Amorphous and Crystalline TiO₂ Nanotube Arrays for Enhanced Li-Ion Intercalation Properties

Dongsheng Guan, Chuan Cai, and Ying Wang

Mechanical Engineering Department, Louisiana State University, Baton Rouge, LA 70803, USA

We have employed a simple process of anodizing Ti foils to prepare TiO₂ nanotube arrays which show enhanced electrochemical properties for applications as Li-ion battery electrode materials. The lengths and pore diameters of TiO₂ nanotubes can be finely tuned by varying voltage, electrolyte composition, or anodization time. The as-prepared nanotubes are amorphous and can be converted into anatase nanotubes with heat treatment at 480 °C. Rutile crystallites emerge in the anatase nanotube when the annealing temperature is increased to 580 °C, resulting in TiO₂ nanotubes of mixed phases. The morphological features of nanotubes remain unchanged after annealing. Li-ion insertion performance has been studied for amorphous and crystalline TiO₂ nanotube arrays. Amorphous nanotubes with a length of 3.0 μm and an outer diameter of 125 nm deliver a capacity of 91.2 μAh cm⁻² at a current density of 400 μA cm⁻², while those with a length of 25 μm and an outer diameter of 150 nm display a capacity of 53 μAh cm⁻². When the 3-μm long nanotubes become crystalline, they deliver lower capacities: the anatase nanotubes and nanotubes of mixed phases show capacities of 53.8 μAh cm⁻² and 63.1 μAh cm⁻², respectively, at the same current density. The amorphous nanotubes show excellent capacity retention ability over 50 cycles. The cycled nanotubes show little change in morphology compared to the nanotubes before electrochemical cycling. All the TiO₂ nanotubes demonstrate higher capacities than amorphous TiO₂ compact layer reported in literature. The amorphous TiO₂ nanotubes with a length of 1.9 μm exhibit a capacity five times higher than that of TiO₂ compact layer even when the nanotube array is cycled at a current density 80 times higher than that for the compact layer. These results suggest that anodic TiO₂ nanotube arrays are promising electrode materials for rechargeable Li-ion batteries.

Keywords: TiO₂ Nanotube Arrays, Anodization, Li-Ion Battery, Cycling Stability.

1. INTRODUCTION

Rechargeable Li-ion batteries have drawn extensive attention due to their high specific capacity, light weight and long lifespan. A Li-ion battery is mainly composed of the cathode, anode and electrolyte. Cathode materials include lithium transition metal oxides (e.g., LiCoO₂ and LiMn₂O₄) and metal oxides (e.g., V₂O₅ and MnO₂). Graphite is the most commonly used anode material in the current commercially available Li-ion batteries. However, the graphite has some limitations which hinder the development of new Li-ion batteries with higher operation voltage and larger power density. For example, lithium dendrites may form in graphite-based Li-ion batteries which can induce an explosion if exposed to air, because the potential for Li-ion intercalation into graphite is close to that of the Li⁺/Li redox couple. Therefore, quite a few new materials have been developed to replace the graphite, such as Si, Sn, Co₃O₄, SnO₂, and TiO₂. Among these materials semi-conducting TiO₂ is a promising alternative to the graphite due to its high operation voltage (~1.75 V vs. Li⁺/Li redox couple), high safety and low self-discharge, and good capacity retention during cycling. For instance, the high operation voltage of TiO₂ makes it possible to combine with novel cathode materials (LiCoPO₄ and LiCo₆Mn₇O_{16}) to achieve Li-ion batteries with high voltage (5 V). In addition, the high chemical stability, low cost and innocuity of TiO₂ are also favorable for its broad applications.

The electrochemical performance of TiO₂ mainly depends on its morphology, structure and phase composition. It has been reported that various polymorphs of TiO₂ display Li-ion insertion/deinsertion properties. For example, Reddy et al. found that a maximum of 0.95 Li/TiO₂ (molar ratio) can be inserted into brookite nanocrystallines with a size of 10 nm and 0.23 Li/TiO₂ into brookite nanocrystallines with a size of 33 nm. Noailles et al.
discovered that hollandite-type TiO₂ shows low Li-ion intercalation capacity. However, nano-structured B-phase TiO₂ shows a large capacity with a theoretical value of 335 mA h g⁻¹ and excellent cycleability when it is used as anode material for Li-ion batteries. Additionally, anatase and rutile TiO₂ are potential anode materials for Li-ion batteries as well.

