

# The effect of changing the electrolyte species volume ratio on the electropolishing of aluminum foil

Dena Pourjafari<sup>a</sup>, Dora Irma Martínez<sup>b</sup>, Alejandro Vázquez<sup>a</sup>, Idalia Gómez<sup>a\*</sup>

<sup>a</sup>Universidad Autónoma de Nuevo León, UANL, Fac. de Ciencias Químicas, Lab. De Materiales I, Edif. CELAES 2do piso, Av. Universidad s/n Cd. Universitaria, San Nicolás de los Garza, N.L. México.

<sup>b</sup>Universidad Autónoma de Nuevo León, UANL, Fac. de Ingeniería Mecánica y Eléctrica, Lab. De Materiales, Av. Universidad s/n, Cd. Universitaria, San Nicolás de los Garza, N.L. México.

\*E-mail: idaliagomezmx@yahoo.com.mx.

Recibido 8 de agosto de 2012, Aceptado 31 de agosto de 2012

## Abstract

In this paper, the electrochemical behavior and surface morphology of AA1100 were investigated in commercial electropolishing electrolyte consisting of perchloric acid ( $\text{HClO}_4$ ) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ). Electropolishing of aluminum foil is a pre-treatment on aluminum surface before anodization process. The electropolishing on Al was carried out in different electrolyte concentrations and proper concentrations were reported by using current density-voltage curves, impedance spectroscopies and AFM images.

**Keywords:** electropolishing; electrolyte; AAO template; aluminum

## 1. Introduction

Aluminum and its alloys are key engineering materials for structural applications in the automotive and aerospace industries due to their high corrosion resistance and thermal stability [1]. Although the performance of these metals is largely governed by their microstructure and is influenced by the environmental conditions [2], high surface quality specifications such as surface smoothness, material cleanness, hydrophilicity and corrosion resistance required for some applications as for electronic devices and medical instruments [3]. There exist several proposed methods to achieve smooth surfaces for different metallic and metalloid materials. Some methodologies include, besides the mechanical polishing, the chemical mechanical polishing [4], the use of magnetic abrasive particles [5], electropolishing [6], laser assisted chemical etching [7] and pulsed laser micro polishing [8]. Electropolishing is a particularly useful machining method because, as non-contact methodology, it produces neither machining heat nor internal stress in the machined materials [9].

Aluminum foil is frequently used for the production of anodic aluminum oxide (AAO), which can serve as template to obtain vertically oriented one-dimensional nanomaterials [10]. AAO template was modified in 1995 by Masuda as a mold and thereafter it has been widely used due to its easy and cost-effective fabrication procedure, its thermal stability, high pore density and easy control of pore size (diameter and length) by changing the experimental conditions [11, 12].

To have a good pore distribution and highly ordered arrangement of pores, pre-treatments on

aluminum foil, before anodization process is necessary [12-14]. Pre-treatments are mechanical polishing, cleaning of aluminum piece ultrasonically in acetone, annealing, chemical polishing and electropolishing [14-16]. Electropolishing is an important pre-treatment process to obtain a smooth and bright surface of metal by passing the current through an electrolyte in which the sample is immersed [17]. There are different experimental parameters such as type, concentration and temperature of the electrolyte, current density, voltage, the anode-to-cathode surface area ratio, their relative position and geometry, process time and agitation of the electrolyte, which must be controlled during the electropolishing process [18-19].

Various investigation groups have reported the effect of electropolishing process on the pores ordering in fabrication of anodic aluminum oxide template. It is mentioned that the key factor to obtain self-ordered AAO template is surface treatment on aluminum foil via a well-controlled electropolishing process [20-21]. In the most cases for electropolishing of aluminum, mixture solution of ethanol and perchloric acid have used as electrolyte [13].

In this article the effect of changing the volume ratio between ethanol and perchloric acid on the surface of aluminum foil is investigated and the optimum volume ratio of acid to ethanol is evaluated by electrochemical measurements.

