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Fabrication of free-standing N-doped carbon/TiO_2 hierarchical nanofiber films and their application in lithium and sodium storages

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ABSTRACT

To simplify the fabrication of electrode in batteries and improve the electrochemical performance, free-standing films composed of N-doped carbon incorporated TiO_2 hierarchical nanofibers were prepared via electrospinning followed by heat-treatment under a nitrogen atmosphere in this study. It is found that hierarchical nanofibers were formed at 700 °C or above due to the phase transformation and the presence of carbon matrix. The as-prepared film was tested as an anode in lithium-ion batteries and sodium-ion batteries. Electrochemical results demonstrate a high rate performance (180 mAh g^{-1} at 5 A g^{-1} in lithium ion batteries) and excellent cycle stability can be achieved in lithium-ion batteries as well as in sodium-ion batteries. This self-standing film is binder free and thus promising for scale-up applications for lithium-ion batteries and sodium-ion batteries with easy fabrication and satisfactory electrochemical performance.

1. Introduction

Lithium ion batteries (LIBs) are high efficiency energy storage devices due to their high gravimetric and volumetric energy, high power density, long cycle life and low self-discharge property, which have been successfully applied for a wide range of portable devices like cellular phones, laptops and digital electronics [1–3]. However, the employment of Li-ion batteries in hybrid electric vehicles (HEV), plug in hybrid electric vehicles (PHEV) and pure electric vehicles (PEV), needs from two to five times more energy density than the present lithium batteries technology can offer (150 Wh kg^{-1}). Especially in the anode, graphite is often used, which has reached to its theoretical limit, in addition there is a safety issue due to the formation of lithium dendrite at low potential [4]. Thus the study of alternative anode materials is urgent.

To date, various novel materials have been studied as anode in LIBs or sodium ion batteries (SIBs). The Si, Ge and Sn based materials in the same group to carbon have much higher theoretical capacities, but these materials exhibited poor rate performance and short cycle life due to the volume expansion during insertion/deintercalation process [5–8].

Titania (TiO_2), as a semiconductor material, has become an appealing anode alternative in LIBs or SIBs due to its good chemical stability, non-toxicity, intrinsic safety, and low cost [9–12]. However, its low electronic conductivity and poor ionic diffusion ability have limited the quick charge-discharge ability, hindering its practical application.

A lot of methods have been proposed to improve the electronic conductivity and/or ion diffusion ability of TiO_2. Several strategies including preparing the nanostructured materials like TiO_2 nanotubes [13–15], element doping, and compositing with conductive materials (such as carbonaceous materials) have been proposed. The compositing with carbonaceous materials like graphene showed very good capability to enhance the electrochemical performance of TiO_2 according to previous reports [16–20]. One-dimensional materials such as nanotubes or nanowires have special properties including high length-radius ratio, high electrolyte-electrode contact area, shortened ion diffusion distance and good strain accommodation, leading to enhanced electrochemical performance [21].

Heteroatom doping can affect the electrochemical performance of materials [22–26]. For example, the doping of nitrogen has been

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proven as an effective way in enhancing electrochemical performance of carbon materials such as carbon nanotubes, because the nitrogen atom can alter the electronic and chemical environment due to its comparable atomic size and five valence electrons available to form strong valence bonds with carbon atoms [27–32]. Ryu *et al* prepared N-doped mesoporous carbon-decorated TiO_2 nanofibers via electrospinning process combined with subsequent heat treatment for the first time, and found the enhanced electrochemical performance for as-prepared nanofibers in LIBs [33].

In general, the LIBs electrodes are typically produced by mixing active materials, conductive additives, and binders into slurry, followed by pasting the slurry on the current collector, and eventually drying the pasted electrode. The process involves in multiple steps and is time-consuming. Furthermore, the binders are poor electronic conductor and provide almost no specific capacity, thus can lower the power density and energy density of the batteries. Consequently, the development of binder-free or free-standing electrodes for rechargeable batteries is an appealing strategy [21]. Yet due to the low electronic conductance, for TiO_2, composition and structuring will be of key importance [34].

Herein, we investigate the preparation and formation of free-standing TiO_2 film electrodes. The binder-free N-doped carbon/TiO_2 nanofiber free-standing films were prepared by electrospinning in which conductive N-doped carbonaceous materials were *in situ* formed in the hierarchical TiO_2 nanofibers film during the annealing. The anode electrochemical performance of the film for LIBs and SIBs at room temperature was investigated in order to illustrate their reversible capacity and rate performance for potential applications.

2. Experimental

2.1. Materials

All reagents were of analytical-grade and used as received except stated otherwise.

