

Contact angle measurement studies on porous anodic alumina membranes prepared using different electrolytes

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ABSTRACT

This paper investigates the effect of pore widening duration on the wetting properties of nanostructured porous anodic alumina (PAA) membranes fabricated using sulphuric and oxalic acid as electrolytes by two step anodization process. XRD analysis shows that prepared PAA membranes were amorphous in nature. With increasing of pore widening durations from 0 to 120 min, the contact angle of PAA membranes varied from 21 to 78°. It was noticed that PAA membranes were hydrophilic in nature in the present of water medium. In the presence of acetone medium, PAA membranes prepared with 1hr pore widening time showed super hydrophilic behaviour. Copyright © 2016 VBRI Press.

Keywords: Anodization; contact angle; porosity; porous anodic alumina; pore widening duration.

Introduction

Aluminum and its alloys are significant industrial materials because of their low weight and high-quality corrosion resistance on account of surface passivation. One of the characteristic properties of aluminum is that when anodized under suitable conditions, a porous structure can be formed on the surface [1]. Porous anodic alumina (PAA) membranes fabricated by the electrochemical anodization of aluminum have turned out into a popular, inexpensive and greatly versatile material for applications in a broad range of fields such as surface tribology [2], filtration [3], catalysis [4], bio sensing [5] and template synthesis of one-dimensional nanostructures [6]. The advanced surface hardness and high porosity along with good thermal strength and chemical resistance are demanding qualities of these inorganic porous membranes. Self-arranged PAA membranes with well-controlled pore diameter (10-150 nm) and interpore distance (25-400 nm) are attained by systematic selection of the processing parameters, such as type and concentration of the acid electrolyte, applied anodization potential, current density, anodizing duration and temperature [7]. Systematically organized hexagonal arrangement of parallel pores aligned normal to the film surface. In the anodization process, there is an equilibrium state among the electric-field-enhanced oxide dissolution at the electrolyte/oxide interface and the formation of oxide at the oxide/metal interface [8]. The growth mechanism by which the porous PAA membranes development has been discussed regularly [9] and many effects have been made to achieve the systematic expressions creating the relations of the pore geometry and the electric field in the oxide with the aspects of the anodization process [7]. A two-step anodizing process [10] is generally used for the formation of high-ordered, porous PAA membranes. Following a

primary anodizing at the preselected potential, a wet chemical etching of the grown aluminum oxide layer is done. This oxide removal results in the production of a periodic concave pattern on the aluminum surface, which acts as a template for the second anodizing step that is completed at the same anodizing potential as used for the first step anodization [10]. Recently the fabrication of surfaces with special wettability, as well as super hydrophobicity, has concerned great research attention because of the promising potential for their use as self-cleaning surfaces and in micro fluidics and droplet based technologies [11]. A surface is called super hydrophobic when the effective contact angle (CA) of a liquid water droplet with the surface exceeds 150° and, on the other hand, super hydrophilic when the CA is smaller than 10°. For the fabrication of super hydrophobic materials a surface behavior with a low surface energy material is regularly merged with a surface structuring with hierarchical geography at the nanometer and/or micrometer scale. Surface wettability of PAA membranes has been studied in recent years. So far, the number of literature reports on the wetting of PAA membranes is limited and most of the studies were paying attention on their surface variation with low surface energy materials rather than scientifically addressing the wetting of the intrinsically porous PAA structures. In the present study, we explain the correlation between the structural attributes and the surface wettability of PAA arrays with changing pore widening duration. In this work, we concentrated on the results on preparation of nanoporous PAA membranes with oxalic acid and sulphuric acid as electrolytes. In particular we focused our attention on wettability analysis of PAA membranes at different pore widening durations. These studies provide the practical instructions for the fabrication of highly porous PAA

arrangements with controlled wettability forming on PAA oxide surfaces.

Experimental

Highly pure aluminium foil (99.999 % Alfa Easer) was used as the initial material. Al foils were annealed in air atmosphere at 500 °C for 5h. The aluminium foils were degreased in acetone washed in distilled water and eliminate the normal oxide layer in NaOH solution. The substrates were then electro polished in a mixture of perchloric acid and ethanol (1:4 vol) for 50 sec at a current density of 250 mA/ cm². PAA films were prepared by two-step anodization process. Working area of aluminium was 1 cm². First step of anodization was conducted about a temperature of 5 °C for 6h in 0.3 M oxalic acid at a potential of 40 V respectively. Subsequently, samples were immersed into a mixture solution of H₃PO₄ (6 wt %) and H₂CrO₃ (18 wt %) at 60 °C to remove the alumina films. The conditions of second anodization were the same as the first step anodization. During anodization, electrolyte was carefully stirred (400 rpm) throughout the experiment. The final step of the experimental sequence includes etching in a solution of H₃PO₄ (5 wt %) at room temperature with different times. The crystallographic analysis were carried out using JEOL X-ray diffractometer (JDX-8030) using Cu-Kawavelength ($k = 1.54059 \text{ \AA}$) with scanning range from 20° to 80°. The surface morphology of the films was studied with JEOL scanning electron microscopy (JSM-6380 LV). The contact angle of water on the PAA templates has been determined using a dynamic contact analyzer (FTA-200 Firsten angstroms). Image analysis (interpore distance and pore diameter) were done with image analysis software Image- J.