## 2. Experimental Procedure

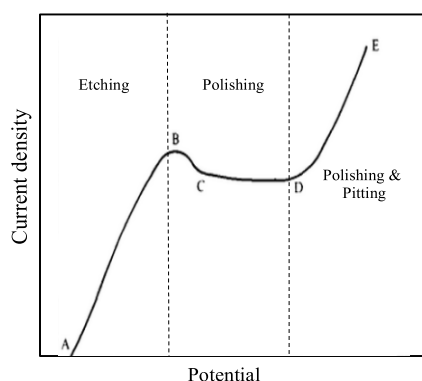
Commercial sheets of aluminum alloy AA1100 with the thickness of 0.5mm were used. This alloy

consists of relatively pure aluminum (99.00 %) with copper (0.12%). Before electropolishing, the samples were cleaned in an ultrasonic bath of acetone for 6 minutes to eliminate the dust, and surface dirt, following by annealing at 450 °C for three hours under nitrogen atmosphere to remove the remained dirt and enhance the grain size of the metal and improve the crystalline quality for pores growth [19, 22]. The annealed aluminum sheets were electropolished in a typical three-electrode cell in which the sample was used as working electrode (anode) with the surface area of 0.8 cm<sup>2</sup> exposed to the electrolyte. The Counter electrode (cathode) was a piece of aluminum foil with the surface area of 3 cm<sup>2</sup> and Ag/AgCl electrode was used as reference electrode. The distance between cathode and anode was adjusted at 4 cm. The electrolyte was a mixture of perchloric acid and ethanol with different volume ratios of 1:2, 1:4, 1:6, 1:8 and 1:10 volume of acid to ethanol. All experiments were carried out at room temperature.

### 3. Results and discussions

#### Current density – Voltage curve

The typical *I* – *V* curve of electropolishing is shown in figure 1. In the A-B region, the metal surface becomes active at low voltage, etching occurs and the surface has dull etched appearance. This region is called the active region. By increasing the voltage, a passivation layer on the anode surface may form at point B. In C-D region, which is called passivation area or plateau region, the experimental parameters reach the equilibrium point and electropolishing occurs. At higher voltage, oxygen evolution takes place and gas bubbles break polishing film and cause pitting [23-26].



**Figure 1.** Schematic diagram of current density versus voltage for electropolishing of a metal [25].

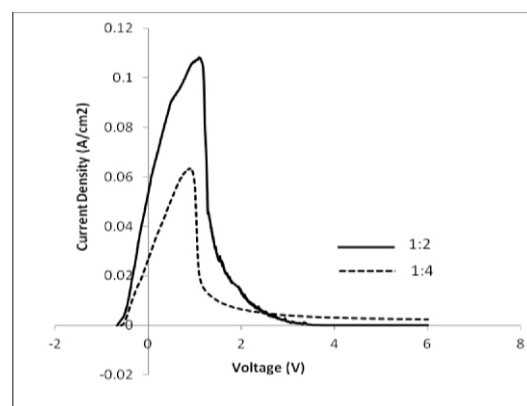
Figure 2 and 3 show the *I*-*V* curves for our experiments, which were obtained by sweeping the

applied potential to 6 V with the scan rate of 1 mV/s.

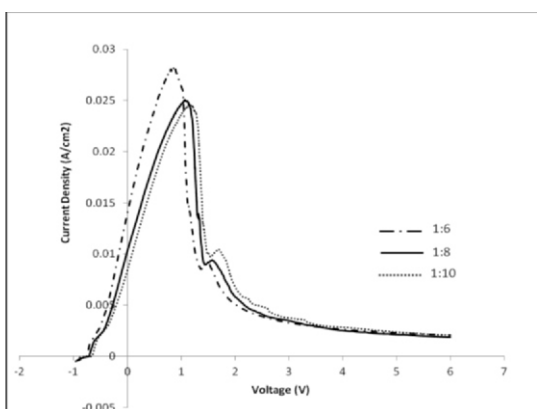
According to the figure 2, for the ratio of 1:2 there is a sharp increase of current density in comparison to other volume ratios at the same voltage (figure 3). It means by the small change in voltage, the current density was highly changed. The reason could be the extremely fast reaction between the electrode (anode) and the electrolyte due to high amount of acid in the solution. The acid in the electrolyte acts as an oxidizer and provides low pH to oxidize Al metal to Al<sup>3+</sup> ion and prevents the formation of other ions or oxides during the process [27]. When the amount of acid is high this may lead to burning of the sample because of the increase in local temperature. In this case, the final product is obtained with non-homogenous surface.

