

# Effect of Low Voltage on Surface Morphology and Electric Properties of Porous Alumina Prepared by One Step Anodizing at Room Temperature

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**Abstract**— Nanoporous anodic alumina (AAO) was fabricated using one-step anodizing at room temperature and low voltage. All specimens were potentiostatically anodized at 5 V for 20 minutes in phosphoric acid ( $H_3PO_4$ ). Morphology of the AAO layers was characterized by scanning electron microscopy (SEM). By anodizing at 20% (by vol.) phosphoric acid, a uniform porous structure with nearly parallel cylindrical pores, ~200 nanometers wide, were detected. The thickness of the porous layer was higher than the barrier layer. The electrochemical impedance test (EIS), using 0.1 M  $Na_2SO_4$  electrolyte, confirmed the presence of a multi layers structure of a barrier layer and a porous layer with the highest resistance value (365.1 k $\Omega$ ). Using AC impedance technique (IS), samples anodized in 20% (by vol.) phosphoric acid, proved to have the highest electrical resistance (26 k $\Omega$ ), reflecting a porous structure formation. The mechanism of pores formation as well as electrical conductivity is to be discussed.

**Keywords:** porous alumina; anodization; electrochemical properties; electrical properties; electrical conductivity

## 1 INTRODUCTION

Electrochemically produced porous anodic alumina (AAO) films [1, 2] have been extensively used as host or template structures for the fabrication of diverse nanometer devices, such as electronic [3], magnetic [4] and photonic [5] devices.

AAO template is an ideal mold because it possesses many desirable characteristics, including tunable pore dimensions, good mechanical property, and good thermal stability [6]. AAO has a low background with respect to many detection techniques, including fluorescence microscopy. Additionally, aluminum oxide does not change volume greatly with temperature changes or wetting, is compatible with a wide range of solvents and is exceptionally thermo-stable (some forms withstand temperatures in excess of 1000 °C. Moreover, aluminum oxide is inert and biocompatible [2].

In recent years, humidity sensors based on nano-structured alumina thin films [7, 8] and other nanometer materials prepared by different methods have also been reported. Polymer sensors, however, usually suffer from low resistance to liquid water and poor mechanical properties. Sensors based on ceramic materials seem to overcome those problems. Ceramic sensors have shown advantages in terms of their mechanical strength, their resistance to chemical attack and their thermal and physical stability. Porous alumina is usually preferred for sensing applications due to the large surface area available for water adsorption [9]. The influence of water vapor on electrical properties of alumina was first reported by Ansbacher and Jason [10], in 1953.

Compared with other humidity sensors, the advantages of an  $Al_2O_3$  humidity sensor arise from simple, low-cost fabrication, thermal and physical stability [11]. It is reported that the microstructure i.e. the pore size distribution, total porosity and

surface area controls the moisture sensitivity and resolution of the ceramic materials [12].

It is widely established that the porosity and morphology of an  $Al_2O_3$  layer is responsible for unique properties of alumina based sensors. Water molecules are absorbed in the sensors porous structure resulting in changes of their electrical properties. The control of pore structure, such as pore diameter, pore diameter distribution, thickness of porous layer, etc., has crucial significance for the sensitivity and selectivity of sensor. Those parameters depend mainly on conditions of the anodizing process [13].

The aim of this work is conducting low voltage one step anodizing of aluminum at room temperature in phosphoric acid. The relationship between the fabrication process parameters and electrical properties of nanoporous alumina membranes will be studied. The mechanism of pores formation as well as electrical conductivity will be discussed.

## 2. EXPERIMENTAL

The samples used for anodizing were made out of 2 cm× 2 cm× 0.01cm pure aluminum coupons (99.999%) supplied by Alfa Aesar-Germany. The specimens were mechanically cleaned with 600-1000 $\mu$ m diamond paste type *Metadi II-USA* in order to remove any surface irregularity and scratches. The chemical polishing approach [14] in the pretreatment phase offering a viable, simpler, safer and faster alternative to electro polishing was applied. The samples were chemically polished in 1:4 mixtures of perchloric acid ( $HClO_4$ ) and ethanol ( $C_2H_5OH$ ) for 5 min for controlling surface roughness. This was followed

again by rinsing with pure ethanol, and then with distilled water.

