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Oxide Growth Efficiencies and Self-Organization of TiO2 Nanotubes

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Self-ordering phenomena during anodic oxidation of metals and the formation of porous oxides have been of a high interest to science and technology for more than 50 years. Particularly, after Masuda et al. demonstrated highly ordered porous alumina by fine tuning the experimental parameters during aluminum anodization, these structures were increasingly used as a template for the deposition and growth of a large variety of 1D functional materials.

For some time, such self-organized oxide structures seemed to be limited to Al2O3, but in 1999 Zwilling et al. reported on self-organized oxide structures (aligned nanotubes) anodically grown on Ti in a dilute fluoride solution. Dilute fluoride electrolytes were then found applicable to grow ordered tubular or porous oxides on a large range of other metals and alloys. Over the past years, the control over the morphology (diameter, length, smoothness of the walls) was strongly improved by continuously optimizing the anodizing conditions (see e.g. reviews in Refs. 16, 17). It was recognized that pore and tube formation follow the same basic concepts and that in certain cases also Cl−, ClO4− or NO3− can provide conditions for self-organization. Nevertheless, the vast majority of research work has been directed toward TiO2 nanotubes, as TiO2 with its semiconducting nature makes the nanotubular structures promising for use in solar cells, photocatalysis, sensors, and also Cl−, NO3− or F− electrolytes can provide conditions for self-organization.

The experimental optimization of growth parameters led to various semi-quantitative or qualitative models that provide a mechanistic reasoning for the occurrence of self-organization. Concepts that mainly originate from porous alumina growth ascribe the key role for self-organization to: stress at the metal-oxide interface (volume expansion/electrostriction), repulsion of electric fields, or establishing maximum current flow conditions.

Theoretical modeling of self-organized structures grown anodically on valve metals started with the discovery of alumina pores several decades ago by Rummel and Baumann. While approaches were increased, a main source of difficulty remained the multitude of experimental factors which influence the growth of self-organized nanostructures. However, recently a comparably simple but fully quantitative model was proposed which provides the necessary boundary conditions to achieve the growth of ordered anodic structures. In essence, the model predicts that self-organization (perceived as a maintained instability) is only possible for a certain narrow range of oxide formation efficiencies. In other words, during anodic oxidation, except for oxide formation, a certain amount of “oxide dissolution” has to be established – which is well in line with early experimental observations. For example, to achieve self-organizing conditions to form TiO2 nanotubes, a steady-state situation according to equations 1-3 is needed, i.e. a certain level of solubility of TiO2 during anodization of Ti49 is required. This is mainly determined by the amount of fluorides present in the electrolyte, as formed TiF62− complexes are highly soluble in many electrolytes.

The theoretically predicted range of self-organization depends on the metal ion charge and on the volume change upon oxide growth (Pilling-Bedworth ratio). For TiO2 the necessary oxide formation efficiency was calculated to be from 0.50 to 0.58. If the dissolution rate is low and thus the efficiencies are higher than the limit, a compact “flat” oxide is expected to form which prevents self-organization and continued oxide production. If dissolution is too high, i.e. the efficiency is below the predicted range, the minimum pore spacing is unrestricted, leading to irregular and branched pore structures or in the extreme case to electropolishing. The goal of the present work is to experimentally investigate the validity of this simple model for the formation of ordered TiO2 nanotube layers and to address empirical issues in determining oxide growth efficiencies.

Experimental

TiO2 nanotube preparation and characterization. — As substrates for TiO2 nanotube growth, we used titanium foil (99.6% purity, Goodfellow) with a thickness of 0.125 mm. Prior to tube formation, the foils were ground with SiC abrasive paper (P2400) and cleaned by sonication in acetone and ethanol, followed by rinsing with deionized water and drying in a nitrogen stream. To grow TiO2 nanotubes, the Ti foils were anodized by using a high-voltage potentiostat (Jaisle IMP 88 PC) in a three-electrode configuration with reference and counter electrodes made of platinum. The anodization area was 0.91 cm². Anodization was carried out at room temperature (22°C) in galvanostatic or potentiostatic modes in ethylene glycol (Fluka, assay ≥ 99.5%, H2O ≤0.1%) with addition of 0.1M or 0.2M (NH4)2F (Fluka) using two different water contents of 1.5 wt% and 5 wt%. For the galvanostatic mode we used currents of 0.5 mA, 1 mA, 2 mA and 3 mA. In potentiostatic mode, the applied voltages were either 20 V or 50 V. The anodization time was varied from 1 min to 16 h.
After anodization, and before the samples were removed from the electrochemical cell, the electrolyte was stirred for 2–4 min to homogenize concentration gradients. This step was found in preliminary experiments very important to minimize a systematic error that can arise from re-precipitation effects during rinsing, due to the high ion concentrations inside the nanotubes. Samples were then removed from the electrochemical cell and cleaned with ethanol, followed by their immersion in a beaker with ethanol for about 1 h - finally they were dried in air.

