

Growth Behavior of TiO₂ Nanotube Arrays in Different Electrolyte pH

Roshasnorlyza HAZAN^{1,2,a*}, Srimala SREEKANTAN^{2,b} and Ishak MAT^{3,c}

¹Materials Technology Group, Industrial Technology Division, Malaysian Nuclear Agency, Bangi, 43000, Kajang, Selangor, Malaysia.

²School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300, NibongTebal, Pulau Pinang, Malaysia.

³Advance Medical and Dental Institute, Universiti Sains Malaysia, 11200, Kepala Batas, Pulau Pinang, Malaysia.

^aroshasnorlyza@nm.gov.my, ^bsrimala@eng.usm.my, ^cddramdi@yahoo.com

ABSTRACT. TiO₂ nanotube arrays grow on Ti metal would be the best candidate as an implant material. The excellent biocompatibility appears to depend on the presence of a passive oxide layer (TiO₂ layer) formed on the surface. In this study, the effect of electrolyte pH (pH 1 up to pH 9) on length of the TiO₂ nanotubes arrays was investigated. The nanotubes length increased significantly with the increase of the electrolyte pH value and the longest TiO₂ nanotubes obtain at pH 8. Lower pH value at the pore tip and higher pH value at pore mouth are necessary to obtain desired TiO₂ nanotubes length. Therefore, it is significantly controlled the electrolyte pH to gain desired TiO₂ nanotubes.

Keywords: Anodization, Biomaterials, Electrolyte, Nanotopography, pH, TiO₂ nanotubes arrays;

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1. INTRODUCTION

Ti implants are commonly used in orthopedics and dentistry for their favorable biocompatibility and corrosion resistance [1]. Upon exposed to the atmosphere, the Ti metal spontaneously forms a thin, dense and protective oxide layer (approximately 10 nm thick) on its surface, which act like a ceramic with superior biocompatibility. When Ti implant is inserted into human body, the surrounding tissue directly contact the TiO₂ layer on the implant surface [2]. In the field of biomaterials and implant technology, nanometric scale of surface topography, roughness and chemical surface modification becoming critical factor for cell survival. The excellent biocompatibility appears to depend on the presence of a passive oxide layer (TiO₂ layer) formed on the surface [3]. In an effort to enhance the cell implant material interaction and increase lifetime, bioactive ceramic based coatings have been applied to Ti implants [4].

Geometry and surface topography are very important parameter for the short and long term success of implant materials [5]. Various nanotopography modifications have been proposed to enhance the cell responses to the Ti-based implant. For example, Ti with micron size rough surface features and higher degree of nanometer surface features were develop by Raimondo et al. [6]. Surface topography such as TiO₂ nanotubes have been shown to alter cell behaviors such as adhesion, orientation, differentiation and migration significantly. It is due to nanotubes topography that can provide more abundant topographical cues

similar to dimensional scale of bone collagen fibrils and elasticity resembling bones [7]. However, the dimensionality (diameter and length) of TiO₂ nanotubes on cell interaction is not well understood.

Raja et al. [8] reported that pH of an electrolyte can affect the formation of nano-porous structure significantly. At lower pH, the length of the TiO₂ nanotubes was limited by higher dissolution rate. On the other hand, increasing the pH value will decrease the chemical dissolution rate and electrochemical oxide formation rate. This will affect the TiO₂ nanotubes length to a certain extent. In order to elucidate the influence of electrolyte pH on the pore morphology, a set of experiments was conducted with different electrolyte pH and discussed in this paper.

2. MATERIALS AND METHODS

High purity titanium foils (99.6% purity) with thickness of 0.1 mm from STREM Chemicals was used in this study. Anodization was done in a standard two-electrode bath with titanium as the working electrode and platinum as the counter electrode. Prior to anodization, Ti foils were degreased by sonicating in acetone for 15 min followed by rinsing in deionised water. After drying, the foil was exposed in glycerol with 0.5 wt.% NH₄F. Different pH of the bath was used in each experiment (pH 1-9) by adding H₂SO₄ (acidic) and NaOH (alkaline). The anodic potential was carried at 20 V with sweep rate of 1 V/sec in room temperature for an hour. The bath was kept at room temperature. After the anodization was completed, the titanium foil was annealed at 400 °C in an air atmosphere furnace for 2 hours. It is anticipated that the formation of anatase phase will lead to enhanced cell growth. The morphologies of the anodized titanium were characterized using a field emission scanning electron microscope (FESEM Supra 35VP ZEISS) operating at working distances down to 1 mm.