For the ratio of 1:4 the slowly increase of current density at the beginning was observed. The graph was reached a plateau, which is in agreement with the typical curve of electropolishing and explains the proper proportion between perchloric acid and ethanol. The electrode (anode) reacted smoothly with the electrolyte, which ensures that there was enough time for charge transfer and reaching the equilibrium between two processes i.e, formation of an oxide layer on the anode surface and dissolution of this layer in electrolyte. The smooth plateau confirms the good quality of the final electropolished product.

For the solutions with ratios of 1:6, 1:8 and 1:10 (figure 3) there are higher amount of ethanol compare to perchloric acid, which prevent to dissolution of formed oxide layer. This results in un-equilibrium condition between two processes of oxide formation and oxide dissolution and not good quality of final product. Also for these ratios, at the voltage between 1.5 and 2 there was a deviation from typical curve of electropolishing, which may because of formation of patterns in the metal surface due to higher amount of alcohol.



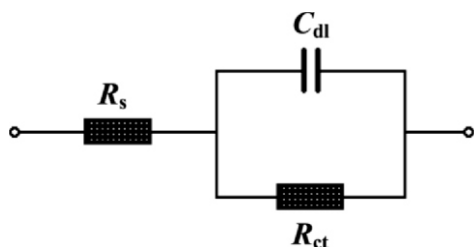
**Figure 2.** Current – voltage curve for electrolytes of 1:2 and 1:4 acid to ethanol volume ratio.



**Figure 3.** Current – voltage curve for electrolytes of 1:6, 1:8 and 1:10 acid to ethanol volume ratio.

### Impedance spectroscopy

To confirm this result we measured the electrolyte resistance for each ratio by considering the circuit model which is shown in figure 4 where  $R_s$ ,  $C_{dl}$  and  $R_{ct}$  are solution resistance, double layer capacitance and charge transfer resistance respectively.

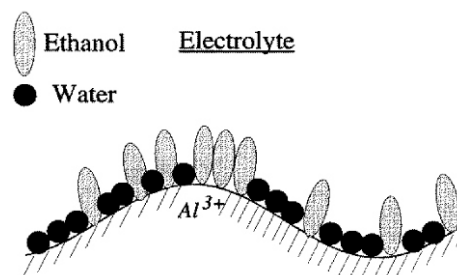


**Figure 4.** Electrical circuit model of the system.

The values for the  $R_s$  are listed in table 1. By increasing the amount of alcohol in the electrolyte, the resistance of solution increases as well. It means there is a higher resistance against passing the current through oxide layer which leads to poor charge transfer through this layer. Hence formation of this layer is more than its dissolution and some patterns on the surface of the metal may form instead of having smooth metal surface. This can be explained by the simple view of the process in figure 5.