Recently, amorphous TiO₂ attracts much interest, because it delivers a large Li-ion intercalation capacity due to the high Li-ion diffusion coefficient. To further enhance the Li-ion intercalation properties of amorphous TiO₂, nanostructured TiO₂ with large surface area has been fabricated, such as nanoparticles and nanotubes. These nanostructures not only provide large surface area for Li-ion insertion/extraction reactions, but also facilitate Li-ion diffusion and electron transport to improve the cell capacity significantly. Meanwhile, less volume change occurs in nanostructured TiO₂ during electrochemical cycling, which is also favorable for the stability of Li-ion batteries. Randomly-dispersed amorphous TiO₂ nanotubes prepared by a hydrothermal method have been reported to deliver a discharge capacity of 168 mA h g⁻¹, while well-aligned TiO₂ nanotubes can deliver a much higher capacity than these disordered nanotubes.

Anodic oxidation of Ti foils, a simpler and cheaper method than the common template-based approach, is often adopted to produce self-ordered TiO₂ nanotube arrays. The metallic Ti beneath the TiO₂ nanotube arrays directly functions as a current collector. More importantly, the growth of anodic TiO₂ nanotube arrays is controllable: their morphology can be optimized by tuning preparation conditions, such as oxidation voltages (DC or AC), electrolyte composition and anodization time. For instance, different electrolyte compositions lead to three generations of anodic TiO₂ nanotube arrays. The first-generation nanotubes only have a length up to 500 nm, due to the high rate of chemical dissolution of TiO₃ in acid HF-based aqueous electrolytes where they are formed. Schmuki et al. found that a reasonable pH gradient within the growing nanotube is critical to the formation of long anodic TiO₂ nanotubes, and thus neutral fluoride-based aqueous solutions were utilized to grow TiO₂ nanotubes with a length up to 6.4 μm. Afterwards, anhydrous glycerol was employed as a solvent in the electrolyte, yielding smooth TiO₂ nanotubes of 7 μm long. Herein, more and more high-aspect-ratio TiO₂ nanotubes have been produced with fluoride-containing organic electrolytes. The most common one is ethylene glycol solution with a small amount of NH₄F and H₂O. TiO₂ nanotubes formed from this electrolyte can be as long as 500 μm and have high-quality surface morphology.

Anodic TiO₂ nanotube arrays show excellent properties for many applications, such as photo-catalysts, solar cells, water splitting, sensors, and biomedical materials. Their electrochemical properties also attract much scientific endeavor when they function as anode materials in Li-ion batteries. Wang et al. set up a lithium-ion cell by incorporating TiO₂ nanotube arrays as the anode and ordered porous carbon as the cathode, which delivered an energy density of 25 W h kg⁻¹ and a power density of 3000 W kg⁻¹ at a current-draining time of 30 s, which is twice higher than previous hybrid electrochemical cells.

