# FABRICATION OF A "CONE PAA NANOSTRUCTURE" BY GRADUAL DECREASE OF VOLTAGE

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**Received: July 2013** **Accepted: Feberary 2014**

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***Abstract:*** *The conical nanostructure improves the applications of alumina membranes and provides three dimensional nanometer scale systems to study the chemical and physical properties. In this study, the nano cone structure is produced in porous anodic alumina (PAA) by two-step anodizing. This conical nanostructure will improve the application of PAA membranes. This approach is novel generation of the so-called "gradually decreased voltage" technique, in which the voltage- time curve is divided into three stages and the effect of each step is investigated for different electrolytes. The effect of the decreasing voltage is examined in two types of electrolytes; oxalic and phosphoric acid with a constant decrease in voltage rate. The results of SEM, FE-SEM images show the slope of the inner cone layer in the oxalic acid to be considerably larger compared with phosphoric acid.*

***Keywords:*** *Porous anodic alumina; anodizing; phosphoric acid; oxalic acid; nanostructures, cone porous*

## 1. INTRODUCTION

Nanotechnology includes many of the world's future technologies and nanostructures are at the heart of the various nano sciences, so their applications vary from solar receivers and magnetic storage media to drug delivery [1]. To develop nanotechnology fabricating the structure which has well-defined with precise dimension is crucial [2].

Anodizing is one of the simple methods to synthesis the nanostructure on surface. This easy electrochemical process which fabricates a densely packed hexagonal array of nano porous structures has been reported for Al, Si, InP, Ti, Zr, Nb, Hf and Sn [3].

Self-ordered nano porous anodic alumina (PAA) membranes have triggered extensive activities in research over recent years, especially in a periodicity lower than 100nm. They have been used widely as templates in chemical and electrochemical deposition of one-dimensional nano wires [4-7].

The potential applications of alumina nanostructures are due to the result of some essential properties of PAAs, such as their corrosion resistance, high strength, low thermal conductivity, good electrical insulation and chemical stability [4].

Self-organized PAA film arranged in a closely packed hexagonal nano channel array with controllable and uniform dimensions can be formed through two-step anodizing under predetermined conditions [8]. It is observed that the PAA structure is influenced both by chemical and electrochemical parameters of anodizing practice. Among the effective parameters, electrolyte composition (phosphoric or oxalic acid), applied voltage, and anodizing temperature have a drastic influence on the pore size, inter-pore distance, pore distribution and symmetry [9].

Nano pores produced by usual methods have a cylindrical shape. However, structures of different shapes have been studied recently [10,11]. For instance, PAA film with tortuous pores was fabricated by AC anodizing in sulfuric acid [12] and also Atashbar et all have fabricated a 'V'-shaped cleaved oriented pyrolytic graphite as a template to prepare palladium nano wires [13].

At table 1. The optimum parameters to gain highly ordered porous anodic alumina by self-organized anodizing have already been reported is shown.

The experimental studies of O'Sullivan and Wood [28] convincingly showed that with increasing the voltage of the anodizing cell, a



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**Table 1.** Selected procedures of two-step anodizing of aluminum conducted in Oxalic and Phosphoric acid

| Electrolyte | Temperature ( C) | Potential (V) | Time of first anodizing (min) | Time of second anodizing (min) | References |
|---|---|---|---|---|---|
| 0.2 M $H_2C_2O_4$ | 18 | 40 | 1800 | 50 | [13] |
| 0.3 M $H_2C_2O_4$ | 0 | 40 | 20 | 120 | [14] |
| | 0–25 | | 600 | 60 | [15] |
| | 1 | | 1440 | 5700 | [16] |
| | 10 | | 120 | 2–10 | [17] |
| | 15 | | 900 | 10–600 | [18] |
| | 17 | | 600 | 5 | [19] |
| | 20 | | 40 | 120 | [20] |
| | 24 | | 300 | 5 | [21] |
| | 5–30 | 20–60 | 120–740 | 740 | [22] |
| 0.5 M $H_2C_2O_4$ | 5 | 40 | 1320 | 5940 | [23] |
| 0.15–0.5 M $H_2C_2O_4$ | 5 | 10–60 | 1200 | 30 | [24] |
| 0.15 M $H_3PO_4$ | 2 | 195 | 1440 | 1200 | [25] |
| 0.5 M $H_3PO_4$ | 0 | 140 | 120 | 5–10 | [26] |

linear increase in the pore diameter, inter pore distance and barrier layer thickness is observed. In contrast, an increase in acid concentration decreases these values [29].

