °C in an ice bath for 2 h before being transferred into distilled water (20 ml) for dilution. After dilution, hydrogen peroxide aqueous solution (10% wt.) was gradually added until the solution turned into yellow paste. The oxidized graphite was repeatedly washed and filtered with distilled water to remove excess acid, and aqueous dispersion of GO was received. The GO dispersion was further diluted with ethanol to form a GO/ethanol solution (1 g/L, volume ratio of ethanol/water = 1:1) after being treated in an ultrasound bath for 10 h. Polyvinylpyrrolidone (PVP, 0.05 g, Sigma–Aldrich) was then added to 5 ml GO/ethanol solution to form GO/PVP in ethanol solution as the precursor for the electrospray process. Antimony trichloride ($SbCl_3$, 0.46 g, Sigma–Aldrich) was first dissolved in N, N-dimethylformamide (DMF, 10 mL, Sigma–Aldrich) to form a $SbCl_3$ in DMF solution. Polyacrylonitrile (PAN, 0.8 g, Sigma–Aldrich) was added in the solution under vigorous stirring; the stirring motion was kept for 12 h at 60 °C to ensure the dissolution of PAN. The obtained mixture was used as the precursor solution for electrospinning. In a typical synthesis process, 1.5 ml $SbCl_3$/PAN in DMF solution was loaded into a 10 mL plastic syringe with a stainless steel voltage receiver, and the syringe was secured to a syringe pump. A piece of aluminium foil attached to a rotating stainless steel drum, which was used as collector, and the distance between the needle tip and the collector was kept at 14 cm. The applied voltage was set to 18 kV for the electrospinning process. During the electrospinning process, the solution was pumped through a blunt-tip syringe needle (gauge 22) at a fixed flow rate of 0.75 mL/h. After the first electrospinning process, the $SbCl_3$/PAN fibers formed white fibrous mats on the surface of the collector. Then, a thin layer of GO/PVP mixture was deposited on top of $SbCl_3$/PAN fibrous mats using an electrospray method. GO/PVP ethanol solution (1.0 mL) was injected through a blunt-tip syringe needle (gauge 25) at a flow rate of 0.5 mL/h. The applied voltage and working distance were 8 kV and 14 cm, respectively. After the deposition of the GO/PVP layer, another layer of $SbCl_3$/PAN fibers further covered the mats with the repeated electrospinning process. The final mat is composed of multi-layered polymer fibers after five steps of the electrospinning process with four steps of electrospray in-between. The obtained mat was vacuum dried at 80 °C for 12 h and then kept under 2 MPa pressure for 1 min to ensure the compact stacking of the $SbCl_3$/PAN fibers and the GO/PVP layer. After cutting composite mat to disks with diameter of 14 mm, the final antimony-carbon-graphene (Sb-C-G) disks were obtained by heating the material in air at 280 °C for 2 h, and calcinated at 600 °C for 3 h in argon balanced hydrogen gas (Volume ratio of H_2/Ar = 1:19). The temperature increasing rate was limited to 2 °C/min for both processes to ensure the integrity of the carbonized polymer fibers. An electrospun $SbCl_3$/PAN fibrous mat without GO/PVP content was also synthesized in same conditions mentioned above. Antimony-carbon (Sb-C) fibrous product was obtained after calcination at 600 °C.

2.2. Material Characterizations

The crystal structure of the Sb-C-G composite was characterized by X-ray powder diffraction (XRD, Siemens D5000). The morphological characteristics of electrospun antimony-PAN nanofibers, electrosprayed graphene-oxide flakes and pyrolyzed fibrous composite were examined by field emission scanning electron microscope (FESEM, Zeiss Supra 55VP) and transmission electron microscope (TEM, JEOL JEM 2011). Thermogravimetric analysis (TGA) was performed with a TA Instruments SDT 2960 analyser in a temperature range from 20 °C to 620 °C at 5 °C/min heating rates in air. Raman spectra of Sb-C-G and Sb-C samples were carried out with a Nishaw system in backscattering geometry, using for excitation the 632.5 nm line of a He–Ne laser.

2.3. Electrochemical Measurements

The electrochemical properties of obtained antimony-carbon-graphene composite for sodium-ion batteries were examined with cyclic voltammetry (CV) and galvanostatic charge-discharge tests. Type 2032 coin cells were assembled with Sb-C and Sb-C-G composites as working electrodes and sodium foil as counter electrode. The Sb-C and Sb-C-G disks after calcination were used directly as freestanding working electrode without using PVdF binder and carbon black additive. Disc glass fiber with a diameter of 18 mm was used as seperator. The electrolyte used for test cells was a solution of 1 M concentration $NaClO_4$ in a mixture of ethylene carbonate and dimethyl carbonate (volume ratio = 1:1).

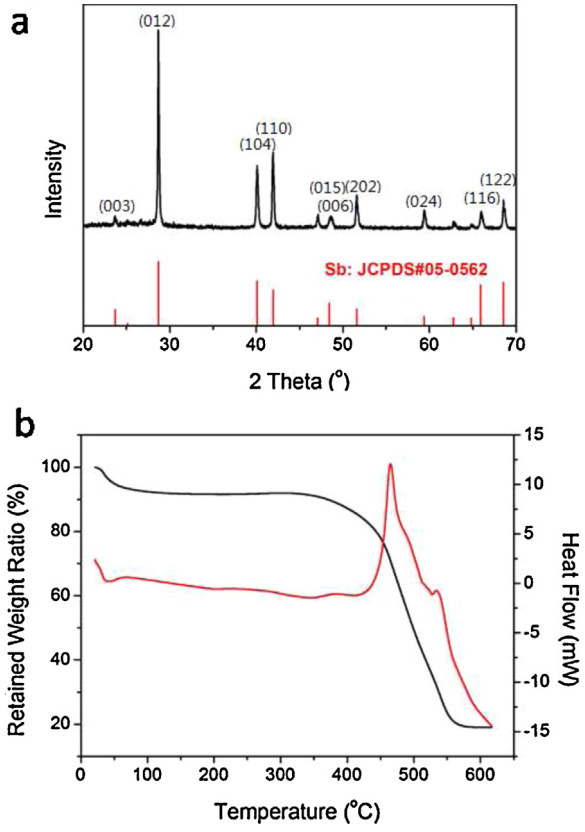

Fig. 1. (a) XRD patterns of antimony-carbon-graphene composite after calcination. (b) TGA curve with heat flow result of antimony-carbon-graphene composite.