Fang et al. found that the capacity of amorphous TiO₂ nanotube arrays is higher than that of anatase TiO₂ nanotubes with identical morphological features, due to the faster Li-diffusion in amorphous TiO₂. Öztürk et al. also compared the capacities of 0.92-μm-long amorphous and anatase TiO₂ nanotubes grown on Ti foils, and found that the former delivers a capacity of 77 μA h cm⁻² in the first reversible discharge at a rate of 5 μA cm⁻², whereas the latter shows a capacity of 68 μA h cm⁻² at the same rate. Interestingly, 0.6-μm-long amorphous TiO₂ nanotubes formed on Ti-coated Si chips exhibit a large capacity of 89 μA h cm⁻² in the first discharge and 56 μA h cm⁻² over 50 cycles, suggesting that such electrode is comparable with IC technology and is an ideal candidate for the fabrication of on-chip 2D micro-batteries. In addition to phase composition, morphology is another factor affecting Li-ion intercalation properties of TiO₂ nanotubes. Wei et al. synthesized amorphous TiO₂ nanotubes arrays with different pore size and wall thickness using voltages of 20~80 V; the authors found the morphological differences are critical to the discharge capacities and the capacities of the nanotubes increase with the formation voltages. Moreover, the influence of chemical composition on the Li-insertion performance of TiO₂ nanotube arrays is also an important issue. For example, the charge-transfer conductivity of anatase TiO₂ nanotube arrays can be enhanced by Ag coating, leading to an increase in the capacity. In a similar concept, 1.1-μm-thick TiO₂ nanotube arrays annealed at 400 °C in CO gas have a larger initial discharge capacity (223 mA h g⁻¹) than those annealed in Ni gas (163 mA h g⁻¹) at a current density of 320 mA g⁻¹.

As we have discussed above, there are several ways to improve the electrochemical performance of anodic TiO₂ nanotube arrays. However, there are few reports on the relationship between tube length and energy storage of the material, though the tube length is a well-known factor that determines the specific surface area of TiO₂ nanotubes where the Li-ion insertion/deinsertion reaction occurs. In addition, anatase TiO₂ nanotubes have some advantages over amorphous nanotubes, such as higher mechanical strength and higher resistance to the erosion of fluoride species; thus it is worth comparing the anatase and amorphous nanotubes and reconsidering the relationship between phase compositions and capacities of TiO₂ nanotubes.

In this paper, we present a study of synthesis and electrochemical characterization of TiO₂ nanotube arrays with...
Fig. 1. Top and cross-sectional SEM images of amorphous TiO₂ nanotubes synthesized at 30 V in EG electrolytes containing 0.3 wt% NH₄F and 10 vol% H₂O for (a-b) 1 h, (c-d) 4 h, (e-f) 10 h, and (g-h) at 60 V in EG electrolyte containing 0.3 wt% NH₄F and 2 vol% H₂O for 3 h.
different dimensions and phase compositions. The lengths and diameters of these nanotubes can be tuned by tailoring several preparation conditions. Heat treatment at elevated temperatures converts the amorphous TiO$_2$ nanotubes into nanotubes of pure anatase phase and nanotubes of mixed phases containing anatase and rutile crystallites. TiO$_2$ nanotube arrays show high thermal structural stability and there is no morphological change after the nanotube arrays are annealed at high temperatures. However, TiO$_2$ nanotubes of different phases show different electrochemical behaviors, and the amorphous TiO$_2$ nanotube arrays demonstrate the highest discharge capacity and the best cycling performance.

2. EXPERIMENTAL DETAILS

The Ti foils (99.5 wt%) (10 × 10 × 0.25 mm$^2$) in this study were purchased from Alfa Aesar. Prior to any electrochemical treatment, Ti foils were first chemically etched by immersing into a mixture of HF and HCl acid. The mixture ratio of HF:HCl:H$_2$O was 1:4:5 in volume. The foils were then degreased in acetone and rinsed by sonicating in deionized water. A two-electrode cell with a Pt mesh (23 × 14 mm$^2$) as the counter electrode was assembled for electrochemical anodization. Electrolytes were anhydrous ethylene glycol (EG) with 0.3 wt% NH$_4$F and 2–10 vol% H$_2$O. All the solutions were prepared from reagent grade chemicals and deionized water. During the anodizing process, a potential ramp from 0 V to 30 V or 60 V with a sweep rate of 1 V/s was first conducted, and then the end voltage was maintained for 1–10 h. The voltage was supplied by a DC power supply with digital display (Model 1623A, PK Precision). All the experiments were carried out at room temperature.

After completing the anodization, the samples were immediately rinsed in deionized water and dried in air. TiO$_2$ nanotube arrays were formed on both front side and back side of Ti foils. Subsequent heat treatments at 110 °C for 1 h, 480 °C for 3 h and 580 °C for 3 h were conducted on these nanotubes in air with heating and cooling rates of 4 °C/min.

