

Room temperature anodization of aluminum and the effect of the electrochemical cell in the formation of porous alumina films from acid and alkaline electrolytes

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ABSTRACT

Nanoporous alumina was produced by anodic oxidation of aluminum in both acidic and alkaline electrolytes. Previous reports indicate that nanoporous alumina is mainly produced from strongly acidic electrolytes, and with the use of a low freezing temperature controlled bath to control the propagation and growth of the pores. We design an in-house electrochemical cell with an electronic circuit box attached, to control the anodization of aluminum at room temperature. The electrolytes used were phosphoric acid solution and sodium hydroxide solution. The pH of the acidic electrolyte was adjusted to 1, 3 and 5 with an applied potential of 50V and anodization time of 1 and 3 hrs, respectively, while the alkaline electrolyte pH was adjusted to 9, 11 and 13 with an applied potential of 40V and the templates anodized for 5 hrs. The micrographs of the nanoporous alumina formed from these electrolytes confirm that the nucleation and growth of nanoporous alumina films is achievable with the aid of the electronic circuit box connected to the electrochemical cell. Copyright © 2012 VBRI Press.

Keywords: Anodization; electrolytes; nanoporous alumina; room temperature.



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coatings.

Introduction

Nanoporous alumina films produced during electrochemical anodization of aluminum has been studied for many years [1], and has continued to attract interest from various researchers because of its unique chemical and physical properties [2-4]. These unique properties have made it possible for a wider application, and there has been numerous reports in the application of nanoporous alumina which are fully documented i.e. Jing et al have reportedly used nanoporous alumina in biodevices; Rumiche et al., have used it as a sensor in hydrogen detection, Mombello et al., used it in the adsorption of volatile organic compounds; Kang et al., used it in drug delivery etc.

The anodization of aluminum is usually performed in a strongly acidic environment and most often, a temperature controlled bath is used to aid the fabrication process [9-11]. It is generally accepted that film structures are of porous-type which develops in phosphoric acid, oxalic acid, sulfuric acid and other strongly acidic solutions [12]. The temperature range during this process is usually below or slightly above the freezing temperature,

while film structure obtained using boric acid, or other organic acid salt produces a barrier-type film with a higher current density supply [13, 14]. There has been considerable effort in providing a proper understanding of the mechanism of formation of nanoporous alumina films during the anodization process, the various informations provided presently have yielded a more understanding and models in some cases have also been developed [15].

The three main acidic electrolytes commonly used for the fabrication of nanoporous alumina are oxalic acid [2, 16, 17]; sulfuric acid [8, 12, 18-20]; and phosphoric acid [21, 22]. Apart from these commonly used acids, there have been reports of researchers using alkaline electrolytes [23] and mixed acids [24, 25] to successfully fabricate nanoporous alumina at room and freezing temperatures. The anodization of aluminum at higher temperatures will make an interesting finding and a possible alternative to the way nanoporous alumina is presently being fabricated. Although, a few researchers have made a report on high temperature fabrication of aluminum [2, 26-28] a detailed study will still be required to identify the key parameters that influence the ordering and structure formation of the pores at those temperatures.

In this study, we report the anodization of aluminum at room temperature using two different types of electrolytes. In order to make it possible an in-house electrochemical cell is designed with an electronic circuit box attached to the electrochemical cell with both inlet and outlet points for the acid and alkaline electrolytes. A schematic diagram of the circuit is shown in Fig. 1. We examine the effect of the electrochemical cell on the fabrication of nanoporous alumina using different electrolytes and operating at room temperature.

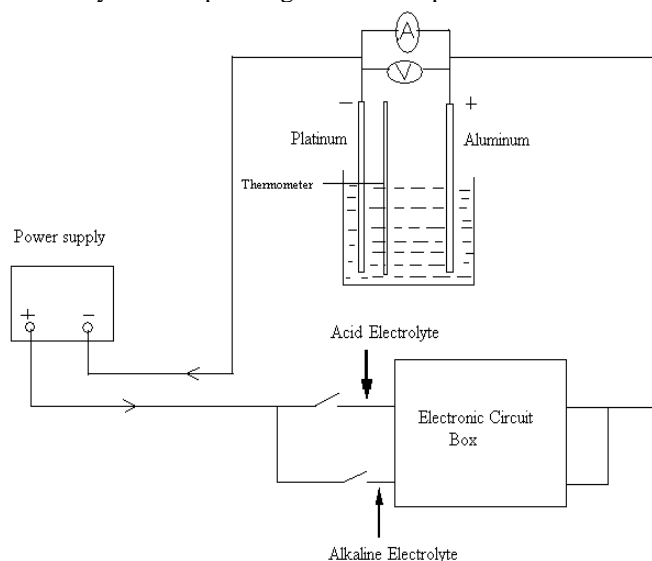


Fig. 1. Schematic diagram of the electrochemical cell.

