

## Preparation and Characterization of Porous Anodic Alumina Membrane

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### ABSTRACT

Porous Anodic Alumina (PAA) was prepared by two-step anodization on both sides of an aluminium foil. The anodization carried out at anodizing temperature 17°C using oxalic acid as an anodizing electrolyte. The (PAA) template was characterized with optical microscope and SEM. The optical microscope image showed two (PAA) layers after the dissolution of the residual aluminium. The average pore diameter was found to be (75) nm. The average interpore distance of (PAA) prepared was found to be (99) nm. The thickness of (PAA) was found to be (59.5) µm.

**Keywords:** Porous Anodic Alumina (PAA)

### تحضير و تشخيص طبقة الألومينا المسامية

#### الخلاصة

عينات الألومينا المسامية حُضرت بعملية الأنودة ذات المرحلتين و على كلا الجانبين لطبقة رقيقة من الألمنيوم. أجريت عملية الأنودة في درجة حرارة (17°C) باستخدام حامض الأوكزاليك. تم تشخيص عينات الألومينا المسامية بواسطة جهاز المجهر الضوئي و المجهر الإلكتروني الماسح. أظهرت صورة المجهر الضوئي وجود طبقتين من الألومينا المسامية بعد إذابة الألمنيوم المتبقي. وجد بأن معدل قطر المسامات (75) نانوميتر ومعدل المسافة البينية بين المسامات لعينات الألومينا المسامية (99) نانوميتر. وجد بأن سمك طبقة الألومينا هو (59.5) مايكرون. تم حساب المسامية لعينات الألومينا المسامية.

### INTRODUCTION

**M**etal nanostructures, such as nanoparticles, nanowires and nanotubes have attracted much attention in recent years due to their extraordinary electronic, magnetic, optical and chemical properties [1].

Metal nanowire arrays have been prepared using a variety of techniques such as: electrochemical methods, chemical vapor deposition, sol-gel and template assisted

electrodeposition. Anodized aluminum oxides (PAA) template is considered an ideal template as it possesses many desirable characteristics including tunable pore dimensions, good mechanical strength, thermal stability, and ordered nanotubes [1].

With the development of the nanoscale material research, porous alumina was paid increasing attention because it is a good template to fabricate nanometer-sized fine structures [2].

The mechanism of nanohole formation by electrical field assisted dissolution was discussed by Hoar and Mott [3]. The occurrence of a periodic pore arrangement in porous anodic alumina (PAA) was reported in 1995 using two-step anodization of high purity aluminum with 0.3M oxalic acid solution, at 40V, 0 °C, 160h [3, 4].

The geometry of anodic porous alumina film may be described as a honeycomb structure, which is characterized by a close-packed array of columnar hexagonal cells, each containing a central pore normal to the substrate [2]. Template assisted methods are commonly used for fabrication of one-dimensional nanostructures such as nanowires, nanotubes, and nanodots. Porous anodic aluminum oxide (PAA) membranes formed by anodization of aluminum in acidic electrolytes has become one of the most versatile template for nanofabrication [5].

The aim of this work is to prepare and characterize porous anodic alumina (PAA).

## EXPERIMENTAL WORK

Aluminium foils of (30 \* 20 \* 0.15) mm and purity of about (99%) was annealed in an electric furnace (Barnstead Thermolyne / 1300, USA) at 500 °C for 3h. Each sample was cleaned with acetone in ultrasonic bath for (5)min before and after annealing to eliminate any grease. The annealed Al samples were then treated with NaOH solution (100ml H<sub>2</sub>O + 5gm NaOH) for (2) min [6], in order to dissolve the Al oxide layer produced during the annealing step. Samples were then washed several times with deionized water and then chemically polished using a solution of (3.5ml H<sub>3</sub>PO<sub>4</sub> + 96.5ml H<sub>2</sub>O + 4.5gm CrO<sub>3</sub>) at (80)°C [6], with magnetic stirrer for 10min. The samples were then washed with deionized water and ready for the anodizing. Two step anodizing technique was used to prepare PAA with highly uniform pores distribution. The first anodizing was performed for 1h at 17°C using oxalic acid 0.3M (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O) as an electrolyte at 40V D.C.

