Alternative Li-Ion Battery Electrode Based on Self-Organized Titania Nanotubes

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We investigate the fabrication of an alternative electrode for lithium-ion batteries. The active material consists of self-organized TiO_2 nanotube layers prepared by a simple anodization process. The performances of this type of nanostructured electrode are studied by the combination of structural techniques (Scanning electron microscopy and X-ray diffraction) and electrochemical tests. The discharge/charge properties and cycling performance characteristics are studied for both amorphous and crystalline titania nanotubes. With a maximum areal capacity of 77 μA h cm^{-2}, a good capacity retention up to 90% over 50 cycles, nanotubular TiO_2 is a promising electrode for rechargeable Li-ion microbatteries.

Introduction

Because of its remarkable physical and chemical properties, TiO_2 has found multiple applications in many domains including medicine, environmental protection, and energy storage and conversion. This transition metal oxide has also attracted a great interest for the fabrication of new electrochemical accumulators especially as active electrode material for Li-ion batteries.[1,2]Titanium oxide thin films can be produced by various techniques such as sol−gel, chemical vapor deposition (CVD), physical vapor deposition (PVD) or electrochemical anodization of Ti foils (galvanostatic, potentiostatic or potentiodynamic experiments). However, the properties of TiO_2 can be drastically improved when the material is porous because of the significant increase of the specific surface area. This is the reason why the fabrication of nanostructured titania and particularly self-organized TiO_2 nanotube layers by electrochemical techniques has been the subject of many investigations[3−8] since Kelly reported for the first time the ability to produce porous nanostructured titania by anodization of Ti foils in fluoride-containing medium.[9] Since Macklin and Neat[10] reported the high capacity and reversibility of lithium insertion into titanium oxide (both rutile and anatase) electrodes in lithium batteries, a considerable research effort has been aimed at optimizing and understanding the titanium oxide anode.[11] Recently, the use of different forms of the anatase phase and the synthetic TiO_2 (B) polymorph as lithium-ion host for rechargeable batteries has gained renewed interest.[12,13] TiO_2 is a promising alternative to conventional anodes, because titanium dioxide can operate at higher voltages (~1.7 V vs Li^+ (1M)/Li) than carbon-based electrodes (~0.1 V vs Li^+ (1M)/Li). Thus, a titania-based anode reduces the overall cell voltage but provides cells with enhanced safety, good capacity retention on cycling and low self-discharge. In addition, TiO_2 is chemically stable, economically competitive, nontoxic, and an environmental "White Knight".

The performances of TiO_2 electrodes depend strongly on the crystalline phase, the morphology, and the porosity of the structure. For instance, Bruce and co-workers have reported that the electrode performances can be improved by using TiO_2 nanowires.[14] Jumas and co-workers studied the electrochemical performance of Anatase electrodes, using tin-doped TiO_2, by Mössbauer spectroscopy.[15] At the moment, the most promising tracks for improving the performances of power sources are based on the fabrication of 3D electrodes using organized nanomaterials. One of the most

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spectacular examples of taking the advantages of such nanostructured materials has been reported by Simon et al. for the fabrication of 3D electrodes using a template-assisted method.[16]These nanomaterials-based electrodes can mitigate the rate-limiting effects of sluggish electron transfer kinetics and mass-transport. The large surface area of nanomaterials serves to distribute the current density improving electrode kinetics, whereas the small size ensures that intercalation sites reside close to the surface. Thus, one-dimensional materials that can be produced by self-organization processes, such as nanowires and nanotubes, have opened promising perspectives.

In this work, we report the fabrication and the electrochemical performances of a self-organized titania nanotubes-based electrode. We propose to use a template-free method to prepare the active materials. Here, layers of nanotubular titania (ntTiO_2) are directly produced by a simple anodization process. We show that this kind of morphology can enhance the electrochemical performances of TiO_2 thin films making the nanotubes-based material a promising electrode for Li-ion microbattery application.