In this paper, we focus on controlling the morphology of the film to produce a cone structure by two-step anodizing in oxalic and phosphoric acid as the electrolyte. The practical condition of fabrication and the morphology of the prepared nanostructures are reported. This novel procedure is based on the gradual and stepwise decrease of the applied voltage.

## 2. EXPERIMENTS

### 2. 1. Materials

High-purity aluminum foils (99.999%, Merck) with 10mm×20mm×0.5mm dimensions were decreased in acetone and washed with distilled water. Subsequently, the specimen was suspended in a NaOH solution for 3 min to remove the oxide layer.

### 2. 2. Synthesis

For reducing the surface roughness, the substrate was electro polished in a mixture of $HClO_4$-$C_2H_5OH$ (1:4 v/v) at 35V in 1min [30].

Al foil was used as the cathode, separated 20mm from the anode. The electrolyte temperature was controlled and kept constant during the anodizing by circulation of isothermal water around the reaction cell. The water was pumped and cooled by a chiller. In order to prevent a temperature increase at the pore bottoms, the electrolyte is stirred vigorously.

First and second anodizing stages were performed at the same operational conditions. Oxalic and phosphoric acid solutions were used

**Table 2.** The applied conditions for the samples using oxalic and phosphoric acid

| Electrolyte | Temperature ( C) | Potential (V) | Time of first anodizing (min) | Oxide removal | | | Second anodizing | |
|---|---|---|---|---|---|---|---|---|
| | | | | Mixture type* | Temperature ( C) | Time (min) | Time (min) | Oxide thickness (mm) |
| 0.5 M $H_2C_2O_4$ | 17 | 40 | 180 | A | 70 | 180 | 55 | 4.4 |
| 1.1 M $H_3PO_4$ | 2 | 165 | 180 | A | 70 | 180 | 180 | 3.7 |



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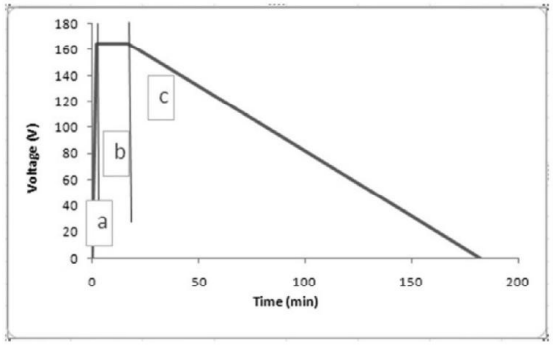


**Fig. 1.** The schematic diagram voltage-time curve for second anodizing in the in 1M phosphoric acid at 165V

as the anodizing electrolytes. The electrolyte concentration, voltage and temperature for the first and second anodizing stages are mentioned in table 2. The first anodizing time was 3hr. After the first anodizing step, the produced oxide film was removed by dipping the specimen in a solution of 0.5M phosphoric acid and 0.2M chromic acid at 70 ℃ for 3hr.

The condition of second anodizing is reported in table 2. In this step, for achieving the cone structure, the voltage was decreased gradually by the time.

In order to compare one- step and two- step anodizing, one sample was anodized in only one step by the same procedure as mentioned in table 2.

### 2. 3. Physical Measurements

A Philips XL30 scanning electron microscope and also Hitachi S-4160 Field Emission Scanning Electron Microscope was used in order to study the cross-sectional and surface morphology of nano porous samples, after Au sputtering on samples that had been rinsed in an ultrasonic bath containing acetone. The anodizing current was monitored and recorded by a PC connected to a Lutron 801 multi meter.

