Effect of electric field strength on the length of anodized titania nanotube arrays

Lidong Sun\textsuperscript{a}, Sam Zhang\textsuperscript{a,b,}\textsuperscript{*}, Xiao Wei Sun\textsuperscript{b}, Xiaodong He\textsuperscript{c}

\textsuperscript{a}School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
\textsuperscript{b}School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
\textsuperscript{c}School of Aeronautics, Harbin Institute of Technology, P.O. Box 3010, Harbin 150008, PR China

\textbf{Abstract}

For application in dye-sensitized solar cells, anodic titania nanotube arrays must have high-aspect-ratio configuration to load more dyes thus result in higher conversion efficiency. Although geometry of the nanotubes is reported to be affected by a variety of anodizing parameters, electric field strength is the essential factor in determining the tube features (length, pore diameter, wall thickness, etc.). In the present work, electric field strength was varied by changing applied potential and working distance. Effect of the field strength on tube length was studied under selected field strengths for prolonged anodization durations. An Ion Flux Model, in consideration of \( F \) and \( H^+ \) concentration profiles within a single tube, is proposed to interpret the influence of the field strength on nanotube growth rate. The results indicate what essentially affects the tube length is the field strength which influences ion migration in electrolyte and ion transport in anodic barrier layer.

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1. Introduction

Titanium dioxide (\( \text{TiO}_2 \)) has been widely employed in dye-sensitized solar cells (DSSCs) \cite{1,2}, biosensors \cite{3}, hydrogen sensors \cite{4}, and water photolysis \cite{5} due to its various intriguing properties. Among diverse one-dimensional nanostructures, highly oriented TiO\textsubscript{2} nanotube arrays prepared by electrochemical anodization have been vigorously investigated since it was first reported in 1999 \cite{6}. This is because the highly ordered structure is favored comparing to the randomly packed configuration prepared by sol–gel method \cite{7}, e.g., in view of application in dye-sensitized solar cells. And the nanotube geometry can be tailored by changing anodizing parameters \cite{8–13}, superior to template-assisted synthesis where the geometry is limited and controlled by the original template \cite{14,15}. In addition, the electrochemical anodization process can be easily performed in a variety of electrolytes with or without fluorine ions in preparation of the nanotubes \cite{16–19}.

For dye-sensitized solar cells, the optimal length of nanotube array was estimated close to 30 \( \mu \text{m} \) \cite{20}. Recently the electron diffusion length of around 100 \( \mu \text{m} \) was also estimated for nanotube array based DSSCs \cite{21}. Therefore, it is crucial to produce high-aspect-ratio nanotubes in consideration of application in DSSCs \cite{21}. For application in dye-sensitized solar cells, anodic titania nanotube arrays must have high-aspect-ratio configuration to load more dyes thus result in higher conversion efficiency. Although geometry of the nanotubes is reported to be affected by a variety of anodizing parameters, electric field strength is the essential factor in determining the tube features (length, pore diameter, wall thickness, etc.). In the present work, electric field strength was varied by changing applied potential and working distance. Effect of the field strength on tube length was studied under selected field strengths for prolonged anodization durations. An Ion Flux Model, in consideration of \( F \) and \( H^+ \) concentration profiles within a single tube, is proposed to interpret the influence of the field strength on nanotube growth rate. The results indicate what essentially affects the tube length is the field strength which influences ion migration in electrolyte and ion transport in anodic barrier layer.

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electrolyte of ethylene glycol and a specially designed electrolytic cell were adopted in the present work, in which the distance between working electrode and counter electrode could be adjusted to vary the field strength. Field emission scanning electron microscopy (FESEM) images were used to examine the nanotube morphology and X-ray photoelectron spectroscopy (XPS) was employed to study chemical composition of the nanotube arrays.

2. Experimental

Titanium foils (0.25 mm, 99.7% purity, Sigma–Aldrich) were cleaned ultrasonically in acetone and ethanol for 10 min, respectively, and rinsed with deionized (DI) water. The foils were dried with air stream. All the experiments were performed in the electrolyte containing ethylene glycol (anhydrous, 99.8%, Sigma–Aldrich) 0.3 wt.% ammonium fluoride (98 + %, ACS reagent, Sigma–Aldrich) and 2 vol.% deionized water. A typical two-electrode configuration was employed with platinum gauze as the counter electrode and titanium foil as the working electrode. After each run, fresh electrolyte was prepared and used for the next. The back side of the Ti foil was also submerged and exposed to the electrolyte during anodization. A Keithley 2400 SourceMeter was used as power supply, and used to record current transients. The target potentials were directly applied onto electrodes without ramping. The distance between electrodes was controlled by a specially designed electrolytic cell. All the experiments were conducted at room temperature, approximately 20 °C, without magnetic stirring except for the highlighted ones mentioned in the result section. After each anodization, the sample was rinsed with DI water and dried in air naturally.

