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Effect of Formation Voltage on the Pore Size of Porous Anodic Aluminum Oxide

Manogari Sianturi^{1,2}, Ariadne L. Juwono¹, Anawati Anawati*¹

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia

²Universitas Kristen Indonesia, Cawang, Jakarta, 13630, Indonesia

Corresponding author: anawati@sci.ui.ac.id

Abstract. This work is aimed to clarify the effect of formation voltage on the pore size of porous anodic aluminum oxide (PAAO) layer formed on commercially pure aluminum. The PAAO layers were obtained by anodization process in 0.3 M sulfuric acid solution at constant voltages of 10, 15, 20, and 25 V at 10°C. The structure and morphology of PAAO layers were characterized by using FE-SEM. The pore diameters which were estimated by using ImageJ software were 19.61 ± 15.35 nm, 20.03 ± 13.59 nm, 20.31 ± 12.36 nm, 25.06 ± 12.10 nm, and the wall thicknesses were 33 nm, 49.99 nm, 74.97 nm, 83.33 nm for the PAAO formed at 10, 15, 20 and 25V, respectively. The structure of the porous oxide layer became more uniform and organized, and the diameter of the pores increased linearly with applied voltage. High anodization voltage is known to cause Joule heating because of the fast movement of electrons and ions. It is believed that the Joule heat was transferred to the bulk electrolyte which results in larger pore diameter and interpore distance. The optimum condition to obtain high order PAAO is at 25 V.

Keywords: Porous Anodic Aluminum Oxide; Anodization; SEM

1. Introduction

In the past decade, there has been a renewed interest for researchers to fabricate porous anodic aluminum oxide (PAAO) layer due to the use of PAAO in various nanotechnology applications such as chemo- and biosensing applications [1], molecular separation, catalysis [2], application of biomedical drug delivery, implants and cell growth, electronic applications [3], hemodialysis, [4]. The unique properties of PAAO membranes such as an ordered pore structure, uniform pore size, controlled pore geometry, surface chemistry, and a large surface area make this material used as a template [5].

The process parameters have been extensively studied to achieve highly ordered pores. The Anodic voltage, temperature, type and concentration of electrolyte have been recognized as the most critical process parameters to control the order and geometry of the pores. The solution of aqueous sulfuric acid (H₂SO₄) at 25 V, oxalic acid (H₂C₂O₄) at 40 V and phosphoric acid (H₃PO₄) at 195 V are the most common electrolytes used to grow PAAO layer. In addition, other acid electrolytes which can also be



used such as selenik, chromate, malonate, tartaric, citrate, malic acid, in which anodic oxide is slightly soluble[6].

The PAAO structure can be defined by the structural parameters namely pore diameter, pore distance, pore length, wall thickness and thickness of the oxide barrier layer. By controlling the process parameter, the structural parameters can be adjusted in the range of 10-400 nm pore diameter, 50-600 nm interpore distance, 10-5000 pore aspect ratio, 10 nm - 150 μm barrier layer thickness, 10^9 - 10^{11} cm^{-2} pore density and porosity from 5% - 50% [6]. Electrolyte concentrations can directly affect pore size and cell diameter; whereas the two of the pore diameters and interpore distances are directly proportional to the anodization voltage [7]. Furthermore, a linear correlation between pore diameter, cell diameter, and voltage is formed in citric acid, malonic, oxalate, phosphate, sulphuric and tartrate. Earlier researchers had used sulphuric acid at voltages of 19-25 volts, oxalic acid at voltages of 40-70 volts, phosphoric acid at voltages of 160 - 195 volts, at a concentration of 0.3 M to obtain optimum structural parameters. The electrolyte temperature was kept as low as 0°C [4][7][8][9]. The low temperature of anodization was not beneficial for mass fabrication of PAAO layer. In this work, the anodization was performed at a higher temperature 10°C , and the formation voltage at the corresponding temperature was optimized in the range 10-25 V.

2. Methods

The sample was a commercially pure aluminum plate with 0.1 cm thickness cut into 1.5 cm \times 3.0 cm. The working area was 5 cm^2 . Before anodization, the sample was degreased with acetone and in ethanol in an ultrasonic bath for 3 min. The Al plate was then electropolished under a constant DC current of 500 mA for 4 minutes in a perchloric acid (HClO_4) solution (Merck) with ratio 1: 4. The sample was then washed in ethanol and then immediately placed in the anodization cell. Anodization was conducted in 0.3M H_2SO_4 (Merck) at 10, 15, 20, and 25 V for 4 h. The sample was placed as anode and platinum, Pt, was placed as a cathode. The distance between the two electrodes was 2,5 cm. The temperature during anodization was maintained at 10°C , and the electrolyte solution was constantly stirred at 300 rpm. The current density was recorded by a Digital Multimeter (DMM, Rigol). After anodization, the sample was immediately rinsed under running water and finally sprayed with DI water before drying with a hair dryer. The porous AAO layer produced from the above anodization process was characterized by using the Field Emission Microscope Electron (FESEM) JEOL type JIB4610F. To determine the average pore diameter, ImageJ software was used to calculate the average area of pore from FE-SEM image.

