

Using Gibbs standard state free energy and a power regulating device to predict and control the fabrication of nanoporous alumina

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ABSTRACT

The basic concept of Gibbs standard state free energy predicts a favorable condition for both room and high temperature fabrication of nanoporous alumina in phosphoric acid electrolyte. The anodization of aluminum foil in acidic electrolytes is made possible by the well known process parameters that have been studied over the years. These parameters i.e. voltage, current density, type of electrolyte etc have been very effective when anodizing aluminum at freezing temperatures. When the operating temperature is raised above the freezing temperature, additional process parameters would be required to make the pore formation possible. The fabrication of the aluminum foil was carried out using phosphoric acid as the electrolyte source. The electrolyte pH was adjusted to 1, 3 and 5 in order to simulate different anodizing conditions. A potential of 50 V from a dc power supply was applied across the electrochemical cell, while a power regulating device with different power rating was attached to the electrochemical cell to provide the operating system with additional parameters that could influence the surface structure of the alumina. The micrographs obtained show that the propagation and growth of the pores at both room and high temperatures was made possible by the power regulating device attached to the cell. Copyright © 2013 VBRI press.

Keywords: Electrochemical cell; Gibbs free energy; Nanoporous alumina; Power regulator; Temperature.



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Introduction

Anodic aluminum oxide (AAO) has always been a template of choice over the years because it is chemically stable, easy to prepare and fabricate, biologically inert and can withstand fairly high temperature [1-5], have found use in different areas that includes magnetic, optical, and electronic devices [6]. The anodization process could be by a single step anodization process [7,8]; two steps anodization process [9-11]; or three steps anodization process [12] have all been reported to obtain disordered and/or ordered nanoporous alumina. Most of the reported operating conditions for the anodization of the aluminum foil have been limited to the freezing of the electrolyte bath despite the prediction by Gibbs standard state free energy of room and higher temperatures to be more favorable. The

successful anodization of aluminum at ambient temperature will make the anodization process cost effective, and a convenient method of controlling the propagation and growth of the nanopores.

The fabrication of nanoporous alumina in an acidic electrolyte proceeds with the gain and lose of electrons which occur at both the anodic and cathodic electrodes. The oxidation process takes place at the anode and the reduction process at the cathode, each of these reactions make up the half cell reaction [13]. The driving force behind this electron transfer across the electrochemical cell is the Gibbs free energy difference between the two half cell reactions. The thermodynamic properties of enthalpy and entropy explain how the different reactions behave under certain conditions [14]. Since Gibbs free energy cannot be measured directly the difference between the enthalpy and entropy of the system provides the Gibbs free energy information if the reaction will be spontaneous or not, but it does not provide information on how fast or slow the reaction will be.

The main objective of this work is to find a way of controlling the kinetics of the chemical reaction by attaching a power regulating device to the electrochemical cell to compliment the analysis obtained from the Gibbs standard state free energy and to provide additional process parameters to the previously known parameters. The analysis of the Gibbs standard state free energy was used to predict the pore formation of nanoporous alumina. The predictions only show that room temperature and high temperature anodization of aluminum are favorable but does not provide more details on how it can be achieved. The temperature of the electrolyte was kept at both room and high temperature respectively. The electrochemical process was easily controlled with the device taking into consideration the different operating conditions as well as the internal resistance generated by the electrochemical cell during the anodization process. The micrographs obtained show the different surface structures that can be obtained when operating above the freezing temperature.

Experimental

Aluminum foil preparation

Aluminum foil with purity of 99.9 % and 0.25 mm thickness was used as the starting material and purchased from Malaysia aluminum and alloys. The different samples before anodization were first degreased in acetone, rinsed with distilled water and then annealed at 400 °C in a programmable furnace (LT furnace purchased from ADV system technology, Malaysia) for 2 hrs [15]. The samples were etched in 1.0 M NaOH for few minutes [16] and electrochemically polished in a 1:4 volume mixture of HClO₄ and C₂H₅OH at constant current density of 500 mA⁻² for 30 sec at 10 °C [17].