The pure aluminum samples were potentiostatically anodized at 5 volt in phosphoric acid solutions, for 20 minutes at room temperature under mechanical stirring conditions at 200 rpm. The electrochemical potentiostatic anodizing cell consisted of aluminum anode and platinum cathode immersed in phosphoric acid with concentrations 15, 20, 30, and 35% (by vol.). The two electrodes were connected to the positive and negative poles of A 30 Volt /6 Amperes DC- power supply type *GW Instek GPC-3030DQ* – Taiwan. The anodizing parameters are summarized in table 1. After anodizing process; further pore adjustment was done by exposure to a chemical solution containing 5wt%  $H_3PO_4$  for 30 min for pore opening.

The surface morphology of anodized samples (AAO) was investigated by Scanning Electron Microscope SEM (*JEOL JXA-840A*) with field emission analysis facility. Pore size as well as cross section images were taken using SEM type *ULTRA 55 Zeiss* field emission.

Electrochemical impedance (EIS) test was conducted using *Zahner Elektrik IM6* electrochemical workstation. The amplitude of the superimposed AC-signal was 10 mV peak-to-peak. The Bode plot method involves direct measurements of the impedance,  $Z$ , and the phase shift,  $\theta$ , of the electrochemical system in the frequency range from 0.1 to 105 Hz. All experiments have been carried out at room temperature,  $25 \pm 1$  °C and the potential was measured against calomel electrode in 0.1 M  $Na_2SO_4$  electrolyte.

The electrical resistance of AAO samples were measured by using AC- Impedance Analyzer *HP-4192A-LF*, interfaced with computer, at frequency range 5 Hz to 13 MHz and the amplitude of applied voltage: 50 mV, at room temperature. The reference electrode (RE) (pt wire) and counter electrode (CE) were connected to one side of the sample, where the working electrode (WE) was connected to other side of the sample.

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### 3. RESULTS AND DISCUSSION

#### 3.1 Surface Morphology

Field emission SEM images in Figure 1a-d illustrate the effect of electrolyte concentration on the surface morphology of porous anodic aluminum oxide formed on pure aluminum substrate. Specimens were tested after anodizing in 35, 30, 20 by volume phosphoric acid. The applied voltage was 5 V with anodizing time 20 min.

A typical barrier layers was detected in case of 35% as well as 30% by volume concentration of phosphoric acid, are illustrated in Figure 1-a and 1-b. Further reduction of electrolyte concentration (20% by vol.), leads to formation of a porous oxide

layer, as presented in Figure 1-c.

Figure 2-a shows a cross-section of the anodic aluminum oxide (AAO), which was formed on pure aluminum substrate in case of 20% by vol. acid medium. A highly uniform porous structure with nearly parallel cylindrical pores of hundreds of nanometers wide, organized in an almost hexagonal structure, was observed. Generally, the oxide layer of aluminum comprises the barrier layer, which acts as an interlayer between the porous layer and the aluminum base. The porous layer thickness is higher than the barrier layer. The cell structure surrounding the pore is composed of randomly oriented crystallites. From Figure 3-b, the measure pore size formed on pure aluminum substrate was 113-386 nm

#### 3.2. Electrochemical Impedance Spectroscopy (EIS)

Figure 3 shows the Bode plot for anodized pure aluminum as a function of acid concentration. Formation of a barrier layer pores using 35% acid concentration of electrolyte was confirmed by the presence of one impedance ( $Z$ ) peak, at frequency 200 Hz and phase angle  $50^\circ$ . This was found to be best fitted to Randle's model, where  $R_s$ ; solution resistance;  $R_b$ , barrier layer resistance and  $C_b$ , barrier layer capacitance (Figure 3-a).

The experimental impedance data for other concentrations were fitted to theoretical data according to the equivalent circuit model presented in Figure 3-b, confirming the presence of a multi layers structure of a barrier layer and a porous layer. In this model,  $R_s$ , solution resistance;  $R_b$ , barrier layer resistance;  $C_b$ , barrier layer capacitance;  $R_p$ , porous layer resistance and  $C_p$ ; porous layer capacitance.

