Anodic-biased titania nanotube growth in low-dielectric viscous media

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The influence was investigated of aqueous electrolytes and organic-based electrolytes on nanopore growth. To create well-defined nanotubes with a high aspect ratio, it is important to maintain equilibrium between field-assisted metal oxide dissolution and field-assisted water dissociation, which influence the temperature and pH levels in TiO$_2$ nanotubes (TiO$_2$ NTs). This sought after balance in the net reactions of the TiO$_2$ NT growth can be achieved by choosing the appropriate electrolytes that are relatively low dielectric viscous media. Viscosity ($\eta$) and dielectrics ($\varepsilon$) can be a priority in designing the experiment since it is closely related to joule-heating, diffusion-driven metal ions dissolution and chemical etching of the metal oxide. Solvation and the hydrogen bonding ability are inter-correlated to the stability of the [TiF$_6$]$^{2-}$ complex. In order to examine various electrolyte effects on the anodic-biased nanotube, different categories of electrolytes, each with different viscosity and dielectric properties, were incorporated in this study.

Keywords: nanoporous material; titanium dioxide nanotube; thin film; anodizing

1. Introduction

Since the first report by Keller et al. in 1953 [1], anodic-biased nanotube (ABNT) formation has been one of the paradigms of self-assembled hierarchical structures. The ABNT has been applied to various fields, such as electronics [2], photoanodes [3] and self-cleaning materials [4]. Also, its recent use in heat transfer augmentation is noticeable [5]. Current studies of the titanium-based tubular structure have focused on well-defined, ultra-long and wide tubes due to potential applications such as dye-sensitized solar cells [6,7] and gas sensing [8]. Grimes and coworkers have created ultra-high aspect ratio TiO$_2$ nanotubes (TiO$_2$ NTs) with $\sim$150 $\mu$m in length [9] and have also created extraordinarily wide TiO$_2$ tubes, measuring 350 nm in diameter [10], in an organic-based electrolyte (OBE). It is significant that most of the well-defined nanotubes with high aspect ratios have been made in OBEs such as ethylene glycol and glycerol [11–13]. This can be attributed to the fact that OBEs have low intermolecular interaction to dissolve the ionophores compared to an aqueous electrolyte (AE) [14]. Despite the high surge of attention in the ABNT with its high aspect ratio, there have been no comprehensive studies regarding the influence of physical and chemical properties of electrolytes on TiO$_2$ NTs. In this study, to examine characteristic electrolyte effects on the ABNT, different categories of electrolytes, each with different
Table 1. Important physicochemical constants of various electrolytes.

| Electrolyte    | pH  | Dielectric constant, $\varepsilon$ | Viscosity, $\eta$ (Pa s) |
|----------------|-----|----------------------------------|-------------------------|
| Water          | 7   | 80.4                             | $8.94 \times 10^{-4}$   |
| Ethylene glycol| 8   | 37.0                             | $1.61 \times 10^{-3}$   |
| Sulfolane      | 8.5 | 43.3                             | $1.01 \times 10^{-2}$   |
| Glycerol       | 3.97| 42.5                             | 1.45                    |

viscosity and dielectric properties, were incorporated with a wide range of parameters (Table 1).

2. Experimental

Titanium foil was obtained from Sigma-Aldrich (99.7%, 0.127 mm thick) and used as received without further surface treatment. The Ti foil was cut into 1 cm × 4 cm pieces and chemically cleaned in acetone and ethanol (1:1 by vol) under ultrasonication for 10 min. Aqueous electrolytes such as 1M H$_2$SO$_4$ and 1M H$_3$PO$_4$ and organic-based electrolytes such as glycerol and ethylene glycol were prepared. The fluoride source concentration was fixed at 0.5 wt % ammonium fluoride in OBEs. In the case of 1M H$_2$SO$_4$, 0.15 wt % HF was added. After the addition of the fluoride source to the solution, the mixture was stirred for 2 h to fully dissolve the salt at room temperature. All experiments were carried out in a potentiostatic mode (10–60 V) at room temperature. An Agilent N5771A DC power supply was used for all tests. In situ pH/temperature measurement was carried out using an Extech Oyster pH/temperature meter. The probe was located at a distance of 1 cm from the Ti anode. After the anodizing process, each specimen was thoroughly rinsed first with ethanol and then with deionized water. Microscopic observations were carried out using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700).

