

# Fabrication of a novel aluminum surface covered by numerous high-aspect-ratio anodic alumina nanofibers



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## ABSTRACT

The formation behavior of anodic alumina nanofibers via anodizing in a concentrated pyrophosphoric acid under various conditions was investigated using electrochemical measurements and SEM/TEM observations. Pyrophosphoric acid anodizing at 293 K resulted in the formation of numerous anodic alumina nanofibers on an aluminum substrate through a thin barrier oxide and honeycomb oxide with narrow walls. However, long-term anodizing led to the chemical dissolution of the alumina nanofibers. The density of the anodic alumina nanofibers decreased as the applied voltage increased in the 10–75 V range. However, active electrochemical dissolution of the aluminum substrate occurred at a higher voltage of 90 V. Low temperature anodizing at 273 K resulted in the formation of long alumina nanofibers measuring several micrometers in length, even though a long processing time was required due to the low current density during the low temperature anodizing. In contrast, high temperature anodizing easily resulted in the formation and chemical dissolution of alumina nanofibers. The structural nanofeatures of the anodic alumina nanofibers were controlled by choosing of the appropriate electrochemical conditions, and numerous high-aspect-ratio alumina nanofibers (>100) can be successfully fabricated. The anodic alumina nanofibers consisted of a pure amorphous aluminum oxide without anions from the employed electrolyte.

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## 1. Introduction

Aluminum oxide films fabricated via anodizing in various electrolyte solutions have been widely investigated in various applied sciences and technologies due to their characteristic nanomorphologies and chemical/physical properties. In general, anodic aluminum oxide can be classified into two different types as follows: barrier and porous oxides [1–3]. Aluminum anodizing in neutral solutions results in the formation of a thin dense barrier oxide that can be as thick as 1  $\mu\text{m}$  on the aluminum substrate [4,5]. Barrier oxides have been widely used for electrolytic capacitor applications due to their high dielectric property [6–8]. In contrast, aluminum anodizing in acidic solutions including inorganic, carboxylic, cyclic oxocarboxylic, and bisphosphonate acid results in the formation of porous oxide that can be as thick as several hundred  $\mu\text{m}$  [9–16]. Porous oxides possess numerous fine hexagonal unit cells that have a nanoscale pore in the center [1–3]. Notably, the hexagonal cells of the porous oxide are self-ordered during anodizing

when aluminum is anodized in the appropriate acidic electrolyte solutions under the appropriate electrochemical conditions, and highly ordered porous oxides with an ideal cell arrangement can be easily fabricated [17,18]. For self-ordering of the porous alumina, several appropriate acidic electrolytes (i.e., sulfuric ( $\text{H}_2\text{SO}_4$ ) [19,20], selenic ( $\text{H}_2\text{SeO}_4$ ) [21,22], oxalic ( $\text{HOOC-COOH}$ ) [23–25], malonic ( $\text{HOOC-CH}_2\text{-COOH}$ ) [26–28], phosphoric ( $\text{H}_3\text{PO}_4$ ) [18,29,30], tartaric ( $\text{HOOC-(CHOH)}_2\text{-COOH}$ ) [27], phosphonoacetic ( $(\text{HO})_2\text{P(O)CH}_2\text{COOH}$ ) [31], and etidronic ( $\text{CH}_3\text{C(OH)[PO(OH)}_2\text{]}_2$ ) acid [32,33]) have been previously reported. In addition, additional acidic electrolytes and the use of organic solvents have also been reported by several research groups for novel porous alumina with different nanomorphologies [34–39]. Anodic oxide including nanoparticles were successfully fabricated by anodizing using sputter coated aluminum alloys and oxide nanoparticle dispersion aluminum [40,41]. Anodic porous alumina has been widely used for various nanoapplications, such as optical devices and nanotemplates [42–51].

The electrolyte used in aluminum anodizing has important effects on the nanofeatures of the anodic oxide. Therefore, the discovery of an additional electrolyte would lead to the formation of different types of anodic oxides with unique nanofeatures. Very recently, we reported the fabrication of a novel anodic aluminum

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oxide, which was called “anodic alumina nanofibers”, by anodizing in a new electrolyte (i.e., pyrophosphoric acid ( $\text{H}_2\text{P}_2\text{O}_7$ )) [52]. Ultra-high density single nanometer-scale alumina nanofibers measuring approximately  $10^{14} \text{ m}^{-2}$  in density are formed on the aluminum substrate during pyrophosphoric acid anodizing. These novel nanostructures are very different from that obtained by typical anodizing for barrier and porous oxides, as previously described. In addition, the aluminum surface that is covered with anodic alumina nanofibers exhibited superhydrophilic behavior with a contact angle of less than  $1^\circ$  within 1 s. This novel third generation anodic oxide can be used for various nanoapplications, such as a catalyst support and wettability control due to their ultralarge surface area. However, the details of the growth behavior of the anodic alumina nanofibers during pyrophosphoric acid anodizing under different experimental conditions, such as voltages, temperatures, and anodizing times, remain unclear. Therefore, detailed investigations of the pyrophosphoric acid anodizing are required for understanding the formation of alumina nanofibers and how to control the nanomorphology.

In the current investigation, we studied the formation behavior of the anodic alumina nanofibers via constant voltage pyrophosphoric acid anodizing under various conditions using high-resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM). We determined that there are appropriate pyrophosphoric acid anodizing conditions, such as time, temperature, and applied voltage, for the formation of uniform anodic alumina nanofibers. We found that the length, density, and nanomorphology of the anodic alumina nanofibers could be accurately controlled by the electrochemical operating conditions. Moreover, we found that numerous high-aspect-ratio anodic alumina nanofibers ( $>100$ ) connected to the aluminum substrate can be fabricated via long-term pyrophosphoric acid anodizing at low temperature of 273 K. These novel alumina nanofibers fabricated via pyrophosphoric acid anodizing will contribute to improving the functional surface materials.