Generally, by reducing the acid concentration, the impedance values were increased. This was also accompanied by peaks broadening of the impedance spectrum. From Figure 3-c, it is evident that the presence of porous of  $Al_2O_3$  layer is accompanied by the appearance of a second phase maximum at higher frequencies, which can be attributed to a second time constant, assigning a porous film formation (phase angle  $60^\circ$ ,  $70^\circ$  and frequency 500 Hz, 1.5 Hz respectively).

The calculated equivalent circuit parameters are listed in table 2. The resistance values for the porous layer ( $R_p$ ) were ranged from 41.5– 365.1 k $\Omega$ . The highest resistance value (365.1 k $\Omega$ ) was registered for 20% (by volume) phosphoric acid, corresponding to the porous film formed on the pure aluminum surface.

#### 3.3 AC Impedance Spectroscopy (IS)

The schematic diagram (Figure 4) of the complex impedance spectroscopy (IS) of a polycrystalline material generally consists of three semicircles; each of them corresponds to a part of the specimen's impedance, expressed by the resistance ( $R$ ) and capacitance ( $C$ ) combination [15]. The first one starting at lower frequency is corresponding to the electrodes. The second one is corresponding to grain boundaries, pores and any microcracks in the microstructure of the material. The third one,

which is at higher frequency, is corresponding to the bulk impedance of the material [16].

Figure 5 illustrates the impedance spectra of the aluminum oxide (AAO) formed on pure aluminum substrate anodizing using phosphoric acid, for 20 min at 5 V. Samples anodized in 20% by volume phosphoric acid had the highest impedance value, reflecting the formation of porous oxide structure. On the other hand, the lowest impedance spectra value was observed at 35% by volume phosphoric acid, reflecting a barrier layer formation. The resistance values obtained from *IS* test were 2.5, 2.8, 26, 5.5 kΩ, for acid concentrations 35, 30, 20, 15% respectively (Table 3).

It can be concluded that nanoporous alumina fabricated by low voltage room temperature anodizing exhibited surface morphology- electrical properties relationship necessary for different industrial applications.

**TABLE 1.** Working parameters of anodizing process

Sample	Pure Aluminum		
Electrolyte	Phosphoric acid		
Voltage, V	5		
Concentration of Electrolyte, %vol.	20	30	35
Working Temperature	(25) °C		
Stirring Speed	200 rpm		

**TABLE 2.** Electrochemical impedance parameters for pure aluminum in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution.

Concentration of electrolyte, %vol.	$R_s$ Ω	$C_b$ μF cm <sup>-2</sup>	$a_b$	$R_b$ kΩ cm <sup>-2</sup>	$C_p$ μF cm <sup>-2</sup>	$a_p$	$R_p$ kΩ.c m <sup>2</sup>
35	88.5	0.66	0.7 3	12. 7	n.a. .	- n.a	n.a.
30	85.5	0.62	0.7 5	59. 7	4.2	0.9 7	175.5
20	116.6	0.13	0.7 3	19. 7	0.9 3	0.9 6	365.1

**TABLE 3.** Ionic Resistance of anodic aluminum oxide (AAO) formed on pure aluminum as well as commercial Aluminum substrate, calculated from AC impedance spectra.

