An Oxygen-bubble-mould-effect Derived Model for Kinetics of Anodic TiO$_2$ Nanotubes under Constant Current

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Abstract. Despite the wide application of anodization, the mechanism is still under debate and requires quantitative analyses. Based on the oxygen bubble mould effect model, the total current contains ionic current and electronic current. The ionic current corresponds to the oxide formation, while the electronic current represents the oxygen bubble generation. In this article, we focus on the galvanostatic anodization of TiO$_2$ nanotubes. We develop a fitting model and simplify it by introducing intermediate parameters. The transients are fitted on 30, 40 and 50 mA, which exhibits high fidelity. The two types of current is also separated mathematically based on the model. The linear relation between nanotube length and the steady value of ionic current are determined, which proves the reasonability and applicability of the model.

1. Introduction
Currently, anodic TiO$_2$ nanotubes (ATNTs) and other anodic oxides are worth to be investigated because of their self-ordered structure and promising application in engineering fields.\cite{1,2} The mechanism of ATNTs has not been determined.\cite{3} So far, the field-assisted dissolution (FAD) model \cite{4,5} has been accepted, which talks about the existence of fluoride ions is a premise of the formation of ATNTs.\cite{6} Below is the assumed formula.\cite{7}

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} \tag{1}
\]

However, the above-mentioned model into doubt because that ATNTs can be obtained in the aqueous H$_2$SO$_4$ solution \cite{8} as well as other fluoride free solutions.\cite{9,10}

It is acknowledged that there are two types of anodic oxide films: compact anodic oxides (CAO) and PAO.\cite{11} Figure 1a and 1b show the current–time curves under a constant voltage and the voltage–time curves at a constant current. It is evident that in both graphs, the curves begin to diverge at a certain point c, which is unexplained in FAD theory. Skeldon et. al\cite{12-14} concluded that the generation and growth of pores are driven by the viscous flow of oxide from the pore base to the pore wall. Nevertheless, the theoretical derivation and quantitative analyses of curves are barely seen in any literatures.

Based on the viscous flow model and relevant findings, Zhu’s group has introduced the oxygen bubble mould effect (OBME) model \cite{15,16}, which reveals that oxygen evolution paves way for PATNT formation. The OBME model emphasizes the existence of ionic and electronic currents ($I_{\text{ion}}$ and $I_e$) in total current ($I_0$) during anodization. The equations have been figured out by Albella et. al.\cite{17} and Diggle et. al.\cite{18}.

\[
I_0 = I_{\text{ion}} + I_e \tag{2}
\]
\[
I_{\text{ion}} = Ae^{BE} \tag{3}
\]
\[
I_e = j_0e^{ad} \tag{4}
\]
The meanings of parameters above will be discussed further in this article. The $I_{\text{ion}}$ corresponds to the formation of oxide, while the $I_e$ gives rise to the release of oxygen.[19] Under OBME model, Zhu’s model has successfully figured out the formula of current-time curves under the constant voltage.[20]

$$i = \frac{U_1}{R_{el}} e^{-\frac{t}{\alpha \beta R_{el}}} + C_{\text{ion}} + i_{\text{eq}} e^{-\eta \alpha \beta k \frac{t}{R_{el}}}(5)$$

Diggle et. al.[11] concluded in early time that there is no essential difference between PAO and CAO films. Based on OBME model, the difference between two types of oxides lies in the proportion of $I_e$.[20]

Herein, this article focuses on the mathematical model of ATNTs growth on the constant current. Two types of models are adopted for ATNTs on 30 mA, 40 mA and 50 mA. By comparing $I_{\text{ion}}$ and $I_e$, the model of low current fits better for our condition. Besides, we measure the length of nanotubes and determine the proportional relation with ionic current. Our work proves OBME model and $I_{\text{ion}}$ and $I_e$ theory.

2. Experimental details

The Ti foil is 100 μm in thickness and the exposure area for anodization is 2 × 1 cm² in each side. The purity is 99%. The Ti is used as a working electrode. Besides, the graphite is applied as a counter electrode, which is 3.5 cm apart from the working electrode. The foils are polished in a mixture solution (40 mL) of deionized water, HF (≥40%, Shantou West Long Chemical Factory Limited) and HNO3 (65–68%, Shantou West Long Chemical Factory Limited) (2:2:1 in volume) for 15 s. Thereafter, the samples are washed with deionized water and dried in the air under room temperature. The electrolyte is composed of 0.4 wt% NH₄F (AR, 98%, Aladdin) and 1.8 wt% H₂O in ethylene glycol (EG). Then, the Ti foils are anodized under the constant currents, which is 30 mA, 40 mA and 50 mA, respectively.

The voltage transients are recorded during the second anodization process. The first anodization is performed at 30 ℃ (in water bath) for 600 s by stirring. Then, we ultrasonically rinse the specimens in the deionized water for 20 min to peel off the as-formed film. The voltage-time transients are recorded automatically by Chroma Programmable DC power supply (62006P-300-8). The morphology of the ATNTs is characterized by field-emission scanning electron microscopy (FE-SEM, Zeiss Supra 55). The nanotube length is measured on each specimen for three times directly on the FESEM images. The average value is taken for the calculation. The curves are fitted by Origin.

