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Tailoring oriented TiO_2 nanotube morphology for improved Li storage kinetics

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ABSTRACT

We report on the syntheses of oriented TiO_2 nanotube (NT) arrays having different geometries and the electrochemical properties as electrodes for lithium rechargeable batteries. The morphology of the NT arrays, which were prepared by electrochemical anodization of Ti foil, is investigated by scanning electron microscopy. X-ray diffraction analysis indicates that annealing the as-grown NT films at a temperature of 400 °C transforms them from an amorphous phase to anatase TiO_2. Analyses of cyclic voltammograms indicate that there is significant capacitive Li^+ storage associated with the NT surface in addition to the Li^+ storage within the bulk material. The NT morphological parameters (e.g. pore diameter, wall thickness, and roughness factor) are found to have significant effects on the Li-ion insertion/extraction kinetics and the performance of the electrodes in lithium-ion batteries.

1. Introduction

Titanium oxides with one-dimensional (1D) nanostructures have received great attention for various applications such as solar cells [1,2], photocatalysts [3], sensors [4], electrochromic [5], and electrochemical energy storage devices [6,7]. Among them, lithium-ion batteries have emerged as a promising energy storage technology for portable electronics, hybrid electric vehicles (HEV), and large-scale energy storage [8]. Titanium oxide has been examined as the Li-ion host materials during the last two decades. Some of the common polymorphs of TiO_2, such as anatase [9–17], rutile [18,19], and TiO_2 (B) [20,21] are considered as good anode materials for Li-ion batteries. Although TiO_2 materials have relatively low theoretical capacities (168 mAh g^{-1} for $Li_{0.5}TiO_2$) as negative electrodes for lithium-ion batteries, they have recently attracted considerable attention [9–21] because of their high-rate capability and enhanced safety, which have become more essential properties of lithium rechargeable batteries and supercapacitors used for HEV applications.

Recently, nanostructured materials of TiO_2 polymorphs or their mixtures have been intensively developed as Li storage materials [13–25]. Nanostructured materials have several features that are suitable for improving electrochemical properties of Li-storage electrodes such as the shorter lengths for both electronic and ionic transport, the higher surface areas of electrodes, and the improved accommodation of the volume changes in active electrode materials during Li insertion/extraction cycling. However, the research focus has usually centered on the disordered nanostructured materials with random structural orientations. A few papers on the aligned TiO_2 NT arrays as anode materials of lithium-ion batteries have recently been reported [22–25]. The oriented nanostructures such as nanotube (NT) arrays might have some merits of fast charge transport along the NT walls and pores. Compared to the randomly mixed structures, the oriented structure can facilitate to investigate the morphology effect on the electrochemical properties of TiO_2 materials for lithium storage. For example, nanoparticle electrodes have randomly mixed pore size and orientation, whereas the NT electrodes have relatively uniform pore size and orientation.

In this study, oriented TiO_2 NT arrays aligned perpendicular to the substrate were fabricated by electrochemical anodization of Ti metal, which is relatively a simple approach to produce NT arrays [1–5,22–25]. The electrochemical properties of Li-ion storage in TiO_2 NT electrodes were investigated. The pore density, pore diameter, wall thickness, intertube spacing, and porosity of the NT films were varied and the effect of the NT geometry on Li insertion/extraction kinetics was studied with cyclic voltammetry.

2. Experimental

Oriented TiO_2 NT arrays were prepared by electrochemical anodization of Ti foils (99.7% purity, Aldrich). The anodization process was carried out in 0.5 wt. % NH_4F in glycerol with a Pt counter electrode. The Ti foils were biased at 10, 20, 30 and 40 V for 10–25 h