Experimental Section

Titanium foils from Sigma-Aldrich, with a thickness of 0.25 mm and 99.7% purity were cut and cleaned by sonicating in acetone, isopropanol and methanol during 30 min. Then, the substrates were rinsed with distilled water, and dried in an Ar stream. The electrochemical anodization of the Ti foils was carried out by potentiostatic experiments in 1 M H_3PO_4 + 1 M NaOH + 0.5 wt % HF electrolyte at room temperature. An electrochemical cell with a two-electrode arrangement was used. The working electrode was a piece of Ti (1.5 cm × 0.6 cm) and a platinum grid of large surface area served as counter electrode. The anodization experiments consisted of applying a constant voltage of 20 V during 240 min using a voltage source (ALS 5010). The anodized Ti samples were immediately rinsed with distilled water and dried in an Ar stream. Optional thermal treatment at 450 °C in air was performed during 3 h. X-ray diffraction (XRD) patterns were recorded at room temperature using a Siemens D5000 diffractometer with Cu Kα radiation (1.5406 Å). Scanning electron microscopy (SEM) images were obtained in a Philips XL-30 FEG SEM.

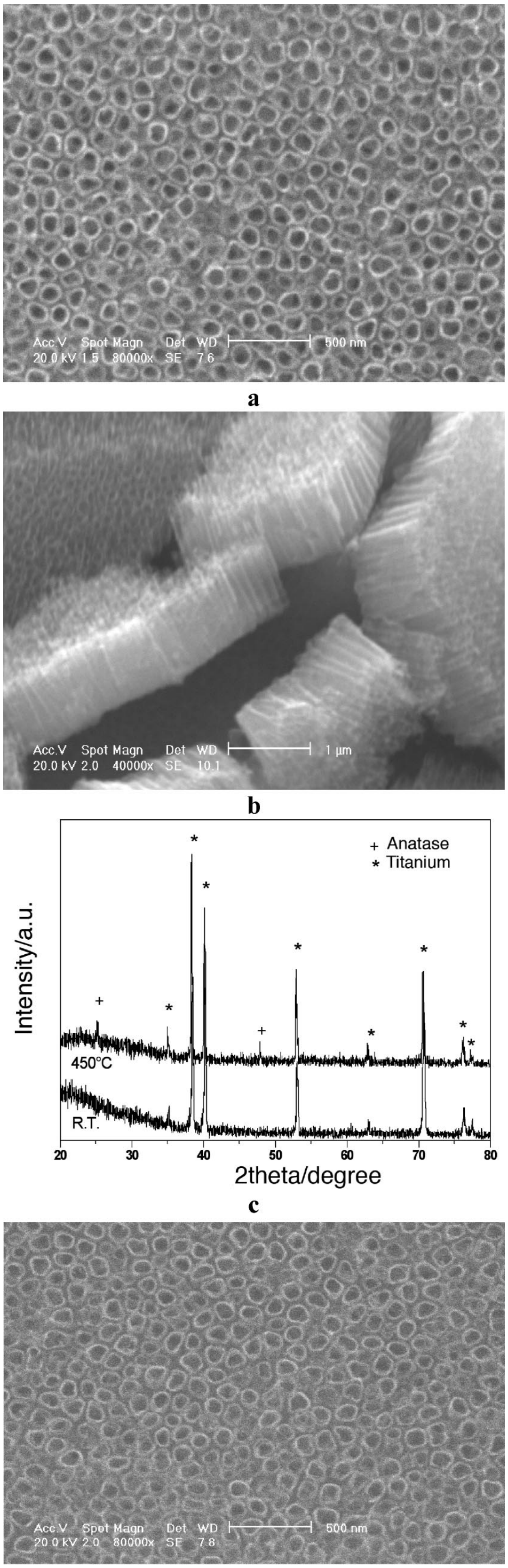
The electrochemical performance of the ntTiO_2 layers was studied by experiments carried out in Li/$LiPF_6$ (EC:DEC)/ntTiO_2 cells. The electrolyte supplied by Merck was embedded in a Whatman glass microfiber acting as a separator and the current collector for the ntTiO_2 was a copper foil (99.99% purity). For these experiments no additives such as poly(vinyl difluoride), that acts as binder agent, and carbon black (conductive agent) were used. Assembling of the cells was performed in a glovebox filled with purified argon in which moisture content and oxygen level were less than 2 ppm. Lithium cells were galvanostatically cycled using an Arbin potentiostat/galvanostat multichannel system. For the discharge/charge reaction a constant current density of 100, 20, and 5 μAcm^{-2} was applied to the assembled cells in the range between 2.6 and 1.0V.