Concentration of electrolyte, %vol.	$R$ , kΩ
35	2.5
30	2.8
20	26

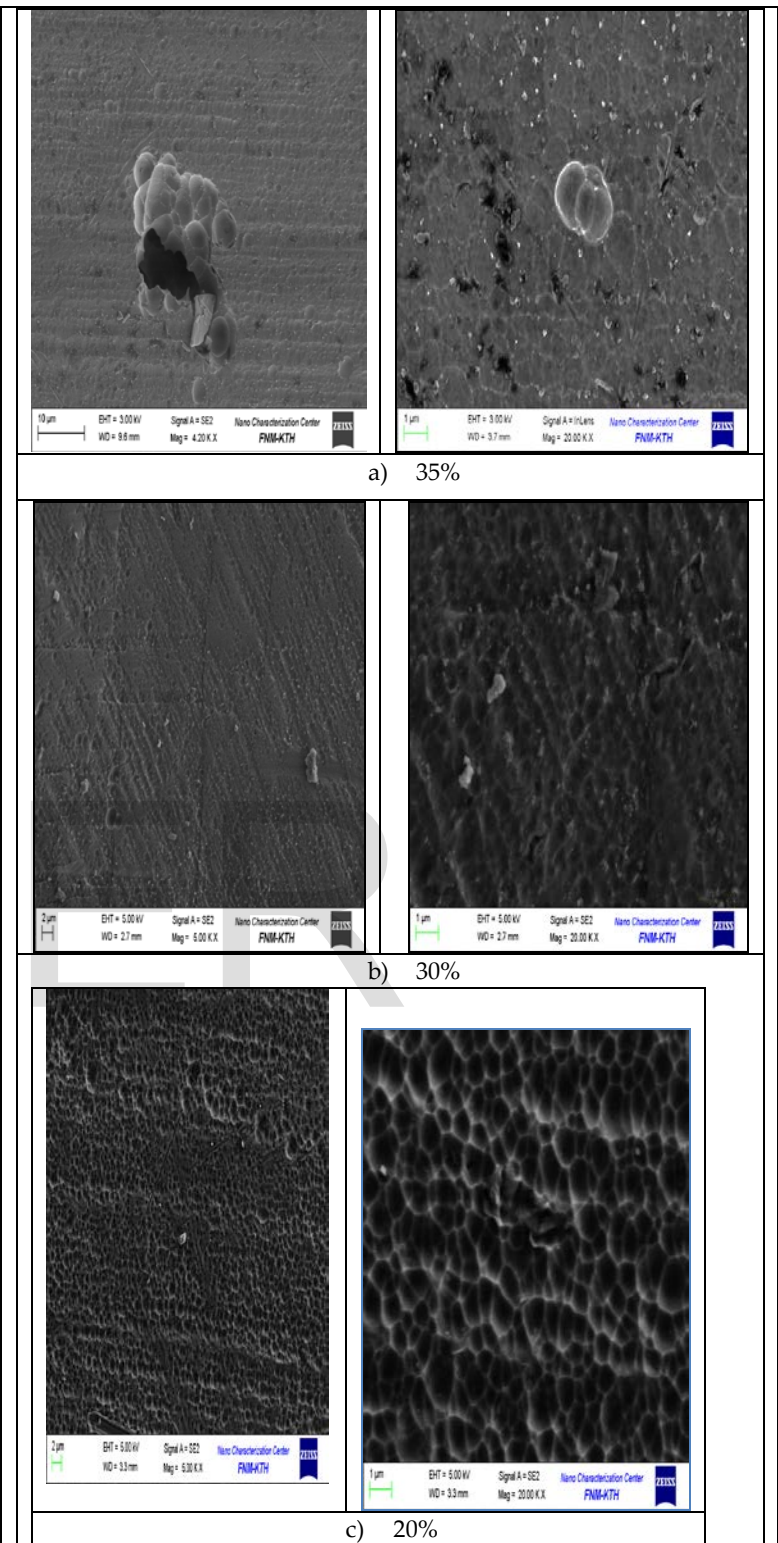
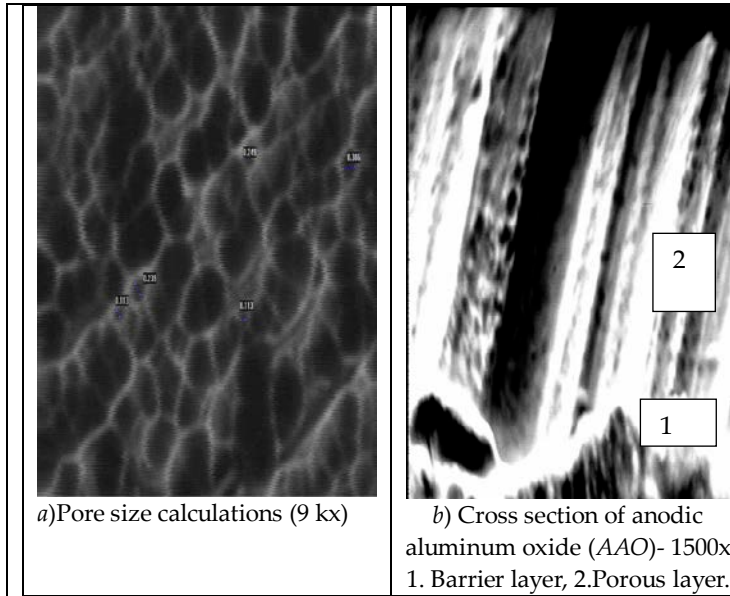


