Diffusion-controlled Growth of TiO$_2$ Mesoporous Anodic Films in Hot Phosphate/glycerol Electrolytes

Etsushi TSUJI,a,* Shiki MATSUURA,b Yoshitaka AOKI,b,c and Hiroki HABAZAKIb,c

**ABSTRACT**

This paper reports unusual diffusion-controlled growth of TiO$_2$ mesoporous anodic films on titanium in hot phosphate/glycerol electrolytes. The formation behavior was investigated by cyclic voltammetry (CV) between 0 and 5 V vs. Pt at 433 K. The current density became almost constant above 1.5 V vs. Pt during the positive potential sweep, and was maintained even during the negative potential sweep. This is contrast to a drastic decrease in current density in changing the direction of potential sweep from the positive to negative in fluoride-containing ethylene glycol electrolyte. The constant current density between 1.5 and 5 V vs. Pt increased with an increase in the basicity of the hot phosphate electrolyte, suggesting that the rate-determining step of the film formation in the hot phosphate electrolyte was diffusion process of oxygen sources in the electrolyte, not the ion migration in the thin barrier layer under the high electric field. When CV measurements were conducted to higher potentials up to 20 V vs. Pt, anatase was developed above 7 V vs. Pt, leading to generate oxygen gas. The film morphology was also potential-dependent and the diffusion current was also influenced by the film morphology as well as oxygen gas generation.

* Corresponding author: e-tsui@chem.tottori-u.ac.jp

1. Introduction

Anodic TiO$_2$ nanotubular (TNT) films have many potential applications such as photocatalysts for decomposition of water$^{1,2}$ and organic compounds,$^{3,4}$ electrodes of dye-sensitized solar cells (DSSCs)$^{5,6}$, electrochromic materials$^{7,8}$ and biological applications$^{9,10}$. Well-ordered TNT films have been formed in the organic electrolytes containing fluorides and a small amount of water at room temperature.$^{5,6}$ The barrier layer thickness, interpore distance and tube diameter of the TNT are controlled mainly by formation voltage, anodizing time and pH of the electrolyte.$^{5,8-10}$ In addition, there are many reports discussing the details of formation behavior of TNT films during anodizing in fluoride electrolytes.$^{5,7,10-12}$ In this case, fluoride ions have an important role to form TNT films. Initially, a protective compact TiO$_2$ film is formed and then the fluoride induced dissolution of the formed TiO$_2$ layers by formation of [TiF$_6$]$^{3-}$ ions (TiO$_2$ + 4H$^+$ + 6F$^-$ → [TiF$_6$]$^{3-}$ + 2H$_2$O). Finally, stable growth conditions are reached due to an equilibrium situation of growth and dissolution of the TiO$_2$ layers. Furthermore, Schmuki et al. reported that the rate determining step (RDS) of the film growth is fluoride ion diffusion to the tube bottom.$^{10}$ The faster migration of F$^-$ in comparison with O$_2^-$ results in a fluoride-rich layer at the metal/oxide interface, leading to high contamination of the anodic films with fluoride and carbon species derived from the electrolyte. Therefore, the as-anodized TNT films are amorphous and post-annealing of them is indispensable for removing such impurities and crystallization of them.$^{13,14}$

On the other hand, recently, TiO$_2$ mesoporous (TMP) films were formed by anodizing of titanium in fluoride-free hot phosphate/glycerol electrolytes.$^{14-21}$ The resultant films showed interesting features, for example: (i) the pore size was as small as ~10 nm, regardless of the formation voltage and (ii) formation of films at an anodizing voltage of 20 V generated the crystalline anatase phase without requirement of post-annealing, whereas the films formed at less than 5 V were amorphous. These characteristic features made the TMP films suitable for fabricating a high efficiency$^{22}$ or size-selective photocatalysts$^{17,18}$ and for applications to DSSCs using heat-labile materials such as ITO conducting glass and plastic substrates.$^{19-21}$ Although the morphology, composition and structure of the crystalline TMP films have been investigated,$^{14-17}$ the growth mechanism and potential-dependent crystal structure of TMP films have not yet been clarified.