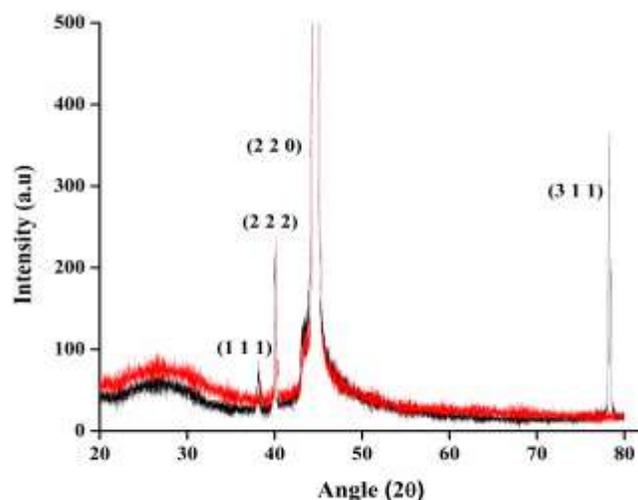


Fig. 1. XRD pattern of the PAA templates prepared using oxalic acid (block) and sulphuric acid (red) as electrolytes.

Results and discussion

X-ray diffraction spectra of PAA membranes made under different electrolytes such as oxalic acid and sulphuric acid as shown in the **Fig. 1**. The (222) and (220) peaks of Al₂O₃ can be observed in the diffraction spectra of PAA membranes with JCPDS data (01 – 1304). These results indicate that the PAA templates amorphous in nature with

aluminium substrate [12]. The other diffraction peaks (111) and (311) can be assigned to the aluminium substrate with corresponding JCPDS data (89-2769).

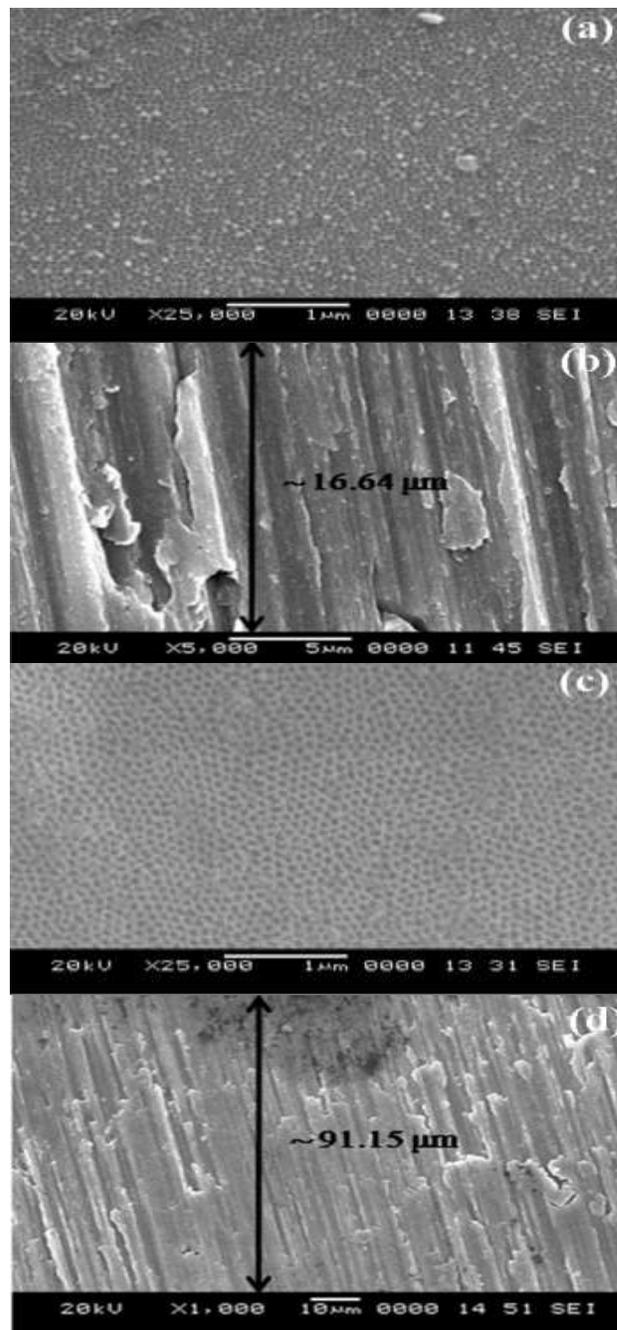


Fig. 2. SEM images of PAA templates fabricated using (a) 0.3 M of oxalic acid at 40V, (b) cross sectional view and (c) 0.3M of sulphuric acid at 20 V, (d) cross sectional view.

