



Carbon treated self-ordered TiO₂ nanotube arrays with enhanced lithium-ion intercalation performance



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ARTICLE INFO

Article history:

Received 17 January 2014

Received in revised form 3 February 2014

Accepted 3 February 2014

Available online 10 February 2014

Keywords:

Li ion battery

Carbon doping

Titanium oxide nanotubes

Anodization

ABSTRACT

Vertically aligned TiO₂ nanotube (TONT) arrays on titanium substrate developed by facile electrochemical anodization in an aqueous solution of 0.5 M Na₂SO₄, 0.5 M H₃PO₄, 0.2 M sodium citrate, and 0.5 wt% NaF were prepared having a pore diameter and thickness of 100 nm and 1.2 μm, respectively. The undoped (*u*-doped) TONT arrays possessing an anatase phase were again annealed at 500 °C under a mixed gas flux of nitrogen (N₂) and acetylene (C₂H₂), to induce the enhancement of electrical conductivity. It was designated as carbon-doped (*c*-doped) TONT arrays. Undoped and *c*-doped TONT arrays were compared using various characterization tools, including X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and X-ray photoelectron spectroscopy (XPS). Furthermore, based on several electrochemical tests (galvanostatic charge/discharge tests, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS)), it was observed that *c*-doped TONT arrays revealed improved charge/discharge capacity, cycle stability, and rate capability, due to the enhanced electrical conductivity of *c*-doped TONT arrays.

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1. Introduction

Among the reliable, quickly rechargeable power sources available, lithium ion batteries (LIB) are the most promising technologies because of their high energy storage density, stable cycle life, little memory effect, absence of poisonous metals and so on. At present, graphite is the commercially used anode material, which has a theoretical specific capacity of 372 mAh/g and quite stable durability. However, several limitations such as electrical disconnection and structural deformation hinder compact LIBs in higher energy density and higher stable cell applications [1,2]. To avoid these limitations, many advanced LIB anode materials, including Si, Ge, and Sn having a high capacity have been examined. However, the decomposition of lithium salt-based liquid electrolyte at low operating voltage (<1 V vs. Li/Li⁺) and the formation of an unstable solid electrolyte interface (SEI) on the electrode surface have been found [3,4]. Therefore, as a new anode material, titanium dioxide (TiO₂) can be suggested due to its high operating voltage (1.75 V vs. Li/Li⁺) in which the electrolyte solution is stable

and has high safety, good cyclability, low self-discharge rates, and small volume change (<3%) during lithiation/delithiation, even though the theoretical capacity of TiO₂ is lower than the Sn, Si, and graphite [5,6]. In addition, TiO₂ shows chemical stability and negligible toxicity, and has relatively simple methods. In terms of the nanostructure, it is well known that the lithium intercalation activity and cycling stability rely significantly on the morphology of electrode materials, and that their properties have dramatically improved with the modification of nanoscale features [7–10].

Above all, one-dimensional (1-D) TiO₂ nanoarchitecture has been of significant interest due to the promotion of ionic and electronic diffusion, increasing the electrode/electrolyte interfacial area and ensuring easy accommodation of strain suffered from the lithium-ion insertion/extraction. Recently, several groups have synthesized 1-D anatase TiO₂ nanostructures such as nanorods, nanowires, and nanotubes (NTs), and assessed their electrochemical properties [11–13].

Especially, anatase TiO₂ nanotubes (TONTs) have shown superior electrochemical properties compared to TiO₂ nanoparticles (such as the discharging capacity maintaining 168 mAh/g in the 30th cycle at 210 mAh/g), representing a high-rate cycling performance, columbic efficiency approaching 98%, and excellent reversibility. TONTs are thus recognized as very attractive anode

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materials for LIB [14,15]. Subsequently, considerable attention has been given to the chemical synthesis of various nanostructure 1-D TiO₂ materials, presenting good electrochemical performance [16]. This still shows that 1-D nanoparticles exist that have a randomly oriented property and poor contact with the current collector, reducing the lithium ionic and electrical conductivities. Consequently, self-ordered 1-D nanoarchitectures grown directly on a current collector such as Cu, Pt, and Ti have been widely studied as a negative electrode for LIB [17–19].