3. RESULTS AND DISCUSSIONS

The different pH levels of the electrolyte lead to different current density profile and TiO₂ surface structure. Fig. 1 shows the current density as a function of the anodization time at pH 1, 6 and 8. The patterns of the curves (Fig. 1) indicating mechanism of TiO₂ nanotubes formation. At pH 1, within 9 min of voltage supply, the current density dropped to 42.7 mA/cm². Fig. 1(i) shows the FESEM micrograph, which was obtained within this range of time upon voltage supply. It confirms that the drastic drop in current density is attributable to the Ti foil oxidation to form TiO₂ barrier layer for pH 1 sample. However, at 30 min, the current density rises to reach a maximum value of 65.3 mA/cm². It was due to chemical dissolution reaction of existing small pits have caused pits enlargement that was induced by F⁻ ions from the electrolyte as shown in Fig.1(ii). Beyond this point, current density drops slowly and became constant with increasing the anodizing time. This observation indicated the growth of nanotube structure. However, very small periodic fluctuation of current density was observed during this stage. This may be due to the competition between the growth and oxide layer dissolution to produce nanotubes. A self-aligned TiO₂ nanotubes with inner diameter of 64 nm and a length of 520 nm was formed after 1 hour of anodization (Fig. 1(iii)).

A relatively constant equilibrium state was maintained after current density drops slowly with increasing the anodizing time. This observation indicated the nanotube structure growth. However, very small periodic fluctuation of current density was observed during this stage. This may be due to the competition between the growth and oxide layer dissolution to produce nanotubes.

On the other hand, the drops in current density were less at pH 6 as compare with pH 1. The current density dropped specifically to 81.7 mA/cm². This indicated that the oxide layer formed in pH 6 (Fig. 1(iv)) is less dense as compared to that in pH 1. Less dense oxide layer mean low ohmic resistance, thus increase current density. The current density started to increase to a certain maximum (96.3 mA/cm²) and could be ascribed to random pits drilling on the oxidized layer of Ti. This event was shown in Fig.1(v). After anodization of Ti for an hour at pH 6, the inner diameter and length of TiO₂ nanotubes produced was 47 nm

(Fig. 1(vi)) and 720 nm, respectively. The inner diameter was smaller and longer nanotubes were formed due to chemical dissolution at the pore mouth was slower than drilling process by F⁻ ions at pore bottom [9]. Fig.1 shows the current density in basic (pH 8) electrolytes during the anodization process. The current density decreases gradually with 15 min during the self-organization process to 85.9 mA/cm². The FESEM micrograph in Figs. 1(vi) and (vii) show the microstructure within 15 min anodization. High current density periodic fluctuation was observed between 85.9 mA/cm² and 104.0 mA/cm². This indicated that both the electrochemical etching rate at the tube bottom and chemical dissolution is higher to form stable nanotubes structure (Fig.1(ix)). In higher pH value (pH 8), the hydrolysis ability of the electrolyte was increased as compared to acidic electrolyte.