Surface morphologies of the nanotube arrays were characterized by field emission scanning electron microscope (FESEM, JEOL, JSM-6340F) at an acceleration voltage of 5.0 kV and working distance of 8–10 mm. Cross-sectional views were examined by scanning electron microscope (SEM, JEOL, JSM-5910LV) at an acceleration voltage of 15.0 kV and working distance of 16 mm. X-ray photoelectron spectroscopic (XPS, KRATOS, AXIS ULTRA) measurements were carried out by using a monochromated Al Kα (1486.7 eV) X-ray source at power of 150 W (15 kV × 10 mA). The XPS analysis was carried out at room temperature under a typical pressure in the range of 4.0 × 10⁻⁷–8.0 × 10⁻⁷ Pa, at take-off angle relative to the surface holder of 90°. A charge neutralizer was employed to neutralize charge accumulation during the analysis. Each sample was measured before and after argon ion etching at 4.0 kV and 15 mA for 5 min to remove possible surface contaminants. Bottom concentration of the nanotubes was obtained by measuring the bottom sides of peel-off pieces.

3. Results and discussion

3.1. Determination of field strength from the current density

Fig. 1a is the time dependence of current density during growth of TiO₂ nanotube arrays under different applied potentials. It shows that the current density at steady-stage anodization increases with the augment of applied potential, owing to the larger driving force of ion transport induced by higher potential. In addition, the initial current density at high voltage is also larger than that at low voltage, as displayed in the inset of Fig. 1a. The relation between anodic current density (i) and field strength (E) can be presented as [31,35,37,38]

\[ i = A \exp(BE) \]  \hspace{1cm} (1)

where A and B are constants related to temperature, and the field strength E is the ratio of the potential drop across the oxide layer to barrier layer thickness. Accordingly, the field strength can be reflected from the current density level for a given temperature. Therefore, from Fig. 1a, it is obvious that the relevant field strength increases with applied potential. For the same electrochemical anodizing system, the applicability of Eq. (1) (or in terms of the High Field Mode [37,38]) has been validated using Macdonald and co-workers’ diagnostic criteria [39] by Prakasam et al. [31].

The current transients for different working distances are shown in Fig. 1b. Clearly the current density at steady stage decreases gradually as the distance increases, so does the electric field strength because of the IR drop in the electrolyte. The IR drop in the present organic solution is substantial and considerable, as a result of relatively low conductivity which is about 460 μS cm⁻¹ [31].

Rewriting Eq. (1) as

\[ \ln i = \ln A + BE \]  \hspace{1cm} (2)

Therefore, field strength is proportional to \( \ln i \) for a given temperature. In Fig. 2, plot of \( \ln i \) vs. time for different applied potentials and working distances is illustrated. Evidently the field strength increases with applied potential whereas decreases with increased working distance. Moreover, the variation of field strength when changing working distance in the range of...
13–40 mm at 60 V corresponds to that when changing applied potential in the range of 60–50 V (keeping distance constant at about 13 mm). To present the field strength effect in a more direct way later, parameters of potential and distance are assigned with $E_n$ ($n = 0–6$) to denote their corresponding field strength with reference to the sequence illustrated in Fig. 2.

Fig. 3 shows the surface morphology of the nanotubes prepared at different potentials and distances, suggesting strong dependence of tube diameter on the relevant anodizing parameters. There is a thin layer of titanium oxides on each surface to be discussed later. The corresponding tube inner (or pore) diameters are summarized in Fig. 4a. It is apparent that pore diameter of the nanotubes increases with applied potential, in agreement with reported results [8,10,22,32–34]. The pore diameter decreases with increased working distance, which can be attributed to the significant IR drop in organic electrolyte [11,23,33] thus reducing effective field strength at the working electrode. Similar trends are also reflected in the nanotube length changes, as illustrated in Fig. 4b. It indicates growth rate of the nanotubes increases with applied potential whereas decrease with increase of working distance.

![Fig. 2](image-url) Re-plotting of data from Fig. 1 in terms of ln $i$ vs. time: the influence of the potential and distance on the logarithm of current density (or electric field strength).

![Fig. 3](image-url) FESEM images of TiO$_2$ nanotube arrays prepared at (a) 25 V, (b) 40 V, (c) 50 V, (d) 60 V with working distances of 13 mm; and at 60 V for different distances between working electrode and counter electrode: (e) 40 mm, (f) 30 mm, (g) 20 mm, (h) 13 mm. The anodization durations for all these experiments are two hours.

