A Study of Titania Nanotube Synthesis in Chloride-Ion-Containing Media

E. Panaitescu, C. Richter and L. Menon

doi: 10.1149/1.2800170

**Email alerting service**  Receive free email alerts when new articles cite this article - sign up in the box at the top right corner of the article or [click here](http://jes.ecsdl.org/subscriptions)

To subscribe to *Journal of The Electrochemical Society* go to:  [http://jes.ecsdl.org/subscriptions](http://jes.ecsdl.org/subscriptions)

© 2007 ECS - The Electrochemical Society
A Study of Titania Nanotube Synthesis in Chloride-Ion-Containing Media

E. Panaitescu,a C. Richter,b and L. Menona,*

*Department of Physics and bDepartment of Chemical Engineering, Northeastern University, Boston, Massachusetts 02115, USA

We have completed a detailed experimental investigation into the recently discovered synthesis of titania nanotubes in chloride-ion-containing media. We show that the role of the chloride ions is catalytic and it has a strong effect in increasing the reactivity of the solution, while the nature of cations has no visible role. We have identified the critical parameters for optimal growth and fast production of nanotubes, and a basic growth mechanism for the tubes is proposed. This opens routes for significant improvements of the method toward uniformity and/or better overall yield, making it a viable alternative to the present established methods.

© 2007 The Electrochemical Society. [DOI: 10.1149/1.2800170] All rights reserved.

Manuscript submitted June 27, 2007; revised manuscript received September 13, 2007.

Titania nanotubes are currently drawing increased interest, as they find numerous applications in solar energy conversion, gas sensing, biophysics,1–3 and others. Fabrication of nanoporous titania and then of titania nanotubes through anodization in hydrotfluoric acid solutions was first reported by Zwilling et al.,4 and by Grimeș and co-workers.5 Furthermore, the research groups of Shankar et al.6 and of Albu et al.7 optimized the growth of long titania nanotubes using alkaline electrolytes with fluorine salts instead of HF as fluoride source and the use of nonaqueous fluoride-containing electrolytes, achieving lengths of over 200 μm and aspect ratios of around 1000:1. Nowadays, about a decade after the first reports, the fabrication of titanium oxide nanotubes in F−-containing electrolytes is a very well-established route and has become the standard for titanium anodization. Systematic experimental studies allowed for tailoring tube characteristics like length, diameter, wall thickness, or shape by identifying the corresponding anodization conditions and new possible applications have been proposed.8

In 2005 Nakayama et al.9 reported that titania nanotubes can be obtained by anodization in a perchloric acid solution.10 Our group recently investigated the rapid synthesis of high-aspect-ratio titania nanotubes by anodization in chloride-containing organic and inorganic acid solutions at voltages lower than 20 V.11 The formation of titania nanotubes using both perchlorate (ClO4−) and chloride (Cl−) solutions and relatively high voltages (over 30 V) was further explored by Hahn et al.12

The present work’s main purpose was to accomplish the systematic study of the anodization conditions and their effect on nanotube formation in chloride-containing solutions. In a previous work13 we studied the role of acid type and of the anodization voltage. We expanded our study to the role of chloride ion concentration and of the cations on the fabrication process. Side experiments also explored pH variation, as well as different titanium foil thicknesses, and viscous electrolytes. From this, we were able to gain a better insight into the synthesis mechanism. A basic synthesis mechanism was subsequently proposed, with an attempt to explain why the tube formation in chloride solutions is much more rapid and violent than in similar fluoride solutions. Critical parameters were also identified, allowing us to optimize the synthesis conditions for better uniformity of nanotubes over the samples and better overall yield.