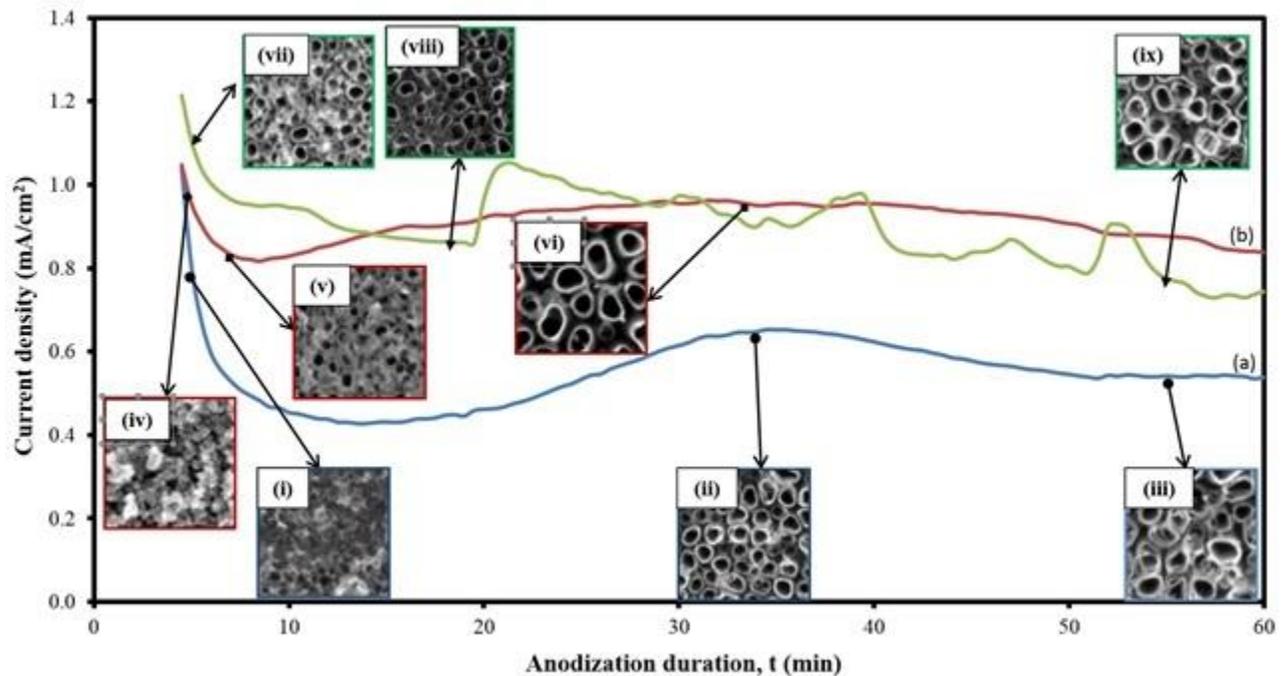


Fig. 1 Lower pH value at the pore tip and higher pH value at pore mouth are necessary to obtain desired TiO₂ nanotubes length

Lower pH value at the pore tip and higher pH value at pore mouth are necessary to obtain desired TiO₂ nanotubes length. Kang et al. [10] reported that longer TiO₂ nanotubes could be achieved by controlling the TiO₂ dissolution rate, which is related to the pH value of the electrolyte. FESEM characterization was performed after an hour of Ti anodization in electrolyte with difference pH. As shown in Fig. 2, TiO₂ nanotubes can be grown in electrolyte within pH 1 to pH 9. The entire samples show formation of well-ordered TiO₂ nanotubes regardless to pH value.

Overall samples are free from debris and the surface was rough. An existence of uneven surface morphology caused uneven H⁺ distribution in the electrolyte or high H⁺ concentration fluctuation due to the relatively low ion diffusion [11]. Local acidification fluctuation had been considerably restrained by decreasing the original H⁺ concentration in the electrolyte. These results confirm that oxide dissolution rate is pH dependence. Lower pH value can accelerate TiO₂ dissolution.

However, it was found that the diameter and length of TiO₂ nanotubes changed with pH variation. The average inner diameter of the nanotubes produced in glycerol solution with initial pH value (pH 6) was ~47 nm. However, when anodized in acidic solution (pH 1-2), the inner diameter increase to ~59-64 nm. It is due to the high chemical dissolution rate of the anodized TiO₂ layer in the enhanced acidic condition. It also been noted that the inner diameter did not significantly change with increasing pH value (pH 7-9).