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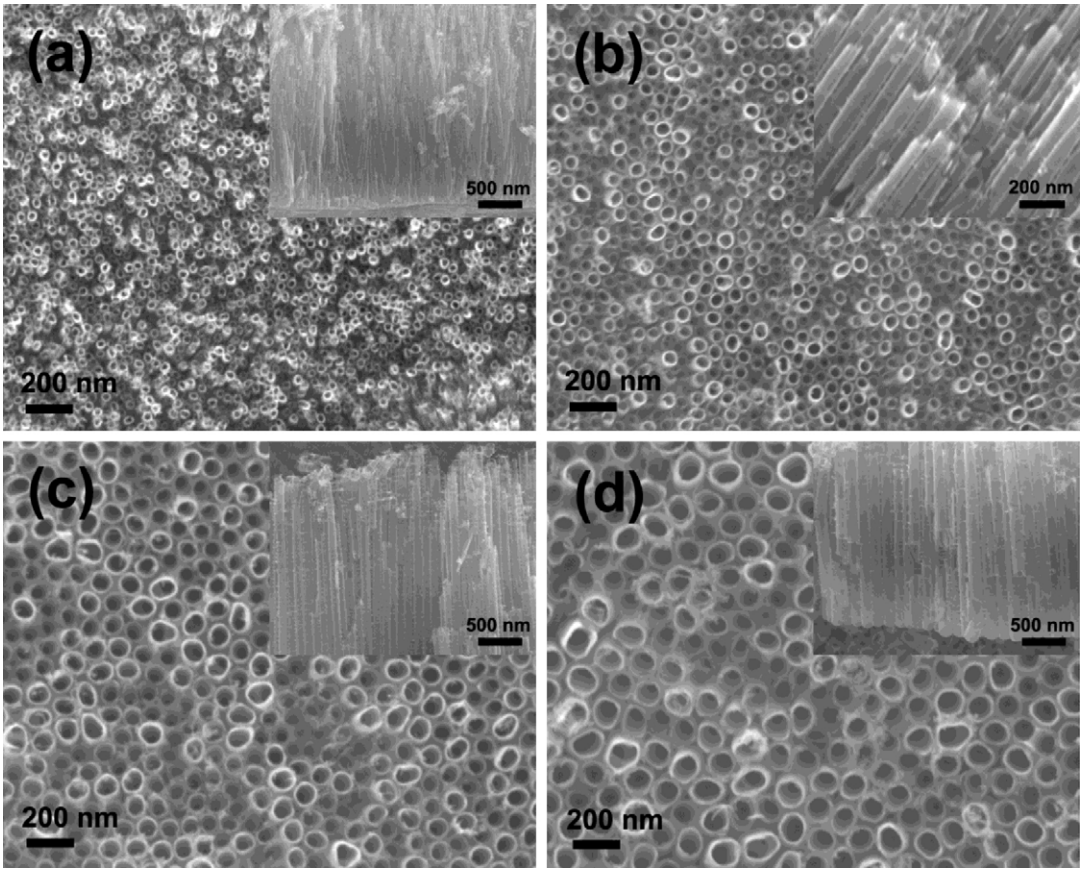

Fig. 1. Surface and cross-sectional (inset) SEM images of oriented TiO_2 NT arrays prepared by applying (a) 10, (b) 20, (c) 30, and (d) 40 V.

at room temperature to produce NT arrays with a length of about 2 μm. After electrochemical anodization, the as-prepared NT arrays were cleaned with distilled water and soaked sequentially in a bath of 20/80, 40/60, 60/40, 80/20, and 100/0 vol.% ethanol/water and then dried using a supercritical CO_2 ($scCO_2$) drying apparatus (SPI-DRY CPD) [2]. The TiO_2 NT films on Ti substrates were heated to 400 °C in air at a heating rate of 2 °C min^{-1}. After annealing at 400 °C for 1 h, the hot plate was cooled to room temperature automatically.

The crystal structure of obtained samples was confirmed using X-ray diffraction (XRD, SCINTAG DMS-2000 diffractometer with Cu Kα radiation). The morphology and microstructure of the prepared NT samples were examined by field emission scanning electron microscope (FE-SEM, JEOL JSM-7000F).

Films of oriented TiO_2 NT arrays grown on Ti substrates were studied as the working electrode using a two-electrode coin-type test cell fixture. A piece of lithium foil (Alfa Aesar) was used as the counter and reference electrode. The electrolyte consisted of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 volume ratio, Novolyte Technologies Inc.). Celgard 480 membranes were used as a separator between TiO_2 NTs and Li foil. All test cells were assembled in an Ar-filled glove box (EE-493, VAC) with moisture and oxygen levels below 0.5 ppm. Cyclic voltammetry (CV) measurements were carried out using a potentiostat/galvanostat (VMC-4, Princeton Applied Research) within a voltage window of 1.0–3.0 V (vs. Li/Li^+). Before the CV measurements, the fresh NT electrodes were cycled at 10 mV s^{-1} for 5 times to remove absorbed water or other impurities on the NT surface, which could have effects to the total current in cyclic voltammograms.

3. Results and discussion

The SEM images of the top view of TiO_2 NT arrays prepared by electrochemically anodizing Ti foils at 10, 20, 30, and 40 V followed by annealing at 400 °C are compared in Fig. 1. The inset images show their cross-sectional views. These NTs are closely packed in approximately hexagonal symmetry [26,27]. No bundles, cracks, or overlayers in NT films were observed as a result of using the supercritical CO_2 drying technique during the NT post-growth cleaning process [2]. Table 1 summarizes the geometric parameters of the TiO_2 NTs such as the inner pore diameter, wall thickness, and center-to-center distance. These parameters were averaged over 40

Table 1
Geometric parameters of the TiO_2 NT arrays produced at different conditions.

Anodization voltage (V)	Inner diameter (nm)	Outer diameter (nm)	Intertube distance (nm)	Wall thickness (nm)	Porosity (%)	Roughness factor (μm^{-1})
10	21.2	40.3	4.8	9.6	47.3	109.8
20	50.6	75.9	5.2	12.7	55.7	69.8
30	73.6	102.9	9.3	14.7	62.6	50.9
40	96.2	131.1	8.8	17.5	63.1	42.2