In this study, we investigated the formation behavior of the TMP films on titanium during anodizing in the hot phosphate/glycerol electrolyte by cyclic voltammetry. We found that the growth of the TMP films was controlled by diffusion of the oxygen sources in the electrolyte, in contrast to the high field ionic conduction-controlled growth of usual anodic oxides. The amorphous-to-crystalline transition occurred at ~7 V vs. Pt, above which an anatase film with phosphate incorporation was developed.

2. Experimental

The specimens used for anodizing were 99.5% pure titanium sheets of 0.5 mm thickness. Prior to anodizing, the specimens were electropolished in 1 mol dm$^{-3}$ NaCl/ethylene glycol solution at 293 K at 20 V for 200 s and, subsequently, at 10 V for 600 s.$^{20}$ A titanium sheet was used as the counter electrode. The electropolished specimens were then anodized in glycerol electrolytes containing 0.6 mol dm$^{-3}$ K$_2$PO$_4$ and 0.2 mol dm$^{-3}$ K$_2$HPO$_4$ or 0.2 mol dm$^{-3}$ K$_2$PO$_4$ and 0.6 mol dm$^{-3}$ K$_2$HPO$_4$ (hereafter denoted as the higher or lower basic phosphate electrolyte, respectively) at...
433 K under a nitrogen atmosphere. The conductivities of the electrolytes were measured by an impedance analyzer (Solartron 1260) combined with a potentiostat (Solartron 1287). The conductivity of the higher basic phosphate electrolyte at 433 K was 0.75 S cm$^{-1}$, while that of the lower basic electrolyte was 0.2 S cm$^{-1}$. The water contents, which were measured by a Karl Fischer titrator (Hiranuma sangyo Co., Ltd., AQUACOUNTER AQV-7S), in both electrolytes was reduced to $\sim$0.03 mass% by heating at 453 K under a dry nitrogen stream for 3 h. Anodizing was performed using a three-electrode system. A platinum sheet and a platinum wire were used as counter and reference electrodes, respectively. The cyclic voltammograms (CVs) during anodizing were obtained with a commercial potentiostat and potential programmer (Toho Technical Research Co., Ltd., Model PS-04) with a potential sweep rate of 30 mV s$^{-1}$ and a constant stirring rate at 330 rpm. Anodizing was also performed at constant potentials between 1 and 20 V vs. Pt till the film thickness became to 5 µm. The CV measurements were conducted at least twice under the same condition to confirm the reproducibility of the results. The variation of current was less than 10%.

For estimation of a RDS during anodizing in the hot phosphate/glycerol electrolytes, the electropolished titanium specimens were also anodized at 3 V vs. Pt without stirring to monitor the current transient behavior. The Cottrell equation is given as the following equation,

$$ I = nFAD^{1/2}C_{p_{0}}^{1/2}j^{1/2} \Rightarrow \left( \frac{I}{A} \right)^{1} = \frac{\sigma^{1/2}}{nF_{0}D^{1/2}}j^{1/2} $$

where $I$ is current, $n$ is the number of electrons to oxide, $F$ is Faraday constant ($= 96,485$ C mol$^{-1}$), $A$ is surface area of a titanium specimen, $D$ is diffusion coefficient, $C_{p_{0}}$ is initial concentration of oxygen sources such as hydroxide ions and water and $j$ is anodizing time, respectively.

For comparison of formation behavior of the TMP film, a TNT film was also prepared as follows; the electropolished titanium specimen was anodized in 0.25 wt% NH$_4$F and 1 vol% water/ethylene glycol electrolyte (denoted as the fluoride electrolyte) at 293 K. In all the experiments, reagent-grade chemicals were used as-received and the deionized water was obtained from a Milli-Q water purification system.

