Fabrication and growth model for conical alumina nanopores – Evidence against field-assisted dissolution theory

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A B S T R A C T

The mechanism of nanopore initiation during anodization remains unclear. Al substrates with a pre-formed compact oxide layer are anodized potentiostatically to decouple dissolution effect and oxide growth. Rather than ordinary cylindrical pores, conical alumina nanopores are fabricated beneath the pre-formed layer. Besides, the current-time transients show an abnormal upward trend compared with transients for ordinary anodization. A mathematical model for nanopore growth is established based on the theory of ionic and electronic current and the oxygen bubble mould effect. The model shows high accuracy when fitting current transients. By simulating the ionic current, electronic current and applied potential across the porous layer, the formation mechanism of conical nanopore embryos is explained. The nanopores beneath the compact layer are separated from the electrolyte, providing further direct evidence against the field-assisted dissolution theory.

1. Introduction

Anodic porous oxides have been intensively studied due to their one-dimensional structure and enhanced surface area, especially porous anodic alumina (PAA) and anodic titania nanotubes [1–6]. However, the mechanism for initiation and growth of the porous (or tubular) oxide layer is still under debate [7–19]. A traditional theory is field-assisted dissolution (FAD), according to which pores are formed due to oxide dissolution at the electrolyte/oxide interface driven by the electric field [8–13]. However, this theory has been questioned for the failure to explain specific structures, such as terminated pores [14–19]. Therefore, more and more theories have been developed to explain the growth of nanopores, including the oxygen bubble mould effect [15, 16], plastic flow model [22, 23], ionic and electronic current theory [24, 25], etc.

Large quantities of research have been done to prove that nanopore formation is not driven by FAD [14–20, 22, 23, 25–27], including tracer study of oxide growth [20, 22, 26], determination of stress inside PAA [23] and analyses of nanopore embryos [15, 18, 28]. Nanopore embryos refer to nanopores (or nanotubes) initiated at the beginning of anodization, which might exhibit different morphology or structure compared with formed nanopores, such as shorter tube length [15], less self-ordering arrays [16] and no-ribbing tube wall [18]. The fabrication and study of embryos may help understand the initiation of anodic oxides. One way to prepare embryos is to decouple the dissolution and oxidation processes at the electrolyte/oxide interface [9, 18, 28]. Usually, the porous layer is exposed to the electrolyte, so the dissolution and oxide growth happen simultaneously, which makes it difficult to study the single effect of oxide growth. By anodizing a substrate with pre-anodized oxide layer, the nanopores can grow beneath the pre-formed layer without interaction with electrolyte.

One of the major differences between porous oxide anodized from Ti and Al is that titania nanotubes are tubular with inter-tube voids, while PAA are pore-arrayed without voids [12–14]. The study of both TiO$_2$ nanotubes and PAA will help understand the tube/pore transition and anodization of other valve metals [14]. Considering promising properties of TiO$_2$ in solar cells and supercapacitors, TiO$_2$ nanotube embryos have been widely observed and studied by the decoupling method [16, 18, 19, 28]. Our recent publication established a growth model for TiO$_2$ embryos to explain the complicated trend of current transients [18]. Nevertheless, to the best of our knowledge, the growth kinetics of PAA has been little studied in recent years [9]. Will PAA have similar parachute-like embryos at the initiation stage as TiO$_2$ [18]? Will the current-time curves show complicated stages with respect to anion incorporation and oxide growth [18, 28]? Fabrication of alumina pore embryos and quantitative analyses are needed to better understand anodization mechanism not only for Al per se, but also for other metals. To quantify nanopore growth, several mathematical models have been developed based on aforementioned theories [29–40]. Our group also derived expression of current-time transient

during potentiostatic anodization [37, 38] according to the theory of ionic and electronic current. The transient trend is easy to record and tightly related to oxide growth. Nevertheless, there has been little research on quantitative analysis of current transients for PAA, which should be studied in detail.

In this study, Al substrates with pre-formed compact layers are anodized to minimize the dissolution effect. Nanopore embryos with a conical top are fabricated beneath the pre-formed layer. Based on our former research, we derive a mathematical model to express current-time transients during embryo growth. According to the model, the conical structure is explained and the mechanism of nanopore initiation under the existing layer is developed, which is evidence against FAD theory.

2. Experimental details

Aluminum foil (200 μm thick, anodizing area 4 cm^2) was used as the working electrode. The counter electrode is graphite 3.5 cm apart. First, samples were anodized in 8 wt% ammonium sebacate aqueous solution at 50–200 V for 180 s. After being soaked by deionized water for 30 min, samples were anodized in 3 wt% oxalic acid aqueous solution at 50–120 V for 100–600 s. The temperature was 30 °C (303 K). Current-time curves were recorded by a computer system. Anodized samples were characterized by scanning electron microscopy (SEM) (FESEM, Zeiss Supra55). Curves were fitted by sciDAVis 1.14. The voltage was simulated by MATLAB_R2015a.

