Quantitative relationship between nanotube length and anodizing current during constant current anodization

Yulian Zhang\textsuperscript{a,b}, Weijie Cheng\textsuperscript{a}, Fei Du\textsuperscript{a}, Shaoyu Zhang\textsuperscript{a}, Weihua Ma\textsuperscript{a,*}, Dongdong Li\textsuperscript{b}, Ye Song\textsuperscript{a}, Xuefei Zhu\textsuperscript{a,*}\textsuperscript{1},

\textsuperscript{a} Key Laboratory of Soft Chemistry and Functional Materials of Education Ministry, Nanjing University of Science and Technology, Nanjing 210094, China
\textsuperscript{b} Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

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The growth kinetics of anodic TiO\textsubscript{2} nanotubes (ATNTs) still remains unclear. ATNTs are generally fabricated under potentiostatic conditions rather than galvanostatic ones. The quantitative relationship between nanotube length and anodizing current (\(J_{\text{total}}\)) is difficult to determine, because the variable \(J_{\text{total}}\) includes ionic current (\(J_{\text{i}}\) also called oxide growth current \(J_{\text{grow}}-J_{\text{ion}}\)) and electronic current (\(J_{\text{e}}\)), which cannot be separated from each other. One successful approach to achieve this objective is to use constant current anodization rather than constant voltage anodization, that is, through quantitative comparison between the nanotube length and the known \(J_{\text{total}}\) during constant current anodization, we can estimate the relative magnitudes of \(J_{\text{grow}}\) and \(J_{\text{e}}\). The nanotubes with lengths of 1.24, 2.23, 3.51 and 4.70 \(\mu\)m, were formed under constant currents (\(J_{\text{total}}\)) of 15, 20, 25 and 30 mA, respectively. The relationship between nanotube length (\(y\)) and anodizing current (\(x\)) \(y = \frac{x}{J_{\text{total}} - \frac{1}{J_{\text{elec}}}}\) can be expressed by a fitting equation: \(y = 0.23(x - 10.13)\), from which \(J_{\text{grow}} = \frac{J_{\text{total}} - \frac{1}{J_{\text{elec}}}}{10.13}\) and \(J_{\text{e}}\) \((\approx 10.13 \text{ mA})\) could be inferred under the present conditions. Meanwhile, the same conclusion could also be deduced from the oxide volume data. These results indicate that the nanotube growth is attributed to the oxide growth current rather than the dissolution current.

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1. Introduction

Anodic TiO\textsubscript{2} nanotubes (ATNTs) and porous anodic alumina (PAA) have been widely investigated for many years due to their various applications [1–3]. Despite many elegant investigations and much deeper interpretation on the nanopores or nanotubes have been reported in many famous journals [4–11], until now, the driving force for the pore formation still remains unclear [4,5,12], because it is hardly derived by direct in-situ methods [11]. The generally accepted mechanism for the pore formation in anodic titania films is the field-assisted dissolution (or preferential oxide dissolution) process (Eq. (1)) [9,12–14], which is similar to that in PAA films (Eq. (2)) [15–17], despite the lack of direct experimental evidence that confirms this expectation [16]. However, this important fact has been ignored for decades, and the Reaction (1) has been cited extensively to explain the growth mechanism of ATNTs.

\begin{equation}
\text{TiO}_2 + 6F^- + 4H^+ \rightarrow [\text{TiF}_6]^{2-} + 2H_2O
\end{equation}

\begin{equation}
\text{Al}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\text{O}
\end{equation}

It is well known that the above field-assisted dissolution processes are acid-catalyzed. Most of H\textsuperscript{+} ions will be driven to gather near the cathode by the electric field, resulting in release of H\textsubscript{2}O gas [15]. As a result, H\textsuperscript{+} ions at the pore bottom are scarce [15]. Moreover, it has been accepted for decades that the pore development was caused by the equilibrium between oxide growth and preferential dissolution at the base of pores where the electric field is high [8,18,19]. Until 2006, an alternative mechanism was discovered successfully by Garcia-Vergara and coworkers [20], which is termed as a field-assisted ‘plastic flow’ model, where the barrier oxide at the metal/oxide interface is considered to be constantly displaced upwards to form the nanotube walls [20,21]. It also indicated that the field-assisted ‘plastic flow’ model was contrary to expectations of the field-assisted dissolution model [20,22].