## 3. RESULT AND DISCUSSION

### 3. 1. Synthesis of Conical Nano Structure

To fabricate a conical nanostructure, two steps of anodizing are done in two different electrolytes (oxalic and phosphoric acid). The applied conditions for the first and second anodizing is mentioned in table 2.

The result of the research till now shows that the diameter pores of each nano channel is dependent on the voltage of second anodizing. To achieve conical nano pores instead of a nano channel, we change the voltage of second anodizing by the time.

Our experiences showed that the variety of the voltage used to obtain the conical structure should have done as schematically for the phosphoric acid shown in figure 1. The anodizing voltage is constant during the first anodizing but the voltage-time curve for second anodizing should be divided to the following three stages:

Linear increase stage: Voltage was gradually increased over two minutes to reach the operational voltage. The experience showed that this stage can be omitted for oxalic acid because of its low operational voltage (40V for oxalic acid), but it is crucial for all of the electrolytes with an anodizing voltage higher than 120V. This regime shouldn't be neglected with phosphoric acid. Also, a high slope in this stage (in V-T curve) leads to surface damage (Fig. 2).

Constant voltage stage: To study the effect of voltage on diameter, decreasing voltage should be exerted when the thermodynamic condition of the system becomes stable. On the other hand, the anodizing at constant voltage for several minutes permits the nano channels growth and the thickness of the anodic alumina layer to get to the critical one. The duration of this stage is caused to steady growth of primitive nano channels. Our experiment shows that the porous oxide layer reaches the necessary thickness in 15 min.

Gradually decrease voltage: Anodizing voltage decreased by a rate of 1Volt/min in two types of electrolyte so anodizing time lasted in oxalic and phosphoric acid for 55 and 180 minutes, respectively. In the first step to form cylindrical pores the aluminum sheet is anodized (Fig. 3A). Subsequently, the anodizing voltage gradually decreases without interrupting the anodizing process (Fig. 3B). Our experience showed that to achieve the best conical structure instead of a stair structure, the voltage decrease rate must be



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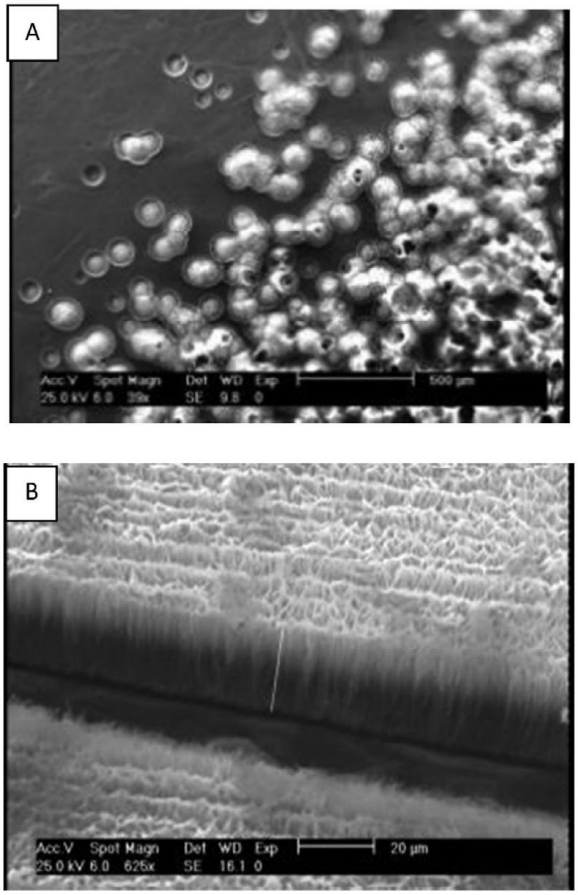


**Fig. 2.** The SEM image of soundness PAA while the last diagram is carried out from stage-c. start second anodizing from stage -c- lead to (A) tough surface at initial time of anodizing (B) non planer surface at the end of second anodizing.

slightly (Fig. 3C).