A FEI Quanta 3D FEG scanning electron microscope (SEM) and a Hitachi S-3600N scanning electron microscope were used to characterize the morphology of TiO$_2$ nanotube arrays. The crystallographic structure of TiO$_2$ nanotube arrays was determined by X-ray diffraction (XRD) using a Rigaku MinIFlex diffractometer with Cu K$_\alpha$ radiation operated at 30 kV and 15 mA with a scan rate of 2°/min.

The electrochemical performance of TiO$_2$ nanotubes was investigated by experiments carried out in anhydrous propylene carbonate electrolytes containing 1 M LiClO$_4$. The TiO$_2$ nanotube arrays on the backside of Ti foils were scraped off before electrochemical measurements. A three-electrode electrochemical cell was constructed for chronopotentiometric and cyclic voltammetric measurements. The cell consists of TiO$_2$ nanotube arrays on the Ti foil as the working electrode, Pt mesh as the counter electrode, and a silver wire in the 0.1 M AgNO$_3$/ethanol solution (Ag/Ag$^+$) as the reference electrode. All the measurements were conducted using an electrochemical analyzer (Model 605C, CH Instruments, Inc.) at room temperature.

3. RESULTS AND DISCUSSION

The morphologies of anodic TiO$_2$ nanotube arrays highly depend on preparation conditions, such as voltage, electrolyte composition and anodization time. Figure 1 presents the SEM images of as-prepared TiO$_2$ nanotube arrays formed in EG electrolytes containing NH$_4$F and H$_2$O at voltages of 30 V and 60 V. These nanotubes are well-aligned with open ends on the top; they are perpendicular to the Ti substrate, with a high aspect ratio up to 158. The shape of the nanotubes resembles bamboo, with ridges on the surface. TiO$_2$ nanotubes formed by anodizing Ti in EG electrolyte with 10% H$_2$O at 30 V for 1 h have an outer diameter of ~106 nm, a wall thickness of ~15 nm and a tube length of ~1.9 µm (Figs. 1(a)–(b)). As the anodization time extends to 4 h, the outer diameter of the formed nanotubes is ~125 nm; the wall thickness is ~15 nm; and the tube length is ~3 µm (Figs. 1(c)–(d)). Anodization of Ti in the same electrolyte at 30 V for 10 h yields nanotubes with an outer diameter of 125 nm, a wall thickness of 15 nm and a tube length of 4.7 µm (Figs. 1(e)–(f)). TiO$_2$ nanotube arrays with an outer diameter of ~158 nm and a length of ~25 µm can be obtained (Figs. 1(g)–(h)) at 60 V in the EG electrolyte with 2 vol% H$_2$O. In addition, it is found that identical TiO$_2$ nanotube arrays are grown on the front side and back side of the bare metal substrate. The nanotube arrays on the backside are removed before electrochemical testing.
Fig. 3. Galvanostatic discharge/charge curves at a current density of 400 μA cm⁻² and cyclic voltammetric curves cycled between −0.6 V and −2.3 V for the three different TiO₂ nanotube arrays: (a–b) amorphous TiO₂ nanotubes, (c–d) anatase TiO₂ nanotubes, and (e–f) TiO₂ nanotubes of mixed phases.

It is obvious that longer anodization time and higher voltages lead to longer nanotubes. According to the field-assisted dissolution model, anodic TiO₂ nanotube arrays result from the competition between electrochemical etching process and chemical dissolution process on Ti. The two processes refer to three simultaneously occurring chemical reactions as follows. (1) Field-assisted oxidation of Ti: Water molecules decompose near the metal and produce O²⁻ ions and H⁺ ions; the O²⁻ ions then travel through an electrolyte-oxide interface to oxidize Ti. (2) Field-assisted dissolution of titanium oxides: Due to electric field, the Ti-O bond undergoes polarization
Table I. The first discharge/charge areal capacities and coulombic efficiencies at a current density of 400 μA cm⁻² for different amorphous TiO₂ nanotube arrays annealed at 110 °C.