Figure 1 FE- SEM of anodic aluminum oxide (AAO) formed on pure aluminum substrate at 5 V and 20 min as a function of acid concentration.



a) Pore size calculations (9 kx)

b) Cross section of anodic aluminum oxide (AAO)- 1500x  
 1. Barrier layer, 2. Porous layer.

Figure 2 FE-SEM of anodic aluminum oxide (AAO) formed on pure aluminum substrate, using 20% phosphoric acid (5 V and 20 min).

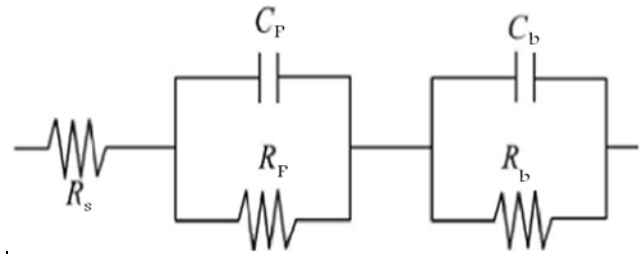


Figure 3-b Equivalent circuit model for data fitting of experimental impedance data, in case of combined barrier and porous layer formation,  $R_s$ , solution resistance;  $R_b$ , barrier layer resistance;  $C_b$ , barrier layer capacitance;  $R_p$ , porous layer resistance and  $C_p$ , porous layer capacitance.

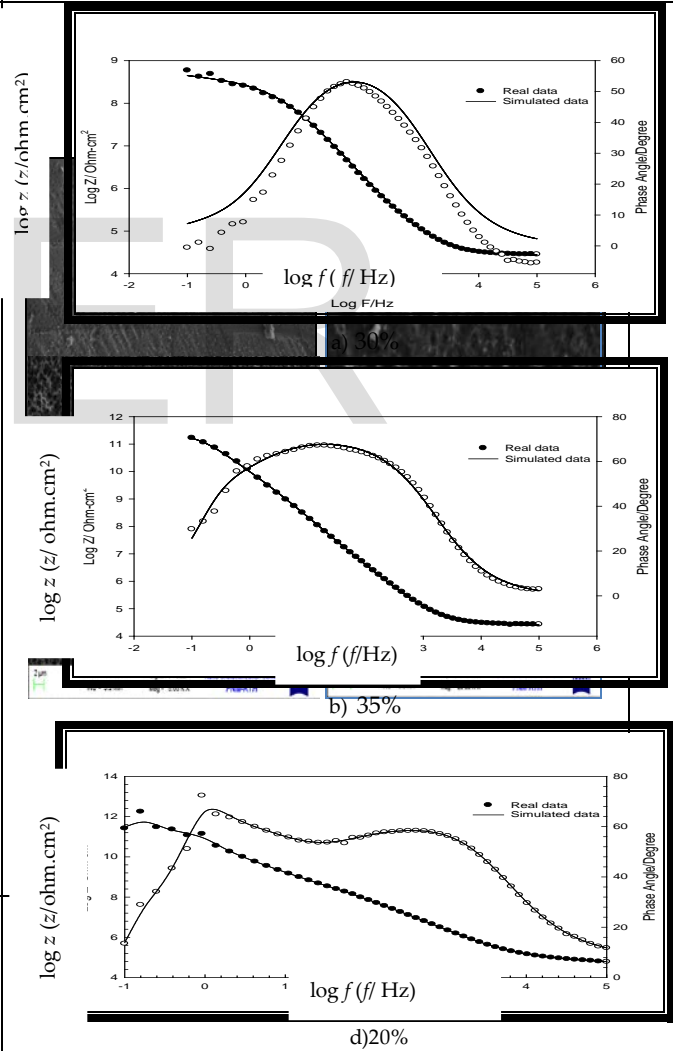


Figure 4 Bode plots of anodic aluminum oxide (AAO) formed on pure aluminum substrate anodizing using phosphoric acid, (5 V and 20 min).