Results and Discussion

The overall cell reaction for the Li insertion/deinsertion into the TiO_2 can be written as:

$$TiO_2 + xLi^+ + xe^- \leftrightarrow Li_xTiO_2 \qquad (1)$$

Insertion of Li into the crystalline anatase phase is possible up to 0.5 Li per Ti reaching a theoretical capacity value of



a

b

c

d

Figure 1. SEM images of TiO_2 nanotube layers after anodization (20 V, 240 min) in a fluoride-containing electrolyte: (a) top view and (b) cross-section of the amorphous titania nanotubes. (c) XRD patterns of TiO_2 nanotube layers obtained at room temperature (RT) and after heat treatment at 450 °C/3 h. (d) Top-view SEM image of ntTiO_2 after thermal treatment.

Table 1. Values of the Reversible and Irreversible Areal Capacities and Efficiency on Cycling of the ntTiO$_2$ Layers Used As Electrodes in Experimental Test Cells at Different Kinetics

electrode	current density (μA cm^{-2})	1st cycle reversible capacity (mA h cm^{-2})	irreversible capacity (mA h cm^{-2})	50th cycle reversible capacity (mA h cm^{-2})	efficiency (%)
amorphous TiO$_2$	5	0.077	0.060	0.055	71
	20	0.050	0.055	0.043	86
	100	0.044	0.036	0.033	75
annealed TiO$_2$	5	0.068	0.027	0.048	71
	20	0.038	0.012	0.031	82
	100	0.030	0.016	0.027	90
amorphous TiO$_2$compact layer	5	0.009	0.008	0.006	67

168 mAhg^{-1} [17]. The anatase phase has a tetragonal structure described by the space group *I*4$_1$/*amd*, in which titanium is surrounded by a distorted oxygen octahedron. Between the TiO$_6$ octahedra, there are vacant octahedral and tetrahedral sites within which Li$^+$ can be accommodated. The electrochemical insertion of lithium ions takes place through a two-phase equilibrium of a Li-poor (tetragonal) and a Li-rich (orthorhombic) phase.[18] It is worth noting that the orthorhombic phase formation is due to the accommodation of donated charge (Li donates an electron to the lattice) in localized Ti-d orbitals with the occupation of degenerate orbitals above a critical intercalation concentration resulting in a cooperative Jahn−Teller-like distortion of the lattice.

SEM images of a ntTiO$_2$ layer electrochemically grown by applying a constant potential of 20V for 240 min are shown in Figure 1. From the top-view (Figure 1a) and the cross sectional (Figure 1b) examination of the layer, it can be observed that the diameter of the nanotubes is about 80 nm, the wall thickness is around 20 nm, and the average tube length is found to be approximately 920 nm. As-formed ntTiO$_2$ nanotube layers are amorphous as determined by XRD (Figure 1c). The annealing of ntTiO$_2$ layers at 450 °C in air during 3 h leads to a partial crystallization into anatase structure. Two new peaks at about 25.3 and 47.9° are detected, corresponding to the (101) and (200) reflections of the anatase phase (JCPDS file 21−1272), respectively. Under these annealing conditions, the microstructure of the nanotubes remains basically unmodified as it can bee seen from the SEM image given in Figure 1d. It is clear that no morphological changes appear in the porous structure after this thermal treatment, which is in agreement with previous data reported by Schmuki's group.[19]