Electrolyte preparation

The type of electrolyte and the pH used for the anodization are aqueous solution of 25 % phosphoric acid electrolyte (Sigma-Aldrich, Malaysia) adjusted to pH1, pH3 and pH5 with NaOH (HmbG chemicals, Malaysia). The anodization process was performed at ambient temperature using dc power source (GW INSTEK GPR-60300 purchased in

Malaysia) with an applied dc potential of 50 V for 5 hrs from the power supply. The samples fabricated at different pH were further treated with 3 % phosphoric acid solution for the enlargement of the pores. For the high temperature anodization, the sample was similarly prepared, the exception was the heating of the reaction vessel to 50 °C and the anodization time reduced to 1 hr. The distance between the platinum cathode electrode and aluminum anode electrode was 3 cm. All the chemicals used were of high grade and purity and purchased in Malaysia.

Characterization

The micrographs obtained during the anodization process with/without the use of the power regulator attached to the electrochemical cell as well as the chemical etching of the nanopores where all characterized using scanning electron microscope (SEM).

Results and discussion

The schematic diagram of the electrochemical cell used for the fabrication of nanoporous alumina at both room and high temperature is shown in Fig. 1.

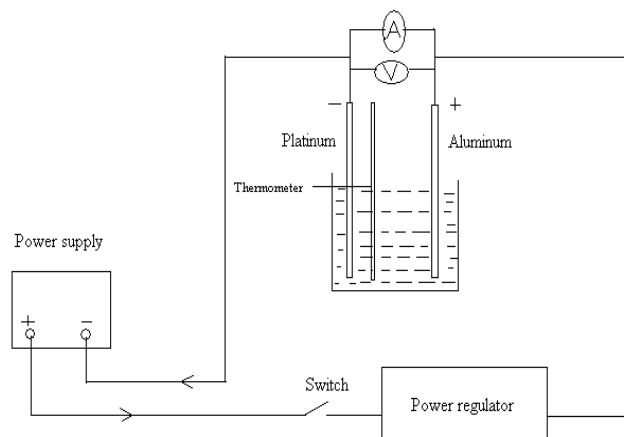


Fig. 1. Schematic diagram of the electrochemical cell.

The electrochemical cell makes use of additional process control parameters provided by the power regulating device. It's a different way of anodizing aluminum which has never been done before, because the electrochemical cell in its present state has the capability to adapt to every change in the kinetics and temperature of the reaction. The operating system implores flexibility that allows the operation of the cell to be tunable in order to provide precise control of the voltage and current density needed during the anodization process. The values of the voltage drop and the internal resistance generated across the circuit during the anodization process can be obtained to allow the necessary adjustments needed by the electrochemical cell.

Fig. 2 shows the FE-SEM of aluminum foil initially anodized at room temperature without the power regulating device attached to the electrochemical cell. The micrograph shows rapid etching of the alumina surface as the reaction process was too fast to allow any form of pore propagation. The result indicates that anodizing aluminum at room temperature without any form of control over the kinetics

most often leads to complete surface etching of the alumina formed. The most ideal approach would be the addition of other suitable process control parameters to reduce the rapid etching of the surface and to enhance the propagation and growth of controlled nanoporous alumina structure.

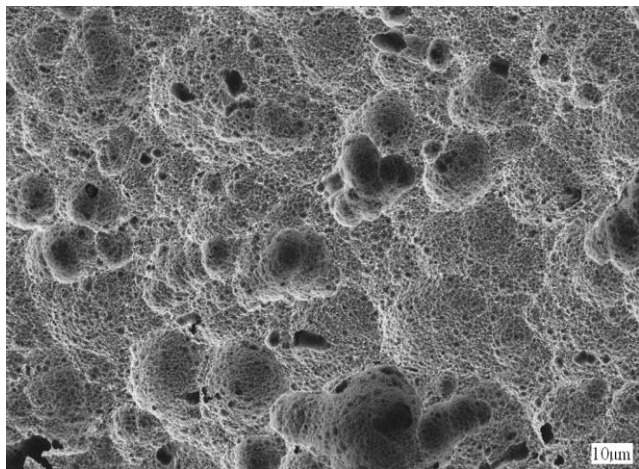


Fig. 2. FE-SEM micrograph of aluminum anodized with a dc power supply at room temperature without the power regulating device attached to the cell.

Fig. 3 (a), (b), and (c) shows FE-SEM of aluminum anodized at room temperature with the power regulating device attached to the electrochemical cell.