In general, most anodizations were performed under constant voltages or pulse voltages [23,24]. However, there has been no...
systematic study of the effect of the applied voltage on the field-assisted dissolution. Obviously, the physical meaning of the field-assisted dissolution is rather complicated and inexplicit until now [16,17,22,25,26] because of the lack of a quantitative correlation between the field-assisted dissolution speed and the variable anodizing current. As Hebert et al. [4,27] indicated that no model has successfully explained the relationship between porous morphology and processing parameters. To the best of our knowledge, satisfactory correlation between the anodizing current and nanotube length (or oxide volume) has not yet been studied.

It is well known that the electrochemical products, including TiO2, Ti(OH)3, [TiF6]3–, and O2 gas, are related to the electric charge. Whereas the total electric charge (Q) is determined by the product of the anodizing current (Qtotal) and the anodizing time (t) (Q = Qtotal). Garcia-Vergara et al. [25] also concluded that the porous layer thickness essentially in proportion to the electric charge transmission during anodization. As Hebert et al. [22] recently indicated that oxide dissolution rates are in fact very low and stress-driven ionic transport toward the pore walls is envisioned to assist pore formation. Here, based on previous literature, an efficient and simple method is first proposed to study the relationship between ATNT morphology (nanotube lengths or diameters) and anodizing current under the galvanostatic condition rather than potentiostatic one. According to the difference of nanotube lengths or oxide volumes, we can identify whether the field-assisted dissolution current (Jdiss) or ionic current (Jion=Jgrow) is the driving force for the nanotube growth. The present results can promote the kinetics research from qualitative level to quantitative level.

2. Experimental details

The commercial Ti foils (100 μm thick, purity 99.5%, Shanghai Shangmu Technology Co. Ltd.) were polished in a mixture solution containing HF, HNO3 and deionized water (1:1:2 in volume) for 10 s. Then the samples were rinsed thoroughly by deionized water and dried in the air. The polished Ti foil was then anodized in an electrochemical cell at 20°C. All anodizing experiments were carried out at 20°C with stirring of the electrolyte. The constant temperature of the cell was controlled using an external cooling circulator (DL3005 Cooling Pump).

The electrolyte was ethylene glycol solution containing 0.3 wt% NH4F and 5 wt% H2O. Prior to anodization, the electrolyte was aged under 60 V for 10 h. The Ti foil as anode was pressed together with a Cu plate (~6 mm thick) against a rubber O-ring in the electrochemical cell. The inner diameter of the O-ring was ~2.0 cm. The anodizing area of Ti foil was maintained constant (~3.14 cm2). A Pt mesh as cathode (area of ~12.0 cm2) was placed ~1 cm away from the Ti anode.

For optimum results, the first anodizations were performed under constant currents of 15 mA, 20 mA, 25 mA and 30 mA for 900 s, respectively. Then, the samples with TiO2 nanotube films were ultrasonically rinsed in the deionized water for ~20 min to peel off the formed film. Then, the new Ti substrates with ordered concaves were anodized for the second time under the same anodizing condition as the first one. The voltage-time curves were recorded automatically by a computer system [17]. The TiO2 film morphologies were characterized by field-emission SEM (FESEM, Hitachi S-4800 II and Zeiss Supra 55). Nanotube lengths were measured directly on the FESEM.

3. Results and discussion

Fig. 1 shows the surface morphologies of the ATNTs formed at four different anodizing currents. In order to obtain precise nanotube lengths, two-step anodizations were adopted in this work. The patterned stripes around the concaves are very clear in Fig. 1. These patterned and raised stripes are ascribed to the residual concaves on Ti substrate after removal of the nanotubes formed in the first anodization. Only if two-step anodization is adopted, these patterned and raised stripes will appear. These patterned stripes around the concaves demonstrate that the chemical dissolution process has not affected the nanotube lengths and the surface morphologies. It is well known that, after longtime anodization, the patterned stripes on the top surface will disappear, some bundling or nanograss will occur on the top surface [8,28], leading to the inexact nanotube lengths. Moreover, based on the classical theory [8], the chemical dissolution has strong influence on the inner diameter of the nanotubes with
increasing anodizing time. The chemical dissolution near the top surface layer is faster and thus contributes more to the fact that the walls become thinner towards the top of nanotubes [8]. In order to avoid the influence of chemical dissolution on the top surface and keep the patterned stripes around the concaves unchanged, the duration of two-step anodization was controlled for only 900s on purpose, because chemical dissolution can be negligible for the present anodizing conditions involving short anodizing periods [25].