Recently, the oriented anatase TONT arrays, prepared using facile electrochemical anodization, have attracted much attention because the several disadvantages induced in the chemically synthesized TiO₂ nanomaterials were overcome and several strong advantages emerged [20]. First, the oriented pore structure of NT arrays is expected to facilitate 1-D electronic/ionic conduction and to accommodate volume change during charging/discharging cycling. Second, the Li⁺ ions in the electrolyte are highly accessible to the interior and exterior surface of the NT walls. Third, the length of the Li⁺ diffusion path in the thin wall of NT arrays is short. Fourth, the electron transport in the environment where the NT arrays are directly grown on the titanium substrate is fast. With these potential advantages associated with oriented NT arrays, it was found that the low electrical conductivity of NT arrays results in unstable capacity retention and poor rate capability, leading to rapid capacity fading during charging/discharging cycling. To increase the electrical conductivity of NT arrays, the doping process can be suggested and applied for various devices such as photocatalysts, photoelectrochemical water splitting, and lithium ion batteries [21–23]. Among various dopants, carbon-doped (*c*-doped) TiO₂ showed improved electrical conductivity, leading to better photocatalytic effect. However, to our knowledge, few reports have been presented on the electrochemical performance of *c*-doped TONT arrays. Herein, *c*-doped TONT was fabricated using a non-destructive thermal-treatment at 500 °C under a 20% C₂H₂/N₂ gas mixture ambient. The *c*-doped TONT arrays showed high capacity and cycling stability from the discharging/charging cycling, cyclic voltammetry, and electrochemical impedance spectroscopy.

2. Experimental

Ti foil (Goodfellow, England) of 0.1 mm thickness and 99.6% purity was used as a substrate. Before each experiment, the Ti foil was cleaned by sonicating sequentially in acetone, isopropanol, and methanol for 10 min each, followed by rinsing in distilled (DI) water and then drying in a nitrogen stream. The electrochemical anodization system was composed of a two-electrode configuration with a working electrode of Ti foil and a counter electrode of Pt mesh. The electrolyte used consisted of 0.5 M Na₂SO₄, 0.5 M H₃PO₄, 0.2 M sodium citrate, and 0.5 wt% NaF in an aqueous bath. Experimental conditions were kept constant with an applied voltage of 25 V, duration of 50 min, temperature of approx. 25 °C, and slow magnetic agitation of 150 rpm to identify the reproducible results. The as-prepared TONT arrays were ultrasonically cleaned in DI water for 1 min to remove the remnants of the anodic reaction and were immediately annealed at 450 °C (heating/cooling rate of 1.5 °C/min) for 3 h under air ambient. For the *c*-doping into TONT arrays, a second thermal treatment was carried out. During the heating process to 500 °C, a heating rate of 5 °C/min was adapted in a N₂ gas flow and during the holding process at 500 °C for 10 min, a 20% C₂H₂/N₂ gas mixture was introduced for *c*-doping. Finally, the samples were naturally cooled in an N₂ atmosphere.

The crystal structures of the as-prepared samples were investigated by X-ray diffraction (XRD) using a Rigaku diffractometer operated with a Cu K α radiation source ($\lambda = 1.541 \text{ \AA}$) at an operating voltage of 50 kV and current of 200 mA. To survey the surface and cross-sectional morphology of TONT arrays, field-emission scanning electron microscopy (FE-SEM; JSM-6330F, JEOL, Japan) was employed. To validate the change of chemical state in the TONT and *c*-doped TONT arrays, X-ray photoelectron spectroscopy (XPS) analyses were performed in a UHV multipurpose surface analysis system (SIGMA PROBE, Thermo, UK) operating at a base pressure of $<10^{-9}$ mbar. The photoelectron spectra were excited by an Al K α (1486.6 eV) anode operating at a constant power of 100 W (15 kV and 10 mA). The binding energy (BE) scale was calibrated from the hydrocarbon contamination using the C 1s peak at 284.6 eV.