In the following, all capacity values (Table 1) are expressed per electrode area to allow better comparison with literature data for thin film microbatteries. Figure 2a shows the galvanostatic discharge/charge curves vs composition of the as-formed ntTiO$_2$-based electrode cycled between 2.6−1.0 V at a rate of 20 μA cm^{-2} (*C*/2). During the first discharge (Li insertion), the voltage plateau at 1.72 V corresponding to lithium insertion into crystalline TiO$_2$ is not present. Only one pseudoplateau at about 1.15 V contributes to a large irreversible reaction of Li. A total capacity of 105 μA h cm^{-2} is measured at the end of the first discharge with a reversible capacity of 50 μA h cm^{-2}, leading to an irreversible capacity of 55 μAhcm^{-2}. After 50 cycles, the as-prepared ntTiO$_2$ layer shows a reversible capacity of 43 μA h cm^{-2}.

Derivative curves of the as-formed ntTiO$_2$ demonstrate clearly that the process at 1.15 V is irreversible (inset Figure 2a). Moreover, a very broad band in the range of 2.4−1.4 V during discharge and charge is still visible on further cycling. Compared with usual large anatase particles, the surface area that the nanotube layers expose to the electrolyte is higher, which leads to a more facile insertion of lithium. Further-

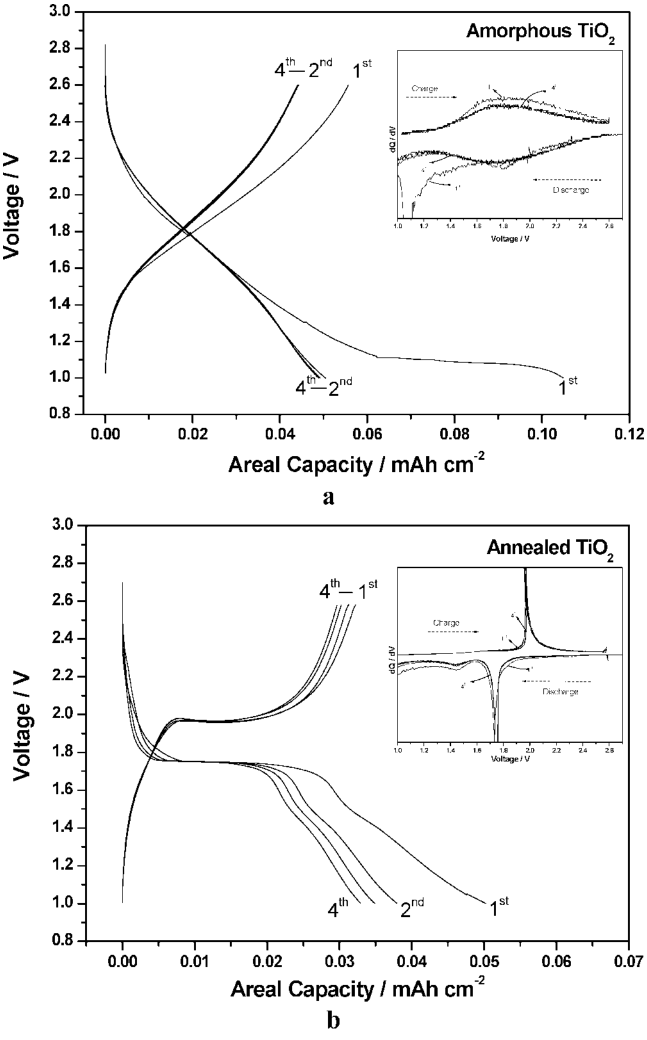


Figure 2. Galvanostatic discharge/charge curves vs composition of TiO$_2$ nanotube layers: (a) as-formed and (b) annealed using 20 μA cm^{-2}. Voltage limits: 2.6−1.0 V. In the insets of the figures are represented the corresponding derivative curves.