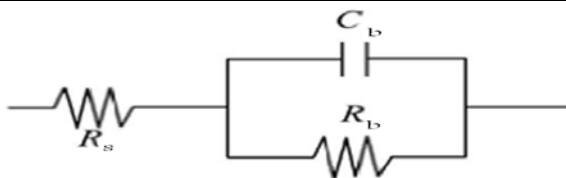


Figure 3-a Equivalent circuit model for data fitting of experimental impedance data in case of barrier layer formation,  $R_s$ , solution resistance;  $R_b$ , barrier layer resistance;  $C_b$ , barrier layer capacitance.

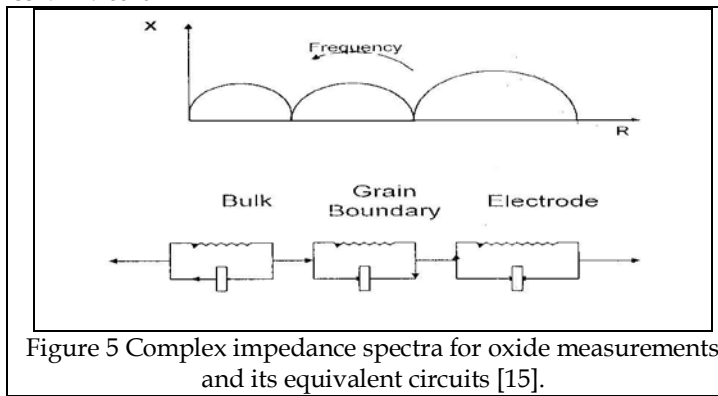


Figure 5 Complex impedance spectra for oxide measurements and its equivalent circuits [15].

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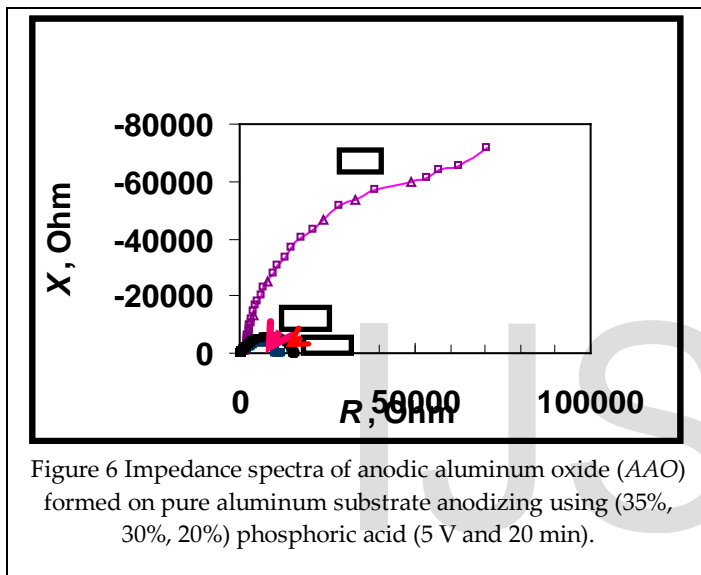


Figure 6 Impedance spectra of anodic aluminum oxide (AAO) formed on pure aluminum substrate anodizing using (35%, 30%, 20%) phosphoric acid (5 V and 20 min).

## 4. CONCLUSION

1. Anodizing process of pure Aluminum was successfully conducted under one step low voltage (5 V) at room temperature.
2. Under this condition, uniform porous structure with nearly parallel cylindrical pores of av. 113-386 nanometers wide. The porous layer thickness was higher than the barrier layer.
3. The electrochemical impedance test (EIS), confirmed the formation of barrier-type layer in case of 35% (by vol.) acid concentration. Other concentrations exhibited a multi layers structure of a porous-barrier type layer.
4. According to AC impedance (IS) test's results, samples anodized in 20% (by vol.) phosphoric acid, proved to have the highest resistance value (26 kΩ), confirming the porous structure formation.