Fig. 2 shows that the inner diameter of the nanotubes near the top layer (~36 nm) is somewhat larger than that of the middle layer (~30 nm) or bottom layer (~26 nm) due to chemical dissolution. These facts indicate that the chemical dissolution enlarges the inner diameter to some extent due to the limited anodizing time. In the direction which is perpendicular to electric filed, the chemical dissolution rate is very low (~1 nm/min=(36 nm-26 nm)/10 min). However, along the direction of the electric field, if the field-assisted dissolution or preferential oxide dissolution existed at the pore bottom, the field-assisted dissolution rate should be very high (3500/15=233 nm/min), based on the field-assisted dissolution [3,8,18]. However, in fact, many previous literature conclude that it is impossible for the field-assisted dissolution rate to reach ~233 nm/min. Diggle et al. [26] considered that the field-assisted dissolution is doubtful. Is the field-assisted dissolution at the same rate as the chemical dissolution? How does field-assisted dissolution rate depend on the anodizing current or electric field [26]? What role does the constant thickness of the barrier oxide layer play in field-assisted dissolution [26]?

In 2015, Hebert et al. [22] also indicated that oxide dissolution rates were demonstrated in fact very small. It is suggested that pore initiation occurs by an instability involving flow of oxide, preceded by accumulation of compressive oxide stress [22], rather than by preferential oxide dissolution, because no significant oxide dissolution was detected at the base of incipient pores [22].

Fig. 3 illustrates the cross sections of ATNTs and the nanotube lengths. When anodized at currents of 15 mA, 20 mA, 25 mA and 30 mA, nanotubes with lengths of ~1.24 μm, ~2.23 μm, ~3.51 μm and ~4.70 μm were obtained, respectively. Obviously, the nanotube length increases with the anodizing current (or called total current, \(I_{\text{total}}\)). but the nanotube length is not directly proportional to \(I_{\text{total}}\). These results are opposite to expectations of the field-assisted dissolution and the ejection models. According to the dissolution theories, there were two competitive reactions, which are barrier oxide growth (\(\text{Ti}^{4+}+2\text{O}^2−\rightarrow\text{TiO}_x\)) at oxide/metal interface and field-assisted dissolution reaction (Eq. (1)) at electrolyte/oxide interface. Therefore, if field-assisted dissolution do exist at the bottom of the pore, there should be a dissolution current, and \(J_{\text{total}}\) should be composed of oxide growth current (\(J_{\text{grow}}\)) and field-assisted dissolution current (\(J_{\text{dis}}\)), i.e., \(J_{\text{total}}=J_{\text{grow}}+J_{\text{dis}}\). \(J_{\text{grow}}\) results from the ion migration across the barrier oxide, and \(J_{\text{dis}}\) results from the field-assisted dissolution of barrier oxide and the field-assisted ejection of \(\text{Ti}^{4+}\) ions into the electrolyte (i.e., \(\text{Ti}^{4+}\) ions were ejected into the electrolyte without oxide formation) [8,18,19,21]. \(J_{\text{grow}}\) will contribute to nanotube growth at the oxide/metal interface, meanwhile, \(J_{\text{dis}}\) should also contribute to nanotube growth (deepening) at the electrolyte/oxide interface both on the top surface and at the nanotube bottom [10,19,29]. If it were true, both \(J_{\text{grow}}\) and \(J_{\text{dis}}\) will yield positive feedback and lengthen the nanotube length. If there were no other types of currents (such as, electronic current), the nanotube length should be directly proportional to the total anodizing current (\(I_{\text{total}}\)) or the total electric charge (\(Q\)) [25]. If this were true, based on the nanotube length of 1.24 μm obtained under 15 mA, the nanotube length formed under 30 mA should be 2.48 μm (1.24 × 30/15 = 1.24 × 2). Obviously, the deducing value (2.48 μm) is much smaller than the experimental findings (4.70 μm) obtained under 30 mA, which indicates that the dissolution current does not exist in fact.