The morphology of the samples (of detached TiO2 nanotubular layers) was evaluated with a Field-Emission Scanning Electron Microscope (Hitachi FE-SEM S4800) equipped with an EDX-detector (Genesis 4000) for compositional analysis.

Data evaluation.— To obtain information on the oxide growth efficiency, electrolyte and oxide were analyzed by two techniques as outlined in Figure 1. The first one was based on combined solution analysis and weight gain/loss measurements. Before anodization, after the tube growth procedure, and after complete mechanical detachment of the nanotubular layer from titanium foil, samples were weighed with METTLER TOLEDO AG135 balance with an accuracy of 0.01 mg. The concentration of titanium dissolved in the electrolyte was measured by Inductively Coupled Plasma Spectroscopy (ICP-AES Spectro Ciros CCD). The second approach is based on determining the weight of the oxide layer, its composition by EDX, and the increase in voltage results in a highly conical shape of the nanotubes originating from thinning (etching) of upper parts of the disordered porous layer. In the galvanostatic mode lower initial dissolution loss occurs, and at low current nanotubes can grow directly from first stage virtually without any initiation layer (compact or porous) (Figure 2f). Additionally, in the galvanostatic mode the slow increase in voltage results in a highly conical shape of the nanotubes (Figure 2b, inset).

Figure 2a and 2b show typical examples of the electrochemical characteristics during TiO2 nanotube formation under potentiostatic and galvanostatic modes, as well as typical morphologies obtained in this process. These anodization reactions were carried out using a set of parameters (voltage, fluoride concentration, water content) where self-organization occurs. Changing parameters such as voltage (potentiostatic), current (galvanostatic), water and fluoride contents, acidity, and temperature over a certain range, still self-organization will occur. However, if parameters are beyond certain values self-ordering is lost, i.e. different defective non-ordered structures are obtained such as sponges, precipitates, localized breakdown events, or for low fluoride concentrations and low voltages simply a compact layer is formed.

In the following we address some features of self-organized tube growth that should be considered when evaluating oxide growth efficiencies. First, it should be noted that, for successful tube formation there are some distinct differences between potentiostatic and galvanostatic approaches. In the potentiostatic mode, the fixed voltage leads to a fast oxide formation in the initial phase, with a typical exponential decrease of the current to seemingly a steady state as in Figure 2a.16 The growth of self-organized tubes follows several stages: First, the surface becomes covered with a compact high field oxide. Then, this layer becomes penetrated by nanoscopic channels and initiation and growth of nanotubes occurs (Figure 2c, 2d), and eventually the growth process reaches a steady-state situation.16,17 The outer diameter of the TiO2 nanotubes remains constant during potentiostatic anodization and is controlled by the applied voltage (Figure 2a, inset).

In the galvanostatic mode, in analogy, an increase in the voltage drop over time is observed that finally reaches a (more or less) steady state plateau. It is evident that surface oxidation in the initial state is better controlled in the galvanostatic mode as typically much less charge is passed in the first stages of anodization – this generally leads to a thinner initiation layer. For example in Figure 2a, in the potentiostatic mode, a high current flow takes place - the peak of about 65 mA is limited by the electrolyte resistance. In the galvanostatic mode (Figure 2b) the current is set to few mA, and a much slower oxide formation occurs. Figure 2e shows typical morphologies obtained for very high anodization rates and Figure 2f for lower anodization rates in the first stages of anodization. High anodization rates generally lead to lower efficiencies of oxide growth as shown previously,58,51 i.e., due to the higher active dissolution the conditions may well be outside of the lower border of predicted range of the model,59 and the obtained initiation layer consists of non-uniform and disordered pores of different sizes (Figure 2e). However, in the later stages as steady-state oxide film growth is established, a decrease and leveling of dissolution losses is expected, and conditions for self-organization can be established. As a result ordered nanotubes then grow underneath the disordered porous layer. In the galvanostatic mode lower initial dissolution loss occurs, and at low current nanotubes can grow directly from first stage virtually without any initiation layer (compact or porous) (Figure 2f). Additionally, in the galvanostatic mode the slow increase in voltage results in a highly conical shape of the nanotubes (Figure 2b, inset).

