



Cavities between the double walls of nanotubes: Evidence of oxygen evolution beneath an anion-contaminated layer

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ABSTRACT

The mechanisms of formation of porous anodic alumina and anodic TiO₂ nanotubes (ATNTs) have attracted increasing attention due to the wide range of application of these materials. The field-assisted dissolution and field-assisted ejection theories are widely supported, despite the fact that many experimental results raise difficult questions. The oxygen bubble mould theory can explain experimental phenomena that contradict the field-assisted dissolution theory, but is controversial as there is a lack of evidence of oxygen evolution. In this work, cavities between the double walls of ATNTs obtained in electrolytes containing NH₄F and H₃PO₄ provide direct evidence of oxygen bubbles resulting in pore formation. Oxygen evolution proceeds at the interface between the anion-contaminated layer and the barrier oxide layer. Small oxygen bubbles that cannot rupture the anion-contaminated layer flow upward with the barrier oxide, resulting in cavities between the double walls of the nanotubes.

1. Introduction

Porous anodic oxides fabricated by anodization, especially anodic TiO₂ nanotubes (ATNTs) and porous anodic alumina, are widely used for a variety of applications [1–5], but their mechanism of formation is still controversial [6–8]. The field-assisted dissolution theory has been widely accepted since it was first proposed in porous anodic alumina by Wood et al. [9]. Even though there is no direct evidence to prove the equilibrium between oxide growth and dissolution, the field-assisted dissolution theory remains the popularly accepted mechanism, although some alternative theories have been proposed [10–13]. Zhu et al. [14,15] have recently presented evidence against the field-assisted dissolution theory: the appearance of terminated nanotubes [14] and observations of oxide growth locations [15] are contrary to the field-assisted dissolution theory. The oxygen bubble mould theory [11–13], combined with a plastic flow model [10], can explain the formation of a porous structure reasonably well. However, this model is questioned by some researchers because it is difficult to obtain evidence of oxygen bubbles by direct in situ methods.

Pore initiation and oxygen evolution are closely related to the incorporation of anions [16–18], but the existence of an anion-contaminated layer is not readily explained by the field-assisted dissolution theory [10,19,20]. Garcia-Vergara et al. [20] indicated that the field-assisted dissolution theory cannot clarify the distribution of anion contaminant species from the electrolyte into the anodic film [20]. If it

is the equilibrium between oxide growth and dissolution that results in pore initiation, the anion-contaminated layer at the bottom must be dissolved first and will not remain. Furthermore, the double-walled structure of porous anodic oxides was reported some time ago [21,22]; the inner wall is actually the anion-contaminated layer [23]. The formation of an anion-contaminated layer is a precondition for oxygen evolution [18,24,25]. Nevertheless, the location of oxygen evolution activity is purely speculative and no evidence of oxygen bubbles has been reported.

In this work, plenty of cavities were discovered between the double walls of anodic TiO₂ nanotubes produced when Ti was anodized in mixed NH₄F/H₃PO₄ electrolytes. As the concentration of H₃PO₄ increases, the nanotube walls get thicker and double-walled nanotubes are observed. These double walls are actually composed of an anion-contaminated layer and a barrier oxide layer. The cavities cannot be explained by the field-assisted dissolution theory and indicate that oxygen evolution occurs at the interface between the anion-contaminated layer and the barrier oxide layer. It is reasonable to conclude that cavities between the double walls of nanotubes are evidence of oxygen bubble formation. The results presented here again raise questions about the field-assisted dissolution theory and for the first time provide supporting evidence for the oxygen bubble mould theory.