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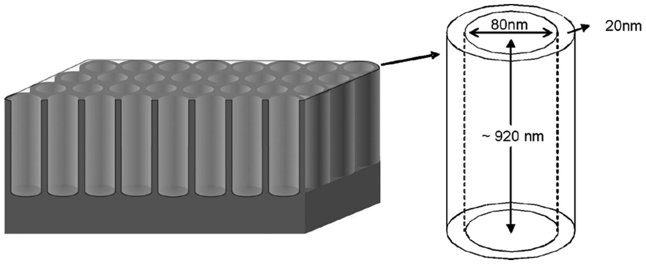

Figure 3. Schematic representation of the self-organized titania nanotubes used for the assessment of the specific area.

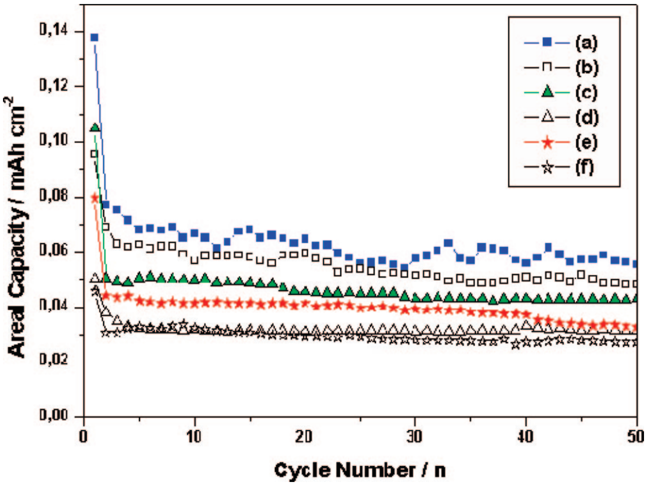

Figure 4. Specific reversible capacity vs cycle number in lithium cells for the as-formed (closed and colored symbols) and annealed TiO_2 (open symbols) nanotube layer cycled at: (a, b) 5 μA cm^{-2} (*C*/8), (c, d) 20 μA cm^{-2} (*C*/2), and (e, f) 100 μA cm^{-2} (2.5*C*).

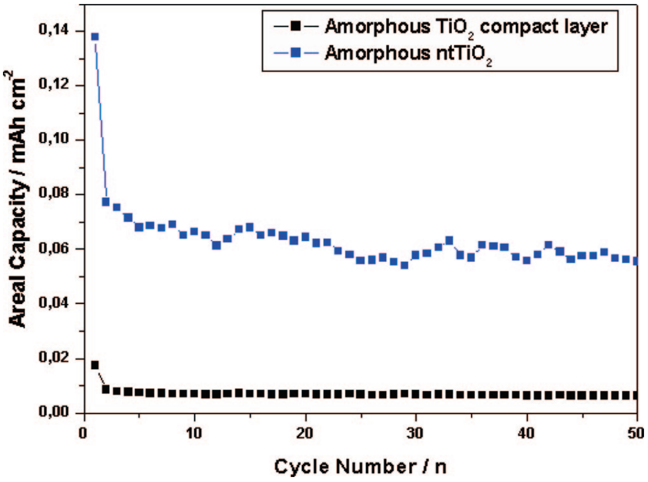

Figure 5. Capacity evolution vs cycle number for an as-formed ntTiO_2 thin film and a TiO_2 compact layer electrochemical grown at 20V during 60 min in 1 M H_3PO_4 + 1 M NaOH electrolyte.

more, the existence of organized 1D nanotubular structures might contribute to a homogeneous insertion process.