3. Results and Discussion

3.1. Current density vs time

The graph of current density output that arises during the anodization process is shown in Figure 1. The graph characteristic was similar at all voltages where a current transient occurred during the first 30 min before stabilized at prolonging anodization time. The formation of porous layers can be divided into two stages: stage I is a linear growth barrier layer, and stage II is the steady-state growth of porous layer. The first stage is characterized by the slope of the current density which was more swooping. At the beginning of the anodization process, the entire metal surface is covered with a compact and uniform oxide layer. The slope of this current density illustrates the mobilization of Al ions and the movement of electrons in the solution to start forming an oxide layer on aluminum metal. The second stage is the distribution of the electric field (E) strongly dependent on inhomogeneities and surface roughness of the oxide layer, which leads to a locally focused electric field and depression at the interface of the electrolyte-oxide. As a result, dissolution assisted by the electric field from the oxide layer occurs, and the first localized pores are formed and become the site for further pore growth. Consequently, an increase in ionic migration will lead to an increase in current density until pores completely cover the entire surface. The anodization process further increases the distribution of individual pores through the oxide layer where the maximum electric field is concentrated at the pore end and decreases towards the pore wall. Prolonged anodization increases the pore order to some

extent. The last stage is a competition between oxide growth at the pore bottom and at the same time oxide dissolution processes at barrier oxide layer interfaces. Finally, the pore growth process reaches a steady state, and uniformly distributed pores are formed. The analysis of this study was similar to earlier report [10].

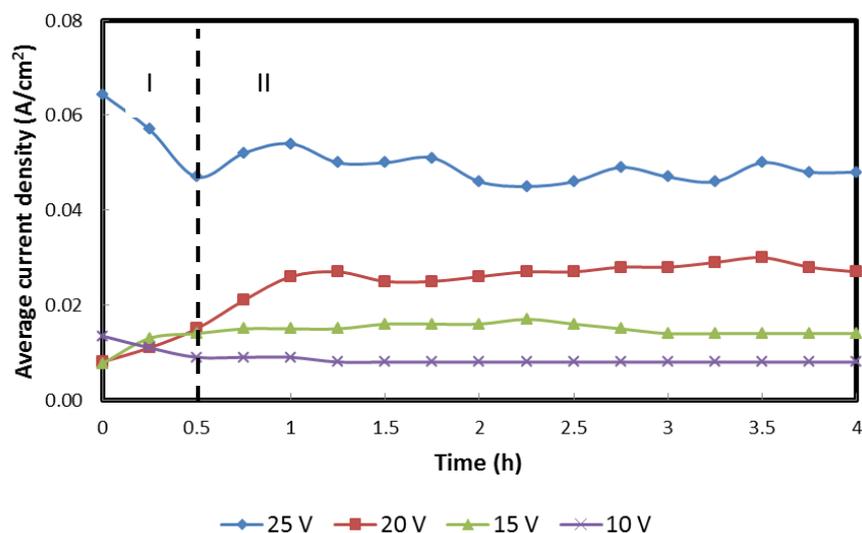


Figure 1. Current density versus time plot at formation voltages of 10, 15, 20, and 25 V in 0.3M H₂SO₄ solution at 10°C.

An interesting phenomenon from this study was that when the formation voltage increased, the current density output increased gradually. The sample anodized at 25 V generated a much greater current density than at lower voltage. The Joule heating which probably occurred at high voltage contributed to increasing the current density. The anodization was conducted at a low temperature of 10°C which slower down the ionic mobility in the electrolyte. The local Joule heating at the metal-electrolyte interface enhanced the ionic mobility which increased the reaction rate for the formation of PAAO layer. The average high current density during anodization gave a more uniform and regular porous oxide growth which also showed greater pore size and interpore distance. The higher regularity of the PAAO pores is required for the application in particular when used as a membrane. A membrane filtered between coarse and fine particles. The higher the regularity of the membrane's pore the better it filtered coarse particles. Figure 2 shows that when the sample was anodized at an increasingly high voltage, the average current density generated increases linearly with slope 0.0027. The average of the current density obtained in this study at various voltages was carried out at a constant temperature of 10 °C. Therefore, the current density generated during the anodization process was strongly influenced by the anodic voltage used.