Furthermore, if there were an equilibrium between barrier oxide growth and field-assisted dissolution at the nanotube base throughout the anodizing process, \(J_{\text{dis}}\) should be equal to \(J_{\text{grow}}\) (\(J_{\text{grow}}=J_{\text{dis}}=0.5I_{\text{total}}\)), i.e., the field-assisted dissolution rate (233 nm/min) should be equal to the oxide growth rate, under the equilibrium conditions. If this were true, the anodizing efficiency (\(\eta\)) or oxide growing efficiency should be defined as \(\eta=J_{\text{grow}}/I_{\text{total}}\%\). However, Proost et al. [30] reported an efficiency value of 66%. Garcia-Vergara and coworkers [31] reported that the efficiencies of PAA growth are 67%, 85% and 93% at the anodizing current densities of 5, 15 and 30 mA cm\(^{-2}\), respectively. They concluded that these findings are consistent.
with the pore development by ‘plastic flow’ of film material, rather than by field-assisted dissolution [31]. Recently, we reported double-layered and triple-layered nanostructures [32–34], where the forming process and corresponding current-time curves could not be clarified by the field-assisted dissolution and ejection models. Because the field-assisted dissolution Eq. (1) only takes

Fig.3. (a–d) FESEM images of cross section of TiO$_2$ nanotubes obtained at different anodizing currents. (e) Voltage-time curves recorded at different anodizing currents. (f) Linear relationship between the nanotube length ($y$) and anodizing current ($x$) after 900 s anodization.

Fig.4. Schematic diagrams showing three stages of the nanotube generation.
place at the electrolyte/oxide interface, which can not supply charge carriers to establish a conductive path across the barrier layer [15,16,33,34]. We also concluded that the chemical dissolution may exist, however, \(J_{\text{ion}}\) across the barrier layer is impossible to generate [15,16,33,34], because the soluble product TiF\(_4^2^-\) anions only enter the electrolyte and cannot run across the barrier layer [33,34]. Therefore, the above experimental results agree well with the conclusion reported by Thompson and Diggle [16,26], that is, the field-assisted dissolution reaction is chemical in nature and hence does not contribute to the anodizing current [16,26].

Fig. 3e shows the voltage-time curves recording four anodizing processes under different currents. Based on the nanotube lengths and the corresponding different currents (15 mA, 20 mA, 25 mA and 30 mA), the fitting curve and equation are shown in Fig. 3f. A relationship between the nanotube length \((y)\) and anodizing current \((x)\) is given by the fitting equation: \(y = 0.23 \times -2.33 + 0.23(x - 10.13)\) \((R^2=0.99)\). The constant \(-2.33\) appears at any anodizing current. The constant term demonstrates that \(J_{\text{total}}\) is composed of two parts: one part plays an important role in the nanotube growth, whereas the other part has little effect on the nanotube growth and is independent of \(J_{\text{total}}\). A key question emerges: which current results in the constant? And what is the physical meaning of the constant term? Obviously, the negative constant \(-2.33\) is independent of \(J_{\text{grow}}\) and \(J_{\text{ion}}\), because both \(J_{\text{grow}}\) and \(J_{\text{ion}}\) yield positive feedback to the nanotube length.