The structure of the anodic films was identified by X-ray diffraction (XRD) (Rigaku, RINT-2000) using CuKα radiation. For evaluating the crystallinity, ~5 µm thick films formed on the titanium sheets at various potentials were used. Elemental depth profiles of the anodized specimens were obtained by a glow discharge optical emission spectroscopy (GDOES) (Jobin-Yvon 5000 RF) with an RF generator (13.56 MHz) in an argon atmosphere of 600 Pa with application of RF of 13.56 MHz and power of 50 W. The anode diameter was 4 mm and the signals of titanium (365.350 nm), phosphorus (178.287 nm), oxygen (130.217 nm) and carbon (165.701 nm) were measured with a sampling time of 0.01 s. The chemical composition of the obtained films was also examined using energy dispersive X-ray spectroscopy (EDS) facilities equipped in a scanning electron microscope (SEM) (JEOL, JSM-6500F). Cross-section morphologies of the anodized specimens were observed using the SEM operated at 10 kV.

3. Results and Discussion

3.1 Formation behavior of TMP films during anodizing at low voltages

Figure 1 shows the CVs during anodizing in (a) the higher and (b) lower basic phosphate electrolytes at 433 K and (c) the fluoride electrolyte at 293 K with stirring. In the higher basic phosphate electrolyte, the current density began to increase at $\sim$0.5 V vs. Pt and became nearly constant above 1.5 V vs. Pt during the positive potential sweep. Interestingly, similar high current density was maintained even in the negative potential sweep from 5 till $\sim$1 V vs. Pt. In contrast, the current decreased markedly when anodic potential sweep was reversed at 5 V vs. Pt in the fluoride electrolyte (Fig. 1c). The current decrease is associated with the reduction of the electric field strength in the barrier layer present beneath the porous layer, being typical in anodizing of valve metals.

The CV curve similar to the higher basic phosphate electrolyte is also observed in the lower basic phosphate electrolyte (Fig. 1b), although the constant current density between 1 and 5 V vs. Pt in the lower basic phosphate electrolyte is much lower than that in the higher basic phosphate electrolyte. The basicity-dependent current suggests that the concentration of OH$^-$ ions influences largely the growth rate of the TMP film. The similar effect of the basicity of the electrolyte was reported in our previous paper.

Figure 2a shows the current transient of titanium during anodizing at 3 V vs. Pt in the higher and lower basic phosphate electrolytes at 433 K without stirring. The current decreases gradually with anodizing time as in our previous papers. The Cottrell plot shown in the inset of Fig. 2a, the reciprocal of current density is approximately proportional to the square root of time, suggesting that the observed current is diffusion-controlled. The slope in the lower basic phosphate electrolyte is approximately twice that in the higher basic electrolyte. This means from the Cottrell equation that the concentration of the diffusing species in the bulk electrolyte is twice higher in the higher basic phosphate electrolyte in comparison with the lower basic phosphate electrolyte. This is consistent with the almost twice higher steady-state current in the higher basicity phosphate electrolyte compared with the lower basicity phosphate electrolyte shown in Fig. 1. When stirring of the electrolyte stopped during potentiodynamic anodizing in the higher basic electrolyte, the anodic current turned to decrease with time (Fig. 2b), confirming the importance of supply of reactive species in electrolyte to the specimen surface. The anodic current density in the lower basic electrolyte also decreased by stopping of stirring.

Figure 3 shows a schematic illustration during the anodic process at the pore base. When TMP films are formed by anodizing, the oxide is formed at the Ti/TiO$_2$ interface and field-assisted dissolution occurs at the pore base, i.e., the oxygen sources such as OH$^-$ and H$_2$O diffuse in the electrolyte, migrate in the barrier
3 V vs Pt during anodizing was different from that in the hot phosphate electrolyte. The current density at 3 V vs. Pt in 0.6 mol dm$^{-3}$ K$_2$HPO$_4$ glycerol and 0.2 mol dm$^{-3}$ K$_3$PO$_4$ and 0.6 mol dm$^{-3}$ K$_3$HPO$_4$ glycerol electrolyte containing 0.03 mass% water at 433 K without stirring. The inset is Cottrell plot of them. (b) The cyclic voltammogram of a titanium specimen during anodizing in 0.6 mol dm$^{-3}$ K$_3$PO$_4$ and 0.2 mol dm$^{-3}$ K$_3$HPO$_4$ with and without stirring.