**Table 1.** Measurement of electrolyte resistance by changing the electrolyte concentration.

Volume ratio	Electrolyte Resistance (ohm)
1:2	12.37
1:4	25.73
1:6	27.5
1:8	38.55
1:10	46.12

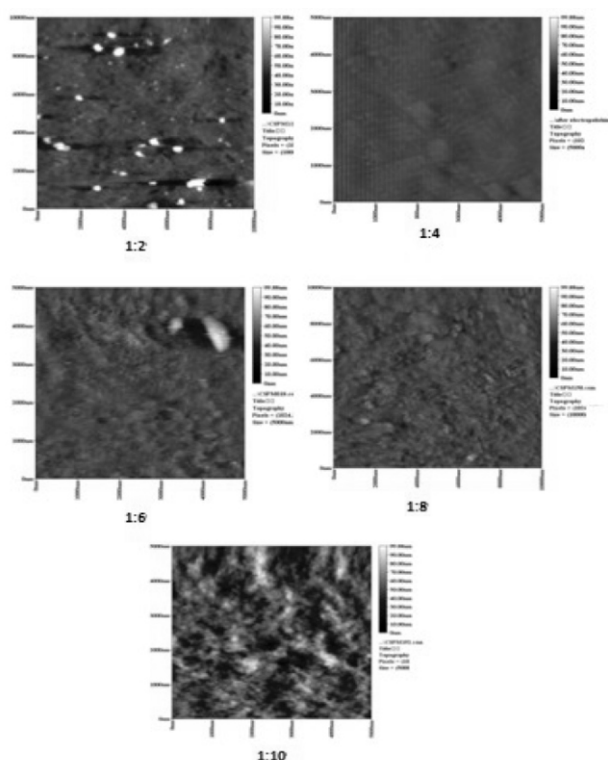


**Figure 5.** Schematic view of electrolyte behavior on metal surface [27]

In electrolyte, there are polar molecules like ethanol and water. By passing the current through the electrolyte, the electrical field is not distributed uniformly on the surface of electrode since the metal surface is not smooth at the beginning and it consists of crests and valleys. There is bigger potential gradient in crests leading to higher electrical field in these areas. This leads to cover the crests by polar molecules, i.e. ethanol. At the same time the aluminum metal is oxidized to aluminum ions, which will form oxide layer on the surface and later will dissolve in the electrolyte. But if the amount of alcohol is high in the solution, these molecules will cover the metal surface and do not allow to  $Al^{3+}$  ions to dissolve. Therefore the incomplete electropolishing process leads to no smooth and un-uniform surface at the end [19, 28].

### Surface characterization

To see the surface morphology of the electropolished samples in different electrolyte, atomic force microscopy images were obtained. These images represent in figure 6. For ratio of 1:2 the surface is not smooth because of high amount of acid and fast reaction of metal with electrolyte. For the ratio of 1:4, the smooth and uniform surface was obtained due to proper volume ratio between perchloric acid and ethanol. For ratios of 1:6, 1:8 and 1:10, the uniformity of the surface is disappearing by increasing the amount of polar molecule i.e. ethanol and some patterns are formed in the surface which results in obtaining not uniform metal.



**Figure 6.** AFM images of Al electropolished surface in different electrolyte concentrations (Scan scope = 1:2 – 10 x 10  $\mu\text{m}$ , 1:4 – 5 x 5  $\mu\text{m}$ , 1:6 – 8.5 x 8.5  $\mu\text{m}$ , 1:8 – 10 x 10  $\mu\text{m}$ , 1:10 – 5 x 5  $\mu\text{m}$ ).

#### 4. Conclusion

The AA1100 foils were electropolished in mixture electrolytes of perchloric acid and ethanol with different volume ratios of the species to find the proper volume ratio for electropolishing process as pre-treatment for fabrication of anodic aluminum oxide template.

From I-V curves and impedance spectroscopies, we analyzed the electrochemical behavior of the metal – electrolyte system. In addition from AFM images, the surface treatment were observed.

The 1:4 ratio has shown better results of electropolishing among the other volume ratios due to proper proportion of oxidizer molecules to polar molecules. The smooth and uniform surface of aluminum foil was obtained after electropolishing at these ratios.

#### 5. Acknowledgement

Authors express their gratitude to PAICYT and CONACYT for the financial support to this work.