As discussed above, the field-assisted dissolution model and dissolution current cannot explain the experimental results and the relationship between the anodizing current and nanotube length [4,27]. We have also clearly demonstrated that the anodizing current \(J_{\text{total}}\) mainly includes \(J_{\text{ion}}\) and electronic current \((J_e)\) [17,32–37]. \(J_{\text{ion}}\) is used to form barrier oxide and \(J_e\) is used to give rise to oxygen evolution as shown in Fig. 4 [17,32–37]. Furthermore, the theoretical derivation of anodizing current and two exact expressions of \(J_{\text{ion}}\) and \(J_e\) have been reported in our recent work [37]. Many groups have demonstrated the existence of the electronic conduction or the \(J_e\) during the anodizing processes [18,38–42]. In contrast, there are very few reports involving the quantitative analysis of the dissolution current. Mazzarolo et al. [38] also proposed that electronic conduction mainly results in oxygen evolution in the anodizing process. Regonini et al. [18,39] indicated that the ingress \(O^2^-\) ions were not solely contributing to the oxide formation, some were instead discharged, generating an electronic current. Vrublevsky and coworkers [40,41] also considered that electronic conductivity did not contribute to the oxide growth. Therefore, the physical meaning of constant in the fitting equation \((y = 0.23 \times -2.33)\) represents the contribution of the electronic current. That is, the electronic current results in the negative constant \(-2.33\).

The anodizing processes of Ti and Al, and the generating processes of \(J_{\text{ion}}\) and \(J_e\) have been studied in our previous works [17,32–37]. The anionic incorporation layer (ANILN, as shown in Fig. 4a) and its influence on the generation of \(J_e\), the oxygen bubble mould and its influence on the embryo of nanotube have been elucidated in detail [33,34]. The distribution of the electric field across the barrier oxide and the pore base, the formation mechanism of gaps and ribs around TiO\(_2\) nanotubes have been discussed in detail [35,36]. Here, Fig. 4 shows schematically the three stages of nanotube formation. Fig. 4a shows the first stage. The barrier oxide layer and ANILN were formed in this initial stage. \(J_{\text{ion}}\) is the predominant mode in charge transport. The driving force for barrier oxide growth is ion conduction which comes from the \(Ti^4^+\) and \(O^2^-\) ions \((Ti^4^+ + 2O^2^- \to TiO_2)\). For the fluoride-containing electrolyte, the barrier oxide would be inevitably contaminated by \(F^-\) and \(OH^-\) ions due to anionic incorporation into the oxide. As a result, three interfaces (electrolyte/ANILN interface, ANILN/barrier layer (BL) interface, BL/metal interface) were formed as shown in Fig. 4a. Fig. 4b shows the process formation of embryo pore and the oxygen bubble mould at the second stage. With the increase of ANILN thickness and anion accumulation near the ANILN/BL interface, a reasonable \(J_e\) must occur within the anodic oxide and result in oxygen evolution and oxygen bubble formation near the ANILN/BL interface [32–37]. As a result, the second stage, the anodizing efficiency \((\theta = J_{\text{ion}}/J_{\text{total}})\) began to decrease as shown in Fig. 3e, because the anodizing current \(J_{\text{total}}\) maintained constant while part of \(J_{\text{ion}}\) was transformed into \(J_e\). Garcia-Vergara et al. [43] indicated that the oxygen gas formed bubbles within the film, with pressures of several hundred MPa. The bubbles impeded ionic migration and affected the distribution of stress in the anodic film, which was critical to the pore formation [43]. As a result, the gas bubble behaves as a mold and grows upward with the growth of barrier oxide. Two mold effects are presented [33]. One is to exert a high pressure on the barrier oxide, causing an arc indentation at the BL/M interface as shown in Fig. 4b, due to the plasticity of the anodic titania and high pressure of the bubbles. The other is to induce the oxide flow around the gas bubble. Fig. 4c shows the third stage. After the pore formation and the electrolyte entrance into the pore bottom, the electric field distribution transforms from the vertical direction (Fig. 4a) to the radial direction (Fig. 4c) across the hemispherical base of nanotube [35]. That is, the vertical direction of electric field \((E)\) is controlled by the macroscopic barrier oxide layer on the macroscopic planar substrate (Fig. 4a), whereas the radial direction of electric field is controlled by the microscopic barrier oxide layer on the microscopic arc (or hemispherical) substrate (Fig. 4c). There is no difference between the growing manner of the macroscopic barrier oxide (Fig. 4a) and the microscopic barrier oxide (Fig. 4c). The only difference between two stages (Fig. 4a and Fig. 4c) is the anodizing efficiency \((\theta = J_{\text{ion}}/J_{\text{total}})\). \(\theta\) at the first stage is higher than that at the third stage, which is because \(J_{\text{ion}}\) decreases and \(J_e\) increases. The appropriate \(J_{\text{ion}}\) is still used to form new microscopic barrier oxide across each pore base and \(J_e\) is high enough to give rise to expansion of oxygen bubbles at the bottom of each pore. The ‘plastic flow’ of the microscopic barrier oxide is mainly ascribed to the presence of gas bubble as shown in Fig. 4c. This manner of ‘plastic flow’ from pore base to the pore walls accords with the flow model [4,20–22,27].