Figure 2. (a) Current transients of titanium specimens during anodizing at 3 V vs. Pt in 0.6 mol dm$^{-3}$ K$_2$PO$_4$ and 0.2 mol dm$^{-3}$ K$_3$HPO$_4$ glycerol and 0.2 mol dm$^{-3}$ K$_3$PO$_4$ and 0.6 mol dm$^{-3}$ K$_3$HPO$_4$ glycerol electrolytes containing 0.03 mass% water at 433 K without stirring. The inset is Cottrell plot of them. (b) The cyclic voltammogram of a titanium specimen during anodizing in 0.6 mol dm$^{-3}$ K$_3$PO$_4$ and 0.2 mol dm$^{-3}$ K$_3$HPO$_4$ with and without stirring.

Figure 3. Schematic illustration showing anodic process at the barrier layer.

Figure 4. Schematic illustration showing film formation during anodizing in the hot phosphate glycerol electrolytes and the fluoride electrolyte. $U_A$, $U_B$ and $U_C$ are applied voltage, $d_A$, $d_B$, $d'_A$ and $d'_B$ are barrier layer thickness and $E_A$, $E_B$, $E_B'$, $E_C$ and $E_C'$ are Electric field strength at barrier layers, respectively.

3.2 Formation behavior of TMP films during anodizing at high voltages

Figure 5 shows the CVs between 0 and 6, 7, 15 and 20 V vs. Pt in the higher basic phosphate/glycerol electrolyte. The current density in the negative potential sweep was almost the same as that in the positive potential sweep at less than 1.5 V vs. Pt, the barrier layer thickness $d_A$ increased with increasing the applied voltage $U_A$ in the both electrolytes (Fig. 4A). However, in the case of the positive sweep at more than 1.5 V vs. Pt, the film growth behavior in the hot phosphate/glycerol electrolytes was drastically different from that in the fluoride electrolyte. In anodizing in the fluoride electrolyte, the barrier layer thickness of the reaction species in the electrolyte.

Layer of the anodic TiO$_2$ film and react with Ti metal at the Ti/TiO$_2$ interface, whereas Ti$^{4+}$ ions migrate in the barrier layer and go into the electrolyte by field assisted dissolution at the TiO$_2$/electrolyte interface of the pore base. Form Fig. 2a, the current density at 3 V vs. Pt during anodizing was diffusion current, suggesting that the RDS was the diffusion of the oxygen sources. In addition, from Fig. 1, the diffusion current density at more than 1.5 V vs. Pt decreased with a decrease in the electrolyte basicity, implying that the oxygen source to form TiO$_2$ may be hydroxide ions. Figure 4 shows schematic illustration during the potentiodynamic anodizing in the hot phosphate electrolytes and the fluoride electrolyte. In the case of the positive sweep at less than 1.5 V vs. Pt, the barrier layer thickness $d_A$ increased with increasing the applied voltage $U_A$ in the both electrolytes (Fig. 4A). However, in the case of the positive sweep at more than 1.5 V vs. Pt, the film growth behavior in the hot phosphate/glycerol electrolytes was drastically different from that in the fluoride electrolyte. In anodizing in the fluoride electrolyte, the barrier layer thickness $d_B$ of TNT is proportional to formation potential $U_B$. Therefore, the electric filed strength $E_B$ at the barrier layer is constant during the positive sweep. However, when the direction of the potential sweep changed from positive to negative, the electric field strength $E_C$ at the barrier layer decreased (Fig. 4B), leading to a drastic decrease in current density. The other hand, in anodizing in the hot phosphate/glycerol electrolyte, the current density did not decrease even in the negative sweep, implying that the ion migration in the barrier layer did not control the anodizing kinetics. These results suggested that the barrier layer thickness $d'_B$ was low and did not increase with increasing the applied potential $U_B'$ in the hot phosphate/glycerol electrolytes (Fig. 4B), in contrast to a continuous increase in barrier layer thickness in the fluoride electrolyte during the positive sweep. Highly enhanced field-assisted dissolution at the pore base in the hot phosphate/glycerol electrolytes containing very low water concentration probably impedes the thickening of the barrier layer. Consequently, the RDS of the film growth was not migration process in the quite thin barrier layer but diffusion process of the oxygen sources in the hot phosphate electrolytes.