Experimental

Titanium sheets 0.127 mm thick (Alfa Aesar, 99% purity) were anodized in chloride ions containing acidic solutions. A titanium sheet was placed at the anode and a Pt mesh served as the cathode. We prepared a series of samples in various electrolytes with the active area of the Ti kept constant at 25 × 10 mm. In the first set of samples, we used electrolytes containing varying concentrations of chloride ion, ranging from 0.01 to 0.9 M. For the second set of samples, we prepared electrolytes with different types of chlorides such as NH4Cl, KCl, and CaCl2, all chemicals being reagent grade and acquired from Alfa Aesar. For each of these samples, bundles of titanium oxide nanotubes (diameter up to several micrometers, length up to 50 μm) were continuously formed on the sheets’ surface and released into solution within 1 min of anodization time after the samples were exposed to a constant anodization voltage. Anodization current was measured and recorded throughout the process by using a computer-assisted power supply (Agilent 6811B, Agilent Technologies). The bundles were recovered from the samples or from solution, sonicated in acetone for up to 2 h using a Branson B1510 Sonifier, and then released on a silicon substrate or directly on a transmission electron microscopy (TEM) grid for further examination by scanning electron microscopy (SEM) (Hitachi S4800) or TEM (JEOL 2010F) imaging and analysis.

Results and Discussion

Characterization of nanotubes—Morphological details of the tubes were obtained from electron microscopy images of the powder recovered from the sample or from the precipitate continuously released in the solution. As in previous reports,11–13 no particular variations of nanoscale properties have been observed while varying the anodization conditions. Bundles made of tightly packed tubes with diameters in the 15–40 nm range with an average around 25 nm were observed by SEM imaging. Measurements made on the top-view images of the tightest packed bundles indicate a coverage density of about 800 nanotubes per μm2. This, considering an average o.d. of 25 nm and i.d. of 17 nm for each tube, corresponds to an estimate of 108 μm−1 (108 μm2 per unit μm3) volumetric surface area of the tubes. Many of the tubes remained in the form of grains up to 50 μm length and several micrometers across, even after several hours of sonication (Fig. 1a). The individual tubes that have been released after sonication were much shorter, of the order of 3 μm (aspect ratio up to 150). This suggests that individual tubes are very brittle (Fig. 1b), as observed also in the case of tubes obtained by the hydrothermal method.14 One can also observe the presence of individual tubes of various lengths before and after sonication, particularly of many hemispherical particles of the same diameter as the tubes, of the order of 20 nm (Fig. 1b, Fig. 7). The latter may provide insight into the strength of the reaction, as we discuss in the next section.

Figure 2 presents high-resolution TEM (HRTEM) images of the individual nanotubes, confirming the diameter of about 20 nm, with a wall thickness of about 5 nm. The tubes are in an amorphous state, similar to those synthesized in fluoride-containing media. The apparent contamination of the tubes with particles up to 5 nm in di-
ameter was not a rule (see, for example, the tubes in Fig. 7), and these impurities could form rather during the sample preparation for imaging (repeated washing, sonication) than during tube formation. However, EDAX measurement confirmed the 1:2 ratio of titanium to oxygen as reported earlier, and traces of chlorine (less than 5%) and carbon content which cannot be analytically interpreted due to the carbon content of the TEM grids.

**Synthesis conditions.**—As discussed in a previous work, anodization current as a function of time can provide good insight into the reactivity of the solution, which in turn can be related to the formation speed and total yield of nanotubes. A typical anodization current vs time plot (Fig. 9) is quite similar to the current vs time plot obtained in the case of porous alumina or titanium oxide nanotubes arrays in fluoride-containing media. Initially, an abrupt initial drop of current is observed which is attributed to the formation of a titanium oxide film on the surface of the sample. This is followed by a plateau region where the nanotubes form. The average magnitude of plateau current is directly related to the reactivity of the solution, while the smoothness of the plateau current can be correlated with the uniformity of tube formation. In a previous work, the chloride ion concentration was maintained at 0.4 M and it was noted that the average plateau current exponentially increases with anodization voltage. For different acids, we identified a threshold voltage around the value of 11 V associated with plateau currents of the order of 1 mA/cm², below which nanotube formation is not detected after the initial formation of oxide layer.