3. Results and discussion

3.1. Electrolyte influence over TiO$_2$ morphology

For TiO$_2$ NT formation, appropriate ionic mobilities, such as those of O$^{2-}$, OH$^-$ and F$^-$, are known to be important. In particular, a fluoride-assisted acidic environment is necessary to avoid the self-limiting growth of TiO$_2$ NTs. Also, it should be noted that the self-limiting growth of TiO$_2$ stabilizes the current density leading to no further growth of TiO$_2$ NT [15,16]. As summarized in Table 2, there were variations in the morphology of TiO$_2$ depending upon the experimental conditions.

While TiO$_2$ nanocrystallites were mostly observed when AEs were used at 30–60 V (Figures 1–2), TiO$_2$ NTs were predominantly observed when OBEs were used (Figures 3–4).

When glycerol was used, for example, a linear proportionality in pore size of the NT was observed in our experiments (Figure 5). It is well accepted that TiO$_2$ NT formation can be explained by the dissolution of a metal oxide (field-assisted metal oxide dissolution, FAMOD) and the dissociation of water (field-assisted water dissociation, FAWD) [17–23]. As the NT grows, the ionic mobilities can be perturbed. Due to this disturbance, the TiO$_2$ NT growth leads to localized pH gradients along the growth direction of the NT. The oxide barriers are relatively more acidic than the pore rim. As Macák et al. [24,25] showed, via simulation results for a local, autocatalytic acidification-induced pH gradient
Table 2. Anodizing results at different conditions (voltage/time/electrolyte).

| Electrolyte | Voltage (V) | Reaction time (h) | Morphology |
|-------------|-------------|------------------|------------|
| Aqueous     | 20          | 15               | Tube       |
|             | 40          | 15               | Crystal    |
|             | 60          | 15               | Crystal    |
| 1.0M H₃PO₄ | 20          | 15               | Tube       |
|             | 40          | 15               | Crystal    |
|             | 60          | 15               | Crystal    |
| Non-aqueous | Glycerol    | 20               | Tube       |
|             | 40          | 8                | Tube       |
|             | 60          | 8                | Tube       |
| Ethylene glycol | 20      | 8                | Tube       |
|             | 40          | 8                | Tube       |
|             | 60          | 8                | Tube       |

*aEach electrolyte contained 0.5 wt % NH₄F but 0.15 wt % HF for H₂SO₄. bAt room temperature*

Figure 1. FE-SEM images of TiO₂ in 1.0M H₂SO₄ with 0.15 wt % HF at (a) 10 V, (b) 50 V and (c) 60 V. Scale bar represents 500 nm.

Figure 2. FE-SEM images of TiO₂ in 1.0M H₃PO₄ with 0.50 wt % NH₄F at (a) 10 V, (b) 50 V and (c) 60 V. Scale bar represents 500 nm.

along the TiO₂ NT in an AE, chemical etching can be accelerated along the nanochannel near the oxide barrier. The study also reported that ABNT growth generates a temperature gradient along the NT. Localized heating can accelerate the chemical etching rate near the oxide barrier. As Keller [1] reported, the temperature increases in the electrolyte during NT growth, and thus temperature measurements of the electrolyte during NT growth could provide an insight on the microscopic phenomena involved in TiO₂ NT film growth.