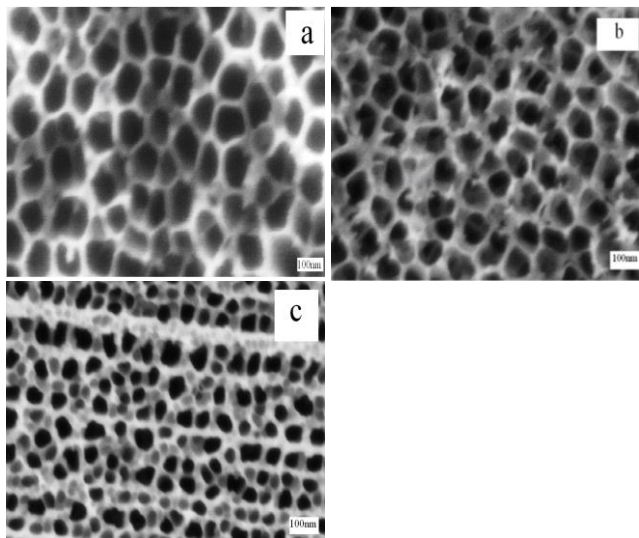


Fig. 3. FE-SEM micrographs of nanoporous alumina produced from an applied potential of 50 V for 5 hrs at different pH. (a) Anodized aluminum foil at pH1, (b) Anodized aluminum foil at pH3, and (c) Anodized aluminum foil at pH5.

It was observed that the power regulating device allows the propagation and growth of nanoporous alumina at pH1 and pH3. In the case of pH5, the internal resistance generated by the cell is much higher when compared to the other pH. Despite the high internal resistance and voltage dropped across the cell, the device was still able to allow the formation of tiny nanopores by controlling the pitting of the aluminum oxide layer on the surface without damaging or etching it off. An advantage of this current approach is that it allows the power regulating device to regulate the

amount of energy (i.e. voltage and current/current density) supplied by the dc power supply, while at the same time it tries to overcome the voltage drop and the internal resistance generated by the electrochemical cell making it possible to operate at room temperature. Most of the excess energy that could etch off the alumina surface is dissipated in the form of heat to the environment. The device is very sensitive to the different electrolyte conditions and the response varies from one condition to another.

Gibbs standard state free energy

The Gibbs standard state free energy predicts a favorable condition for room temperature fabrication of the aluminum foil, while the power regulating device in the closed circuit ensures the propagation and growth of the nanoporous alumina structure. Gibbs free energy (G) reflects the balance between spontaneous and non spontaneous reactions in terms of the enthalpy, the temperature and the entropy of the system [18,19]. This can be expressed as the difference between enthalpy and the product of temperature and entropy.

$$G = H - TS \quad (1)$$

If the data are collected under standard-state conditions, the result is the standard-state free energy of reaction (G°).

$$\Delta G^\circ = \Delta H^\circ - \Delta T S^\circ \quad (2)$$

The Gibbs standard state free energy of reaction can also be obtained from the sum of the free energies of formation of the products minus the sum of the free energies of formation of the reactants:

$$\Delta G^\circ = \sum \Delta G^\circ_{\text{products}} - \sum \Delta G^\circ_{\text{reactants}} \quad (3)$$

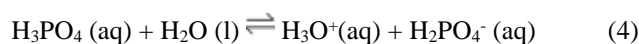
Any reaction for which ΔG° is negative should be favorable, or spontaneous. Favorable or spontaneous reactions: $\Delta G^\circ < 0$

Any reaction for which ΔG° is positive is therefore unfavorable. Unfavorable or non-spontaneous reactions: $\Delta G^\circ > 0$

The temperature of a chemical reaction has effect on the free energy of that particular reaction, and the balance between the contributions from the enthalpy and entropy terms to the free energy of that reaction depends on the temperature at which the reaction is run. The Eqn. (1), (2) and (3) used to define the free energy of a system suggests that the entropy term will become more important as the temperature increases [18, 19].

Standard state free energy (ΔG°) of the metal and the electrolyte

The phosphoric acid used as the electrolyte source in an aqueous form produces an acid with its conjugate base from the reaction shown



The enthalpy and entropy are governed by the difference in the summation of the products and reactants shown below:

$$\text{Enthalpy } \Delta H^{\circ} = \sum n\Delta H^{\circ}_{\text{products}} - \sum m\Delta H^{\circ}_{\text{reactants}} \quad (5)$$

$$\text{Entropy } \Delta S^{\circ} = \sum n\Delta S^{\circ}_{\text{products}} - \sum m\Delta S^{\circ}_{\text{reactants}} \quad (6)$$