After the sample is heated at 450 °C, voltage plateaus are observed during the discharge and charge (Figure 2b) at 1.72 and 2.0 V, respectively, which are attributed to insertion and deinsertion of Li^+ from tetrahedral and octahedral sites of crystalline anatase TiO_2 nanotubes (see also the inset of Figure 2b). The deinsertion potential is slightly higher than in crystalline anatase.[20] After the first discharge, the capacity is 50 μA h cm^{-2} and the reversible capacity is 38 μA h cm^{-2} leading to an irreversible capacity of 12 μA h cm^{-2}. From these results, the irreversible capacity is strongly dependent on the structure of ntTiO_2. To explain the relatively high irreversible capacity, the influence of the reaction between adsorbed water molecules onto the ntTiO_2 electrode and Li^+ has been considered.[21] From the SEM image (Figure 1a) and assuming that the nanotube is a perfect cylinder (Figure 3), it is apparent that the nanotubes are not connected along the vertical axis, leading to a specific area of about 40 cm^2. Assuming that 1 × 10^{15} H_2O molecules/cm^2 can be adsorbed onto the nanotubes, the number of H_2O molecules present onto the nt TiO_2 electrode should be around 4 × 10^{16}, which can react with Li^+ ions according to the following reaction:

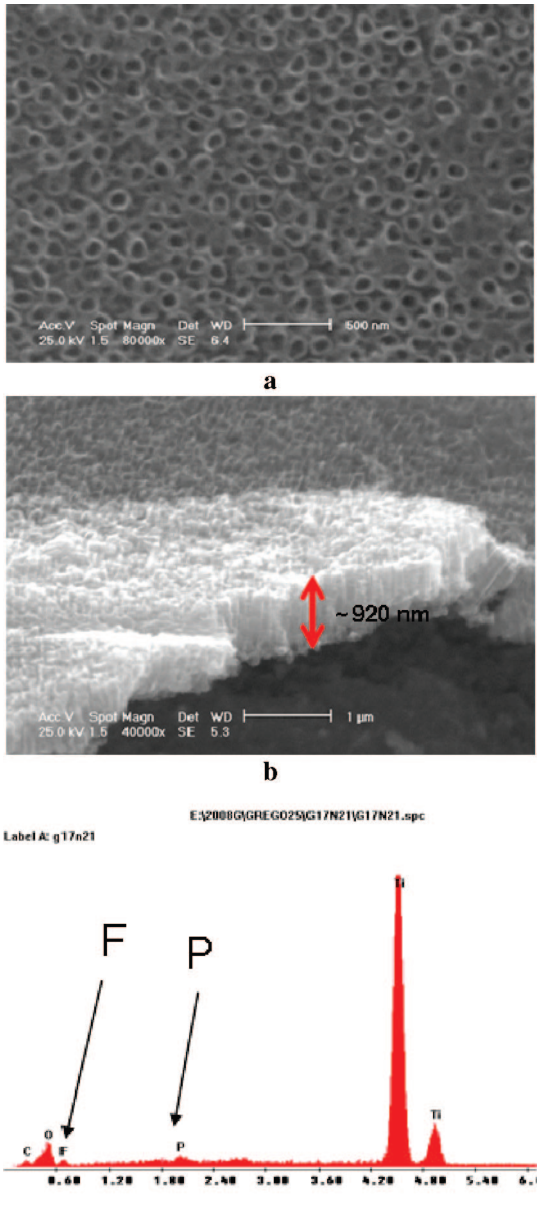

Figure 6. Ex situ SEM measurements from (a) top-view and (b) cross-section of the ntTiO_2 nanotube layer stopped at 2.6 V in the charged state and after the 50th cycle. (c) EDX analysis of the electrode.

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$$H_2O + Li^+ + xe^- \leftrightarrow LiOH + 1/2H_2 \qquad (2)$$

However, the number of Li^+/cm^2 corresponding to the irreversible capacity of 55 and 12 μA h cm^{-2} for both amorphous and crystalline materials is significantly higher, i.e., 1.26×10^{18} and 2.7×10^{17} Li^+/cm^2, respectively. Therefore, the large irreversible capacity obtained for both samples cannot be only attributed to the presence of adsorbed water but also to the formation of a very thin disordered layer at the electrode surface. Considering the numbers given above for irreversibly inserted Li ions and available sites per unit area, this would correspond to insertion in about 30 atomic planes for amorphous tubes and 7 atomic planes for crystalline nanotubes.