Electrochemical measurements were executed in two electrode cells using Li foil as both the reference and counter electrodes. The coin-type half cells were assembled using Li foil, an electrolyte of 1 M LiClO₄ in a 50:50 (w/w) mixture of ethylene carbonate and dimethyl carbonate, and polyethylene film (Celgard 2300) as the separator in an Ar-filled glove box. The cells were charged and discharged at a constant current density of 42, 84, 168, and 336 mA/g between 1.0 V and 2.5 V vs. Li⁺/Li on a TOSCA-3100 battery cycler (Toyo Co., Japan). Cyclic voltammetry (CV) was carried out in the potential range of 1.0 V–2.5 V vs. Li⁺/Li at a scan rate of 0.1 mV/s on a Solartron multi-state instrument (Model 1480, UK). Electrochemical impedance spectroscopy (EIS; IM6, Zahner, Germany) was carried out by applying an alternating current (ac) voltage of 5 mV in the frequency from 100 kHz to 0.01 Hz.

3. Results and discussion

Fig. 1 compares the typical top and cross-sectional FE-SEM images of the *u*-doped and *c*-doped TONT arrays with the length of approximately 1.2 μm , which enables uniform carbon doping through the inner and outer walls. The pore diameter and wall thickness were observed to be 100(\pm 25) nm and 25(\pm 5) nm, respectively. Furthermore, it was observed that the irregular shaped pores were not perfectly round in shape. After a 20% C₂H₂/N₂ gas treatment, no morphological modification was observed, confirming that the acetylene thermal treatment did not induce the morphological change of the TONT arrays.

In order to determine the crystallinity of the *u*- and *c*-doped TONT arrays, XRD measurements were performed as shown in Fig. 2. The as-anodized TONT arrays exhibit an amorphous structure without any detectable crystalline phases, since only the peaks associated with the Ti substrate were evident. This is consistent with reports by other researchers that only amorphous titania can be produced via anodization without high-temperature annealing. Annealing the as-prepared TONT arrays at 450 °C for

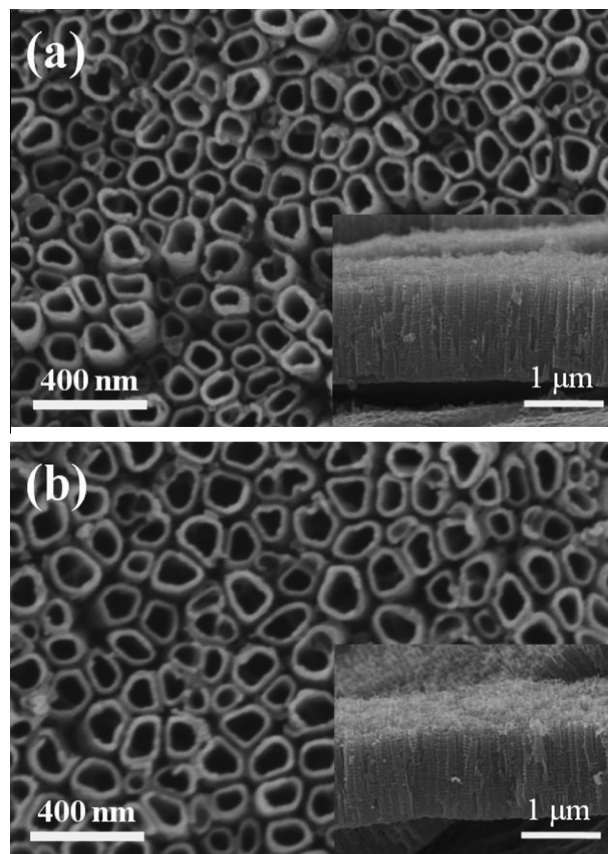


Fig. 1. FE-SEM images of (a) *u*- and (b) *c*-doped TONT arrays annealed at 500 °C in a C₂H₂/N₂ atmosphere for 10 min.

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