Experimental

Materials and methods

High purity aluminum (99.9 %, 0.25 mm thick) was purchased from Malaysia aluminum and alloys, and anodized in both acidic and alkaline electrolytes using a

single step anodization procedure. The templates were purged by acetone in ultrasonic cleaner to clean out possible grease on its surface [15]. Before anodizing, the electrochemical polishing of samples was carried out in a 1:4 volume mixture of HClO_4 and $\text{C}_2\text{H}_5\text{OH}$ at constant current density of 500 mAcm^{-2} for 30 sec at 10°C [29]. The samples were later rinsed with distilled water, and a single-walled electrochemical cell with a magnetic stirrer (500 r.p.m.) was used. Pt electrode served as the cathode electrode and the distance from the aluminum anode electrode was 3 cm.

Preparation of the acidic electrolytes

The strongly acidic electrolyte was prepared by using 25 % phosphoric acid aqueous solution (Sigma-Aldrich, Malaysia) and the pH adjusted to 1, while pH3 and pH5 electrolytes were prepared by adjusting the acidic electrolyte with 1M of sodium hydroxide. A 50V potential at ambient temperature was applied across the electrochemical cell on the templates for 1 and 3 hours, respectively.

Preparation of the alkaline electrolytes

2.5M of sodium hydroxide electrolyte (HmbG chemicals, Malaysia) was prepared, and a certain amount of acid was used to adjust the pH to 9, 11 and 13. A lower potential of 40 V at ambient temperature was applied across the cell for 5 hrs during the anodization process.

Post anodization treatment

Nanoporous alumina films produced from the acidic electrolytes was further treated with 3 % phosphoric acid solution for the enlargement of the pores. The porous alumina templates fabricated from pH1 and pH3 electrolytes were treated for 30 min, while the template fabricated from pH5 electrolyte was treated for 40 min.

Characterization

The characterization of the samples anodized at different pH in both acidic and alkaline electrolytes were by X-ray diffractometer (XRD) and scanning electron microscope (SEM). The X-ray diffractometer used is to obtain the X-ray diffraction patterns of the samples covering the 2θ range from 10 to 90° , and the surface microstructure (pore diameters) of the anodized aluminum films was observed using high resolution SEM.

Results and discussion

Porous alumina films from strongly acid electrolyte

Fig. 2 (a-d) shows the surface micrographs of the porous alumina anodized at room temperature with a 50 V potential for 1 and 3 hrs respectively. The pores formed on the surface are randomly distributed not ordered, not uniform and with pore diameters in the range of 70 – 100 nm similar to what other researchers have also reported [2, 30, 31]. The propagation and growth of these nano pores was made possible by the dissolution of the oxide layer with H^+ ions present in the solution [32]. The pores in Fig.

2 (b) are of circular shapes after the initial anodization and are distributed all over the surface of the template. A slight change in the shape was observed in **Fig. 2** (d) which might be due to prolong anodization time and change in the growth velocity.

The anodization of aluminum in the strongly acidic electrolyte starts with the addition of phosphoric acid to water which dissociates into its ions according to the equation below;

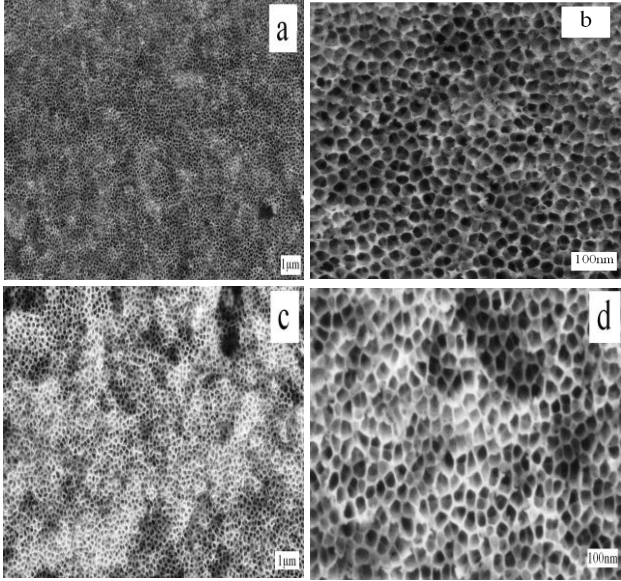
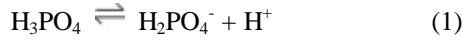


Fig. 2. FE-SEM images of the top view of anodized aluminum from pH1 electrolyte and 50V potential (a) and (b) low and high magnification of aluminum anodized for 1 hr, (c) and (d) low and high magnification of aluminum anodized for 3 hrs.