Another point that should be considered in galvanostatic and potentiostatic modes is that after extended anodization the typical surface morphologies of the tubes show “grass” formation (Figure 3) – this morphology originates from thinning (etching) of upper parts of the TiO2 nanotubes that reside the longest in the electrolyte and collapse in bundles. The length of nanotubes increases linearly with the total passed charge (Figure 3a) until this tube collapse occurs (Figure 3b).

In this context, to evaluate the rate of purely chemical dissolution we exposed a freshly prepared nanotube layer to an anodization electrolyte for 16 h and determined the Ti4+ content via ICP. The measured chemical dissolution amount resulted as 2.6% of the total dissolved titanium during anodization, i.e. this error on growth efficiency measurements is comparably small.

In contrast to this, a main source of error is caused by precipitates during the anodization process that shift experimental values to a too high value. Figure 3c and 3d illustrate these precipitates if very high fluoride contents are used (e.g. 1 mol L−1). The crystallites visible in the image are (NH4)2TiF6, as analyzed before.17 The formation of such crystallites to a large extent depends on the current density: for the higher current densities and larger anodization times considerable amounts can be detected in SEM investigations (local Ti4+ concentration, the NH4+ concentration, and the fluoride concentration in the electrolyte).

In general one may consider to evaluate growth efficiencies from faradaic currents plus microscopic measurements. In this case one could evaluate the thickness of the nanotube layer and the thickness of...
Figure 2. a) I-t curve of TiO2 nanotubes grown under potentiostatic mode at reference voltage of 50V. The inset represents SEM cross-section view of the nanotubes after 1h of anodization at 50V; b) Typical U-t curve of TiO2 nanotube growth under galvanostatic mode at set current of 1 mA. The insets represent HR-SEM cross-section view near the top and bottom of nanotubes after 1h of anodization at 1 mA; c) Top view of the compact initial oxide formed in a potentiostatic mode at 50V; d) Bottom view of nanotubes formed at 50 V; e) Example of disordered porous layer formed on top of nanotubes in galvanostatic mode at 1 mA; f) Example of SEM top view of nanotubes formed in galvanostatic mode at 0.5 mA, where because of the low current density no disordered initiation layer was produced. The used electrolyte for a)–e) was EG + 0.1M (NH4F) + ∼1.5wt%(H2O) and for f) was EG + 0.1M (NH4F) + ∼5wt%(H2O).

Consumed metallic titanium (Figure 1a). However, such an evaluation turns out to be very unreliable. An important point is that during TiO2 nanotube growth an unusual length expansion occurs – i.e. the tubes grow significantly longer than expected from the Pilling-Bedworth-ratio – this finding was used to support the field-assisted flow of oxide during nanotube growth.37,52 For the nanotubes grown in fluoride-containing ethylene glycol the expansion factor is 2.7–3.1 and it is similar to nanotubes grown in glycerol.52 Nevertheless, the expansion ratio is, for example, time dependent52 and due to the uncertainties involved, a direct deduction of oxide efficiency based on SEM cross-sections was found very difficult (due to different degree of layer porosity, incorporation of electrolytes species in the oxide layer and assumptions on faradaic efficiencies etc.).

Nevertheless, by combining Faraday’s law with total consumed titanium from weighing analysis one may calculate the current efficiency (Figure 4a).17,53–57 From Figure 4a it can be seen that a side reaction (likely O2 evolution58) occurs and its contribution is higher in the beginning of the anodization process, especially in potentiostatic mode when a high voltage is applied. This effect can also be observed by naked eye, as visible gas evolution takes place at the anode until the surface is covered with a sufficiently thick oxide layer. After the initial stage the amount of charge lost in side reaction is more or less constant (Figure 4a) – with a charge that is going into Ti oxidation of ≈92% (extracted from linear approximation shown in Figure 4b) – this ratio of 92% was found to hold for all anodization conditions in this study if the initiation phase was disregarded.

Experimentally, a reliable approach to determine the efficiency of the oxide growth was judged to be weight loss measurements of Ti combined with solution analyzes, but it turned out that a second approach based on determining the Ti lost by weight measurements and determining the Ti in the oxide was found to be similarly reliable. As mentioned before, in the latter approach the true composition of the oxide has to be taken into account. The reason for this is evident from the EDX measurements in Figure 5, where the elemental composition of typical nanotubes is measured from the cross-section in the middle of a thick TiO2 tubular layer. Clearly there is a high amount of carbon and fluoride incorporated in nanotube walls. As discussed in earlier work, C mainly resides in inner shell of the wall59 and leads to an over-estimation of the high weight of the tube layers. Therefore the mass was corrected using the fraction of Ti measured by EDX.