3.2. Physicochemical influence over TiO₂ growth

In the previous section, it was indicated that local pH gradients and Joule-heating induced temperature change are closely related to TiO₂ NT growth during an anodizing reaction.
In order to elucidate the relationship between TiO$_2$ NT growth and physicochemical properties, such as local pH gradients and temperature, microscopic level *in-situ* measurements can provide useful information on TiO$_2$ NT growth. Since it is experimentally restricted, *in-situ* measurements of bulk fluid properties might be another strategy to obtain relevant information. In order to measure physicochemical properties (pH and temperature profiles), 1.0M aqueous phosphoric acid solution and ethylene glycol were used as representative AE and OBE, respectively. Figure 6a shows measured temperature profiles for the AE and OBE solutions, respectively. A faster temperature rise in the AE relative to the OBE can be clearly observed within 30 min. This can be interpreted in terms of the faster acid-catalyzed exothermic reactions (FAWD/FAWD) and predominant joule-heating being important for TiO$_2$ NT formation in AEs. According to Li et al. [26], the localized
heating-induced concentration gradient of the metal ions ($\text{Ti}^{4+}$) along the NT is significant in AEs. Also, it should be noted that the dielectric constants ($\varepsilon$) of AEs are much higher than those of OBEs (Table 1). Thus, in an AE with lower viscosity, the $\text{Ti}^{4+}$ dissolution into the electrolyte becomes predominant and results in a shorter NT film. Figure 7 supports the $\text{Ti}^{4+}$ dissolution-induced NT length difference in an AE and an OBE, respectively. Additionally, the precipitate layer (titanium oxyhydroxide) on top of the $\text{TiO}_2$ NT is often observed in an OBE since the solubility of the metal ions decreases compared to that of AEs (Figures 3 and 7).

For $\text{TiO}_2$ NT growth, pH is another important factor since acid catalyzed pH accelerates $\text{TiO}_2$ NT etching. The time-dependent pH for AE and OBE is shown in Figure 6. For an AE (1.0M $\text{H}_3\text{PO}_4$), a pH drop was observed within an initial half hour; however, the pH then slowly increased. After an hour, the pH reached a plateau. Right after applying an electrical potential, the vigorous FAWD/FAMOD on the anode surface and the acid-catalyzed

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**Figure 6.** *In situ* temperature and pH measurements at 20 V at room temperature in an aqueous (■) and organic-based electrolyte (●) with 0.5 wt % $\text{NH}_4\text{F}$.

**Figure 7.** FE-SEM images of $\text{TiO}_2$ NT length at 20 V in: (upper row) 1.0M $\text{H}_3\text{PO}_4$ with 0.50 wt % $\text{NH}_4\text{F}$ for (a) 0.5 h, (b) 1 h and (c) 3 h; (lower row) ethylene glycol with 0.50 wt % $\text{NH}_4\text{F}$ for (d) 0.5 h, (e) 1 h and (f) 3 h. Scale bar represents 500 nm.
pH drop assists in the \([\text{TiF}_6]^{2-}\) complex formation, which occur simultaneously. The pH behavior in the early stages of the reaction is consistent with current density measurements obtained in previous studies [26]. After the metal oxide formation, there are pH reactions between the FAWD and the acid dissociations creating conjugate base anions. Most of the \(\text{O}^{2-}\) and \(\text{OH}^-\) ions migrate into the oxide, and hydronium ions migrate toward the cathode causing hydrogen evolution. The remaining biphosphate/phosphate anion enhances the pH level and impurities of the metal oxide by replacing the \(\text{O}^{2-}\) [26]. The reaction rate of the conjugate base is accelerated by the diffusion-induced concentration gradient on the anode surface until it reaches equilibrium. While the pH level increase is detrimental to the \([\text{TiF}_6]^{2-}\) complex formation, the pH level of an AE remains acidic (\(<\)pH 4), as accelerating chemical etching. Similarly, the pH change in an OBE is of significance within the same time frame (within a minute) compared to the AE. Due to the extremely limited amount of water molecules in OBE, the pH drop was not low enough to accelerate chemical etching. This means that the FAWD/FAMOD is restricted due to inefficient current density in less conductive medium. The organic electrolyte rarely dissociates into conjugate acid and base. Although the \([\text{TiF}_6]^{2-}\) complex formation in an OBE is unfavorable, the conjugate base-induced impurities and acid-assisted chemical etching of the metal oxide are predominantly reduced. Also, no significant hydrogen evolution occurs on the cathode due to slow diffusion of hydronium ion.