The enthalpy and entropy of the products formed is as follows:

$$\Delta H^{\circ} (\text{H}_3\text{O}^+) = -285.84 \text{ KJ/mol}; \Delta H^{\circ} (\text{H}_2\text{PO}_4^-) = -1302.6 \text{ KJ/mol};$$

$$\Delta S^{\circ} (\text{H}_3\text{O}^+) = 69.940 \text{ J/mol K}; \Delta S^{\circ} (\text{H}_2\text{PO}_4^-) = 92.5 \text{ J/mol K}.$$

The enthalpy and entropy of the reactants is shown in the equation:

$$\Delta H^{\circ} (\text{H}_3\text{PO}_4) = -1277.4 \text{ KJ/mol}; \Delta H^{\circ} (\text{H}_2\text{O}) = -285.84 \text{ KJ/mol};$$

$$\Delta S^{\circ} (\text{H}_3\text{PO}_4) = 222 \text{ J/mol K}; \Delta S^{\circ} (\text{H}_2\text{O}) = 69.940 \text{ J/mol K}.$$

$$\Delta G^{\circ} = 13.41 \text{ KJ/mol}.$$

The standard-state free energy for this reaction is positive, while the introduction of Al to the reaction produces a favorable Gibbs free energy as shown:



$$\text{products: } \Delta H^{\circ} (\text{AlPO}_4) = -1733.8 \text{ KJ/mol}; \Delta H^{\circ} (\text{H}_2) = 0$$

$$\Delta S^{\circ} (\text{AlPO}_4) = 90.79 \text{ J/mol K}; \Delta S^{\circ} (\text{H}_2) = 130.59 \text{ J/mol K}.$$

$$\text{reactants: } \Delta H^{\circ} (\text{Al}) = 0; \Delta H^{\circ} (\text{H}_3\text{PO}_4) = -1277.4 \text{ KJ/mol};$$

$$\Delta S^{\circ} (\text{Al}) = 28.32 \text{ J/mol K}; \Delta S^{\circ} (\text{H}_3\text{PO}_4) = 222 \text{ J/mol K}.$$

$$\text{Free energy } \Delta G^{\circ} = -934.49 \text{ KJ/mol}.$$

Since the reaction is favorable and spontaneous at room temperature it further confirms that nanoporous alumina fabrication at room temperature is achievable if the kinetics of the reaction can be properly controlled. If the temperature is changed from room to a higher temperature of 50 °C or 323.15 K the entropy becomes more favorable as the degree of disorder increases. The free energy is negative and the value obtained shows that the reaction is more spontaneous when compared with room temperature. $\Delta G = -936.31 \text{ KJ/mol}$

Although the Gibbs standard state free energy predicts the reaction processes to be favorable it does not provide information on how the kinetics can be controlled. This is the reason why a regulating device was introduced to control the rate of the electrochemical reaction.

Power regulating device

The power regulating device which is an electronic device used for the anodization process is very sensitive to changes in electrolyte concentrations, the type of electrolytes, and the temperature of the electrolytes. The sensitivity of this device to the different electrolyte

conditions is displayed during the anodization process. The functioning of the electrochemical cell is based on the knowledge of the standard equations to provide the device with suitable power rating required for the control of the reaction kinetics.

The standard equations that govern the use of the power regulating device during the anodization process are listed as follows:

$$P = V^2 / R \quad (8)$$

$$P = V \times I \quad (9)$$

$$V = I \times R \quad (10)$$

$$V_f = V_a - I (R + R_i) \quad (11)$$

Where P = power (watts), V = voltage (v), I = current (A), R = resistance (Ω), V_f = final voltage (v), V_a = applied voltage (v), and R_i = internal resistance (Ω). These standard equations apart from the control it provides it also makes it possible to know the values for the internal resistance generated by the electrochemical cell. The internal resistance is usually as a result of the difference between the electrodes (anode and cathode) as well as the difficulty of ion movement in the electrolytes. A suitable power regulating device with known electrolyte sensitivity and the right rating is able to overcome the internal resistance while still providing control over the anodization process to create a suitable condition for the growth of the pores.

Fig. 4 (a) shows FE-SEM of aluminum anodized at 50 °C without the power regulating device attached, and **Fig. 4** (b) with the device attached to the electrochemical cell. It was observed that the surface of **Fig. 4** (a) was completely etched off as the reaction process was too fast for the propagation and growth of the pores to be sustained. In order to reduce this surface etching the device with a suitable rating was placed in series with the power supply. It was able to sustain the fabrication of nanoporous alumina structure shown in **Fig. 4** (b) by controlling the rate of the chemical reaction.