Analysis of recorded Current- Time anodizing curve

The recorded current- time anodizing curve and also Top-view SEM micrograph of PAAs for one-step and two-step anodizing in this study exactly follow the theory.

The curve of recorded current-time is divided into three independent stages. The transient recorded current-time in oxalic and phosphoric acid follows the same trend discussed on one-step and two-step anodizing at oxalic acid results for simplicity.

In Fig. 4 Current- Time graph is shown. With starting anodizing, the current density drastically increases then considerable reduction is observed. This reduction is due to a formation of barrier layer with high electric resistance on aluminum surface. Minimum current density corresponded with maximum thickness of oxide layer. Also the current density increases because of some cracks from the oxide layer [31]. Crack formation in barrier layer is the initial step in pores making. Along with pores growth I-t curve reaches a steady state.

In two-step anodizing process, the time duration in which the steady state current density has been achieved, is notably shorter than the time duration for the one-step anodizing process. In addition, the amount of the minimum current density is greater than the one-step anodizing process (Fig. 4). These phenomena are due to the fact that the primitive tiny holes are not yet formed at the beginning. Therefore the time duration for pores nucleation and growth is

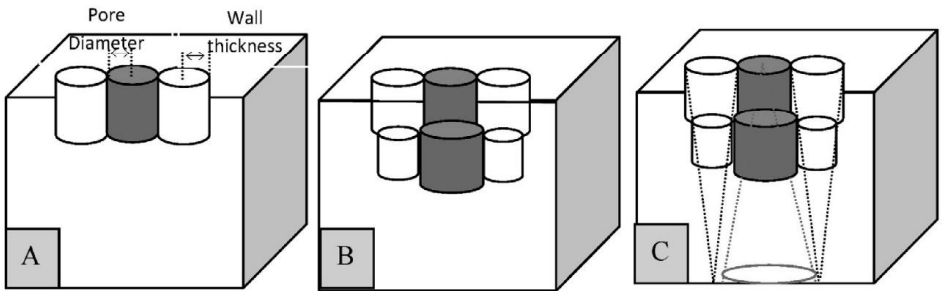


**Fig. 3.** the schematic model of fabrication process for multi-step nanostructure. (A) Formed nano pores in constant voltage with minimum diameter. (B) Decreased anodizing voltage leads to increase in diameter and the formation of two-step stair nanostructure. (C) Exposed samples to gradually decreased voltage in order to produce a cone nanostructure.



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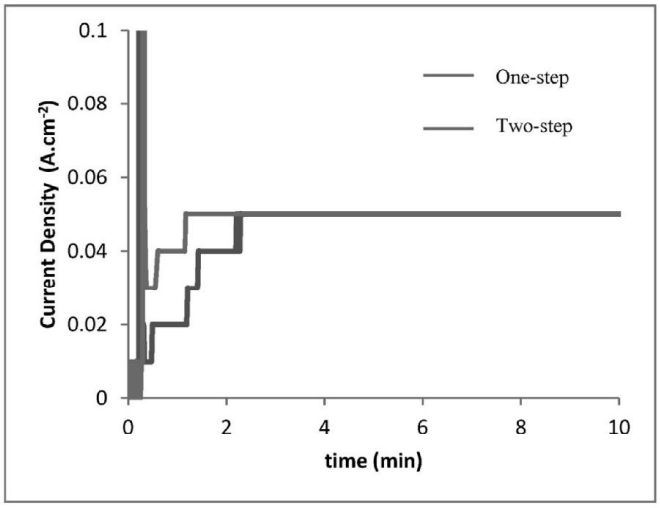


**Fig. 4.** The magnification of current in the range of 0-0.06A/cm$^2$ versus anodizing time for the prepared samples in 0.5M oxalic acid

longer in one-step anodizing process. Moreover, the change in diffusion mechanism from planar to spherical diffusion increases the diffusion rate of ions to the oxide-solution zone [32].

Studies Top-view SEM micrograph of PAAs for one-step and two-step anodizing

SEM images of Fig. 5 show that the pores in two–step anodized sample (Fig. 5B) has much better order than in the one-step anodized sample (Fig. 5A). This result is completely conformed to the results of the previous research.