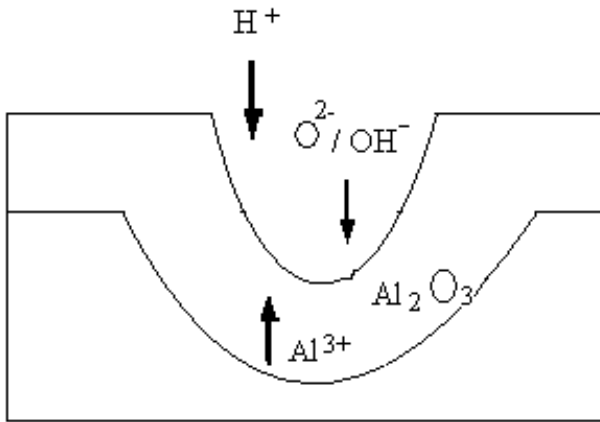
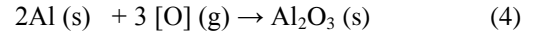
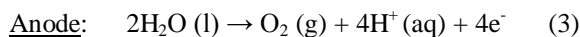
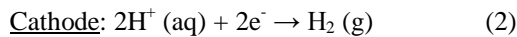


Fig. 3. Dissolution of the oxide layer by H^+ ions.

Equ. 1 shows that the dissociation of the acid produces a very strong acid and its conjugate base. The forming of the film is shown in the equation (2), (3) and (4)-



The dissolution of the film shown in **Fig. 3** is due to the presence of high concentration of H^+ ions which easily ionizes and dissolves the oxide layer [32]. The equation of the dissolution is shown in **Equ. 5**.



Porous alumina films from pH3 and pH5 electrolyte

The nanoporous alumina structure obtained from the anodization of aluminum in pH3 and pH5 electrolytes shows a promising result with the aid of the electrochemical cell. The FE-SEM micrographs of figures iv and v shows nanoporous alumina with pore range between 50 – 120 nm and 10 – 40 nm distributed over the surface of the template. The pores produced in **Fig. 4a** are small and of irregular shapes, while prolong anodization enables more dissolution of the oxide layer by H^+ [32] which increases the size of the pores significantly as shown in **Fig. 4b**. The fabrication of nanoporous alumina in weak acids is slow due to the deprotonation of H^+ ions in the electrolyte. The addition of sodium hydroxide to the strongly acid electrolyte neutralizes the protons of the acid in a step wise fashion, thereby reducing the concentration of the H^+ ions in the electrolyte.

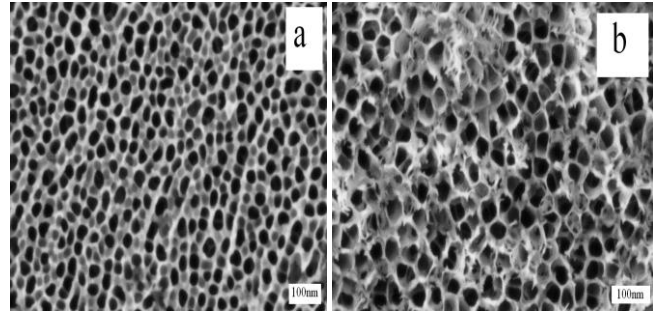
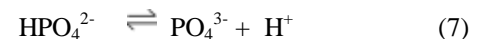
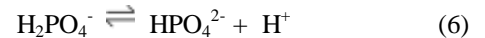


Fig. 4. FE-SEM images of the top view of anodized aluminum from pH3 electrolyte and 50V potential (a) 1 hr anodization time, and (b) 3 hrs anodization time.

The initial preparation of the acid at the beginning of the anodization produces a very strong acid with its conjugate base. Further addition of the base to the acid result in more deprotonation of the acid and either of the **Equ. 6** or 7 below is likely to occur for pH3 or pH5 with a weak acid being formed with its conjugate base.



