



Morphological and crystallite size impact on electrochemical performance of electrospun rutile and rutile/multiwall carbon nanotube nanofibers for lithium ion batteries

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Abstract

A sol–gel based route was used to produce TiO₂ based nanocomposites. Sols were electrospun into continuous nanofibers and calcined to get rutile phase. Fibers with diameter around 100 nm and crystallites size between 10 and 50 nm were obtained. The morphological impact and crystallites size dependence of the electrochemical performance for as-synthesized materials are reported. Enhancements using inert calcination atmosphere and incorporation of multi-wall carbon nanotubes (MWCNT) into the system are also presented.

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1. Introduction

Marked improvements in higher stability and enhanced kinetics for various electrical and chemical processes were obtained in electrospun fiber materials, as confirmed by several reports [1,2]. The 1-dimensional hierarchical structure was also found to enhance the electrochemical performance of electrode materials in lithium ion batteries by diminishing the severe aggregation often associated with common sol–gel and heat-treatment technique [3,4]. Shorter diffusion distances were expected with the increased electrolyte-active electrode material-electronic conductor ternary interfaces. This is beneficial in Li⁺-intercalation materials especially those with 1-dimensional lithium transport paths [5].

Titanium oxide (TiO₂) was studied extensively for its potential applications in photocatalysis, electronic devices, solar cells, photovoltaics and recently, lithium ion batteries [6–10]. TiO₂ was considered as one of the most promising anode materials in the future for its abundance in nature, environmental benignity, low cost and stability during lithium

intercalation process [9,11–13]. This was especially important for applications coupling with high voltage cathode materials, where safety was the primary concern, e.g. battery for plug-in hybrid vehicles (PHV) [12,14,15].

Among the eight commonly acknowledged polymorphs of TiO₂, rutile had the most stable structure [16–18]. However, anatase phase was previously the most studied candidate as lithium insertion hosts [19–21]. They can be more easily synthesized into nanosize and exhibited significant electrochemical activity. Micron size rutile particles only had very limited galvanostatic capacity at room temperature [8,22]. This could mainly be attributed to 1-dimensional lithium transport channel along *c*-axis, whereas the octahedral sites were hardly reachable from other directions [23]. The highly anisotropic lithium ion diffusion mechanism was often accused to limit the realizable charge–discharge capacity of the rutile phase, as the channel could be easily blocked with impurity ions or dislocations [24,25].

However, from theoretical calculation, it was found that rutile should have a lower charge/discharge voltage as compared to the anatase phase of TiO₂ [26]. The lower voltage is beneficial for the material to be used as anodes in lithium ion batteries. Recently, rutile phase TiO₂ with improved electrochemical performance was reported. Various

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synthetic routes were used to obtain nanomaterials with controlled morphology in rutile phase TiO₂, especially with a limited width in *c*-direction, which could enhance their charge–discharge capacity [27–31]. A shorter lithium transport lengths was believed to be the key factor for these improvements. However, most of these reports involved sophisticated design of material preparation and did not have a solid build of how morphology and crystallites size could affect the electrochemical performance of rutile TiO₂.

Here we presented our latest work explaining the morphology and structure impact on electrochemical performance of electrospun rutile and rutile/MWCNT (multiwall carbon nanotube) nanocomposite for lithium ion batteries. A simple electrospinning setup based on sol–gel chemistry was used to fabricate the rutile phase TiO₂ fibers. This is the first report where electrospun rutile nanofibers were prepared for the application in lithium ion batteries. Depending on the synthesis condition, rutile TiO₂ with significantly different electrochemical performances was obtained. The crystallites size dependence of the charge–discharge capacity was discussed. The introduction of MWCNT into the rutile system and their enhancement in materials performance were also presented.