All the descriptions above clearly show that the nanotube length is independent of \(J_{\text{ion}}\), but depends on \(J_{\text{ion}}\) and \(J_e\). Although many groups have recognized that \(J_e\) and oxygen evolution indeed exist during anodization [15,18,38–45], it is hard to distinguish \(J_e\) from \(J_{\text{ion}}\). Here, we provide a method to estimate the \(J_e\) magnitude. The \(J_e\) magnitude can be estimated from the nanotube length and corresponding \(J_{\text{total}}\). Given that oxide growth rate (i.e., the length of nanotubes grown at per unit \(J_{\text{ion}}\)) is essentially constant for a given electrolyte at a constant temperature, six equations can be obtained through permutation and combination of four length values and four values of \(J_{\text{ion}}\) \((J_{\text{ion}} = J_{\text{total}} - J_e)\), because the transfer charge number of the ions \((Ti^4^+ + O^2^-)\) is directly proportional to the anodic current \(J_{\text{ion}}\). That is, the anodic current contributes to the oxide growth \((Ti^4^+ + 2O^2^- \to TiO_2)\), whereas the electronic current does not contribute to the oxide growth. The nanotube length \(y\) is only proportional to the ionic current, \(y = \text{const} \times J_{\text{ion}} = \text{const} \times (J_{\text{total}} - J_e)\). Compared with the fitted equation, \(y = 0.23(x - 10.13)\), it can be deduced that \(J_{\text{ion}} = J_{\text{total}} - J_e\). The electronic current is approximately equal to 10.13 mA.

Table 1 lists the calculating equations and the corresponding parameters. Six values of the \(J_e\) can be estimated from the six equations, their average value is approximately 10.07 mA. Compared with the fitting equation \(y = 0.23(x - 10.13)\), the average value of 10.07 is approximately equal to the constant term of 10.13. Both results provide the direct quantitative evidence that \(J_e\) indeed exists in the anodizing process, and \(J_e\) may maintain with an
appropriate value in spite of the different anodizing currents (15–30 mA) in anodization with a given electrolyte at 20°C. We conclude that the oxide growth rate (or efficiencies $\theta$=$J_{\text{ion}}/J_{\text{total}}$) increases with the increase of anodizing current $J_{\text{total}}$, because the increase of $J_{\text{total}}$ mainly results in the increase of $J_{\text{ion}}$ ($J_{\text{ion}}$=$J_{\text{total}}$–$J_{\text{ele}}$). This conclusion is entirely consistent with the experimental results reported by Garcia-Vergara and coworkers [31]. They reported that the efficiencies are 67%, 85% and 93% at the anodizing current densities of 5, 15 and 30 mA cm$^{-2}$, respectively [31]. According to equations $\theta$=$J_{\text{ion}}/J_{\text{total}}$ and $J_{\text{ele}}$=$(1-\theta)J_{\text{total}}$, one can calculate that the electronic currents are 1.65, 2.25 and 2.10 mA cm$^{-2}$ at $J_{\text{total}}$ of 5, 15 and 30 mA cm$^{-2}$, respectively. The average value of $J_{\text{ele}}$ is nearly constant, approximately 2.00 mA cm$^{-2}$. That is to say, for a given electrolyte and under a given anodizing condition, the electronic current $J_{\text{ele}}$ is essentially independent of the anodizing current $J_{\text{total}}$. It must be emphasized that the complication of anodizing process arose from the complicated field-assisted dissolution current ($J_{\text{dis}}$) so that quantification of anodizing current and oxide growth rate were always difficult in the past decades [10,15–17,25–27,29,31]. A challenge in this field of the metal anodization is how to separate the ionic current, dissolution current and electronic current [10,15,16,19]. Here, the ionic current was easily derived from the nanotube length. It was demonstrated that this is an interesting and efficient method to determine the ionic current and electronic current in the anodizing process. This calculating process seems to be too simple. However, the quantitative relationship between nanotube length and anodizing current is elucidated for the first time. In fact, similar results may also be deduced from the oxide volume of the nanotube walls. Fig. 5 shows the inner diameter ($i$) and outer diameter ($R$) of TiO$_2$ nanotubes formed under different currents. Based on the cross-section area ($\pi R^2$ – $\pi r^2$) and nanotube length (listed in Table 1), the oxide volumes of the nanotube walls are depicted in Table 2.