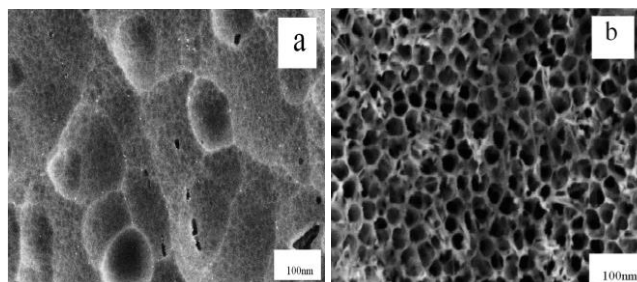


Fig. 4. FE-SEM micrographs of aluminum foil anodized at high temperature (50 °C) for 1hr. (a) Without the power regulating device attached, and (b) With the power regulating device attached.

The pore diameters obtained when anodizing at 50 °C is about 100 nm not ordered because of the single step anodization process employed, and the porous structure obtained has similar surface characteristics to the foils anodized at ambient temperature.

Nanoporous alumina pore diameters can be increased after the anodization process with the use of a suitable

etchant. **Fig. 5** (a), (b) and (c) shows FE-SEM of etched alumina surface initially anodized at different pH.

The pores were observed to increase significantly due to the presence of the H^+ ion in the aqueous solution [7]. The use of a mild etchant which can be easily controlled enables the possibility of having a controlled pore size suitable for the different area of applications. The etching process basically removes the alumina pore walls in a step wise process [8] shown in **Eqn. 12**. If the process is prolonged the pores formed starts to collapse as it is observed in **Fig. 5** (c).

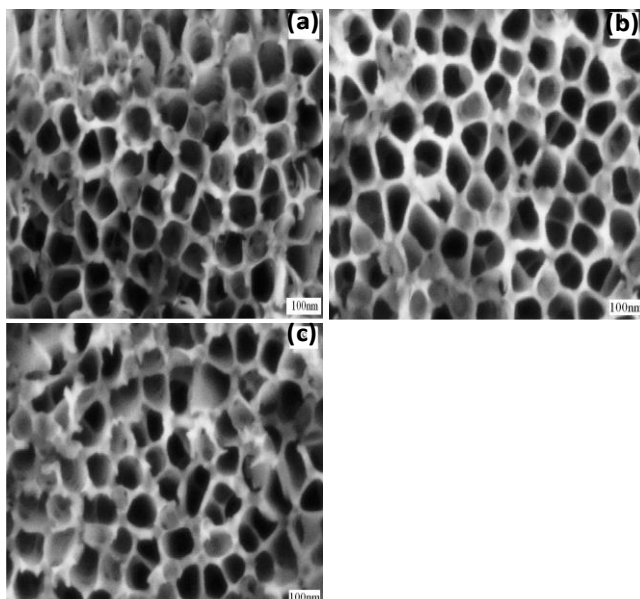
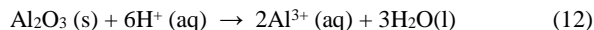


Fig. 5. FE-SEM of anodized aluminum foil etched in 3 % phosphoric acid at different pH. (a) Aluminum foil anodized at pH1 and etched for 30 min, (b) Aluminum foil anodized at pH3 and etched for 30 min, and (c) Aluminum foil anodized at pH5 and etched for 40 min.

Fig. 6 shows the pore size distribution of the nanopores formed during the anodization process. The pore size is influenced by the choice of electrolyte as increased pore diameters have been reported to be obtainable from foils anodized in phosphoric acid electrolyte [20,21], while lower pore diameters have also been reported from oxalic and sulphuric acids [22-25]. The pore diameters obtained at pH1 is in the range of 150 – 200 nm, because the oxide layer formation and the breakdown of the barrier layer occur simultaneously as soon as the aluminum foil comes in contact with the electrolyte under the control of the regulator. The attack on the foil leads to several pitting of the oxide layer on the surface by the H^+ ion, as the process continues the pores increases in diameter with time.

The pores produced at pH3 are in the range of 80 – 120 nm smaller in diameter when compared with pH1 with the same anodizing time. The pores from pH3 electrolyte are less because there is slight restriction of ion movement as a result of high resistance experienced during the anodization process. The rating of the power regulating device had to be change because of its sensitivity to the different electrolyte condition, to allow the propagation and growth of the pores without etching off the surface. The resistance

of ion movement in the electrolyte continued to increase as the pH is further increased. The pores produced from pH5 electrolyte are in the range of 10 – 30 nm much smaller when compared with the other pH. The regulating device still made it possible to generate the pits on the surface of the template but at a much slower rate and with care not to etch off the oxide layer. The etching of the foils shows an increase in the size of the pores regardless of the pH used. The pore diameters from pH1 and pH3 increased in size to about 300 nm while pH5 although with prolong etching time also increased to 250 nm. The etching process which basically involves thinning of the alumina pore walls can be used to control the diameters of the porous structure. A shorter time anodization procedure can be performed while the etching of the foil can be used to produce the required size of pores.