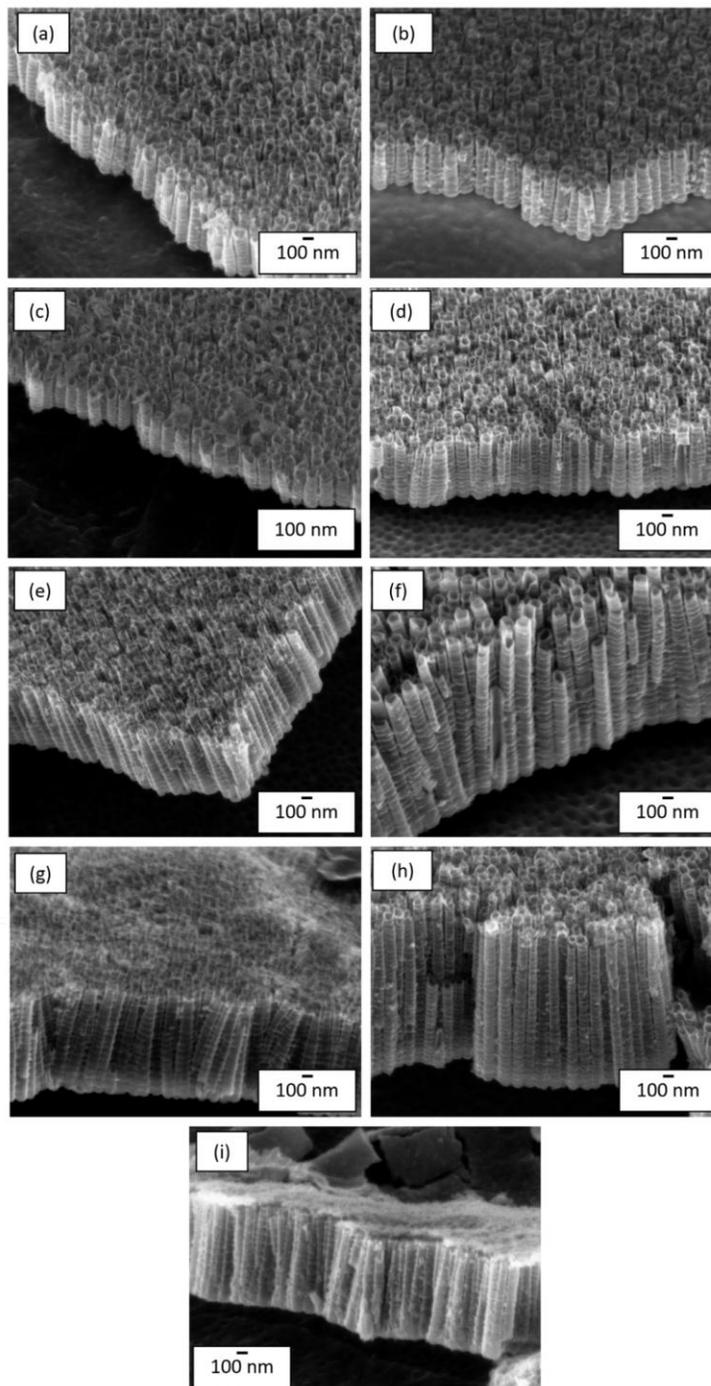


Fig. 2 Microstructural topography at different electrolyte pH (a) pH 1, (b) pH 2, (c) pH 3, (d) pH 4, (e) pH 5, (f) pH 6, (g) pH 7, (h) pH 8 and (i) pH 9

Fig. 3 shows correlation of TiO₂ nanotubes length with regards of pH value. The nanotubes length increased significantly with the increase of the electrolyte pH value. In acidic electrolytes (pH 1), the TiO₂ layer was thinner compare to TiO₂ layer in neutral electrolyte (pH 6). The shortest TiO₂ nanotubes were achieve because chemical dissolution at the pore mouth was faster than drilling process by F⁻ ions at pore bottom. As the low pH value induces a high chemical dissolution rate, the as-anodized nanotube tip is dissolved away gradually. This phenomenon prevents the TiO₂ nanotubes to grow longer.

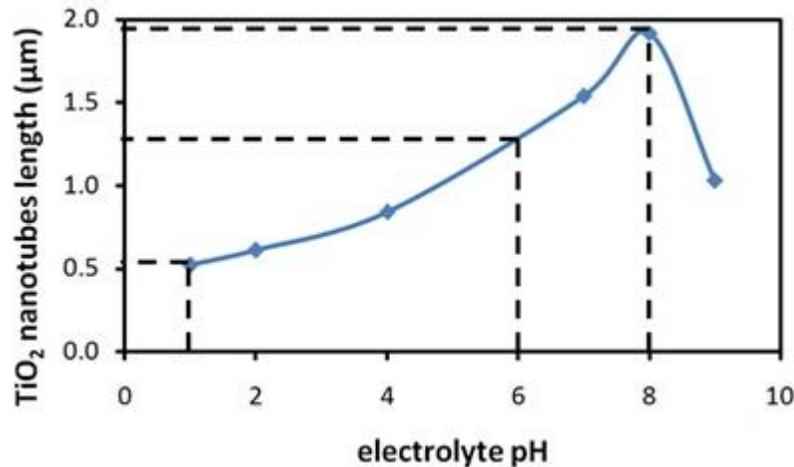


Fig. 3 Correlation of TiO₂ nanotubes length with regards of pH value

A relatively longer tube length of 1.98 μm could be obtained when the Ti foil was subjected to anodize in pH 8 electrolyte. By increasing pH of the electrolytes, chemical dissolution of TiO₂ was reducing. However, when increasing pH value to 9, the TiO₂ nanotubes became shorter. It is believed that with increasing pH, chemical dissolution rate was slow resulting slower growth kinetic for TiO₂ nanotubes formation. This process can also be expressed as electrochemical oxidation (Eq. 1) and chemical dissolution (Eq. 2) competition [12].



At the beginning, Ti oxidized to TiO₂ and then selectively dissolved by F⁻ ion. Thus, the pore became deeper and deeper. The reason for this reaction is OH⁻ in the bulk solution and H⁺ produced via reaction process (Eq. 1) show lower diffusion rate in viscous electrolyte. The pH value at tube bottom controlled by self-acidification process (Eq. 1) and less influences by bulk electrolyte pH value. This effect prevents passivation at the pore bottom even in basic solution (pH 8). Generally, the chemical dissolution reaction (Eq. 2) is also occurring at the tubes mouth during the growth process. The pH value at the tubes mouth is controlled by the bulk solution. In basic electrolyte, the chemical dissolution reaction (Eq. 2) at the tubes mouth is extremely slow. This resulting, the as-formed TiO₂ nanotubes can survive for longer anodization period [12]. Therefore, longer TiO₂ nanotubes produced.

4. SUMMARY

The nanotubes length increased significantly with the increase of the electrolyte pH value and the longest TiO₂ nanotubes obtain at pH 8. Increment of pH value to 9, the TiO₂ nanotubes became shorter. Lower pH value at the pore tip and higher pH value at pore mouth are necessary to obtain desired TiO₂ nanotubes length.

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