In this work we analyzed the role of chloride ion concentration, nature of the cations, pH of the solution, and nature of the electrolyte on the tube formation. The plots in Fig. 3 show the dependence of the plateau current on chloride concentration for two different anodization voltages. This in turn may be related to the dependence of the reactivity on the chloride ion concentration. For anodization voltage, \( V_a = 11 \) V, identified as a threshold value in previous experiments at 0.4 M [Cl⁻], we observed nanotube formation for concentrations above 0.5 M for hydrochloric acid and 0.7 M for formic acid. Thus, a decrease of the threshold voltage is seen at high concentrations. Conversely at 13 V, a value well above the thresh-

**Figure 2.** HRTEM images of the amorphous TiO₂ nanotubes.

**Figure 3.** Dependence of the average plateau current with the chloride ion concentration of the solution for different anodization voltages: (a) \( V = 11 \) V and (b) \( V = 13 \) V. The plateau current displays a slow almost linear value increase with voltage below the threshold linear value. At and above the threshold potential an “exponential-like” increase is obtained, critical behavior that is consistent with the mechanism proposed.
old at 0.4 M [Cl\textsuperscript{−}] barely leads to tube formation for small concentrations around 0.1 M. This suggests that the threshold voltage is higher at smaller concentrations.

A similar experiment has been carried out in order to identify the influence of cation nature on nanotube formation. For this, the “standard” ammonium chloride salt has been replaced by potassium chloride and calcium chloride, respectively, keeping constant the other conditions such as voltage and chloride ion concentration. Figure 4 is a plot of the anodization plateau for the three different salts at three different voltages. No significant dependence with the cation nature can be identified in the 11–16 V range. Slight variations are thought to be a result of different dissociation constants of the salts.

Experiments have also been conducted in order to identify the role of other parameters, such as pH of the solution. Using slight variations in the hydrochloric acid concentration while keeping constant the overall chloride ion concentration and the anodization voltage, we varied the pH of the solution in the range 1–3 without significant variations in other parameters. As expected, a slight increase of reactivity is observed with increasing acidity of the solution (decreasing the pH), but no significant role can be attributed to this parameter.

As a conclusion, the previously introduced notion of threshold voltage can be generalized to include a whole set of threshold parameters, the anodization voltage, and chloride concentration being the most important.

Discussion.—Synthesis mechanism.—From the above analysis, we have obtained important insight into the mechanism, resulting in the extremely rapid etching and nanotube formation apparently catalyzed by chloride. First of all, as is the case with other anodization methods, we are dealing with a competition between two main processes: formation of an oxide layer at the surface of the sample (oxidation) and its dissolution in chlorine species (corrosion). Extreme conditions (e.g., very low or very high anodization voltage) can decisively turn the balance in favor of oxidation or corrosion, respectively. For intermediate conditions, a local equilibrium is reached, giving birth to patterns such as the porous alumina or titania nanotubes or nanopores.

The simplest explanation for the high reactivity is that chloride ions penetrate and break down the pacifying titanium oxide layer under sufficiently high bias voltage. Although such chloride-induced oxide dissolution has indeed been observed in the case of aluminum oxide,\textsuperscript{17} the strongly hygroscopic nature of the chlorination products of titanium make this mechanism very unlikely.\textsuperscript{18} In the case of titanium chlorination products rapidly react with water to form oxy-

chlorides and hydrated oxides that typically build up on the surface and stop further chlorination. Also weighing in against this “simple explanation” of the chloride-induced reactivity underlying nanotube formation is the finding by D’Agostino et al.\textsuperscript{19} that chloride ions are a lot less mobile and able to penetrate titanium oxide than ions like fluorine or oxygen species (OH\textsuperscript{−}, O\textsuperscript{2−}, etc.). Hence, based on this finding one may expect that a higher bias voltage should perhaps favor the supply of oxygen species above chlorine species and thus have a stabilizing effect on oxide formation.

A possible clue to the mechanism responsible for the high chlorine reactivity observed is supplied by the findings of Rojas et al.\textsuperscript{20} and Arikawa et al.\textsuperscript{21} Rojas and co-workers studied the relative evolution of O\textsubscript{2} and Cl\textsubscript{2} on TiO\textsubscript{2}-Pt electrodes. As one would expect, they found that the rates of both gas evolution reactions decrease as the titanium oxide layer thickness is increased, inhibiting electron transfer. However, they found that the reduction in the rate of oxygen evolution with oxide thickness is much more rapid than that of chlorine, that is, thicker oxide shifts the selectivity of the gas evolution reaction away from oxygen toward chlorine. A similar result was reported by Arikawa et al.\textsuperscript{21} They found that the threshold bias potential at which oxygen and chlorine evolution starts increases as the width of the initial titanium oxide layer is increased. Moreover, they found that this increase in threshold is significantly more rapid for oxygen than it is for chlorine. These results indicate that the oxidation of chloride ions (Cl\textsuperscript{−}) gains in prevalence relative to the oxidation of oxygen species (primarily OH\textsuperscript{−}) as oxide thickness increases. We have recently shown that the titanium oxide barrier layer thickness of titania nanotubes increases with increasing anodization voltage,\textsuperscript{22} a result that is analogous to the anodization behavior of aluminum and other metals.\textsuperscript{23} Together, these experimental observations suggest the following:

1. When a new titanium foil is first introduced into the electrolyte, the oxide layer is thin and the oxidation of oxygen species proceeds much more rapidly than that of chlorine species, resulting in the evolution of oxygen and, more importantly, rapid oxidation and thickening of the oxide layer by the overall anodic reaction

\[
2 \text{OH}^{−}(\text{aq}) + \text{Ti}(s) \rightarrow \text{TiO}_2(s) + 2\text{H}^{+}(\text{aq}) + 4e^{−}
\]

2. The barrier oxide thickness (δ) increases by this mechanism until a steady-state barrier thickness (δSS) is reached, where electron transfer becomes sufficiently slow so that titanium atoms at the electrolyte surface are preferentially dissolved instead of being reincorporated into the oxide layer. This steady state with very slow titanium etching is what the system evolves to if there is no chlorides present in the electrolyte. This slow-etching steady state can apparently also be maintained even in the presence of chlorides, as long as the voltage is low enough, below the system-specific threshold voltage discussed above. If chloride is present in the electrolyte, the chlorine species competes with oxygen species for oxidation at the anode. This can have one of two outcomes.

For a low anodization voltage δSS(V) is thin enough so that oxidation of oxygen species still dominates that of chlorine species, even after the oxide thickness reaches the steady-state value δ = δSS. Hence, in spite of the presence of chlorides the barrier layer thickness will, at low applied voltages, approach a steady-state thickness that is close to its steady-state thickness [δSS(V)] in a chloride-free electrolyte. Subsequently, reactivity is low and etching slow. This is indeed what we observe if subthreshold voltages are used.

For higher anodization voltages, a critical point is reached where δ becomes sufficiently large so that chlorine chemistry begins to be competitive with oxygen chemistry. This reduces the rate of oxida-

---

Figure 4. Average plateau current for different cations. No significant dependence is observed in the range of voltages 11–16 V.
ortion of oxygen species and interferes with the mechanism responsible for oxide growth in step 1. That is, as relatively less hydroxyl ions are oxidized there are fewer oxygen ions and radicals at the electrode surface. A decrease in these oxygen species at the surface leads to a relative decrease in the fraction of Ti$^{4+/3+}$ that gets reincorporated into the oxide layer with an increase in the relative number of Ti$^{3+/4+}$ ions that are etched (i.e., dissolve into the solution, forming complexes like TiF$_n^{3+}$, TiOH$^{+}$, TiF$_3$(OH)$_2$$^{−}$, etc.,$^{24,25}$ Hence, under the influence of chloride ions we expect that the oxide thickness will approach a new thinner, steady-state oxide layer ($\delta_{SS}$) as the balance is swayed toward the etching of, and away from reincorporation of, Ti ions.

The situation can be summarized as follows

\[ V \text{ low } \Rightarrow \delta \rightarrow \delta_{SS} \approx \delta_{SS} \]
\[ V \text{ high } \Rightarrow \delta \rightarrow \delta_{SS}^* < \delta_{SS} \]

However, higher $V$ means that the rate of inward migration or diffusion of oxygen atoms is sped up. In fact, to a first order the solid diffusion of these atoms through the oxide layer is proportional to the gradient of the potential (i.e., the force), and because most of the potential drop occurs across the barrier layer, we can write for the diffusive flux

\[ \phi \propto \frac{V}{\delta} \]

Therefore, it is clear that the combination of a higher potential and a thinner barrier layer ($\delta \rightarrow \delta_{SS} < \delta_{SS}$) results in a very reactive situation. At higher anodization voltages chlorine inhibits the growth of a pacifying oxide layer, with the result that the inward migration of oxygen atoms and oxidation of titanium are maintained at their rapid initial levels. At the same time, titanium atoms at the electrolyte–oxide interface can be swept away, either by dissolution with chlorine species or with hydroxyl ions that are, at higher voltages, less likely to be oxidized themselves than is Cl$^−$. Because of the hygroscopic nature of most chorine products, the latter mechanism is likely to dominate.