2.2. Synthesis of free-standing carbon-decorated TiO_2 nanofiber

TiO_2 nanofiber film was fabricated according to previous literature with some modifications [33]. The typical procedure is as follows. A solution of titanium tetraisopropoxide (1.6 mL) and acetic acid (3 mL) were first stirred in ethanol (3 mL) for 2 h. Then, 0.9 g polyvinyl pyrrolidone (PVP, Mw = 1,300,000) was dissolved in ethanol (0.7 mL). The PVP solution was added into titanium solution, stirring for 5 h to get electrospinning solution. The prepared electrospinning solution was then transferred into a plastic syringe equipped with an 18-gauge metal nozzle made of stainless steel. The solution was electrospun at a direct current (DC) voltage of ~12 kV and a flow rate of 0.5 mL h^{-1}. Copper foil was placed ~12 cm from the tip of the nozzle to collect the nanofibers. First, the electrospun nanofibers were dried under ambient environment overnight and then heated at 500 °C for 3 h at a heating rate of 1 °C min^{-1} under a nitrogen atmosphere, respectively, yielding black free-standing film. The film was denoted as NCTN5. The NCTN5 films were further heated at 600, 700 and 800 °C for 3 h under nitrogen atmosphere, respectively, denoted as NCTN6, NCTN7 and NCTN8.

2.3. Characterization

Powder X-ray diffraction (XRD) measurements of the samples were carried out on a D-max 2500 X-ray powder diffractometer using a graphite monochromator with Cu Kα radiation ($\lambda = 1.5406$ Å). The data were collected between scattering angles (2θ) of 20–80° at a scanning rate of 4°/min. Thermogravimetric analysis (TGA) measurements were recorded on a NETZSCH5 STA 449C thermogravimetric analyzer at a heating rate of 5 °C·min^{-1} under air atmosphere from room temperature to 800 °C. Field emission scanning electron microscope (FE-SEM, Hitachi-4800S) was used to observe the morphology. Transition electron microscopy (TEM) and high resolution transition electron microscopy (HRTEM) was performed on the FEI Tecnai F20 and JEM 2010F. TEM specimens were obtained by drop-casting the as-prepared sample dispersions in ethanol onto carbon-coated TEM grids and dried in ambient environment. Raman measurements were performed on a PerkinElmer Raman Station 400 (USA). X-ray photoelectron spectroscopy (XPS) was obtained on the ESCALAB 250XI in which the binding energy is calibrated with C1s = 284.5 eV.

2.4. Electrochemical measurements

The as-prepared free-standing film was placed between two pieces of nickel foam and pressed to form sandwich-like configuration. The cells were assembled inside the argon-filled glove box with water and oxygen less than 1 ppm, employing a lithium or sodium metal foil as the counter electrode and the reference electrode. The electrolyte for Li-ion batteries was 1 M $LiPF_6$ in a mixture solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v:v), and microporous polypropylene (Celgard 2400) was used as the separator. The electrolyte for Na-ion batteries was 1 M $NaClO_4$ in propylene carbonate (PC)/DMC (1:1, v:v) with 3% (v:v) fluoroethylene carbonate (FEC) as additive. Galvanostatic charging/discharging for the assembled cells was performed on a 2000 battery testing unit (Arbin, USA) at varied current density between voltage limits of 0.01 and 1.5 V (vs. Li/Li^+, or Na/Na^+) at room temperature. The cyclic voltammetry (CV) measurements were performed in the potential window of 0.01–1.5 V (vs. Li/Li^+, or Na/Na^+) at 0.1 mV^{-1} on an electrochemical workstation (P4000, Princeton Applied Research, USA). The capacity is calculated based on the total weight of TiO_2 and carbon in the film. The active materials refer to both TiO_2 and carbon in the film. Electrochemical impedance spectroscopy (EIS) was obtained on the P4000 electrochemical workstation in the frequency range of 0.1–10^5 Hz with an amplitude of 5 mV at the open-circuit potential.

3. Results and discussion

As shown in Scheme 1, nanofiber films were prepared by spinning titanium tetraisopropoxide/PVP solution. Then, the electrospun films were heated under a N_2 atmosphere at varied temperature to yield N-doped carbon/TiO_2 free-standing films. The as-prepared films were used as binder-free electrodes in batteries after cutting.

Fig. 1 presents the XRD patterns of the as prepared TiO_2/carbon nanofibers. For NCTN5, no strong peaks can be observed except those assigned to double-sided adhesive. In contrast, the XRD patterns of the electrospun nanofiber, which was heated at 500 °C for 3 h under air atmosphere, showed typical characteristic peaks of anatase TiO_2 (JCPDS 21-1272), shown in Fig. S1. Notably, the nanofiber heated in air is very brittle and is hardly to be usable as film. During annealing, PVP will transform into CO_2 rapidly and TiO_2 grain will grow gradually under air atmosphere. On the contrary, a certain amount of PVP will transform into N-doped amorphous carbon under nitrogen atmosphere. Notably, to prepare N-doped carbon/TiO_2 nanocomposites, Ryu *et al* introduced an ionic liquid as N-doped mesoporous carbon precursor source to form a conducting network on the TiO_2 nanofibers [33], whereas N-containing PVP was used as N-doped amorphous carbon source for our case. The presence of amorphous carbon is one reason of the low