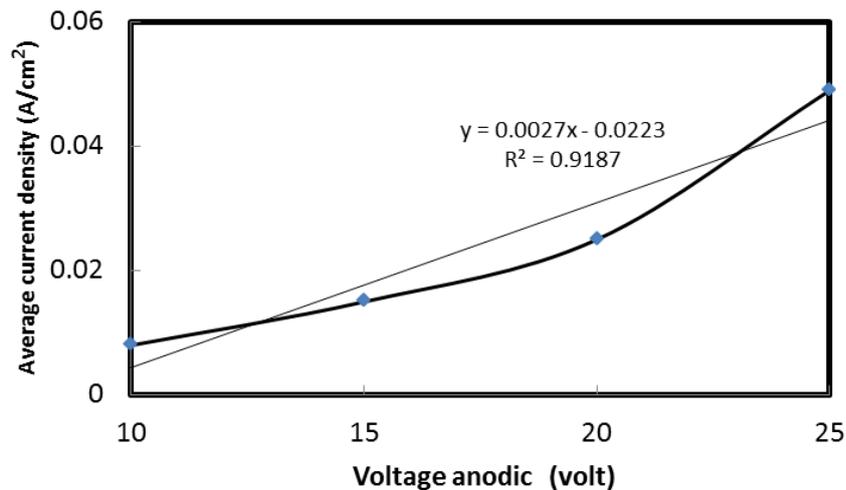
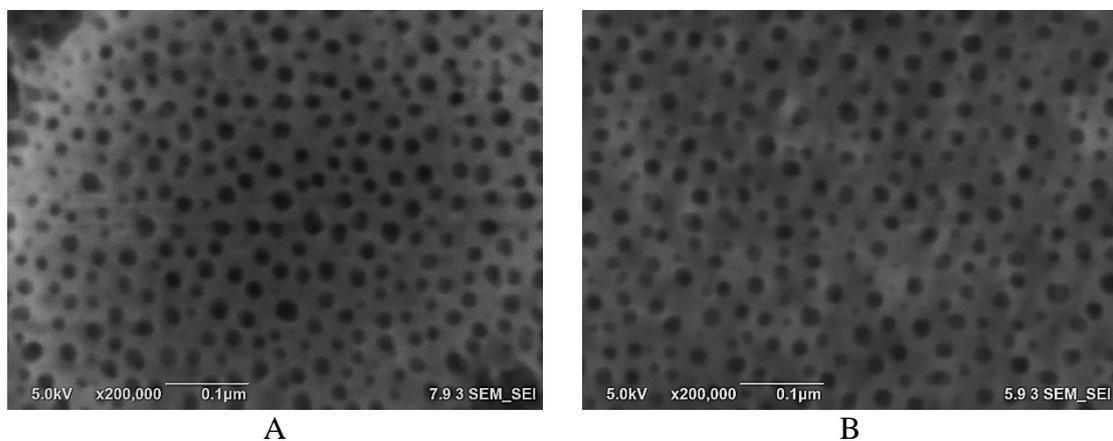


Figure 2. Graph of average current density versus anodization voltage.

3.2. Morphology of porous AAO layers

Figure 3 shows the morphology of PAAO layers produced from the anodization process at 10, 15, 20, and 25 V in 0.3 M H₂SO₄ solution. The average pore diameter sizes were 19.61 ± 15.35 nm, 20.03 ± 13.59 nm, 20.31 ± 12.36 nm and 25.06 ± 12.10 nm for anodization process voltage 10, 15, 20 and 25V, respectively and the interpore distance was 33 nm, 49.99 nm, 74.97 and 83.33 nm respectively, as measured by using ImageJ software. FE-SEM results revealed that the porous oxide layer morphology grew more regularly and uniformly with increasing formation voltage.

In this study, it was proved that the size of the pore diameter and interpore distance is greater with increasing applied voltage was confirmed in previous studies [11]. The effects of changes in anodization parameters directly affect the characteristics of the pore structure. The pore diameter and interpore distance are directly proportional to the applied voltage [7, 12]. Although other researchers also reported oppositely that anodization in oxalic acid the pore diameter and density increased with decreasing applied voltage[13]. Figure 3 shows that the size of the pore diameter and interpore distance tended to increase with applied voltage.