As a result of high deprotonation of the acid by the base, to produce weak acids and its conjugate base the pores formed at pH5 are very small shown in **Fig. 5a**. The breakdown of the oxide layer by low concentration of H^+ ions becomes difficult even with prolong anodization shown in **Fig. 5b** in which minimal increase in the size of the pores was observed.

Nanoporous alumina pore widening

The post anodization treatment of the templates in an acidic electrolyte is shown in **Fig. 6**. The FE-SEM micrographs of the porous alumina formed after 3 % phosphoric acid treatment for 30 min and 40 min shows an increase in the size of the pores. The pores formed were observed to be well distributed all over the surface of the template. The pore diameters of **Fig. 6a-b** are in the range of 200 – 300 nm, while **Fig. 6c** is in the range of 100 – 250 nm.

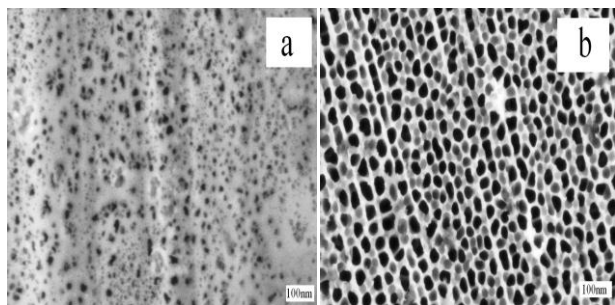


Fig. 5. FE-SEM images of the top view of anodized aluminum from pH5 electrolyte and 50V potential (a) 1 hr anodization time, and (b) 3 hrs anodization time.

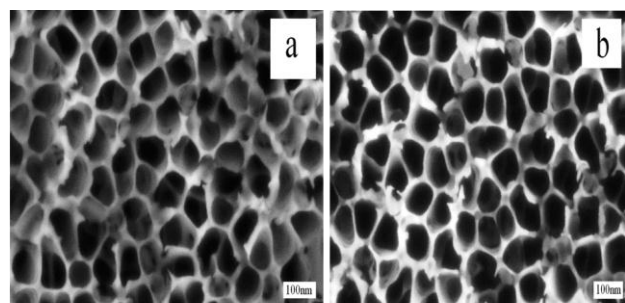


Fig. 6. FE-SEM micrographs of nanoporous alumina from post anodization treatment with 3 % phosphoric acid solution for 30 and 40 min (a) etched surface of porous alumina initially anodized for 3 hrs from pH1 electrolyte, (b) etched surface of porous alumina initially anodized for 3 hrs from pH3 electrolyte, (c) etched surface of porous alumina initially anodized for 3 hrs from pH5 electrolyte.

The phosphoric acid solution used as the etchant in the widening of the pores is mild, more effective and can easily be controlled. It is known that the addition of 3 % phosphoric acid to water produces H^+ ions in the solution, the concentration of these H^+ ions produced from this etchant is suitable for the enlargement of the pores [8]. When the templates from the different pH electrolytes are placed into the solution, the H^+ ions present in the solution migrate into the pores, the migration of these highly

concentrated H^+ ions attacks and dissolves the alumina pore walls continuously, thereby increasing the size of the pores [17]. It is possible to achieve different pore diameters mainly by controlling the duration and concentration of the solution.

X-ray diffraction spectra

The X-ray diffraction spectra of anodized aluminum templates at 50 V is shown in **Fig. 7**; we observed a change in the crystalline FCC structure to amorphous alumina at 1 1 1 and 2 0 0 planes which corresponds to 39° and 45° on the 2- θ scale [33]. The broadening of the peaks at 39° and 45° indicates that the phase transformation from Al to Al_2O_3 occurs more easily [34]. The patterns produced are similar to all the templates fabricated from the different electrolytes and only one is shown here.

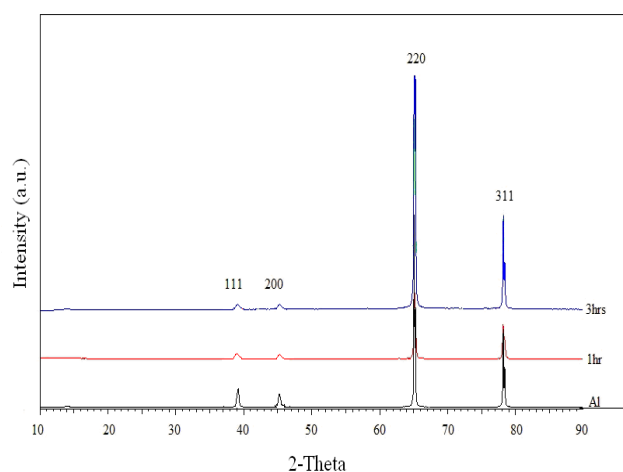


Fig. 7. XRD patterns of anodized aluminum at pH1 for 1 hr and 3 hrs.