The pores nucleation patterns, in one-step anodizing are not regular but in two-step anodizing is shaped in ordered pattern. After the first anodizing and removing the initial oxide coat, well-ordered concave pattern remains on the aluminum substrate. In first anodizing the site for nucleation is random but in second anodizing some preference site is formed. This is the reason that why the pores nucleation isn't haphazard and get modified shape.

Effect of decreasing anodizing Voltage on PAA nano structures

Until now, all researches focused on the constant voltage in the second anodizing process but the novel result in this study reveals a simple method to fabricate the other shape except nano channel in PAAs.

In this step, the anodizing voltage decrease step by step in rate of 1 volt per minute in two

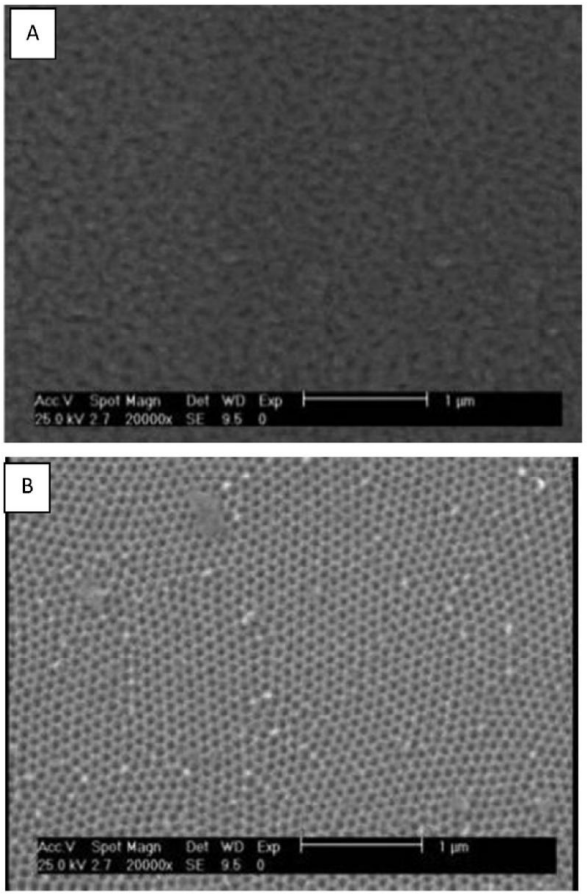


**Fig. 5.** Top-view SEM micrograph of PAAs for one-step (a) and two-step (b) anodizing process in 0.5M, oxalic acid.



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types of electrolyte. Second anodizing stage in phosphoric acid was carried out in 165 steps (from 165V to 0V). The large quantity of gradually decreased voltage and the large pore diameter are caused to the nano conical and nozzle structure in phosphoric acid electrolyte. This phenomena is clearly distinct in the Fig.6.