<table>
<thead>
<tr>
<th>TiO₂ nanotubes on the surface of Ti foils</th>
<th>Tube length (μm)</th>
<th>The first discharge capacity (mA h cm⁻²)</th>
<th>The first charge capacity (mA h cm⁻²)</th>
<th>Coulombic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-side</td>
<td>1.9</td>
<td>0.0460</td>
<td>0.0421</td>
<td>92</td>
</tr>
<tr>
<td>Single-side</td>
<td>3.0</td>
<td>0.0912</td>
<td>0.0792</td>
<td>87</td>
</tr>
<tr>
<td>Single-side</td>
<td>4.7</td>
<td>0.1154</td>
<td>0.1049</td>
<td>91</td>
</tr>
<tr>
<td>Single-side</td>
<td>25</td>
<td>0.5330</td>
<td>0.4678</td>
<td>88</td>
</tr>
<tr>
<td>Double-side</td>
<td>3.0</td>
<td>0.1583</td>
<td>0.1533</td>
<td>85</td>
</tr>
</tbody>
</table>

and is weakened, promoting dissolution of the oxides. (3) Chemical dissolution of titanium oxides: Herein, Ti⁺⁺⁺ cations become soluble hexafluorotitanium complexes [TiF₆]³⁻ that go into the electrolyte, while the free O²⁻ anions transfer to the oxide-metal interface and react with Ti. When the electrochemical etching rate of Ti metal equals the chemical dissolution rate of entrance of TiO₂ nanotubes, the tube length remains unchanged. At this point, increasing anodization voltage to enhance the etching rate, or decreasing the water content in electrolytes to reduce the chemical dissolution rate, will facilitate the formation of long TiO₂ nanotubes.

Figure 2 shows the XRD patterns of Ti substrate, TiO₂ nanotubes anodized at 30 V in EG electrolytes containing 0.3 wt% NH₄F and 10 vol% H₂O, and anodic TiO₂ nanotubes annealed at 110 °C for 1 h, 480 °C for 3 h and 580 °C for 3 h in air. The XRD patterns of Ti substrate and as-prepared nanotubes only have Ti diffraction peaks, such as the typical peak (101) at 2θ = 40.0°, which indicates that the as-prepared nanotubes are amorphous. This is in agreement with previous reports.⁶¹,⁶² TiO₂ nanotubes annealed at 110 °C for 1 h are also amorphous, as evidenced by their XRD pattern where anatase peaks or rutile peaks cannot be found. On the other hand, the heat treatment at higher temperatures can convert the amorphous nanotubes into crystalline ones. Metastable anatase crystallites are found to emerge at 480 °C, which is evidenced by its typical diffraction peaks (101) at 2θ = 25.2° and (200) at 2θ = 47.4°. The diffraction peaks of Ti substrate are also found in the XRD pattern of TiO₂ nanotube arrays annealed at 480 °C. Due to heat treatment at 580 °C, stable rutile phase appears in TiO₂ nanotube arrays, which is shown by its representative diffraction peak (110) at 2θ = 27.5° in the XRD pattern of annealed TiO₂ nanotube arrays. The anatase phase is also found in TiO₂ nanotube arrays annealed at 580 °C. The intensity of anatase (101) peak is much higher than that of rutile (110) peak, which suggests that only a small portion of anatase crystallites transform to rutile phase at 580 °C resulting in TiO₂ nanotube arrays of mixed phases.

The reaction for Li⁺ insertion/removal into anode TiO₂ can be written as follows.⁶³

\[ \text{TiO}_2 + x \text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2 \]

Both anatase phase and rutile phase have tetragonal structures, which are described by the space group I4/m am and P₄/mnm, respectively. In such a structure, a Ti ion is surrounded by a distorted oxygen octahedron, and numerous vacant octahedral and tetrahedral sites exist between these octahedrons. Li ions can be accommodated in these vacant sites. It should also be noted that Li⁺ insertion can lead to a phase transition from a Li-poor (tetragonal) phase to a Li-rich (orthorhombic, cubic spinel, cubic rocksalt, etc.) phase.⁶⁴,⁶⁵

