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

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ABSTRACT

The growth kinetics of anodic TiO_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 ($\boldsymbol{J}_{total}$) is difficult to determine, because the variable $\boldsymbol{J}_{total}$ includes ionic current ($\boldsymbol{J}_{ion}$) (also called oxide growth current $\boldsymbol{J}_{grow}$=$\boldsymbol{J}_{ion}$) and electronic current ($\boldsymbol{J}_{e}$), 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 $\boldsymbol{J}_{total}$ during constant current anodization, we can estimate the relative magnitudes of $\boldsymbol{J}_{grow}$ and $\boldsymbol{J}_{e}$. The nanotubes with lengths of 1.24, 2.23, 3.51 and 4.70 μm, were formed under constant currents ($\boldsymbol{J}_{total}$) of 15, 20, 25 and 30 mA, respectively. The relationship between nanotube length (y) and anodizing current (x =$\boldsymbol{J}_{total}$=$\boldsymbol{J}_{grow}$+$\boldsymbol{J}_{e}$) can be expressed by a fitting equation: y=0.23(x-10.13), from which $\boldsymbol{J}_{grow}$ ($\boldsymbol{J}_{grow}$ = x -10.13) and $\boldsymbol{J}_{e}$ (~10.13 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.

1. Introduction

Anodic TiO_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.

$$TiO_2+6F^-+4H^+ \rightarrow [TiF_6]^{2-} +2H_2O \quad (1)$$

$$Al_2O_3+6H^+ \rightarrow 2Al^{3+}+3H_2O \quad (2)$$

It is well known that the above field-assisted dissolution processes are acid-catalyzed. Most of H^+ ions will be driven to gather near the cathode by the electric field, resulting in release of H_2 gas [15]. As a result, H^+ 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

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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 TiO_2, $Ti(OH)_x$, $[TiF_6]^{2-}$ and O_2 gas, are related to the electric charge. Whereas the total electric charge ($\boldsymbol{Q}$) is determined by the product of the anodizing current ($\boldsymbol{J}_{total}$) and the anodizing time ($\boldsymbol{t}$) ($\boldsymbol{Q}$ $=\boldsymbol{J}_{totalt}$). Garcia-Vergara et al. [25] also concluded that the porous layer thickens 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 ($\boldsymbol{J}_{dis}$) or ionic current ($\boldsymbol{J}_{ion}$=$\boldsymbol{J}_{grow}$) 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, HNO_3 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 (DL3005Cooling Pump).

The electrolyte was ethylene glycol solution containing 0.3wt% NH_4F and 5wt% H_2O. 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 cm^2). A Pt mesh as cathode (area of ~12.0 cm^2) 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 TiO_2 nanotube films were ultrasonically rinsed in the deionized water for ~20 min to peel off the formed film. And 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 TiO_2 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

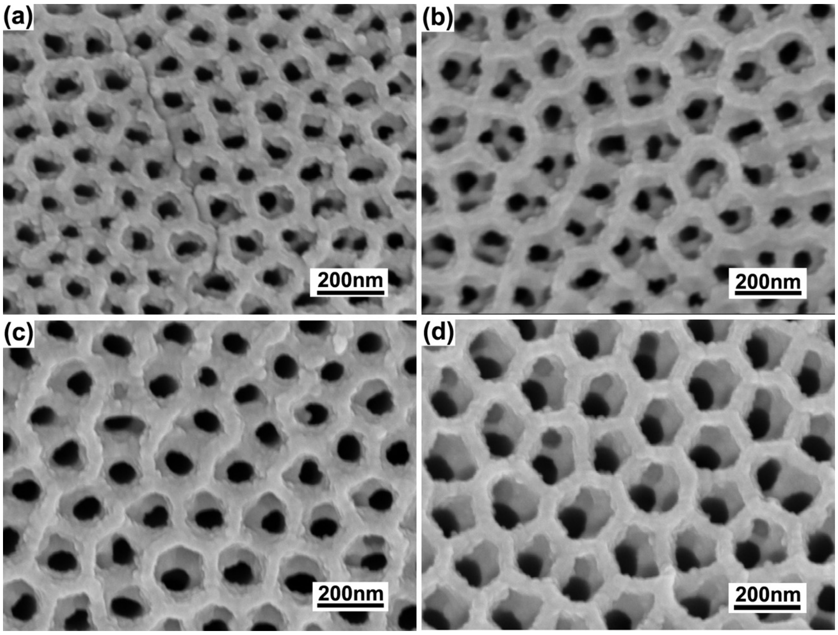

Fig.1. FESEM images showing the top views of TiO_2 nanotubes formed at different anodizing currents: (a) 15 mA, (b) 20 mA, (c) 25 mA, (d) 30 mA.