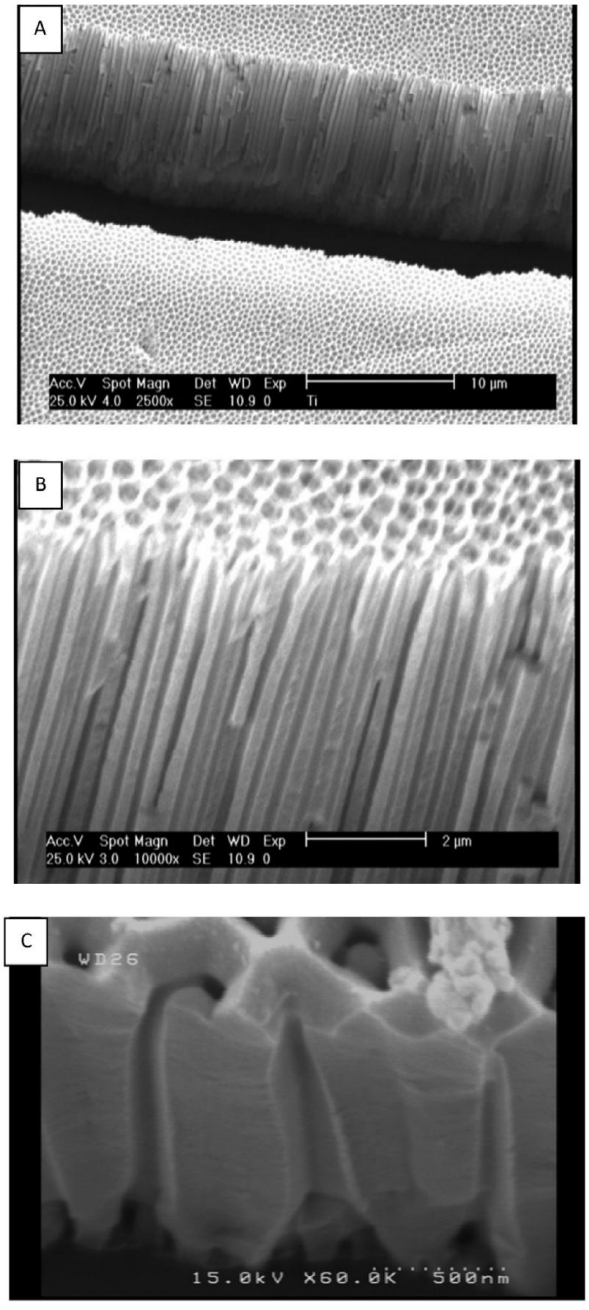


**Fig. 6.** (A), (b) SEM and (C) FE- SEM cross section views of anodic alumina after second anodizing at 165V in 1M phosphoric acid at 2℃.

In Fig. 6 (A) the cross section of porous oxide layer is shown and nano cone have been exhibited. As clearly illustrate in Fig. 6 (C) the cone structure is obtained.

In this method, anodizing voltage decreased with rate of 1Volt/min in phosphoric acid as an electrolyte lead to cone structure in oxide layer so our claim proved.

The conical structure in one cross sectional SEM image in oxalic acid is not seen. In order to illustrate the conical structure formation along the decreasing voltage, SEM images are taken in nano tubes striate continuously and just decreasing in wall thickness is observed. Its prominent reason is the cone slope in oxide film and the number of steps for decreasing voltage is a few in oxalic acid.

Any other shape with different application in porous anodic alumina oxide layer can be produced with this novel procedure. To achieve in this method just simple equipment and a simple set up for different rate decreasing of voltage are needed. In other methods like multi-steps anodizing in phosphoric acid [33], anodizing and leaching both were employed to produce conical structure. In such a method, the time duration for transferring of sample from anodizing cell to pore-widening cell in multi-step process is very long. Moreover, in order to produce each sample it is needed to occupy two cells whereas, the proposed method in this article has the advantage of time saving and the least cost of equipment.

## 4. CONCLUSION

A new method has successfully presented for fabricating of cone nanostructure PAA films in phosphoric acid, using of two-step anodizing with voltage gradual decreasing. The proposed voltage- time curve includes three stages; linear increase, constant voltage and gradually decreased voltage stage. Our investigations on the behavior of the voltage- time curve in both two types electrolytes and also the observations on the cross-sectional SEM, FE-SEM images enable us to obtain the following conclusion:

Gradual increase of voltage is done to achieve operation voltage across two minutes. This process



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can be omitted in oxalic acid (40V) whereas ignoring this stage in phosphoric acid (165V) results in chiefly surface damage.

The oxide film thickness in phosphoric acid electrolyte under the condition of decreased voltage rate of 1 volt per minute is equal to 3.7μm and the alternation is in the range of 0-400nm.

In comparison with oxalic acid the slope of inner layer cone in phosphoric acid is considerably larger.

By the above mentioned process, the different shapes with defined application can be produced in PAA film just using simple equipment. Several nano devices such as electronic transformations, fluid flow systems through nano gaps and medical equipment can be designed base on the inverted cone nanostructures.

## ACKNOWLEDGMENT

The authors would like to thank Dr. S. Saramad, Dr. F. Javanmardi, M. H. Rahimi for valuable comments and suggestions.

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