Figure 3 shows the galvanostatic discharge/charge curves at a current density of 400 μA cm⁻² and cyclic voltammetric curves cycled between −0.6 V and −2.3 V for the three different TiO₂ nanotube arrays with a tube length of 3 μm. The nanotubes of the back side of Ti foils after anodization are removed for these tests. The absence of voltage plateaus in the curves for amorphous TiO₂ nanotubes (Figs. 3(a)–(b)) is attributed to the considerable disordered structures and defects contained in them. The disordered structures and defects provide many sites for Li⁺ insertion at relatively higher potential during discharging, and thus expand the potential range for Li⁺ insertion reaction. The shape of curves for crystalline TiO₂ nanotubes (Figs. 3(c)–(f)) is in accordance with those reported earlier for anatase TiO₂,⁶¹ and rutile TiO₂ electrodes. Voltage plateaus can be observed in the curves for crystalline TiO₂ nanotubes, which correspond to Li⁺ insertion into or deinsertion from the crystal matrix of anatase or rutile TiO₂. In addition, the first discharge capacity of amorphous nanotubes (0.0912 mA h cm⁻²) is apparently higher than that of anatase nanotubes (0.0538 mA h cm⁻²) and nanotubes...
of mixed phases (0.0631 mA h cm$^{-2}$) at the same current density of 400 $\mu$A cm$^{-2}$, due to the higher Li-ion diffusion coefficient in amorphous TiO$_2$. The disordered structures and defects in amorphous TiO$_2$ not only create large spatial channels for Li-ion diffusion, but also function as scattering sites for electron transport resulting in low electronic conductivity. However, for the nanotubes which are not very long, the Li-ion diffusion coefficient plays a more important role in the cell capacity than the electronic conductivity of the material. Moreover, the Li-ion diffusion coefficient in rutile TiO$_2$ is found to be larger than that in anatase by 4~5 orders of magnitude at room temperature, which may explain why nanotubes of mixed phases have higher capacity than that of anatase nanotubes. In other words, the rutile crystallites in anatase nanotubes facilitate the Li-ion transportation in TiO$_2$.

It can be understood that the Li-ion insertion reaction occurs at the electrolyte-oxide interface on the anode.
Large surface area is beneficial for TiO₂ nanotube arrays to work as a medium that accommodates Li ions, because there are more sites for the Li-ion insertion/deinsertion reaction. Table 1 summarizes the electrochemical performance of different amorphous TiO₂ nanotubes with various tube lengths at a current density of 400 μA cm⁻². Clearly, for the nanotubes on the single side (front side) of Ti foils, the first discharge capacity of nanotubes increases by 11.6 times as the tube length extends from 1.9 μm to 25 μm to create more reaction sites per electrode area. TiO₂ nanotube arrays on double sides of the Ti foil yield more reaction sites resulting in a higher discharge capacity (0.1583 mA h cm⁻²). It has been reported that the amorphous TiO₂ compact layer delivers a capacity of 0.009 mA h cm⁻² at a current density of 5 μA cm⁻². The amorphous TiO₂ nanotubes with a length of 1.9 μm exhibit a capacity of 0.0460 mA h cm⁻² at a current density of 400 μA cm⁻², as shown in Table 1. Hence, the nanotube array shows a capacity five times higher than that of TiO₂ compact layer even when the nanotube array is cycled at a current density 80 times higher than that for the compact layer. These results also indicate that the surface area of TiO₂ nanotube arrays does have significant influence on their areal capacity. Since the length of the nanotubes can reach up to hundreds of micrometers, their discharge capacity may be further improved drastically. The charge process (Li-ion deinsertion) charged to ~0.6 V for these TiO₂ nanotubes delivers charge capacities in a range from 0.0421 mA h cm⁻² to 0.4678 mA h cm⁻², indicating the influence of the lengths of TiO₂ nanotubes on their charge capacities. Moreover, these amorphous nanotubes all exhibit good coulombic efficiency (ratio of charge to discharge capacity) up to 92%, which is beneficial to their cycling performance.