3. Results and discussion

3.1. Morphology and current transients of nanopores

SEM images and current-time transients of samples are shown in Fig. 1. Without the compact layer (noted as pre-layer), uniform cylindrical nanopores are formed without interpore voids (Fig. 1a) [41–43]. In contrast, the nanopores formed under the pre-layer have a different structure from ordinary PAA. Under the pre-layer (Fig. 1b–d), nanopores with a conical top are developed. The conical pores are shorter and less ordered than ordinary nanopores, which means they are still in the initiation process [28]. When the pre-layer is formed at 200 V, the self-ordering nanopores are not formed and only cavities are discovered (Fig. 1e). Since most theories focus on the growth of self-ordering, hexagonal-packed PAA, the formation mechanism of conical nanopores cannot be explained by existing theory and needs detailed explanation.

Besides, the current-time transient for conical pores is different from that for ordinary nanopores. For ordinary anodization, the current-time curve is divided into three typical stages (Fig. 1a). The transient drops exponentially in stage I, slightly increases in stage II and remains stable in stage III, which has been clearly clarified in our previous study [15, 16, 18]. As for conical nanopores (Fig. 1b–e), in stage I, the current rapidly decreases within a short time. Afterwards, the total current slowly rises in stage II and steeply increases in stage III. Besides, the current in Fig. 1b–d is much lower than that in Fig. 1a, owing to resistance of the pre-layer. Although the upward transient was recorded by Thompson et al. [9] in H$_3$PO$_4$, the mechanism of nanopore growth in stage II and III still remains unclear. Usually, for Al, Ti and other metals, the current curves show a steady trend after certain anodizing time (Fig. 1a), where chemical equilibrium is reached at the electrolyte/growing-oxide interface [38, 39]. The ever-increasing transient for nanopore embryos means the system is in an unstable state (Fig. 1b–e), which should be quantitatively analyzed.

3.2. Derivation of current-time transient of nanopores

The theory of ionic and electronic current divides total anodizing current (J) into two parts – ionic current (J_{ion}) and electronic current

(J_e), which represent oxide growth and oxygen generation at the anode, respectively [39].

$$J = J_{ion} + J_e \tag{1}$$

J_{ion} is related to the exponential of average electric field (E) across the whole oxide layer (including pre-layer) [44], while J_e is related to the exponential of growing layer thickness (d) [30].

$$J_{ion} = Ae^{BE} \tag{2}$$

$$J_e = j_0 e^{\alpha d} \tag{3}$$

where A, B and α are coefficients and j_0 is initial electronic current.

For TiO$_2$ embryos, the relation between J_{ion} and d is established to solve the model. However, since the electrolyte/oxide/substrate system is in an unstable state as mentioned in Section 3.1, the relation does not apply. During anodization, J_e derives from oxidation of O^{2-}, so the electric charge of J_e is related to the amount of yielding O$_2$.

$$Q_e = \int J_e dt = zn(O_2)F \tag{4}$$

where t is anodizing time, F is Faraday constant, z is the number of electron transferred for every O$_2$ molecule, and $n(O_2)$ is the amount of O$_2$.

According to the Clapeyron equation,

$$n(O_2) = \frac{pV}{RT} \tag{5}$$

where p and V are pressure and volume of O$_2$, T is Kelvin's temperature and R is universal gas constant. Then

$$Q_e = \frac{zpVF}{RT} \tag{6}$$

The embryo is a conical structure filled with oxygen gas. The volume of O$_2$ (V) is related to length of the embryo (l).

$$V = k_1 l^m \tag{7}$$

Here m is the index. Theoretically, if the embryo is standard spherical, $m = 3$. For cylindrical or conical pores, $m = 1$.

The length of embryo is proportional to porous layer thickness [37].

$$l = k_2 d \tag{8}$$

Therefore, charge of J_e is related to layer thickness.

$$Q_e = \frac{zpFk_1k_2}{RT}d = kd \tag{9}$$

This corresponds with that pore thickness is related to electric charge [45]. Then

$$\int J_e dt = \int j_0 e^{\alpha d} dt = kd \tag{10}$$

$$d|_{t=0} = 0 \tag{11}$$

Solve the differential equation

$$j_0 e^{\alpha d} dt = kdd \tag{12}$$

$$\frac{j_0}{k}dt = e^{-\alpha d}dd \tag{13}$$

$$\frac{j_0}{k}t = \int_0^d e^{-\alpha \delta}d\delta \tag{14}$$

So

$$d = -\frac{1}{\alpha}\ln\left(1 - \frac{\alpha j_0}{k}t\right) \tag{15}$$

J_e can be expressed as

$$J_e = \frac{j_0}{1 - \frac{\alpha j_0}{k}t} \tag{16}$$