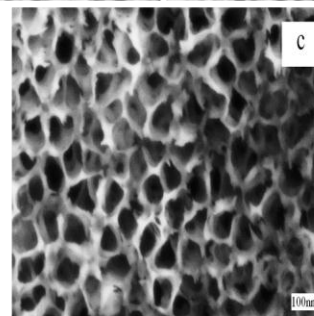
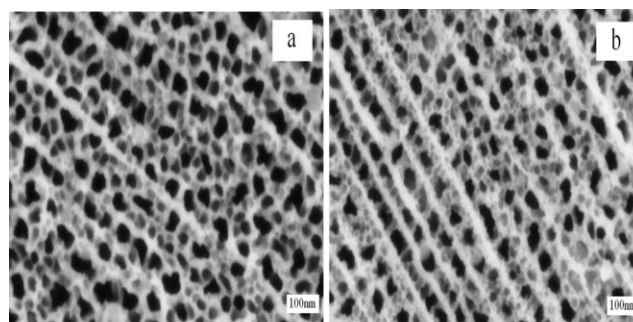


Fig. 8. FE-SEM micrographs of nanoporous alumina produced from 2.5 M sodium hydroxide electrolyte (a) 5 hrs anodization from pH9 electrolyte, (b) 5 hrs anodization from pH11 electrolyte, and (c) 5 hrs anodization from pH13 electrolyte.

The FE-SEM micrographs of aluminum anodized in alkaline electrolyte for 5 hrs are shown in **Fig. 8a-b**, and **c**. The anodization of aluminum in alkaline solutions mainly produce barrier oxide films [35] but the addition of the electronic circuit box to the electrochemical cell enables the formation of nanoporous alumina in the alkaline solution. The nano pores produced from the alkaline electrolyte increases in size as the pH is increased. The addition of sodium hydroxide to water leads to the dissociation of its ions shown in **Equ. 6**; the concentration of the OH⁻ is crucial in the dissolution of the oxide films in the alkaline electrolyte [23].

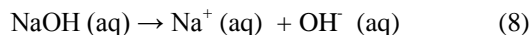


Fig. 8a-b shows very tiny pores on the surface of the alumina, these pores are of irregular shape and unevenly distributed across the surface of the template as a result of slow dissolution process of the oxide layer. The concentration of OH⁻ at pH9 and 11 were observed to be less effective in breaking down the oxide film which is the reason why small pores were seen to be present on the surface of the templates. The pH of the alkaline electrolyte was further increased to 13 to produce higher concentrations of OH⁻. This strongly alkaline electrolyte was able to dissolve the oxide layer to produce nanoporous alumina shown in **Fig. 8c** with pore size in the range of 100 – 150 nm.

The nano pores produced from pH13 electrolyte have disordered nanoporous alumina structure similar to the nano pores fabricated from the acidic electrolytes.

Conclusion

In this work, nanoporous alumina was successfully fabricated at room temperature in both acidic and alkaline electrolytes with the aid of an in-house electrochemical cell. The SEM micrographs obtained during the anodization process in the acidic electrolytes show how effective the H⁺ ion in the dissolution of the oxide films and the growth of the nano pores. The deprotonation of the H⁺ ions by the addition of a base solution reduces the concentration of H⁺ ions to produce weak acid solutions that becomes less effective in breaking down the oxide layer. The post anodization treatment of the templates in the acidic solution produces a very significant result with the enlargement of the pores; this was also made possible by the H⁺ ions present in the aqueous solution of the phosphoric acid solution. The micrographs obtained from the anodization in the alkaline electrolyte provide an interesting finding since alkaline electrolytes are not known to produce nanoporous alumina. The SEM shows the effect of both high and low concentration of OH⁻ in the barrier oxide film breakdown and the propagation and growth of the nano pores. Presently, the templates used for magnetic storage devices, catalytic membranes, and photonic crystals are fabricated from strongly acidic electrolytes, the nano pores obtained from the alkaline electrolytes which is similar to pores fabricated from the

acidic electrolytes could either serve as an alternative or also find use in other areas of application.

Acknowledgement

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