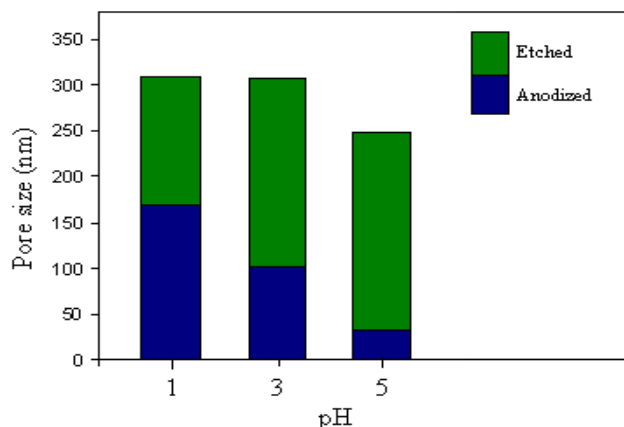


Fig. 6. Pore size distribution of both anodized and etched aluminum/alumina foils at different pH.

Fig. 7 shows the current density pH diagram of the anodized aluminum foils; for all the samples, pH1 sample exhibits the highest current density in the range of 1.66 – 3.3 A/cm² due to easy ion movement which allows the power regulating device to supply a substantial amount of current with less resistance to the electrochemical cell. The current density value from the graph for pH3 and pH5 is lower and in the range of 1 – 2 A/cm² and 0.17 – 0.3A/cm² respectively.

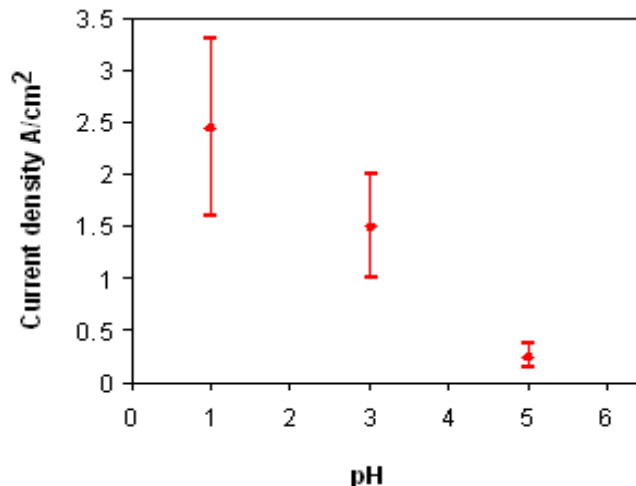


Fig. 7. Graph of current density vs pH of anodized aluminum foil.

The resistance from the pH 3 and 5 electrochemical cell is higher when compared with pH 1 but the power regulating device was able to supply the required current to overcome the cell resistance and to produce the nanopores without etching off the pores. The most important observation when operating the electrochemical cell at ambient temperature is the high current density which is necessary for pore formation, the device attached is able to maintain this high current density required while it dissipates all the excess current in the form of heat to the environment from getting to the aluminum foil. This form of control over the anodization process allows for pore propagation at the same time prevents the etching of the alumina surface.

Conclusion

In conclusion, we show first; the limitation associated with Gibbs free energy prediction of a favorable temperature condition but it provides no more details on how it can be achieved, and secondly the importance of the attached power regulating device during the fabrication of nanoporous alumina operating at both ambient and high temperature. We show that the power regulating device compliments the prediction from the Gibbs free energy. The sensitivity of the power regulating device to different electrolytes and temperature conditions makes it suitable to provide a form of control over the electrochemical process. We observed that the nanoporous alumina structure obtained with different pore diameters for the different pH is as a result of the resistance generated by the electrochemical cell. This resistance leads to the decrease in the size of pores and increase in the heat that is dissipated to the surrounding with every increase in pH. If this resistance is reduced and a suitable voltage and current/current density is supplied as we have shown there is a high tendency of obtaining a nanoporous alumina structure with every change in the electrolyte conditions.

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