Figure 5 shows the CVs between 0 and 6, 7, 15 and 20 V vs. Pt in the higher basic phosphate/glycerol electrolyte. The current density in the negative potential sweep was almost the same as that in the positive potential sweep at less than 1.5 V vs. Pt, the barrier layer thickness $d_A$ increased with increasing the applied voltage $U_A$ in the both electrolytes (Fig. 4A). However, in the case of the positive sweep at more than 1.5 V vs. Pt, the film growth behavior in the hot phosphate/glycerol electrolytes was drastically different from that in the fluoride electrolyte. In anodizing in the fluoride electrolyte, the barrier layer thickness $d_B$ of TNT is proportional to formation potential $U_B$. Therefore, the electric filed strength $E_B$ at the barrier layer is constant during the positive sweep. However, when the direction of the potential sweep changed from positive to negative, the electric field strength $E_C$ at the barrier layer decreased (Fig. 4B), leading to a drastic decrease in current density. On the other hand, in anodizing in the hot phosphate/glycerol electrolyte, the current density did not decrease even in the negative sweep, implying that the ion migration in the barrier layer did not control the anodizing kinetics. These results suggested that the barrier layer thickness $d'_B$ was low and did not increase with increasing the applied potential $U_B'$ in the hot phosphate/glycerol electrolytes (Fig. 4B), in contrast to a continuous increase in barrier layer thickness in the fluoride electrolyte during the positive sweep. Highly enhanced field-assisted dissolution at the pore base in the hot phosphate/glycerol electrolytes containing very low water concentration probably impedes the thickening of the barrier layer. Consequently, the RDS of the film growth was not migration process in the quite thin barrier layer but diffusion process of the oxygen sources in the hot phosphate electrolytes.
Figure 7 shows the X-ray diffraction patterns of the titanium specimens anodized in the higher basic electrolyte at various constant voltages. The peaks of crystalline anatase TiO₂ appeared in the specimens anodized at and above 7 V vs. Pt, indicating that an amorphous-to-crystalline transition occurs between 6 and 7 V vs. Pt. The most intense peak was the 004 peak of anatase, besides the substrate peaks, whereas the most intense 101 peak for randomly oriented anatase was missing. The orientation of anatase is the characteristic of the TMP film formed in hot phosphate/glycerol electrolytes. The intensity of the peaks became stronger with increasing formation potential. Since the film thickness was controlled to ~5 µm regardless of the formation potential, the crystallinity of the films improved at higher formation potentials.
Interestingly, the initial potential of the film crystallization is well consistent with that at which the current density decreased (Figs. 5c–d), suggesting that the decrease of the current density during negative sweep is induced by crystallization of the films. Oxygen generate on the anatase crystalline TMP films during the anodizing in the hot phosphate/glycerol electrolyte at 20 V, whereas no obvious oxygen gas generation occurred on the amorphous TMP films formed at less than 5 V. The rate of the crystalline TMP film growth at 20 V was less than one fourth that of the amorphous TMP film at 5 V, implying that significant amount of oxygen may be generated during the anodizing. Therefore, one of the possibilities of the current decrease is that oxygen gas trapped in the pores of the TMP film impedes the diffusion of oxygen sources to the pore base between 7 to 20 V vs. Pt.

To get insight into the crystallization mechanism of the TMP films, their chemical composition was evaluated by GDOES and EDS. Figure 8a shows the GDOES elemental depth profiles of the film anodized by the CVs between 0 and 20 V vs. Pt in the higher basic phosphate electrolyte. An oxide-based film is formed throughout the film thickness, since the intensity ratio of oxygen to titanium was almost constant. In contrast, phosphorus intensity changes in depth. The highest phosphorus intensity is obtained at middle part of the film, where film is developed at the highest formation potential of 20 V vs. Pt. The phosphorus intensity is low below 7 V vs. Pt. The similar result was observed by EDS analysis of the TMP films formed at each constant voltage in the higher basic phosphate electrolyte. Figure 8b shows the plot of formation voltage vs. the amount of phosphorous in the TMP films, examined by EDS. The amount of phosphorous increased at more than 6 V vs. Pt and tends to be constant at about 2 at% ([P]/([Ti] + [O] + [P])) above 10 V vs. Pt. There is a good correlation between the XRD peak intensity of anatase (Fig. 7) and the amount of phosphorus (Fig. 8b). The correlation may be associated with the increased electric field strength in the crystalline oxide film; the electrolyte anion incorporation is enhanced with an increase in the electric field.