Table 1
Anodizing parameters, nanotube lengths and calculating equations (0.3 wt% NH$_4$F, 20°C)

<table>
<thead>
<tr>
<th>Nanotube length</th>
<th>$J_{\text{total}}$</th>
<th>$J_{\text{ion}}$</th>
<th>$J_{\text{ele}}$</th>
<th>Calculating equation</th>
<th>Estimated value of $J_{\text{ele}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.24 μm</td>
<td>15 mA</td>
<td>$\frac{1.24}{15}$</td>
<td>$\frac{2.21}{15}$</td>
<td>$J_{\text{ele}}=\frac{10.25}{15}$</td>
<td>0.75 mA</td>
</tr>
<tr>
<td>2.3 mA</td>
<td>20 mA</td>
<td>$\frac{2.3}{20}$</td>
<td>$\frac{2.31}{20}$</td>
<td>$J_{\text{ele}}=\frac{10.07}{20}$</td>
<td>0.50 mA</td>
</tr>
<tr>
<td>3.51 mA</td>
<td>25 mA</td>
<td>$\frac{3.51}{25}$</td>
<td>$\frac{2.67}{25}$</td>
<td>$J_{\text{ele}}=\frac{10.07}{25}$</td>
<td>0.40 mA</td>
</tr>
<tr>
<td>4.70 mA</td>
<td>30 mA</td>
<td>$\frac{4.70}{30}$</td>
<td>$\frac{4.70}{30}$</td>
<td>$J_{\text{ele}}=\frac{9.54}{30}$</td>
<td>0.32 mA</td>
</tr>
</tbody>
</table>

Fig. 5. FESEM images showing the diameters of TiO$_2$ nanotubes formed under different currents: (a) 15 mA, (b) 20 mA, (c) 25 mA, (d) 30 mA. (e) Linear relationship between the outer diameter ($Y$) and steady voltage ($X$). The insets in (a–d) show the inner diameters and the scale bars represent 100 nm.
Similarly, six other equations can be obtained through permutation and combination of four volume values and four $J_{\text{ion}}$ values ($J_{\text{ion}} = J_{\text{total}} - J_e$), because the oxide volume formed at per unit area (1 mm$^2$) is directly proportional to the ionic current $J_{\text{ion}}$. That is, the ionic current contributes to the oxide volume, whereas the electronic current does not contribute to the oxide growth. Table 2 lists the calculating equations and the corresponding parameters. Six values of $J_e$ can be estimated from the six equations, and their average value is 10.22 mA. Compared with the above two methods, the three average values (10.13, 10.07 and 10.22) are approximately equal to each other. It must be emphasized that all these findings remain valid in the range of 15–30 mA for a given electrolyte (0.3 wt% NH$_4$F) at a certain temperature. Fig. 5e shows the relationship between the outer diameter ($Y$) of nanotubes and the steady voltage ($X$) and the fitting equation is $Y = 2.50X + 37.89$ ($R^2 = 0.998$). The fitting equation indicates that the diameter increases with the increase of the steady voltage. The steady voltage increases with increasing anodizing current as shown in Fig. 3e. It must be pointed out that both nanotube length and outer diameter increase with the increase of the anodizing current. On the other hand, there is a constant ($+37.89$) in the fitting equation. It is very difficult to quantitatively clarify the fitting equation based on the dissolution model [19,26]. Here, based on the electronic current and the ‘oxygen bubble mould’, a quantitative description of the fitting equation is originally proposed. The fitting equation and the constant demonstrate that two events contribute to the outer diameter of the nanotubes. One is the constant barrier oxide growth which is dependent on the steady voltage [32] and the other is the oxygen bubble mould which is independent of the steady voltage [33–35,37]. Hence, the constant ($+37.89$) may result from ‘oxygen bubble mould’ at the pore bottom due to the constant electronic current [17,32–35]. In fact, Fig. 2 and Fig. 5 show that the inner diameters of the nanotubes are limited approximately to the range of 30–40 nm for the present anodizing time (900 s). If the inner diameter does not result from the ‘oxygen bubble mould’ at the pore bottom, it is difficult to account for the constant inner diameter near the bottom of the nanotubes formed under different anodizing currents (15–30 mA).