2. Experimental

Precursors for electrospinning were prepared based on a sol–gel chemistry. 1 g polyvinylpyrrolidone (PVP, average M.W.=1,300,000, Acros Organics), 2.7 ml acetyl acetone (Certified, Fisher Scientific) and 1.3333 g titanium (IV) isopropoxide (Ti(OiPr)₄, 98+%, Acros Organics) were added to 12 g ethyl alcohol (absolute, 200 proof, 99.5%+, Acros Organics) sequentially with 1 h time interval in between. The precursor solution was mixed homogeneously using vigorous magnetic stirring and then loaded into a 20 ml plastic syringe with an 18-gauge stainless steel nozzle. 20 kV DC voltage and 10 cm spacing between the nozzle tip and aluminum collector were used for the electrospinning. The flow rate was set to be 0.5 ml/h. The whole process was conducted in air. Upon completion the fiber mats were calcined in air or flowing argon atmosphere at 800 °C (10 °C/min ramping rate for both heating and cooling) to obtain the rutile crystal phase. For particle samples the electrospinning setup was not used. As-prepared sol–gel solution was dried in vacuum oven at 60 °C overnight and directly calcined. For rutile-MWCNT nanocomposite fibers, the functionalized MWCNTs, prepared in the route as described in Lee et al.'s paper [32], were ultra-sonicated into the solvent before other reactants were added. Other synthesis condition remained the same.

The fiber diameter was obtained via ImageJ analysis on scanning electron microscopy (JEOL 6335F FEG-SEM) picture of the as-prepared samples. Crystal phase of the materials was confirmed by X-ray diffraction technique (Panalytical x'pert powder) on a 2θ angle from 10° to 80°. Using Scherrer equation the crystallites size for the samples was calculated.

CR2016 type coin cells were assembled for electrochemical tests. The cells were fabricated into a half-cell setup using lithium metal as the counter-electrode. The active-electrode

consisted of as-synthesized rutile nanofibers, polyvinylidene fluoride (PVDF) binder and carbon black in 60:20:20 weight ratio. The slurry was tape-casted on aluminum foil and dried overnight in oven at 70 °C. 1 M LiPF₆ in ethylene carbonate-dimethyl carbonate (EC-DMC) electrolyte was directly purchased and used in the cells. Celgard 260 membrane was used as the separator. The coin cells were cycled at 30 mA/g (corresponding to a rate of C/10) between 0.5 and 3.5 V using Arbin Instrument 3000 battery testing system for the evaluation of their electrochemical performance.

3. Results and discussion

Fig. 1 showed TiO₂ nanofibers in the green state and those after calcination in air or argon. The diameter for as-prepared TiO₂ nanofibers (Fig. 1a) was measured to be 258 ± 47 nm and decreased to ~100 nm after heat treatment in air because of the burn out of organic compounds, as shown in Fig. 1b. Due to the presence of residual surface carbon rendered from the inert atmosphere, rutile fibers calcined in argon atmosphere (Fig. 1c) exhibited a larger diameter and also smaller crystallites size as compared to those heat-treated in air, as suggested by XRD calculation in later section. All fibers displayed a continuous 1D geometry with loosely interwoven morphology. This type of structure helped to keep substantial porosity in the calcined samples which was beneficial for their electrochemical performance.

Powder diffraction pattern for air calcined TiO₂ particles and fibers as well as fibers prepared in argon are shown in Fig. 2. It was found that all the peaks could be indexed to a single phase of ordered rutile TiO₂ structure for sample from all the preparation routes. No observable alternative phase was found in the diagram.

Based on the XRD diagrams, the crystallites size for calcined rutile samples was calculated, using Scherrer equation

$$\tau = K\lambda/\beta \cos \theta$$

where *K* is the shape factor with a value of 0.9 for spherical samples; λ is the X-ray wavelength, being 1.54 for CuK α X-ray source; β is the line broadening (FWHM) width at half maximum intensity in radians, and θ is the Bragg angle. τ is the calculated mean size of the crystalline domains, equal to the particle size of single crystallites. The results were summarized in Table 1. It clearly showed the impact of calcination atmosphere on crystallites size. The residual carbon that usually burnt out in air atmosphere still presented and significantly hindered the crystal growth in inert gas atmosphere. This was crucial in enhancing the electrochemical performance of rutile which has a 1-D lithium transport channel. Smaller crystallites size greatly decreased the chance that the channel was blocked by misplaced atoms and dislocations. Also comparing the particle sample and the electrospun nanofiber sample, it was observed that the fiber morphology was beneficial in preventing crystal growth due to the limits from the fiber diameter so that smaller crystallites were obtained.

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