Fig. 2 shows the top – view SEM images of the PAA membranes prepared at various electrolytes such as 0.M of oxalic acid at 40 V (**Fig. 2c**) and 0.3 M of sulphuric acid at 20 V (**Fig. 2a**) and cross sectional images of oxalic acid (**Fig. 2d**) and sulphuric acid (**Fig. 2b**) respectively. The barrier layer thickness of PAA membranes are 16.64 μm and 91.15 μm for sulphuric acid and oxalic acid respectively. In **Fig. 2** PAA membranes shows that size of the pores in 0.3m sulphuric acid is very tiny so the density of pores is high the fabricated pores are arranged in

hexagonal structure as shown in **Fig. 2**. Pores are more regular in oxalic acid, but their sizes are bigger in comparison with sulphuric acid as electrolyte. Pore diameter and inter pore distances of PAA membranes were calculated using Image J software and the distribution figures were shown in **Fig. 3**.

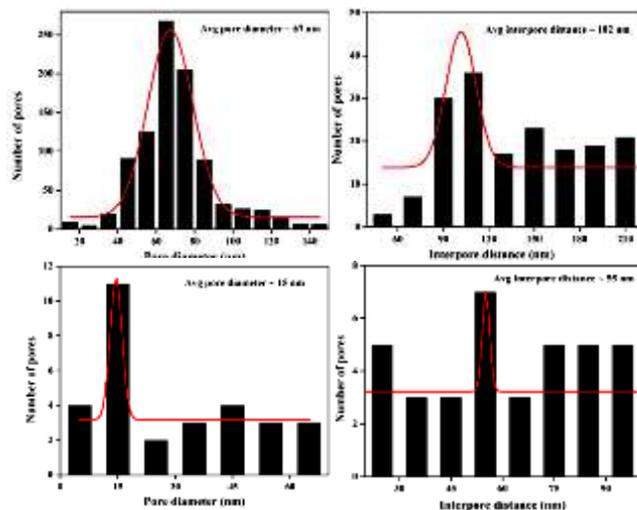


Fig. 3. Pore diameter and inter pore distance distribution diagram of PAA membranes formed in 0.3 M oxalic acid (3a,b) and 0.3 M sulphuric acid (3c, d).

Table 1. Average pore diameter, inter pore distance, pore density and porosity of PAA membranes.

Sample	Pore diameter (nm)	Inter pore distance (nm)	Porosity (%)	Pore density ($\times 10^9 \text{ cm}^{-2}$)
OA	67	102	59.40	11.0
SA	15	55	24.64	38.1

The average pore diameter and inter pore distance of pores was 67 nm, 102 nm and 15 nm and 55 nm respectively, for PAA membranes which were anodized in 0.3 M oxalic acid, 0.3 M sulphuric acid (**Table 1**). PAA membranes show the uniformity in pore size and distribution in both oxalic and sulphuric acid cases. Sulphuric acid can generate the smallest diameter pore at lower voltages [12]. In the anodization process of PAA membranes, there is a balance among the dissolution of field-enhanced oxide in the interface electrolyte/oxide and oxide creation at the interface oxide/metal. This balance is important for the formation of porous alumina because it causes the width of the barrier to remain constant throughout the anodization process [13]. In recent years, solids with nanometer-scale pores have become well-known members for producing super hydrophobic surface due to their inherent surface roughness [14]. Surface wettability property is considered to be managed by both the chemical composition and geometrical arrangement of solid surfaces [15]. To study the effect of a pore widening on the wetting properties of PAA membranes, we etched the PAA membranes in 5 wt % phosphoric acid at 30° C. The wetting of the PAA surfaces is largely dependent on the surface porosity [16]. With increasing pore widening duration, the pore wall thickness decreases and as a result of both the average pore diameter and the surface porosity

increases [17]. The pore widening results in a shift of the contact angle (CA) toward higher values for PAA membranes.

Table 2. Contact angle as a function of pore widening for PAA membranes formed in 0.3 M of oxalic and sulphuric acid.