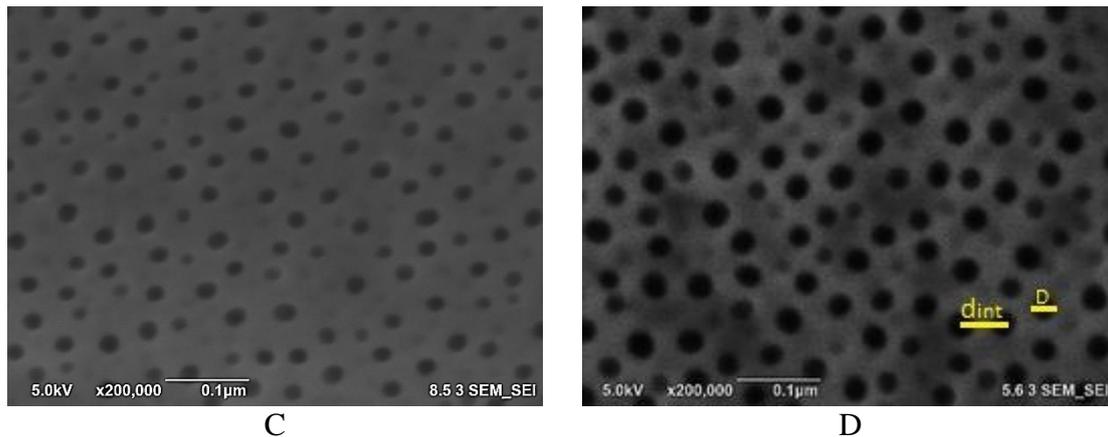


Figure 3. FE-SEM image of the surface morphology of anodic aluminum oxide at A. 10, B. 15, C. 20 and D. 25 V in 0.3 M sulfuric acid.

Table 1 shows the PAAO structure parameters, namely average pore area, average pore diameter (D), and pore distance (d_{int}) obtained from Figure 3. Anodization at an anodic voltage range of 10-20 volts increased the average pore diameter linearly. When the sample was anodized at an anodic voltage greater than 20 volts the average diameter of pore increased rapidly, the phenomenon shows that the voltage anodic used has approached the breakdown voltage of the aluminum sample in the sulfuric acid solution. The interpore size also increased with increasing applied voltage.

Table 1. PAAO parameters of image A, B, C and D

PAAO parameters	Image A	Image B	Image C	Image D
Average pore area (μm^2)	$3.02 \times 10^{-4} \pm 1.85 \times 10^{-4}$	$3.15 \times 10^{-4} \pm 1.45 \times 10^{-4}$	$3.24 \times 10^{-4} \pm 1.2 \times 10^{-4}$	$4.93 \times 10^{-4} \pm 1.15 \times 10^{-4}$
D (nm)	19.61 ± 15.35	20.03 ± 13.59	20.31 ± 12.36	25.06 ± 12.10
d_{int} (nm)	33	49.99	74.97	83.33

This study reveals that the morphology of the pores from the results of the characterization of FE-SEM that the average pore diameter, the inter pore distance, and the uniformity of pore increases with the increasing the anodic voltage used [14]. Figure 4 shows that the obtained inter-pore distance increases linearly with a slope of 3.5194. The image D from Fig. 3 shows that the average diameter of the pore and interpore distance were the largest, and most uniform when the sample was anodized at a voltage of 25V.

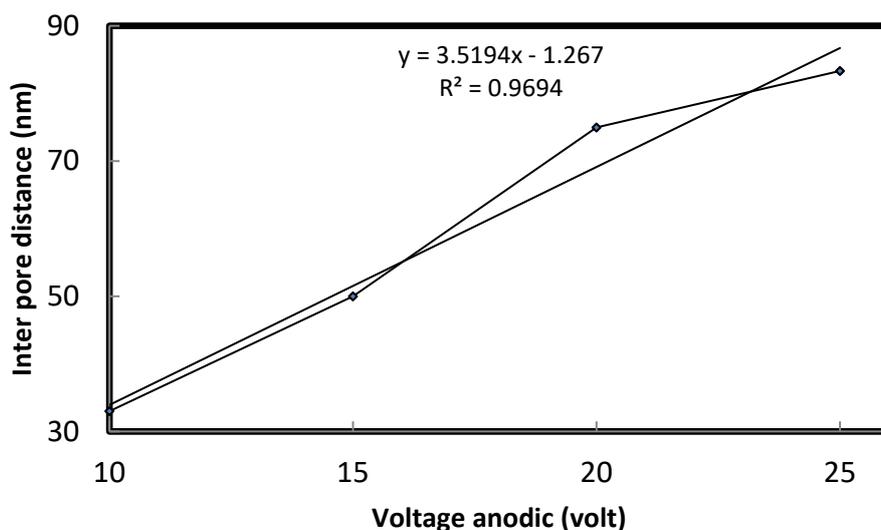


Figure 4. Graph of inter pore distance versus anodization voltage.

4. Conclusions

We have successfully fabricated porous anodic aluminum oxide (PAAO) layers at various formation voltages of 10, 15, 20, and 25 V in a 0.3 M sulfuric acid electrolyte solution at a 10°C. Surface characterization by FE-SEM and further analysis with ImageJ software indicated structural parameter of the PAAO layer increased with applied voltage. The pore diameter, interpore distance, and pore regularity increased with increasing applied voltage. Therefore, the optimum voltage to grow a regular PAAO layer at 10°C in 0.3 M H₂SO₄ solution is at 25 V.

5. References

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