Both methods were used to extract growth efficiencies for a large number of experimental conditions, with a variation of applied voltage.
or current, of fluoride concentration and of water content – the data are compiled in Figure 6. From the data of the potentiostatic mode one can see that the initial compact oxide film is forming with an efficiency approaching unity (Figure 6a). Upon onset of growth of nanotubes, a substantial dissolution of titanium occurs, i.e., tubes grow by partial use of the formed Ti$^{4+}$ for oxide formation and part of the Ti$^{4+}$ is ejected to the electrolyte (and solvatized). Therefore there is an error on the total measurements by initial layer formation that with time strongly decreases and steadily drops to a range of 0.6 to 0.5.

This range shows slightly higher values than the predicted range of efficiency (0.5 to 0.58). Except for the already mentioned contribution of the initiation layer, another factor is that under some conditions some precipitates are still present in the nanotubes (leading to an apparently too high growth efficiency). These findings turned out to be the most important source of experimental complications when comparing the results with the theoretical model. Nevertheless, similar trend of the efficiency with time in the potentiostatic mode was measured via RBS (Rutherford backscattering spectroscopy) for nanotubes grown in glycerol at 20V. For very extended anodization times, chemical etching may contribute and thus yield a too low growth factor. But as mentioned before, under the conditions of our measurements, we estimate this error to be only in the few % range.

In the galvanostatic mode the picture of efficiency is only somewhat different (Figure 6b). In the first moments of anodization, the applied current leads to a relatively low voltage drop at the liquid/solid interface. The growth of the oxide is slow in time and it competes from very first moment with the dissolution process, and quickly self-organized tube growth is established. However, for some conditions (such as higher fluoride content in the electrolyte), a higher dissolution rate occurs and it results, in the first stage, in a porous disordered layer before tubes start to grow (Figure 2e). In this case the efficiency is below the lower limit of the predicted range (Figure 6b, circled data). Otherwise the data lie in a similar range as for the potentiostatic mode. Detailed experimental conditions are provided in the Table I. The common feature for points around an efficiency value of 0.7 is that they are obtained with a high current density or for extended periods of time.
Figure 5. EDX measurements of thick TiO₂ nanotube cross-section.

Figure 6. a) Efficiency of TiO₂ NT growth in potentiostatic mode at 50V in EG+0.1M(NH₄F)+1.5 wt%(H₂O); b) Growth efficiency of NTs in galvanostatic mode at different current densities (0.5 mA, 1 mA, 2 mA and 3 mA) in EG with different ammonium fluoride content (0.1 or 0.2 M) and water content (1.5 wt% and 5 wt%). The open stars and circles show the EDX and ICP measurements for the samples with observed crystallites on top. The full symbols represent crystallite free samples. The solid lines represent the range of efficiency where experimentally self-organization occurs; c) Efficiencies of the samples free of precipitated crystallites. The dashed lines represent the threshold values according to theoretical approach in Ref. 49.
Table I. Exact anodic conditions for the galvanostatic mode.

<table>
<thead>
<tr>
<th>Pt. #</th>
<th>Current</th>
<th>Electrolyte</th>
<th>Q/C</th>
<th>ε, ICP</th>
<th>ε, EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>2.69</td>
<td>0.70</td>
<td>0.66</td>
</tr>
<tr>
<td>2</td>
<td>2 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>3.60</td>
<td>0.66</td>
<td>0.65</td>
</tr>
<tr>
<td>3</td>
<td>1 mA</td>
<td>EG+0.2M(NH4F)+1.5wt%(H2O)</td>
<td>3.60</td>
<td>0.41</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>1 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>3.60</td>
<td>0.51</td>
<td>0.67</td>
</tr>
<tr>
<td>5</td>
<td>3 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>5.39</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>6</td>
<td>0.5 mA</td>
<td>EG+0.1M(NH4F)+5wt%(H2O)</td>
<td>5.40</td>
<td>0.53</td>
<td>0.52</td>
</tr>
<tr>
<td>7</td>
<td>2 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>7.19</td>
<td>0.66</td>
<td>0.69</td>
</tr>
<tr>
<td>8</td>
<td>1 mA</td>
<td>EG+0.2M(NH4F)+1.5wt%(H2O)</td>
<td>7.20</td>
<td>0.50</td>
<td>0.46</td>
</tr>
<tr>
<td>9</td>
<td>0.5 mA</td>
<td>EG+0.1M(NH4F)+5wt%(H2O)</td>
<td>9.00</td>
<td>0.56</td>
<td>0.58</td>
</tr>
<tr>
<td>10</td>
<td>1 mA</td>
<td>EG+0.1M(NH4F)+5wt%(H2O)</td>
<td>10.80</td>
<td>0.66</td>
<td>0.63</td>
</tr>
<tr>
<td>11</td>
<td>1 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>10.80</td>
<td>0.59</td>
<td>0.61</td>
</tr>
<tr>
<td>12</td>
<td>1 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>10.81</td>
<td>0.58</td>
<td>0.60</td>
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<tr>
<td>13</td>
<td>1 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>10.81</td>
<td>0.60</td>
<td>0.64</td>
</tr>
<tr>
<td>14</td>
<td>2 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>14.38</td>
<td>0.70</td>
<td>0.71</td>
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<tr>
<td>15</td>
<td>0.5 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>14.48</td>
<td>0.57</td>
<td>0.58</td>
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<tr>
<td>16</td>
<td>1 mA</td>
<td>EG+0.1M(NH4F)+5wt%(H2O)</td>
<td>17.99</td>
<td>0.64</td>
<td>0.63</td>
</tr>
<tr>
<td>17</td>
<td>1 mA</td>
<td>EG+0.1M(NH4F)+1.5wt%(H2O)</td>
<td>18.00</td>
<td>0.64</td>
<td>0.68</td>
</tr>
</tbody>
</table>