![Fig. 4](image-url) Tube diameter (a) and length (b) of TiO$_2$ nanotube arrays as a function of applied potential (bottom axis) and working distance (top axis). The anodization durations for all these experiments are two hours.
To uncover the effect of electric field strength, Eq. (2) is formulated in the following forms:

$$\Delta \ln i = B\Delta E$$

$$\ln i_B - \ln i_0 = B(E_n - E_0)$$

where $E_n (n = 0–6)$ is the pertinent field strength at different applied potentials or working distances, as illustrated in Fig. 2, and $\ln i_B$ is the corresponding ordinate (in Fig. 2) at steady-state anodization. In Eq. (4), the field strength at 25 V (i.e., $E_0$) is designated as the ground field strength, while the others are presented with relative values with reference to $E_0$. In this case, variations of nanotube length and pore diameter are plotted against this relative field strength, as shown in Fig. 5. Obviously, pore diameter presents a linear increase with relative field strength, as a result of proportionally enhanced lateral components of the field. In contrast, the tube length (also growth rate in the first 2 h) displays an exponential relationship with the relative field strength. Taking into account the exponential relation (1), it suggests that growth rate of the nanotubes is proportional to the anodic current density, i.e., the higher the current density the higher the growth rate. On the other hand, the current density is a reflection of the ion transport in the anodic barrier layer (or ion migration in the electrolyte) which is strongly associated with the field strength in this layer (or field strength in the electrolyte). In other words, it is the field strength that essentially affects the nanotube growth rate as well as the length.

### 3.2. Growth process

Fig. 2 reveals the maximum and minimum field strength is produced at 60 V and 25 V, respectively. In view of this, to further figure out the effect of field strength, titania nanotubes were produced and studied at 60 V and 25 V (with respective working distance of 13 mm) at prolonged anodization durations.

It is widely recognized that there are three key processes during the growth of nanotube arrays, i.e., field-assisted oxidation at metal/oxide interface, field-assisted dissolution at oxide/electrolyte interface at tube bottom and chemical dissolution of produced nanotubes at tube mouth [22, 24, 28, 29]. And these processes are responsible for two crucial rates which in turn determine the final length of nanotube arrays. One is the electrochemical etching rate, determined by field-assisted oxidation and dissolution, being constant when these two processes reach equilibrium. The relevant chemical reactions are as follows [10, 26, 40, 41]:

$$\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}$$

(5)

$$\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O}$$

(6)

The other is the chemical dissolution rate, the speed under which the fashioned TiO$_2$ nanotube array is dissolved through the same reaction (6). As a consequence, longer nanotubes are attainable for a given duration if the electrochemical etching rate at tube bottom is faster than the chemical dissolution rate at tube mouth, otherwise shorter or even no nanotubes are obtained [22].

Fig. 6 illustrates nanotube length as a function of time at selected potentials which produces desired maximum and minimum field strengths. Growth rate of nanotubes can be attained from the slope, which is the combined result of electrochemical etching rate and chemical dissolution rate. The slope is positive if the former is faster than the latter, and it is negative if the former is slower than the latter and equals to zero if these two rates are comparable. Moreover, the larger is the slope, the more apparent is the discrepancy between these two rates. The figure reveals that the growth rate at 60 V in the initial 2 h is ~7.81 μm/h, more than nine times higher than that at 25 V (which is only ~0.80 μm/h), and it increases slightly as duration extends and decreases finally for long anodization periods. The growth rate at 25 V shows the same trend in the primary hours, whereas becomes negative for long anodization periods. The results suggest electrochemical etching at high field strength is prominent, while chemical dissolution at low field strength dominates the growing process.