In summary, the combination of ‘plastic flow’ model [20,21,27] and ‘oxygen bubble mould’ [17,32–37] can be used to successfully explain the nanotube growth. The driving forces of the nanotube growth are the ionic current and the electronic current. The ionic current results in the oxide growth, the electronic current results in the oxygen evolution, and meanwhile oxygen bubble that can cause high pressure on the barrier oxide always acts as the ‘oxygen bubble mould’ at the pore bottom, where the barrier oxide constantly embraces the ‘oxygen bubble mould’ and then grows upwards to form the nanotube walls. This growing manner of the porous anodic oxides has been intensely investigated in our previous works [32–37,46–49]. These concerned viewpoints have received considerable attention and citation [15,18,40,44,45,50–53].

### 4. Conclusions

In order to study the growth kinetics of anodic TiO$_2$ nanotubes, the titanium anodizing processes under different constant currents have been investigated. Both nanotube length and outer diameter increase with the increase of the anodizing current $J_{\text{total}}$. These results demonstrated that the chemical dissolution has no contribution to the $J_{\text{total}}$ but is mainly composed of ionic current $J_{\text{ion}}$ and electronic current $J_e$. For a given anodizing process of constant current, three interesting schemes are first proposed to estimate the relative values of $J_e$. Three average values of $J_e$ are approximately equal to each other, and it was demonstrated that the estimate values and the experimental error are reasonable. Furthermore, a relationship between the nanotube diameter ($Y$) and steady voltage ($X$) is given by the fitting equation $Y = 2.5X + 37.89$, the constant term ($+37.89$) may result from oxygen bubble mould at the pore bottom. It is very difficult to quantitatively clarify the present results based on the traditional model. These results may open up some new opportunities for fabricating anodic TiO$_2$ nanotubes and help to understand the yet-unclear growth kinetics of other porous anodic oxides.

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### References


#### Table 2

<table>
<thead>
<tr>
<th>$J_{\text{ion}}$ (mA)</th>
<th>Inner diameter (nm)</th>
<th>Outer diameter (nm)</th>
<th>Oxide Volume of one nanotube (108 nm$^2$)</th>
<th>Number of nanotubes (106 nm$^{-2}$)</th>
<th>Calculating equation</th>
<th>Estimated value of Je (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 mA</td>
<td>30</td>
<td>151</td>
<td>0.85</td>
<td>13.97</td>
<td>$J_e = 8.55$</td>
<td></td>
</tr>
<tr>
<td>20 mA</td>
<td>38</td>
<td>164</td>
<td>1.78</td>
<td>11.84</td>
<td>$J_e = 11.87$</td>
<td></td>
</tr>
<tr>
<td>25 mA</td>
<td>34</td>
<td>193</td>
<td>3.98</td>
<td>8.55</td>
<td>$J_e = 10.19$</td>
<td></td>
</tr>
<tr>
<td>30 mA</td>
<td>37</td>
<td>208.5</td>
<td>6.21</td>
<td>7.33</td>
<td>$J_e = 9.71$</td>
<td></td>
</tr>
</tbody>
</table>

Note: $0.85 \pm 13.97 \pm 11.87$ $3.98 \pm 8.55 \pm 14.03$
$b_{1.78} \pm 11.84 \pm 21.07$ $6.21 \pm 7.33 \pm 45.52$
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