Dielectric constant is closely related to thermodynamic energy. Since dielectric constant \(\varepsilon\) of the electrolyte is inversely proportional to the Gibbs free energy in ionic species reactions [14], the Gibbs free energy in an OBE is expected to be larger than that in an AE: \(\Delta G_{\text{OBE}} > \Delta G_{\text{AE}}\). This inequality implies that the \([\text{TiF}_6]^{2-}\) complex in an AE is efficiently solvated by the surrounding water molecules and the complex stability can be increased. Additionally, complex stability is closely related to the hydrogen bonding in the ionic interactions. Since water and most alcohols are good hydrogen bonding donors (HBD), \(\text{F}^-\) is more effectively solvated by the HBD solvents. The OH group of alcohols, ethylene glycol and glycerol are electrolyzed into aldehyde under basic conditions (Figure 6b) [27,28]. Therefore, the HBD ability of the OH group becomes weaker than in water. The TiO\(_2\) NT formation is accelerated in OBEs.

It is noteworthy to compare the grown TiO\(_2\) NTs in various OBEs. As listed in Table 2, ethylene glycol and sulfolane are less viscous than glycerol. Knowing that the liquid viscosity is a dominating factor in chemical etching process, Ti\(_{4+}\) dissolution can be accelerated in lower viscous electrolytes. Comparison of the TiO\(_2\) NT wall thickness can be indicative of the chemical dissolution rate of the metal oxide. For instance (Figures 5 and 8) at 20 V, the grown TiO\(_2\) NT in ethylene glycol (\(\sim 14\) nm) and sulfolane (\(\sim 13\) nm) have much thinner walls than that in glycerol (\(\sim 19\) nm). The precipitate layers observed in Figures 3 and 8 are a clear evidence of the rapid metal dissolution that causes the local concentration increase of Ti\(_{4+}\) to reach beyond the limit of the solubility [29].

Figure 5b shows the average wall thickness and pore diameter of TiO\(_2\) grown in OBEs. At lower voltage regimes (\(< 40\)V), Ti\(_{4+}\) dissolution is slow. This results in preferential formation of titania. As the voltage increases, both the ion mobility and water dissolution accelerate. The net results are a steep pH gradient and an enhanced heating inside the NTs. This could lead to damaged TiO\(_2\) NTs as also noticed by Yoriya [10] and Lim [30].

High voltage accompanies the TiO\(_2\) NT wall thickness change (Figure 5). Mohapatra et al. [31] reported that the pore wall thickness became saturated beyond a specific voltage. Since the titanium oxide is a passage for ion mobility, the thicker pore wall can prevent the vertical NT film growth since the ionic path is longer. Therefore, beyond a certain voltage limit the oxide film prefers NTs with thinner pore walls of a longer tube. These observations are consistent with the former report [31]. The significant voltage and thickness, 30–40 V
and 20–30 nm, can be seen as a point of the saturation curve. The wall thickness of the NTs in ethylene glycol is 50% thinner than NTs grown in glycerol (Figure 5). A linear proportionality in voltage and pore size could be maintained under an optimized condition of fluoride concentration, voltage and time, as also noted by Yoriya and Grimes [10].

4. Conclusion

In the present work, the influence of AEs and OBEs on nanopore growth has been studied. To create well-defined nanotubes with a high aspect ratio, it is important to maintain equilibrium between FAMOD and FAWD, which influence the temperature and pH levels in an electrolyte. This sought after balance in the net reactions of TiO₂ NT growth can be achieved by choosing appropriate electrolytes that have a relatively low dielectric constant. Viscosity and dielectric properties can be a priority in designing the experiment (larger pore size and longer nanotube) since they are closely related to joule-heating, diffusion-driven metal ion dissolution and chemical etching of the metal oxide. Solvation and the hydrogen bonding ability are inter-correlated to the stability of the [TiF₆]²⁻ complex. In order to eventually achieve the goal of an ultra-long and wide TiO₂ channel, the relationship between the temperature of the electrolyte, the fluoride source and the [TiF₆]²⁻ complex must be investigated further.

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