The anodizing cell (anode, cathode, electrolyte and the beaker) was cooled in a bath of liquid mono-ethylene glycol with inhibitors which ensure long lasting protection against freezing and corrosion. The temperature of the cell was measured using k-type thermocouple. The current density (J), which is current (mA) passing through a unit area (cm<sup>2</sup>) of the sample was calculated and plotted against the anodizing time (sec). After the first anodizing, the sample was washed with deionized water and then dried. The porous oxide film that was formed after the first anodization process must be removed to get better pores uniformity during the second anodization process. So to remove the porous oxide film, a solution of (8.75ml of H<sub>3</sub>PO<sub>4</sub>, 241.25gm of H<sub>2</sub>O and 5gm of Cr<sub>2</sub>O<sub>3</sub>) at 50 °C was used for (10) min [6]. The sample was then washed in deionized water and dried. The second anodizing was performed under the same conditions of the first anodizing process except anodization time was (11) h. This long anodizing time will help to increase the thickness of the porous aluminium oxide. The anodizing current was also recorded during

the second anodizing process. The sample was washed with deionized water after each anodizing process to eliminate the residual electrolyte. In order to make sure that PAA has been prepared on both sides, the remaining aluminium of one sample was eliminated by immersing the PAA template in a solution of (0.1M of CuCl + 20% vol of HCl).

Pores widening process was performed after the second anodizing process using a solution of (5ml of H<sub>3</sub>PO<sub>4</sub> and 95ml of H<sub>2</sub>O) at (50) °C for (10) min was used [6].

The SEM micrograph was used to measure the pore diameter ( $D_p$ ), the interpore distance ( $D_c$ ).

## RESULTS AND DISCUSSION

Two step anodizing process (first and second anodizing) was carried out using Al foil with oxalic acid as an electrolyte. The current density (J) mA/cm<sup>2</sup> of the Aluminum sample with area of (3 \* 2) cm<sup>2</sup> was calculated by recording the cell current (I) mA during anodizing time (t) sec. First anodizing was carried out for one hour. The current density versus anodizing time is shown in Figure (1). This behavior of the first anodizing process shows three different stages at all temperatures. The same three different stages as shown in Figure (1) were observed during both first and second anodizing process. In the first stage of the first anodizing process a compact oxide layer called (oxide barrier layer) starts to form as a result of oxidation of Al surface with accompanying increasing in oxide thickness and continuous falling in current density with time. At the beginning of this stage, the current density is at a maximum because of the direct contact between the aluminium surface (anode) and the electrolyte (oxalic acid). At the end of this stage, the oxalic is temporarily isolated from the Al substrate surface and the current density will be at its lowest value. The variation of current density with anodizing time is exponential in nature and can be expressed as [6]:

$$J = C \text{Exp} (BT) \quad \dots (1)$$

Where: J= current density, mA/ cm<sup>2</sup>, t= anodizing time sec, C and B are constants. The value of C and B was found to be (8.25 (mA/cm<sup>2</sup>)) and (-0.16 sec<sup>-1</sup>) respectively. The second stage represents the oxide pores initiation. After the oxide barrier layer has reached a maximum thickness, an electrical breakdown occurs because of the insulating nature of this oxide barrier layer. As a result a propagation of individual paths through this oxide begins which indicates an increasing in the current density, and so pores are formed. In the third stage, the current density reached a maximum value and the variation of the current density with the anodizing time is minimum. A continuous porous film starts to grow on the surface of the aluminium foil. The same three stages were found in the second anodizing but with higher current density values. As stated earlier, the PAA film formed in the first anodizing was removed chemically to be ready for second anodizing process. The remaining aluminium surface contains pits that act as seeding area for the next pores formation in the second anodizing. These concave pits areas possess high energy leading to pores formation with more uniformity. SEM was used to analyze the PAA samples. A SEM image for porous alumina prepared at 17°C (the temperature was controlled using chiller system) is shown in Figure (2). The honey-comb hexagonal closed packed structure is shown.

The porosity is calculated from the following equation[6]:

$$P = 0.907 (D_p/D_c)^2 \quad \dots (2)$$

Where  $D_p$  and  $D_c$  are the pore diameter and interpore distance in (nm) respectively. High anodizing temperatures frequently used for shorten the anodizing duration and this is important from economic point of view because the less the time the lower the cost. The area occupied by pores (porosity) has been more spread with high anodizing temperature.

Figure (3) shows SEM image was taken for vertically positioned samples to measure the PAA thickness.

Indescribing the anodic porous alumina structure, researchers usually list the outer layer diameter of oxide close to the surface, and the inner layer diameter close to the pore bottoms [7].

As mentioned in the experimental, the residual aluminium was removed after the second anodizing and an optical microscopy image was taken, and proved the occurrence of two separated PAA layers. Figure (4) shows the optical microscopy image.

## CONCLUSIONS

The Conclusions of this work are:

- 1-The pore diameter of the prepared PAA at 17°C was (75) nm and interpore distance was (99) nm.
- 2-The thickness of PAA is (59.5) µm at 17°C.
- 3-The porosity of PAA was calculated from the previous equation and it is found to be (52) %.
- 4-Optical microscopy image revealed the formation of two PAA layers after the removing the residual aluminium.