## 2. Experimental

High-purity aluminum foils and plates (99.99 wt%,  $20 \text{ mm} \times 20 \text{ mm}$  with a handle,  $110 \mu\text{m}$  thick from Showa Aluminum, Japan,  $400 \mu\text{m}$  thick from Nippon Light Metal, Japan) were used as the anodizing specimens. The aluminum specimens were ultrasonically degreased in an ethanol solution for 10 min, and then, a silicone resin was coated on the bottom of the handle. After drying the coated silicone resin, the specimens were electropolished in a  $13.6 \text{ M CH}_3\text{COOH}/2.56 \text{ M HClO}_4$  mixture ( $T = 280 \text{ K}$ ) at a constant voltage of 28 V for 1 min. An aluminum plate was used as a cathode for electropolishing. Then, the specimens were washed with distilled water and dried.

The electropolished specimens were immersed in a concentrated pyrophosphoric acid solution (74.0–78.0 wt%,  $100 \text{ cm}^3$ ,  $T = 273\text{--}313 \text{ K}$ , Kanto Chemical, Japan), and then, the samples were anodized at a constant voltage at 10–95 V for up to 72 h using a PC-connected direct-current power supply (PWR-400H, Kikusui, Japan). The electrolyte solutions were slowly stirred ( $1 \text{ s}^{-1}$ ) with a magnetic stirrer during anodizing and maintained at a constant temperature using a water bath (UCT-1000, AS ONE, Japan). A platinum plate was used as the cathode for pyrophosphoric acid anodizing. The corresponding current during the constant voltage anodizing was recorded by a digital multi-meter (DMM4040, Tektronix, USA). After pyrophosphoric acid anodizing, the specimens were washed with distilled water and dried in a desiccator.

The surface nanomorphology of the anodized specimens was examined by field emission SEM (JIB-4600F/HKD and JSM-6500F, JEOL, Japan) and TEM (Titan Cubed G2 60-300, FEI, USA). For the SEM

observations, a thin platinum conductive layer was coated on the specimens by a sputter coater (MSP-1S, Vacuum Device, Japan). The density of the anodic alumina nanofibers was calculated by the SEM observation of the lower honeycomb structures. For the TEM observations, the specimens were embedded in an epoxy resin, trimmed mechanically, and then sliced into thin sections using an ultramicrotome (PT-X POWERHOME, Boeckler, USA) with a diamond knife. Qualitative analysis of the incorporated anions in the anodic oxide was performed using energy-filtered TEM (EFTEM) and electron energy-loss spectroscopy (EELS).

## 3. Results and discussion

### 3.1. Typical formation behavior of anodic alumina nanofibers

To understand the formation behavior of the anodic alumina nanofibers, the electropolished aluminum specimens were anodized in pyrophosphoric acid under various experimental conditions, such as applied voltages, temperatures, and times. Fig. 1 shows the electrochemical results and the changes in the current density,  $j$ , with anodizing time,  $t$ , at different constant voltages,  $U$ , during pyrophosphoric acid anodizing ( $T = 293 \text{ K}$ ). At a low voltage of 10 V, the current density increases and decreases rapidly to approximately  $6 \text{ A m}^{-2}$  immediately after the voltage was applied. Then, the current density decreases gradually with the anodizing time through a slight up-and-down variation for 5–10 min. The current density at other voltages during the initial 10 min increases with anodizing voltage, and key peaks were observed for 15 min at 25 V, 7 min at 50 V, and 3 min at 75 V. The position of the peak shifts with anodizing voltage toward the initial stage of anodizing. In contrast, the current densities become nearly the same values of approximately  $2\text{--}3 \text{ A m}^{-2}$  for longer periods of anodizing. These current-time transients and peak shifts were very similar to that obtained by typical anodizing for anodic porous alumina [1]. However, the current density increases rapidly to over  $2500 \text{ A m}^{-2}$  in the very initial stage at 90 V, and active anodic dissolution of the aluminum substrate was observed during anodizing. High-voltage anodizing above 95 V at different temperatures in the range of 273–313 K resulted in similar active dissolution of the aluminum substrate. Therefore, the application of a high voltage in concentrated pyrophosphoric acid is inappropriate for the formation of anodic oxide on aluminum. The changes in the surface nanomorphology under each of the anodizing conditions were examined by SEM.

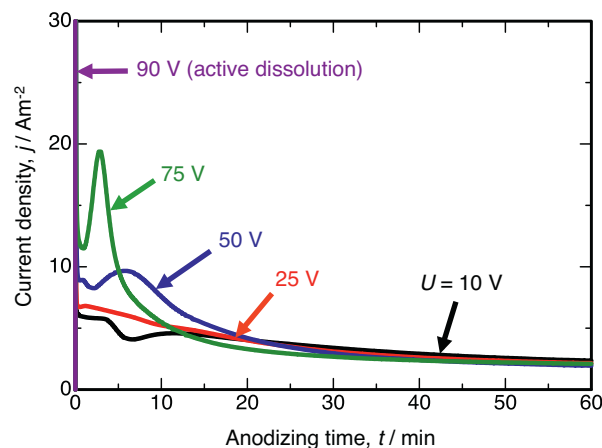


Fig. 1. Changes in the current density,  $j$ , as a function of anodizing time,  $t$ , during anodizing in concentrated pyrophosphoric acid at 293 K and constant voltages ranging from 10 to 90 V.

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