3. Results and discussion

3.1. Mechanism and morphology of ATNTs

Figure 1c illustrates the apparatus of anodization. During anodization, the Ti foil loses electrons and turns to TiO₂ nanotubes on the surface. Based on OBME model, this process is divided into three stages. Figure 1d shows schematic diagram of OBME. In stage I, Ti anode is oxidized into Ti⁴⁺ and drifted into the electrolyte under the applied filed, which corresponds to the ionic current (Ion). Reacted with the electrolyte, compact TiO₂ layer is formed rapidly on the surface of the anode. During the meantime, the O₂⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-~(in the form of H₂O) is oxidized into O₃, which corresponds to electronic current (Ie). In stage II, the oxygen bubble is egressed into the oxide layer, which works as the mould for nanotube growth. Nanotubes grow from the bottom to the top based on the plastic flow model. In stage III, the oxide layer on the top of nanotubes will be cracked. And oxygen bubbles at the bottom will be released into the electrolyte. Besides, the electrolyte will enter into the nanotubes. Therefore, there will be an equilibrium between Iion and Ie. The process of anodization can be quantifiably analyzed based on the Iion and Ie theory, which will be discussed in detail in the following context.

Figure 2a shows the picture of TiO₂ nanotubes. Figure 2b – 2d shows the SEM images of nanotubes on 30, 40 and 50 mA, respectively. We can see independent nanotubes with voids on SEM. Also, there are semi-spherical bottoms. In addition, typical inter-tube ribs are observed. At the
meantime, the length of nanotubes are measured. The length of nanotubes on 30, 40 and 50 mA are 1.48, 2.72 and 2.87 μm, respectively. Generally, longer nanotubes are obtained on higher current.

Figure 1. (a) The current–time curves under potentiostatic anodization and (b) the voltage–time curves under galvanostatic anodization. (c) The apparatus of anodization. (d) Schematic diagram of OBME.

Figure 2. (a) Digital photos of TiO$_2$ nanotubes. SEM images of ATNTs on (b) 30, (c) 40 and (d) 50 mA.
3.2. The model and fitting

Based on OBME model and Iion and Ie theory, Zhao et al.[21,22] developed the mathematical model of voltage-time transients under constant current.

\[ U = (I_0 - \frac{j_0}{I_{e\text{max}}} + (1 - \frac{j_0}{I_{e\text{max}}})e^{-akt_{e\text{max}}t})(R_{el} + \frac{1}{\alpha\gamma S} \ln \frac{j_0}{I_{e\text{max}}} + (1 - \frac{j_0}{I_{e\text{max}}})e^{-akt_{e\text{max}}t}) \]

\[ U = R_{el}(I_0 - \frac{j_0}{I_{e\text{max}}} + (1 - \frac{j_0}{I_{e\text{max}}})e^{-akt_{e\text{max}}t}) + \frac{1}{aB} \ln \frac{j_0}{I_{e\text{max}}} + (1 - \frac{j_0}{I_{e\text{max}}})e^{-akt_{e\text{max}}t} \cdot \ln \frac{1}{A}(I_0) \]

Eq. (6) is the model of low current density (< 10 mA cm$^{-2}$), labelled as CC1. Eq. (7) is the model of high current density (> 10 mA cm$^{-2}$), labelled as CC2. Specifically, 10 mA cm$^{-2}$ is an empirical value. The selection of low or high current model should be based on the analyses of ionic and electronic current. In Eq. (6) and (7), $I_e$ soars from a tiny initiation ($j_0$) steeply to a certain maximum ($I_{e\text{max}}$). $\gamma$ is the conductivity, and $S$ is the anodic area. $\alpha$, $k$, $B$ are coefficient. $R_{el}$ means resistance of electrolyte. The formula can be simplified for convenience of fitting.

Let

\[ \varepsilon = e^{ad} = \frac{n}{1 + (n - 1)e^{-a\text{mt}}} = \frac{1}{\frac{j_0}{I_{e\text{max}}} + (1 - \frac{j_0}{I_{e\text{max}}})e^{-akt_{e\text{max}}t}} \]

Let

\[ M = \alpha k I_{e\text{max}} \]

\[ N = \frac{j_0}{I_{e\text{max}}} \]

\[ D = \frac{1}{\alpha\gamma S} \]

\[ F = \frac{1}{A} \]

\[ G = \frac{1}{aB} \]

then

\[ \varepsilon = \frac{1}{N + (1 - N)e^{-Mt}} \]

The two models are

\[ U = (I_0 - j_0\varepsilon)(R_{el} + D \ln \varepsilon) \]

\[ U = R_{el}(I_0 - j_0\varepsilon) + G \ln \varepsilon \cdot \ln F (I_0 - j_0\varepsilon) \]

Simplified formulas of fitted CC curves is listed in Table 1. The variation curve of voltage with time, and the variation curve of ionic and electronic currents with time are depicted in figure 3, respectively. According to Table 1, both CC1 and CC2 model exhibit high R2 (goodness of fitting).
The model corresponds to the trend of voltage vs. time during anodization, and separates the ionic and electronic current mathematically.