#### 6. References

- Roy, S.; Nataraj, B. R.; Suwas, S.; Kumar, S.; Chattopadhyay, K. *Mater. Des.* **2012**, 36, 529–539.
- Cai, M.; Langford, S. C.; Dickinson, J. T.; Cai, M.; Langford, S. C.; Dickinson, J. T. *J. Appl. Phys.* **2012**, 110, 063509.
- Hryniewicz, T.; Konarski, P.; Rokosz, K.; Rokicki, R. *Surf. Coat. Technol.* **2011**, 205, 4228–4236.
- Chen, X.; Zhao, Y.; Wang, Y. *Appl. Surf. Sci.* **2012**, 258, 8469–8474.
- Givi, M.; Tehrani, A. F. *Int. J. Adv. Manuf. Technol.* **2012**, 61, 989–998.
- Roy, R. K.; Das, S. *J. Mater. Sci.* **2006**, 41, 289–292.
- Dandekar, N.; Chivas, R.; Silverman, S.; Kou, X.; Goorsky, M. *J. Electron. Mater.* **2012**, 41, 2790–2794.
- Vadali, M.; Ma, C.; Duffie, N.A.; Li, X.; Pfefferkorn, F.E. *J. Manuf. Processes* **2012**, 14, 307–315.
- Lee, E. S.; Shin, T. H. *J. Mech. Sci. Technol.* **2011**, 25, 963–969.
- Chung, C. K.; Liao, M. W.; Chang, H. C.; Lee, C. T. *Thin Solid Films* **2011**, 520, 1554–1558.
- Masuda, H.; Fukuda, K. *Science* **1995**, 268, 1466.
- Ali, G.; Ahmad, M.; Akhter, J. I.; Maqbool, M.; Cho, S. O. *Micron* **2010**, 41, 560–564.
- Alam, K. M.; Singh, A. P.; Bodepudi, S. C.; Pramanik, S. *Surf. Sci.* **2011**, 605, 441–449.
- Ma, D.; Li, S.; Liang, C. *Corros. Sci.* **2009**, 51, 713–718.
- Jessensky, O.; Muller, F.; Gosele, U. *Appl. Phys. Lett.* **1998**, 27, 1173–1175.
- Le Coz, F.; Arurault, L.; Datas, L. *Mater. Charact.* **2009**, 61, 283–288.
- Eliaz, N.; Nissan, O. *J. Biomed. Mater. Res.* **2007**, 83A, 546–557.
- Bandyopadhyay, S.; Miller, A. E.; Chang, H. C.; Banerjee, G.; Yuzhakov, V.; Yue, D. F.; Ricker, R. E.; Jones, S.; Eastman, J. A.; Baugher, E.; Chandrasekhar, M. *Nanotechnology* **1996**, 7, 360–371.
- Yu, C.; Hu, C.; Bai, A.; Yang, Y. F. *Surface & Coatings Technology* **2007**, 201, 7259–7265.
- Rauf, A.; Mehmood, M.; Rasheed, M.A.; Aslam, M. *J. Solid State Electrochem.* **2009**, 13, 321–332.
- Montero-Moreno, J. M.; Sarret, M.; Müller, C. *Surface & Coatings Technology* **2007**, 201, 6352–6357.
- Jessensky, O.; Müller F.; Gösele, U. *Electrochem. Soc.* **1998**, 145, 3735–3740.
- Mathad, G. S.; Electrochem. Soc. **2003**, 245.
- Watanabe, T. *Nano plating - microstructure formation theory of plated films and a data base of plated film microstructure*, Elsevier, 2004; pp 215.
- Vander Voort, G. F. *Metallography, principle and practice*, The Materials Information Society, 2007; pp 122.
- Mathad, C. G. *The electrochemical society*, 2003; pp 228.
- Yuzhakov, V. V.; Chang, H. C.; Miller, A. E. *Phys. Rev. B* **1997**, 56, 12608–12624.
- Wang, X.; Lib, C.; Yu, Z.; Yongbin, H. Z.; Ping, J.; Chen, J. Z.; Fan, Z. *Mater. Chem. Phys.* **2012**, 133, 212–217.