The prevailing process of electrochemical etching at high field strength can be seen from the steep slope at 60 V in contrast to that at 25 V (see Fig. 6). The dominant process of chemical dissolution at low field strength can be deduced from the changes in surface morphology with prolonged duration. In Fig. 3, the pore diameters of TiO$_2$ nanotube arrays anodized for two hours cannot be seen clearly and the wall thicknesses cannot even be distinguished, except for some special regions such as within the cracks. Because there is a thin layer of TiO$_2$ oxides on top of the nanotube arrays formed in the first few tens of seconds (see the drastic drop of current density in the insets of Fig. 1) after commencement of anodization. Although the pores are partially shaded, nanotube arrays grow beneath the initial oxides, and the pore entrances (the initial oxides) are not affected by field-assisted dissolution and hence remain relatively narrow [11, 24, 42]. Therefore, the initial oxides on the surfaces can only be eliminated by chemical dissolution that mentioned above [41]. Fig. 7 is top and lateral view of TiO$_2$ nanotube arrays prepared at 25 V for different durations. It reveals that...
the surface becomes much planar as time increasing, and the pores gradually become clear, as visible from the insets. In particular, the remnant initial oxides present on the surface of 2 h anodization (Fig. 7a) are dissolved after long anodizing periods (e.g., 14 h in Fig. 7b). Moreover, nonuniform and relatively thick-wall nanotubes are observed after anodization for 24 h, which can be attributed to the permanent chemical dissolution of the nanotubes in consideration of the characteristic V-shape profile in wall thickness [13,30,43,44]. In addition, progressively decreased tube length is exhibited in Fig. 7d–f, which is adopted in the plot of Fig. 6. All these results demonstrate that chemical dissolution is substantial at low field strength.

3.3. Ion profile in a single tube (ion flux model)

To elucidate the influence of electric field on the growth rate of the nanotubes, it helps to look into the details of ion migration under electric field in the electrolyte. (This electric field originates from IR drop in the organic electrolyte, which is the driving force of ion migration. Although it is different from the electric field in the oxide layer discussed afore, the relationship of field strength between different parameters is consistent with that illustrated in Fig. 2.) Reported results [11,13,33] indicate, in aqueous electrolyte, steady-state growth of anodic nanotubes is controlled by ion diffusion. However, in organic electrolyte, the effect of electric field should be considered. This is exactly the case of the present work. In principle, the flux of ions in the presence of electric field can be expressed as

\[ J_i = -D_i \frac{\partial c_i}{\partial x} - u_i c_i E \]  

where \( J_i \) is the flux of species \( i \) of concentration \( c_i \), in direction \( x \), \( \frac{\partial c_i}{\partial x} \) the concentration gradient, \( D_i \) the diffusion coefficient, \( u_i \) the mobility of species \( i \), and \( E \) the electric field strength. Evidently
ion transport in electrolyte is significantly affected by field strength, since ion migration under electric field is considerable in comparison to the process of ion diffusion under concentration gradient. In addition, Eqs. (5) and (6) suggest $\text{H}^+$ and $\text{F}^-$ ions play an important role in growth of the nanotubes. As the reaction products, $\text{[TiF}_6\text{]}^{2-}$ ions also influence the growth process, which will be discussed later. Let the vertical axis be the length of the tube, and the horizontal axis the concentration of ions. Let us consider $\text{H}^+$ and $\text{F}^-$ ion concentration profile within a single nanotube: $\text{H}^+$ ions are produced during anodization only at tube bottom [26], and the concentration is constant at steady-state anodization. Under electric field, $\text{H}^+$ ions migrate in the electrolyte towards negative electrodes (the estuary direction). Therefore, $\text{H}^+$ concentration decreases from the tube bottom to the mouth. $\text{F}^-$ ion concentration, on the other hand, is the maximum at the estuary, i.e., comparable with that in the bulk electrolyte thus remains constant. Under electric field, $\text{F}^-$ ions migrate in the electrolyte towards the positive electrode (the bottom direction). As such, the concentration of $\text{F}^-$ ions decreases from the tube mouth to the bottom. This is illustrated as Fig. 8.

In Fig. 8a, as tube length increases (from solid line to dot line, then to dash line and to dash-dot line), the $\text{F}^-$ concentration at the bottom decreases gradually because of the increase in ionic migration pathway (increase of tube length). The variation of $\text{H}^+$ profile strongly depends on the $\text{F}^-$ concentration at the bottom. From Eqs. (5) and (6), it can be seen that most $\text{H}^+$ ions produced through reaction (5) immediately participate in reaction (6) as long as there is enough $\text{F}^-$ ions (e.g., at the intersection of solid line in Fig. 8a). As such, there is not much accumulation of $\text{H}^+$ ions, i.e., $\text{H}^+$ concentration profile is small and is in the vicinity of the tube bottom (solid line in $\text{H}^+$ profiles). At this stage, electrochemical etching is dominant as there is almost no $\text{H}^+$ ion at tube mouth. In this scenario, the tube grows at nearly constant rate (cf., Fig. 6).