Taking nanotubes anodized on 40 mA, by CC1 model as an example. Figure 3b shows the variation curve of voltage with time on 40 mA, figure 3e depicts the variation curve of ionic and electronic currents with time on 40 mA. In stage I, the voltage increases rapidly, which is in accordance with the compact oxide layer formation. During this stage, $I_{ion}$ decreases from 40 mA due to increasing resistance of oxide. Meanwhile, $I_e$ starts from small $j_0$. In stage II, the voltage begins to decline, which is in accordance with the nanotube growth. During this stage, $I_{ion}$ keeps decreasing, and $I_e$ starts to increase because the oxygen bubbles are generated and expanded. During this process, the oxygen bubbles function as mould for the nanotube growth from bottom to the top.

In stage III, the voltage becomes steady, corresponds to the equilibrium between $I_{ion}$ and $I_e$ (18 mA vs. 22 mA from figure 3e). For CC2, the ratio of $I_{ion}$ and $I_e$ is disproportional. Therefore, we adopt CC1 as the final model.

Table 1. Expressions of fitted CC curves. The expressions are simplified with intermediate $\varepsilon$.

| $I_0$ (mA) | CC1 | CC2 |
|------------|-----|-----|
| 30         | $\varepsilon = \frac{1}{0.03292+0.96708e^{-0.1035t}}$ | $\varepsilon = \frac{1}{0.00414+0.9586e^{-0.1011t}}$ |
|            | $U = (30 - 0.4818\varepsilon)(0.3832 + 0.7252 \ln \varepsilon)$ | $U = 0.4083(30 - 0.0075\varepsilon) + 2187.13 \ln \varepsilon \cdot \ln 0.0337 (30 - 0.0075\varepsilon)$ |
|            | $R^2 = 0.9942$ | $R^2 = 0.9955$ |
| 40         | $\varepsilon = \frac{1}{0.05235+0.9476e^{-0.0911t}}$ | $\varepsilon = \frac{1}{0.0668+0.9332e^{-0.0857t}}$ |
|            | $U = (40 - 1.1687\varepsilon)(0.2056 + 0.9454 \ln \varepsilon)$ | $U = 0.1791(40 - 0.0638\varepsilon) + 991.04 \ln \varepsilon \cdot \ln 0.02600 (40 - 0.0638\varepsilon)$ |
|            | $R^2 = 0.9697$ | $R^2 = 0.9955$ |
| 50         | $\varepsilon = \frac{1}{0.1518+0.8482e^{-0.1023t}}$ | $\varepsilon = \frac{1}{0.06648+0.93352e^{-0.1724t}}$ |
|            | $U = (50 - 4.6003\varepsilon)(0.3246 + 1.2261 \ln \varepsilon)$ | $U = 0.4423(50 - 0.1328\varepsilon) + 459.25 \ln \varepsilon \cdot \ln 0.021245 (50 - 0.1328\varepsilon)$ |
|            | $R^2 = 0.9955$ | $R^2 = 0.9828$ |
Figure 3. The variation curve of voltage with time under the constant current condition (a) 30, (b) 40 and (c) 50 mA. The variation curve of ionic and electronic currents with time under constant voltage condition (d) 30, (e) 40 and (f) 50 mA.

Figure 4. The relation between the length of the TiO$_2$ nanotubes (L) and the steady value of ionic current ($J_{ionst}$).

3.3. Relation between nanotube length and ionic current

Figure 4 explains relation between the length of the ATNTs and the steady value of ionic current. The nanotube length is observed proportional to the steady value of ionic current. This is due to that ionic current is in accordance to the oxide growth. This relation proves the CC1 model and connects the current and nanotube growth.
4. Conclusion
In summary, we focus on three stages of nanotube growth based on OBME model and the ionic current and electronic current theory. The morphology and length of TiO$_2$ nanotubes are determined by SEM. We apply the fitting model of galvanostatic anodization under different current conditions and make the simplification by introducing intermittent parameters.

Then, the transient of voltage vs. time is fitted based on CC1 and CC2 model on 30, 40 and 50 mA, which exhibits high goodness of fit. The ionic current and electronic current is also separated mathematically based on the models. During anodization, the ionic current decreases rapidly to a quasi-steady value, while the electronic current increases from a tiny initial value and keeps rising with oxygen bubble generation to a steady value. Comparing $I_{\text{ion}}$ and $I_e$ from CC1 and CC2, CC1 illustrates more appropriate relation between $I_{\text{ion}}$ and $I_e$, which should be adopted in this work.

Finally, the linear relation between nanotube length and the steady value of ionic current are observed, which proves the reasonability and applicability of OBME model. This work may help understand the relation between nanotube growth and current trend.

5. References
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