It can also be noted that the ratio between the irreversible capacity of the amorphous and the annealed materials is around 5. This difference can be explained by the fact that annealing treatment of the amorphous electrode removes structural and chemical defects that act as Li^+ ion traps, which are responsible for the irreversible insertion of Li^+.

The cycle performance of as-formed and annealed ntTiO_2-based electrodes at different kinetics is illustrated in Figure 4a−f for 50 cycles. First, these results suggest that ntTiO_2 can be used as an alternative electrode for rechargeable Li-ion microbatteries. The specific capacity obtained for the as-prepared samples is higher than for the annealed materials confirming that the amount of lithium ions inserted into amorphous ntTiO_2 is higher than in the crystalline structure. The highest specific capacity is obtained with as-prepared ntTiO_2 layers using a relative slow kinetic (5 μA cm^{-2} or C/8), which delivered a maximum reversible capacity of 77 μA h cm^{-2} after the first cycle and 55 μA h cm^{-2} after 50 cycles (see Figure 4a). The average capacity loss of 0.45 μA h cm^{-2} per cycle leads to a cycling efficiency of 71%. Although lower values of specific capacity are observed using faster kinetics, the efficiency on cycling is improved and can reach 90% in the case of crystalline ntTiO_2 at a rate of 100 μA cm^{-2} or 2.5 C (Figure 4f). The higher efficiency on cycling obtained with crystalline materials compared to amorphous structures is due to the lower amount of structural defects and Li ion trap sites.

To demonstrate that ntTiO_2 layers show enhanced electrochemical properties, the variation of the areal capacity vs cycling has been studied for an as-formed ntTiO_2 thin film and a TiO_2 compact layer electrochemically grown at 20V during 60 min in 1 M H_3PO_4 + 1 M NaOH electrolyte. From Figure 5, it is clearly apparent that the presence of nanotubes leads to a significant improvement of the areal capacity. Compared with other thin layer-based electrodes that have been reported in literature (e.g., MoS_2-based planar Li-ion battery [22]), ntTiO_2 thin films show an areal capacity of 55 μA h cm^{-2} after 50 cycles, suggesting that this electrode can be a potential candidate for the fabrication of 2D microbatteries.

"Post mortem" ex situ SEM images of the electrodes (images a and b in Figure 6) were obtained after the end of the 50th charging cycle at 2.6 V. It is observed that the characteristic nanotube geometry is unchanged after cycling: a tube diameter of about 80 nm, wall thickness of 20 nm (top view), and nanotube length of 920 nm (cross-sectional view). The chemical analysis carried out using energy dispersive X-ray (EDX) spectroscopy (Figure 6c) reveals that there are phosphorus and fluorine impurities. These analyses demonstrate the robustness of the nanotube morphology, which survives after repeated cycling.

Conclusions

We studied the possibility of using self-organized TiO_2 nanotubes as an alternative electrode for lithium-ion batteries. The ntTiO_2 layers are prepared by a simple anodization procedure providing subsequent good electrical contacts between the active materials and the current collector. The powder-free fabrication method used to prepare the active material directly on the current collector tackle the use of additives such as polymer binders and conductive agents (e.g., carbon black).

A specific reversible capacity up to 77 μA h cm^{-2} is achieved in lithium test cells for as-formed ntTiO_2 layers that were 80 nm in diameter and 920 nm in length. We show that using a relatively fast kinetic (100 μA cm^{-2}), the efficiency after 50 cycles is 75%. The possible reasons for the high experimental capacity values are the high surface area and highly organized 1D structure of titania nanotube layers. After thermal treatment, the efficiency on cycling is 90% using faster kinetic (100 μA cm^{-2}) for crystalline nanotubes, suggesting that ntTiO_2 can be used an alternative electrode for rechargeable batteries. Postmortem analysis shows that the ntTiO_2 morphology survives at least 50 cycles.

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