For this situation formation of crystallites as discussed in Figure 3c, 3d is common. Therefore, if one omits points that are significantly affected either by remnants of the initiation layer, crystallites on the surface, and obviously wall etching at high fluoride concentration, one obtains the picture shown in Figure 6c. These points are well in line with the theoretical prediction of a recently published model.99 Another factor that is noteworthy is that in the galvanostatic mode, the tube diameters increase during growth (as the diameter is directly dependent on the voltage). In the galvanostatic mode the voltage in the system increases according to a logarithmic law in line with high-field conditions31,60 (Figure 7a), and consequently the outer diameter of nanotubes is logarithmically increasing (Figure 7b). Moreover, similar to potentiostatic regime there is a maximum admissible power that can be applied for the certain electrolyte. For example, in a set-up as shown in Figure 7a, and consequently the outer diameter of nanotubes is logarithmically increasing (Figure 7b). Moreover, similar to potentiostatic regime there is a maximum admissible power that can be applied for the certain electrolyte. For example, in a set-up as shown in Figure 7a, such crystallites to a large extent depends on the current density: for high current densities and long anodization times the crystallites visible in the image are (NH4)2TiF6 as analyzed before.17 The formation of such crystallites to a large extent depends on the current density: for the higher current densities and larger anodization times considerable amounts can be detected in SEM investigations (local Ti4+ concentration, the NH4+ concentration, and the fluoride concentration in the electrolyte).

Overall, the present work illustrates critical issues if one tries to determine correct growth efficiency values for TiO2 nanotube growth. Clearly, within the system NH4F/H2O/EG some effects (initiation layers, chemical dissolution, reaction product precipitation) can interfere with commonly used approaches to determine growth efficiency values. Nevertheless, for the values determined under most reliable conditions, a remarkable agreement with theoretical predictions exists.

Conclusions

In the present work we examined growth efficiencies of titanium nanotubes grown under various conditions in both potentiostatic and galvanostatic modes. Typically we obtained, over a wide range of experimental conditions, growth efficiencies of 0.5–0.65. These efficiency values are in good agreement with a recently published theoretical model (0.5–0.58), considering the typical errors affecting the practical determination of growth efficiencies.

In contrast to this, a main source of error is caused by precipitates during the anodization process that shift experimental values to a too high value. Figure 3c and 3d illustrate these precipitates if very high fluoride contents are used (e.g. 1 mol L−1). The crystallites visible in the image are (NH4)2TiF6 as analyzed before.17 The formation of such crystallites to a large extent depends on the current density: for the higher current densities and larger anodization times considerable amounts can be detected in SEM investigations (local Ti4+ concentration, the NH4+ concentration, and the fluoride concentration in the electrolyte).

The formation of a compact initiation layer mostly affects the measurements for short anodization times. Precipitation of (NH4)2TiF6 crystallites is for high current densities and long anodization times the largest source of error. Under the present conditions, chemical dissolution of the oxide seems comparably small except for electrolytes...
containing a high fluoride concentration. It is also demonstrated how important it is to consider the true composition of the nanotube layer, if one operates with weight measurements to determine the mass of the formed oxide layers.

Nevertheless, the present work indicates, given the experimental uncertainties, that self-organization and formation of ordered TiO2 nanotube layers are well in line with theoretical approach provided in Ref. 49.

References