The experimental data are in agreement with the mechanism proposed. No nanotubes are formed at lower voltages, and after an initial surge the anodization current approaches a very low steady-state value, typically less than 1 mA/cm². Beyond a threshold voltage the anodization current rapidly increases by at least one order of magnitude. The rapid evolution of hydrogen at the cathode is visible as vigorous bubbling of the reaction vessel. That a significant amount of chlorine gas is also evolved at the anode is indicated by a distinctive chlorine odor.

- It is true in the case of both porous alumina and titania nanotubes grown in fluoride electrolytes that a thinner barrier layer and smaller pore or tube diameters are obtained. The mechanism proposed here is consistent with the fact that the new chloride nanotubes have smaller diameters than any other grown in fluoride-based electrolytes is consistent with this trend. We have found that nanotubes anodized at 15 V in fluoride electrolytes typically have diameters of $\sim$50 nm (nanotubes were fabricated in a 0.5 wt % HF solution as described elsewhere).$^{16}$ In fact, the smallest diameter fluoride-based tubes obtained by us with hydrogen fluoride (HF) electrolytes$^{16}$ are on average $\sim$30 nm. At lower voltage there is a transition from tubes to pores that can have diameters down to 15 nm.$^{16,26}$

- The chloride tubes reported here, anodized at 15 V, have diameters of around 25 nm. Hence, the mechanism proposed here, suggesting that in chloride ion containing electrolytes a thinner barrier layer with higher voltage gradient forms, is consistent with the fact that these tubes consistently have small diameters and are long (very rapidly etched).

Although one should perhaps be careful in drawing parallels between dielectric or passivity breakdown as it occurs in the context of macroscopic phenomena like pitting and corrosion, the mechanism proposed above (responsible for creating a very nonpassive/reactive surface) has some features in common with mechanisms proposed for the above-mentioned phenomena in chloride media. In particular, the findings of Ahn et al. (leading to a hypothesis similar to the earlier work of Foroulis and Thubrikar$^{17}$), supporting the theory that it is metal cation vacancy generation at the barrier layer/solution interface that is responsible for the depassivation of iron and nickel oxide films, are very similar to the mechanism described above where chlorine-enhanced cation dissolution also plays a critical role.
Discussion.— Process optimization.— Our experimental investigation into the synthesis conditions offers a statistically averaged view of the phenomena involved by dealing with macroscopic quantities such as average anodization current, anodization voltage, and average chloride concentration. The values of these quantities show good reproducibility, so they offer an accurate global view of the anodization process. The anodization of titanium in chloride aqueous solutions occurs in a much more violent way than in fluoride, with several orders of magnitude bigger speeds of tube formation. This provides an important advantage regarding the synthesis time, but the trade-off is a dramatic loss in the uniformity of the tube formation, both individually for each tube and globally over the sample surface. As observed also by Hahn et al.,12 the dissolution action of chlorine species under voltage bias is much more sensitive to slight variations in the electric field and/or in the sample uniformity, local behavior being drastically different from one place to another. This imposes a more careful study of the local phenomena involved.

Figure 5 provides visual information regarding localized tube formation in chloride-containing media. It occurs more likely in pre-existing sites of local disruption of the titanium foil uniformity, such as the edges (Fig. 5c) or along linear patterns formed during the titanium sheet fabrication (Fig. 5b). These disruptions are also the sites of local spikes in the electric field, the combination of the two most important factors in tube formation generating an avalanche effect in that area and leaving neighboring areas less affected (Fig. 5a). Experiments with various thickness of the initial titanium foil further highlight this trend, as very thin (32 μm) foils were found to need smaller anodization voltages for the breakdown of the titanium oxide pacifying layer, and the tube formation occurred practically only at the edges of the samples.