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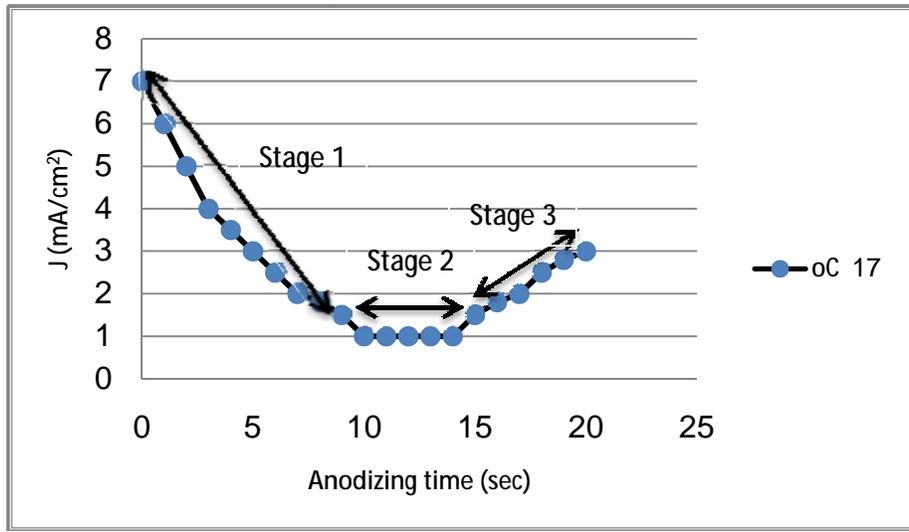


Figure (1) Current density versus anodizing time for the First anodizing at 17°C.

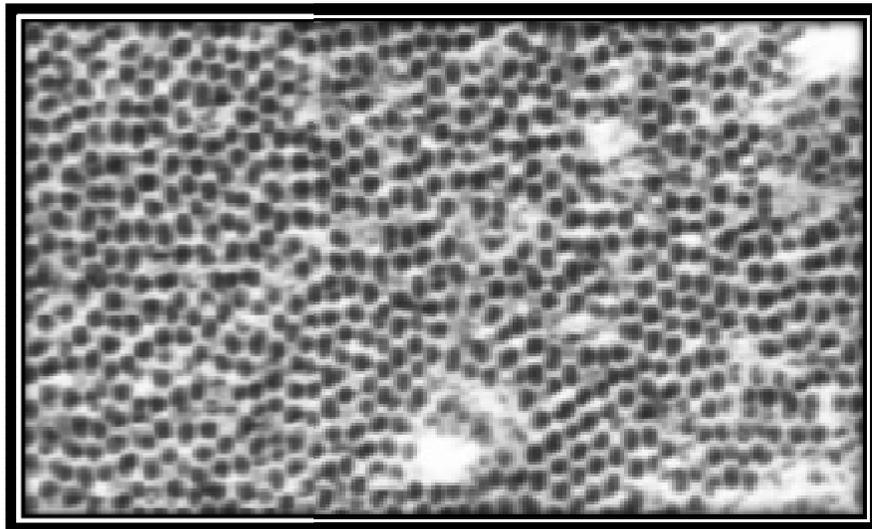


Figure (2) SEM image of PAA after second anodizing at 17°C.

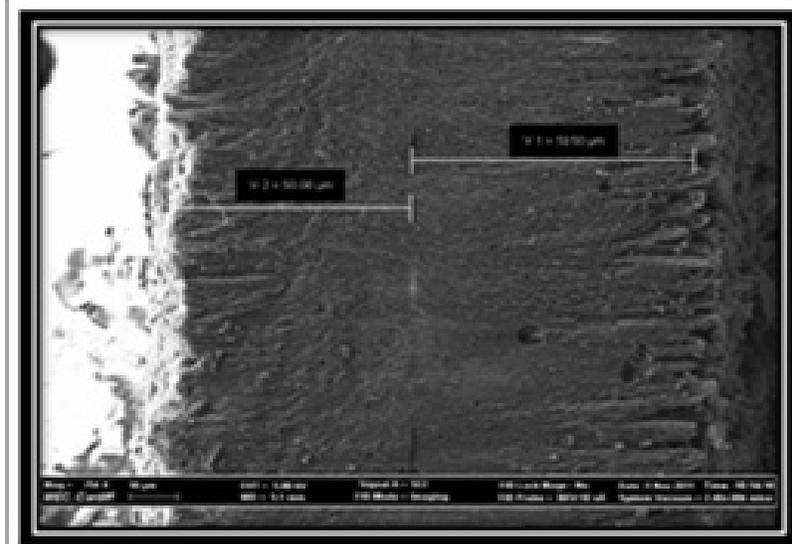


Figure (3) SEM image of PAA thickness after second Anodizing at 17°C.



Figure (4) Optical microscopy image of single and Double PAA membrane.