As tube length increases, the $\text{F}^-$ concentration at the bottom decreases while the $\text{H}^+$ concentration keeps constant at the steady state. Therefore, there exists a critical concentration of $\text{F}^-$ ions, which is approximately $[\text{H}^+]/[\text{F}^-] = 2:3$ according to Eq. (6). At this point (marked with a cross in Fig. 8a), the $\text{F}^-$ concentration is just enough to meet the needs of reaction (6) (in addition to possible direct reaction in $\text{Ti}^{4+} + 6\text{F}^- \rightarrow \text{[TiF}_6\text{]}^{2-}$ [40] or migration into the oxides under the electric field). At this point, the concentration gradient of $\text{H}^+$ ions is still small and confined at the bottom area, as shown in the dot line of the $\text{H}^+$ profiles in Fig. 8a. The electrochemical etching is still prevailing at this stage.

Further increase in the tube length results in $\text{F}^-$ concentration falling below the critical point at the bottom. When this happens, the $\text{F}^-$ ions at tube bottom can no longer meet the needs of reaction (6). Consequently, extra $\text{H}^+$ ions at the bottom will migrate towards the estuary under the electric field, giving rise to significant change in $\text{H}^+$ concentration profile to the dash line in Fig. 8a. At this stage, though electrochemical etching is still dominant, the nanotube growth rate is decreased (due to slowdown of reaction (6)). This can be confirmed from the turning point in Fig. 6 (at 60 V after 8 h the slope of curve is dipped).

As the process continues and the $\text{H}^+$ ion accumulates at the estuary (dash-dot profile of $\text{H}^+$), chemical dissolution of the fashioned nanotubes takes place, again through reaction (6), but this time the tube at the mouth ($\text{TiO}_2$) is consumed, resulting in decreased growth rate. At the steady state, where the rate of reaction (6) at the tube mouth (dissolution) increases to that at the tube bottom (tube growth), the net growth of the tube stops. This has been widely observed in the growth of anodic nanotubes [11,17,18,22,34]. At the bottom of the tube, the reaction product $\text{[TiF}_6\text{]}^{2-}$ accumulates gradually, which reduces the chemical reaction rate. At certain extent, the dissolution at the top becomes faster than the growth at the bottom, a negative net growth occurs, i.e., reduction of the total tube length (as happened at 25 V during long time anodization in Fig. 6).

The role of the electric field strength can be clearly seen in Fig. 8b. According to Eq. (7), higher field strength results in higher ion flux in the electrolyte. At the same tube length, under high field strength, $\text{F}^-$ concentration at tube bottom will be higher than that under low field strength. Therefore, it requires longer time for bottom $\text{F}^-$ concentration to drop to the critical value. In this process, the $\text{H}^+$ ions are mainly confined in the vicinity of tube bottom. As a result, electrochemical etching (or tube growth) process maintains for a longer time. As is shown in Fig. 6, at 60 V, the tube still grows after 10 h but at 25 V the tube growth stops at around 5 h (and further increase in time only results in shortening of the tube). Therefore, at low field strength, the chemical dissolution kicks in much faster than at high field strength. Since the chemical dissolution takes place at the tube estuary and depends on the accumulation of the $\text{H}^+$ ions, reduction in the $\text{H}^+$ concentration at the mouth should effectively prolong the growth. As such, an anodization run at 25 V was continuously stirred for 24 h. Without stirring, the final tube length is only ~2.5 μm, whereas with stirring, the final tube length becomes 8.4–12.7 μm, or an increase by a factor of three to five. Of course, this increase of length did not come from the reduction in chemical dissolution alone: the other reason is the increase in flux as a result of enhanced ion diffusion (first term in Eq. (7)) [11,13,33,45] due to stirring.

As an evidence of the fluorine ion concentration gradient in the electrolyte during the anodization process, the fluorine gradient in the as-grown tubes is observed via X-ray photoelectron spectroscopy. In the nanotube array prepared at 60 V for 8 h (length of ~120 μm), the XPS composition analysis reveals 13.52 at.% F at the mouth and 8.38 at.% at the bottom (or, 28.68 at.% Ti, 57.80 at.% O and 13.52 at.% F at tube mouth; 30.76 at.% Ti, 60.86 at.% O and 8.38 at.% at tube bottom).

4. Conclusions

In the present work, the role of electric field strength was studied on growth of titania nanotubes through electrochemical anodization. Pore diameter of the nanotubes increases linearly with field strength. The tube length (also the growth rate) exponentially increases with the field strength. What essentially affects the
length of the tube is the field strength, which influences ion migration in electrolyte and ion transport in anodic barrier layer. At higher field strength, growth of the tube maintains longer time as a result of higher ion concentration at the bottom of the tube. The growth and the influence of the electric field strength are elucidated by the Ion Flux Model (Fig. 8) where H⁺ and F⁻ ion concentration profiles are considered in a single tube.

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