Pore widening time (min)	Contact angle (°)		Surface energy (mJ/cm^2)	
	SA	OA	SA	OA
0	21.50	21.30	66.87	66.96
60	32.15	37.03	61.19	58.04
120	54.02	72.07	45.23	30.69

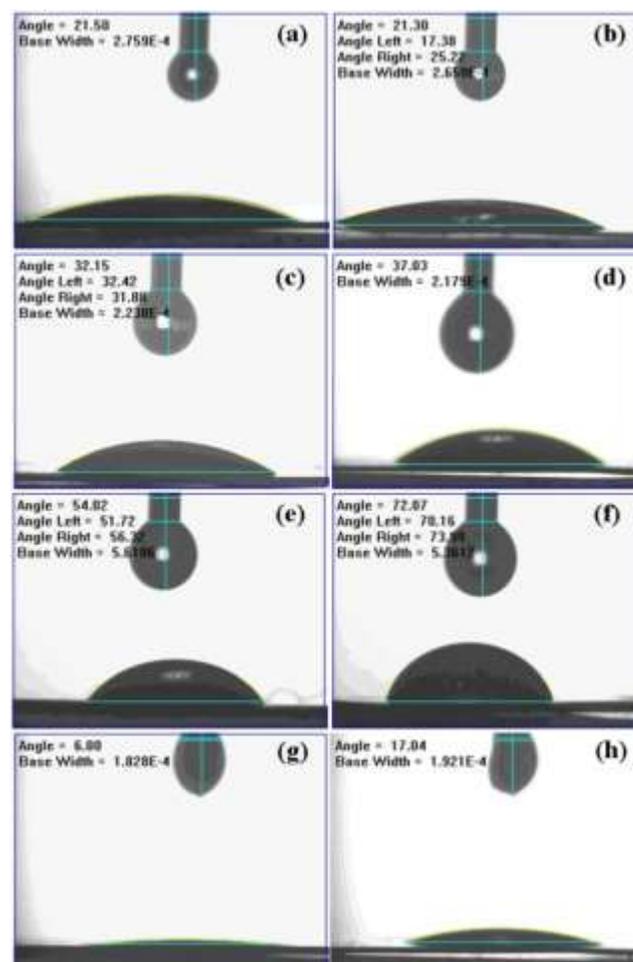


Fig. 4. Contact angle measurement images of PAA membranes formed at different pore widening durations: Without pore widening (a) sulphuric acid and (b) oxalic acid; 1 hr pore widening (c) sulphuric acid (d) oxalic acid; 2 hr pore widening (e) sulphuric acid and (f) oxalic acid; in acetone medium (g) sulphuric acid (h) oxalic acid.

To examine the effect of the pore opening on the wetting of PAA in more detail, we varied the etching time (60 min, 120 min) and the resulting oxide structures were studied. **Fig. 4** shows the wettability behaviour of PAA membranes formed at different pore widening durations. The measurement on water contact angles (CA) at room temperature are recorded in the **Table 2**. From **Fig. 4**, it is evident that, PAA membranes shows hydrophilic behaviour with contact angle 21.50° and 21.30° for sulphuric acid and oxalic acid respectively without pore widening.

Furthermore with increasing pore widening duration from 0 min to 120 min contact angles varies from 21.50° to 54.02° for sulphuric acid and to 21.30° to 72.07° for oxalic acid with hydrophilic nature. In addition, PAA membranes prepared using oxalic acid shows hydrophilic behaviour and sulphuric acid shows super hydrophilic nature with contact angles 17.04° and 6.00° in acetone medium. The surface energy of the PAA membranes was then calculated from Young's equation [17]. It showed variation between 45.23 to 68.67 mJ/cm² for sulphuric acid and 30.69 to 66.69 mJ/cm² for oxalic acid respectively (**Table 2**). From the wettability studies in acetone medium, the surface energy values for oxalic acid was found to be 68.67 and for sulphuric acid 71.39 mJ/cm² respectively. From the SEM images and the obtained values of contact angle, we can notice that the contact angle directly associates with the surface structure of the film.

Conclusion

In summary, we have reported the synthesis of PAA membranes by two-step anodization of aluminium in sulphuric acid and oxalic acid electrolytes using optimized process parameters. The anodizations were performed in 0.3 M oxalic acid at 40 V and 0.3 M sulphuric acid at 20V. It was found that density of pores is higher in sulphuric acid case as compared with that of oxalic acid. As the pore widening duration was increased, the pore diameter and contact angle were found to increase in both oxalic acid sulphuric acid in water medium. In fact, PAA membranes produced in sulphuric acid exhibited super hydrophilic nature which was confirmed through contact angle measurements in the acetone medium.

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