Finally, we investigated the effect of formation voltage on morphology of the TMP films. Figure 9 shows scanning electron micrographs of the cross-sections of the film anodized by the CVs between 0 and 20 V vs. Pt. The film thicknesses to 7 and 20 V vs. Pt during positive and negative sweeps were calculated using the electric charge values passed and growth rates of amorphous (2.3 × 10−11 m C−1 m2) and crystalline (5.5 × 10−12 m C−1 m2) TMP.

Figure 8. (a) GDOES depth profiles of the film anodized in 0.6 mol dm−3 K3PO4 and 0.2 mol dm−3 K2HPO4 glycerol electrolytes containing 0.03 mass% water at 433 K after the cyclic voltammogram between 0 and 20 V vs. Pt. (b) Plot of formation voltage vs. amount of phosphorous, examined by EDS, contained in the films anodized in 0.6 mol dm−3 K3PO4 and 0.2 mol dm−3 K2HPO4 glycerol electrolytes containing 0.03 mass% water at 433 K.

Figure 9. Scanning electron micrographs of the fractured cross-sections of the film anodized in 0.6 mol dm−3 K3PO4 and 0.2 mol dm−3 K2HPO4 glycerol electrolytes containing 0.03 mass% water at 433 K after the cyclic voltammogram between 0 and 20 V vs. Pt.
films as reported in our previous paper. As shown in Fig. 7, the film formed at less than 7 V vs. Pt was assumed to be amorphous and that above 7 V vs. Pt was crystalline TiO₂. It is obvious that the film morphology is potential-dependent in Fig. 9. The regions of (a) and (f) formed at less than 1 V vs. Pt have sponge-like morphology, whereas the other regions of (b)–(e) formed above 1 V had relatively straight porous structure. In the amorphous regions of (b) and (e) formed at less than 7 V vs. Pt, the pore size appeared to be ~50 nm. In potentiostatic anodizing, the pore size of the TMP films was ~10 nm regardless of the formation potential. The larger pore size may be characteristic of the potentiodynamic anodizing. In the crystalline regions of (c) and (d) formed above 7 V vs. Pt, the pore size was reduced to 10–30 nm. The reduced pore size of the crystalline TiO₂ layer formed above 7 V vs. Pt probably also contributes to the reduction of current.

The sponge-like TiO₂ layer formed at less than 1 V vs. Pt also reduce the current. Figure 10 shows the CV curves between 0 and 5 V vs. Pt. At each cycle, the current density in the positive sweep reduces the current. Figure 10 shows the CV curves between 0 and 5 V vs. Pt even after changing to the negative potential sweep.

The cyclic voltammograms of titanium specimens are drawn.

1) Nearly constant current density was obtained between 1.5 and 5 V vs. Pt even after changing to the negative potential sweep.

The current decay curves at a constant potential follows the Cottrell equation. The results indicate that the film growth is diffusion-controlled in the hot phosphate/glycerol electrolytes with a highly reduced water concentration.

2) The diffusion-controlled current increases as the basicity of electrolyte increases. The diffusion of oxygen species, such as OH⁻, appears to control the growth rate.

3) The TMP films are amorphous below 7 V vs. Pt, while anatase is developed above 7 V vs. Pt. Associated with film crystallization, phosphate concentration in the TMP films is increased.

4) The film morphology is also potential dependent. A sponge-like layer is formed below 1 V vs. Pt. An amorphous layer with cylindrical pores is formed at 1–7 V vs. Pt. The crystalline layer formed above 7 V vs. Pt has smaller pore size compared with the amorphous porous layer. The change in the pore morphology as well as oxygen gas generation above 7 V vs. Pt influences the diffusion current.

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