Figure 4 shows the cycling performance of amorphous and crystalline TiO₂ nanotube arrays at a current density of 400 μA cm⁻² for 50 cycles. The nanotubes on the back side of Ti foils are removed for these tests. The results clearly confirm that the specific capacity of amorphous nanotubes is much higher than that of crystalline nanotubes, which suggests that many more Li ions are inserted into amorphous TiO₂ than into crystalline TiO₂. The capacity retention efficiencies measured for amorphous nanotubes, anatase nanotubes and nanotubes of mixed phases are 77%, 67%, and 72%, respectively. The capacity retention efficiency of our amorphous TiO₂ nanotubes is compatible with previous results obtained at a much lower current density. The poorer cycling performance of anatase TiO₂ nanotube array is possibly attributed to the smaller quantity of structural defects in the crystal that favor Li-ion insertion and deinsertion.

The structural stability of TiO₂ nanotube arrays during cycling is also explored. Figures 5(a), (c), and (e) present SEM images of various TiO₂ nanotube arrays (amorphous, anatase, and mixed phases) before electrochemical cycling. These nanotubes are synthesized at 30 V in the EG electrolytes containing 0.3 wt% NH₄F and 10 vol% H₂O, and subsequently annealed at 110 °C for 1 h, 480 °C for 3 h or 580 °C for 3 h. It can be clearly seen that the tubular structure is well-retained despite the annealing process. These anatase and crystalline TiO₂ nanotubes stand separately and are well-aligned, with an average outer diameter of ~119 nm and a length of ~3 μm. A small amount of flocules appear on the surface, possibly due to the shrinkage of the nanotubes during heat treatment. Overall, the morphology of TiO₂ nanotube arrays almost remains unchanged after annealing, showing a high structural stability at elevated temperatures. Figures 5(b), (d), and (f) show the SEM images of these nanotube arrays (amorphous, anatase, mixed phases) after electrochemical cycling at a current density of 400 μA cm⁻² for 50 cycles. It can be seen that both amorphous and crystalline tubular structure are well preserved after cycling, and no discernable damage is found on the walls of these nanotubes. Such high structural stability of TiO₂ nanotube arrays will lead to good capacity retention efficiency as shown in Figure 4.

4. CONCLUSIONS

In summary, we have successfully synthesized high-aspect-ratio TiO₂ nanotube arrays by anodizing Ti foils in EG electrolytes containing NH₄F and H₂O. The dimensions of these nanotubes are controllable by tuning synthesis conditions, such as voltage, electrolyte composition and anodization time. The as-prepared nanotubes are amorphous, and heat treatment can convert them into crystalline nanotubes with identical morphologies. During the annealing process, TiO₂ nanotube arrays show high structural stability.

The amorphous nanotubes, anatase nanotubes, and nanotubes of mixed phases (anatase and rutile) exhibit excellent electrochemical properties. Among the three, the amorphous TiO₂ nanotubes deliver the largest Li-ion intercalation capacity because the Li-ion diffusion coefficient is higher in amorphous TiO₂ than that in crystalline TiO₂. The TiO₂ nanotubes of mixed phases have higher capacity than pure anatase nanotubes, because the formation of rutile phase in anatase nanotubes facilitates the Li-ion transportation. The amorphous TiO₂ nanotube array shows good cycling performance, with a capacity retention efficiency of 77% after 50 cycles. The anatase nanotube array shows less good capacity retention, possibly due to fewer structural defects for Li-ion diffusion in anatase TiO₂. However, all amorphous and crystalline nanotubes show excellent structural stability during cycling tests. Our results further confirm that anodic TiO₂ nanotube arrays could be a potential alternative material for the anode of high-performance Li-ion batteries.

Acknowledgment: Dongsheng Guan would like to acknowledge the LSU Graduate School Supplementary
Awards and Chuan Cai would like to acknowledge the LSU Graduate School Enhancement Award. This work is financially supported by the Louisiana State University Junior Faculty Start-up Funds. The authors would like to thank Materials Characterization Center at LSU for the technical support in using the XRD and SEM.

References and Notes


Received: 15 March 2010. Revised/Accepted: 22 July 2010.