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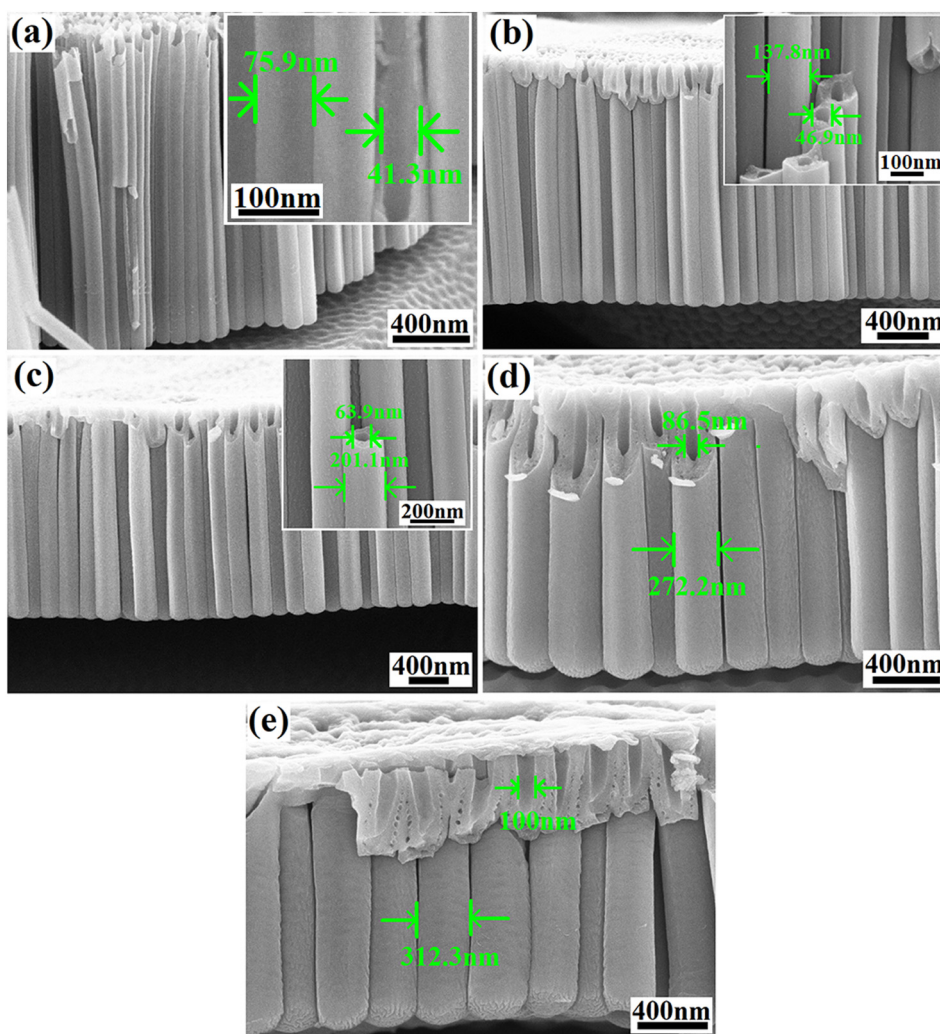


Fig. 1. FESEM images showing the morphology of cross-sections of ATNTs fabricated in a mixed electrolyte containing 0.5 wt% NH_4F and n wt% H_3PO_4 ($n =$ (a) 0, (b) 2, (c) 4, (d) 6, (e) 8, respectively).

2. Experimental details

The titanium foils (100 μm thick, purity 99.5%) were polished with a mixture of HNO_3 , HF and deionized water (1:1:2 by volume) for about 10 s. All specimens were then rinsed thoroughly with deionized water and dried in air prior to anodization. The titanium foils were used as the anode and another titanium foil served as the cathode. The pretreated specimens were anodized in a mixed electrolyte containing 0.5 wt% NH_4F and n wt% H_3PO_4 ($n = 0, 2, 4, 6, 8$, respectively) for 600 s. The solvent was ethylene glycol with 2 vol% water. The anodizing temperature was 30 $^\circ\text{C}$ and the anodizing current density was maintained at $5 \text{ mA}\cdot\text{cm}^{-2}$. The voltage vs time curves were recorded via the automatic computer system during anodization. All the samples were rinsed using deionized water after anodization and dried in air. Finally, all of the specimens were characterized by FESEM (Zeiss Supra 55) without annealing. The anodized specimens were bent into a V shape before observation.

3. Results and discussion

Fig. 1 shows the cross-sections of ATNTs obtained in electrolytes containing different concentrations of H_3PO_4 . All the anodizing processes were otherwise the same, with the current density maintained at $5 \text{ mA}\cdot\text{cm}^{-2}$ for 600 s. As H_3PO_4 was added to the NH_4F /ethylene glycol, all the ATNTs have a normal porous structure. However, the inner and

outer diameters of the nanotubes become larger with increasing H_3PO_4 concentration. The nanotube wall thickness can be calculated using the inner and outer diameters and are 17.3 nm, 45.4 nm, 68.6 nm, 92.8 nm and 106.1 nm for the H_3PO_4 concentrations studied. It is clear that the wall thickens with increasing H_3PO_4 concentration. According to the field-assisted dissolution theory, H^+ concentration increases with H_3PO_4 concentration, hence the dissolution ($\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O}$) should be accelerated. The wall should then be thinner and the barrier oxide thickness should decrease with higher H^+ concentration, but the experimental result shows the opposite.

Fig. 2 shows the corresponding voltage vs time curves for the five anodizing processes obtained in different electrolytes. All the curves show the three typical stages. Based on the field-assisted dissolution theory, as the H^+ concentration increases the dissolution should be more intense. Then the equilibrium voltage (which is proportional to the barrier oxide thickness) should be lower. However, the equilibrium voltage is actually higher. A higher equilibrium voltage results in a thicker barrier oxide and the outer diameter is bound to increase. Furthermore, in electrolytes with a higher H_3PO_4 concentration, the inflection point of the voltage vs time curve occurs later, which is also difficult to interpret by the field-assisted dissolution theory. The later appearance of the inflection point means that the oxygen bubbles are staying under the anion-contaminated layer for a longer period of time, so the inner diameter becomes larger.

It is surprising that there seem to be plenty of cavities within

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