In addition, the ultrarapid reaction leaves no time for relaxation of the processes and accommodation of the increased volume associated with the nanotube formation, so that the uniform tube arrays tend to form locally on areas several square micrometers wide (Fig. 6a). These areas experience a violent burst of material, possibly due to some local gas bubbling, but more probably due to the local mechanical stress imposed by surrounding areas of unaffected titanium oxide which are not allowing the increase in volume associated with the formation of the nanotubes. The result is a periodic release of tubes in the solution, as debris of these local “explosions” most often in the form of grains or bundles of various sizes, leaving part of them still attached to the sample, usually in a flowerlike pattern (Fig. 6b).

The reaction speed can also play an important role in the formation of defects in individual tubes, causing segmentation and brittleness. These effects can proceed to such an extent that they cause interruption in tube formation right from the start and the release in the solution of the initial layer made of hemispherically shaped particles of the same diameter as the tubes (Fig. 7).
A possible solution for a smoother and a more uniform tube formation is the extensive cleaning and polishing of the sample, and careful setup for uniform distribution of electric field and chloride concentration. The use of nonaqueous electrolytes may extend the range of equilibrium conditions in the same way as for fluoride media, preliminary experiments showing a much smoother shape of the plateau current vs time, but with formation of only sponge-like structures, without any tubular organization. These optimizations can ultimately lead to uniform arrays of nanotubes but may also increase the time of fabrication up to tens of hours.

Another solution is to prepattern the sample in order to provide a uniform distribution of defects all over the foil. To test this idea, we preanodized the samples first in a hydrofluoric acid solution (0.5 wt %) for several minutes, resulting in the covering of the sample with a thin nanoporous/nanotubular titanium oxide film (Fig. 8a). The second anodization in standard conditions ($V = 13 \text{ V}$) in a chloride-based solution ($\sim 0.02 \text{ M HCl, 0.2 M NH}_4\text{Cl, pH 1.65}$) yielded a total, more uniform coverage of the sample with tube formation sites (for a comparison of sample coverage without and with preanodization in HF, one can check Fig. 5b and Fig. 8b, respectively). This would result in a more efficient usage of the titanium foil, and in a production of large quantities (of the order of grams) titanium oxide tubes precipitate/powder in less than 2 h. Further optimization of this method may provide a fast alternative route for the production of titanium oxide nanotube powders, now routinely synthesized via a hydrothermal method derived from the one pioneered by Kasuga et al. 28

Finally, another indication of the fact that the prepatterned anodization indeed leads to a more uniform tube formation is provided by the current vs time plot (Fig. 9). For similar anodization conditions, the preanodized foil exhibits a higher value of the plateau current (more formation sites present) and also a smoother evolution of anodization current (three times smaller percentage standard deviation), indicating that the tube formation process occurs closer to the desired steady-state rate.

**Conclusion**

In conclusion, we have carried out an extensive investigation into the synthesis of titanium oxide nanotubes in chloride-ion-containing solutions. This helped us to propose a basic electrochemical model of the nanotube formation. The anodization voltage and chloride concentration of the solution have been identified as the most important parameters which trigger tube formation and furthermore, the reactivity, speed, and smoothness of the process. When triggered, the very high speed and reactivity of the process make the task of adjusting the conditions in order to achieve a steady state and to obtain ordered arrays of nanotubes much harder than in the case of anodization in fluoride media. On the other hand, we demonstrated that by using a simple prepatterning method, we increased dramatically the uniformity of tube synthesis over the sample, thus increasing the total yield of nanotubes containing precipitate and achieving an optimal usage of the initial titanium sheet.

**Northeastern University assisted in meeting the publication costs of this article.**

**References**


![Figure 8](Image 75x437 to 315x755.png)

Figure 8. SEM images of the sample surface (a) after the first anodization in a HF solution and (b) after the second anodization in a chloride-containing solution.

![Figure 9](Image 342x564 to 582x755.png)

Figure 9. Current vs time plot for two samples anodized in “standard” chloride-containing solutions ($\sim 0.02 \text{ M HCl, 0.2 M NH}_4\text{Cl, pH 1.65}$), with and without preanodization in 0.5 wt % hydrofluoric acid solution.