

Parameters and Underlying Mechanisms Affecting the Morphology of Bifurcating TiO₂ Nanotubes

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Self-organized TiO₂ nanotubes created from anodized Ti sheets were first reported by Zwillling *et al* [1], which opened avenues of research aimed at exploiting their properties for various applications. TiO₂ nanotubes increase reaction efficiencies and are therefore deemed as a suitable substitute for TiO₂ nanoparticle layers within Grätzel-type solar cells [2]. Reaction efficiencies have been demonstrated to be augmented by the morphology of the nanotubes reducing both the distance traversed by mobile electrons and electron/inter-crystalline interactions [3]. This concept highlights the importance of the morphology of the TiO₂ anode within a Grätzel-type solar cell, and provides credence to research aimed at controlling the morphology of TiO₂ nanotubes. Optimization of length, diameter, smoothness of the tube side walls, and self-ordering has been regulated by selectively determining the appropriate anodizing conditions. The main factors controlling the morphology of nanotubes are: the electrolyte, water content of the electrolyte, applied voltage/current, and temperature. However, despite a large degree of control over the morphology of TiO₂ nanotubes being possible, vertically aligned nanotubes with large aspect ratios have been predominantly investigated. Only a minority of papers have examined the possibility of exotic morphologies such as bifurcating (branching). Furthermore, the underlying mechanism describing the formation of such morphologies has not been examined in depth. This study aims at examining the parameters which affect the formation of bifurcating nanotubes, in order to obtain a greater understanding of the mechanisms behind their formation, and superior control over their final morphology.

Degreased Titanium foil (99.5%) was placed into a poly (methyl methacrylate) specimen holder to form a two electrode cell with a platinum foil counter electrode. The specimens were anodized in a 0.3 wt.% NH₃F solution in ethylene glycol containing 2 - 9 wt.% deionized water, with the applied potential utilized varying between 30 - 70 V. Anodizing was carried out via a “two-step” method which involved anodizing the specimen at an initial voltage for 3600 s and then removing the produced oxide layer via adhesive tape. The second step of anodizing was then carried out on the exposed metal/oxide interface under the same conditions as the first step for 600 s. This was immediately followed by a subsequent period of anodizing under a reduced applied voltage in the same electrolyte. The applied voltage was reduced by a factor of $1/\sqrt{n}$; where $n = 2, 3, \text{ or } 4$. The specimens were then analyzed via SEM, STEM and HR-TEM to determine the resulting nanotube morphology.

SEM cross sectional analysis of the oxide film revealed that the nanotubes generated in electrolytes containing only 2wt. % deionized water did not bifurcate when the voltage was reduced. These observations were later reconfirmed by in depth analysis of the metal/oxide interface after the oxide layer had been peeled off. This result is contradictory to the idea that the diameter of the cell is proportional to the applied voltage and implies

there is an underlying mechanism that allows this proportionality to vary depending on growth conditions. Analysis of nanotubes generated in electrolytes with higher water contents revealed that bifurcation became progressively more global as the water content was increased. Additionally, the introduction of a ramped voltage induced less localized bifurcation, as has been previously reported by Chen and Lu [4]. Both, situations imply that an elevated dissolution of the barrier layer plays an important role in the processes leading to a “smooth” bifurcation of nanotubes (figure 1a).

Contrary to these results, it was observed that for higher factors of n , bifurcation occurs without a ramped voltage if the voltage remains applied for an extended period of time. This data was in accordance with results published by Albu *et al* [5] and imply a “non-smooth” bifurcation based on penetration paths forming within the barrier layer (figure 1b). By observing the metal/oxide interface at various times during the develop of bifurcation, it was possible to determine that penetration paths are more likely to form at the saddle points of the cell and less likely to form at the triple point. This phenomenon generates distinctive patterns within the scalloped surface of the metal/oxide interface, if the bifurcation process is terminated prematurely (figure 2).

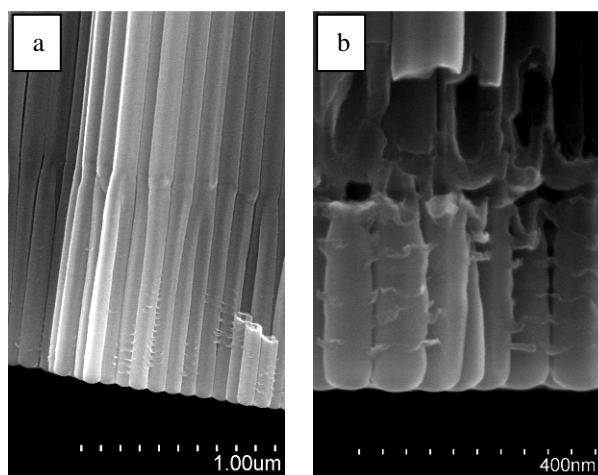


Fig 1. SEM images of a) “smooth” and b) “non-smooth” bifurcating TiO₂ nanotubes

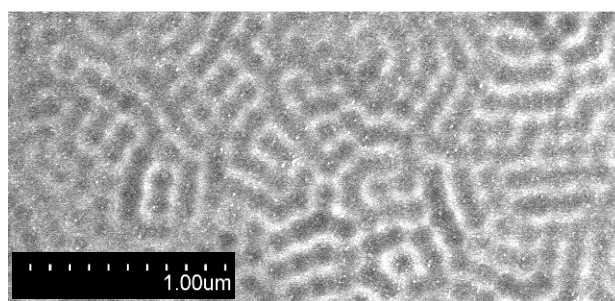


Fig 2. SEM image of a metal/oxide interface with a scalloped pattern generated by incomplete bifurcation.

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