THE EFFECT OF VARIOUS FACTORS ON THE FABRICATION OF ANODIZED ALUMINUM OXIDE

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ABSTRACT

Anodization is a process to produce a thick oxide layer on the surface of metal by inducing an ionic current through the layer. A two-step anodization is used to fabricate the anodic aluminum oxide template. This process occurs under suitable conditions, such as 0.3M oxalic acid with a voltage of 40 volts applied across the cell. However, it is not know what combination of temperature and current strength is the most suitable. In this study the anodization was done at 16 °C, 21 °C and 26 °C and with the currents of 50 mA, 70 mA, 90 mA, and 110 mA. The morphologies of anodized aluminum oxide in various conditions were obtained diameters of the holes on the surface of anodized aluminum oxide in order to ascertain which combination of temperature and current produced the best results.

The quality of the anodized aluminum oxide at 16 °C and 90 mA was the highest but only marginally more than other combinations. The initial temperature was seen to have the greatest effect on the size of holes' diameters. The sizes of holes' diameters did not show any correlation with the current. Current densities decreased when the temperature decreased. The current densities at the equilibrium points were the same when the same temperature was used.

KEY WORDS: A TWO-STEP ANODIZATION/ANODIZED ALUMINUM OXIDE

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บทคัดย่อ

การอะโนไดซ์ (anodization) เป็นกระบวนการหนึ่งในการผลิตชั้นของออกไซด์ที่มีความหนาบนผิวหน้าของโลหะ ด้วยวิธีการให้กระแสไฟฟ้าผ่านไปในชั้นของโลหะ การอะโนไดซ์สองขั้นตอน (a two-step anodization) ถูกใช้ในการสร้างแม่พิมพ์อลูมิเนียมออกไซด์ (aluminum oxide template) กระบวนการนี้ จะเกิดขึ้นภายใต้สภาวะที่เหมาะสม เช่น ภายใต้กรดออกซาลิก (oxalic acid) ความเข้มข้น 0.3 โมลาร์ โดยให้ความต่างศักย์ 40 โวลต์ ตกคร่อมขั้วของเซลล์ แต่ยังไม่ทราบว่าอุณหภูมิและกระแสเท่าไรเหมาะสมที่สุด ในการทดลองนี้ เราทำการอะโนไดซ์ที่อุณหภูมิ 16, 21 และ 26 องศาเซลเซียส ด้วยกระแส 50, 70, 90, และ 110 มิลลิแอมแปร์ สัณฐานของอลูมิเนียมออกไซด์ในสภาวะต่าง ๆ ถูกนำมาวิเคราะห์หาเส้นผ่านศูนย์กลางของรูที่อยู่บนอลูมิเนียมออกไซด์ เพื่อให้แน่ใจว่าที่อุณหภูมิและกระแสเท่าไรที่ทำให้ผลออกมาดีที่สุด

คุณภาพของอลูมิเนียมออกไซด์ ที่อุณหภูมิ 16 องศาเซลเซียส และที่กระแส 90 มิลลิแอมแปร์ ให้ผลออกมาดีที่สุด แต่ไม่ได้ต่างจากอันอื่นมากนัก อุณหภูมิเริ่มต้นมีผลกระทบอย่างมากต่อเส้นผ่านศูนย์กลางของรู และขนาดของรูไม่แสดงสหสัมพันธ์กับกระแส ความหนาแน่นกระแสจะลดลงเมื่อลดอุณหภูมิ และความหนาแน่นกระแสที่ภาวะสมดุลจะมีค่าเท่ากันที่อุณหภูมิเดียวกัน

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CHAPTER I
INTRODUCTION

Exposing various metals to air leads to the formation of metal oxides on the surface. After the metal-oxide layer is formed, the reaction process ceases since the metal no longer comes into contact with the oxygen. For aluminum, the layer can be anywhere between 5 to 50 nm. The thickness of these metal oxide layer does not provide much protection of the metal from the environmental corrosion. If the metal ions can be brought to the top of the oxide layer, they would be free to react with the oxygen in the air, thus increasing the thickness of the layer, up to several μm. The metal ions can be transported across the oxide layer by placing a voltage across the layer. The voltage drop creates an electric field $E = V/d$ (where d is the thickness of the layer). The electric field produces a force (qE) which acts on the ion, thus causing it to move across the layer. Once it reaches the top of the layer, it is then free to chemically interact with the oxygen ions in the electrolyte and a thicker oxide layer would ensue. This would lead to a greater protection if the metal from the environment corrosion. The process is called anodizing [1]. Anodize coatings of aluminum and magnesium are done on a large scale while coating of zinc, titanium, and some of the other metals is done on a lesser scale [2].

1.1 History of anodization

Since 1800s, many scientists have developed experiments which have lead to a better understanding of how electrolytic cells work [3]. They describe the reaction which takes place using the terminology of electrochemistry. In other words, they described the reaction in terms of ionic current flow in an electrolyte solution between two electrodes connected to each other via an external circuit with an electrical load or current source [4]. One of the electrodes is called the anode and it is where the oxidation reactions occur and other is called the cathode. At this latter electrode, a reduction reaction occurs. Examples of where electrochemistry is used are:

electrolysis, electroplating (that convert electrical energy to produce a net chemical change), batteries, corrosion process (that convert the energy of chemical reactions into electrical energy).

Anodic reactions involve the oxidation of materials produced when the electrons at a solid-electrolyte interface removed. Much of the early interest in anodic surface layer has been centered in their use in capacitors. Oxides on aluminum, tantalum and niobium are primarily used as dielectrics [5]. Dielectric films are used in electronic, optical circuits and display devices.

1.2 History of anodization of nanoparticle

At first anodizing of metals was investigated by optical microscope [5]. At that time, the morphology of metal oxide layer was referred to as films (called anodic films). Later the scanning electron microscope (SEM) was used [6] which had high magnification power. The SEM revealed the true nature of the anodic film. In 1953 Keller et al. [7] was among the first to report the details of anodic aluminum oxide surface. In 1970 O'Sullivan & Wood presented the mechanism of anodic oxidation of alloys. In 1995 Masuda [8] succeeded in producing an array of nano hole on the anodic aluminum surface having a honeycomb structure of anodic aluminum by using a two-step anodizing process. The anodized aluminum oxide (AAO) membranes are now widely use as template for depositing metals into the nano hole in order to create nano array of metals such as cobalt [9,10], iron [11], nickel [12], CoPt [13].

1.3 Mechanism

The beginning of anodization process starts whereas anodic voltage is applied to the metal surface. The formation of barrier oxide layer on the surface is signaled by a drop in voltage. Very small pits will appear on the surface of the oxide/electrolyte interface. Those pits will widen and become nanoporous as anodization's time is increased. After some time, the rate of growth nanoporous becomes stable when dissolution of the oxide at the oxide/electrolyte interface is equal accumulation speed at the metal/oxide interface. By then a hexagonal pore structure will be formed. This is seen as closely packed cylindrical cells (see Figure 1.1). Each cell will contain a pore whose bottom is the shape of hemisphere (see Figure 1.2).

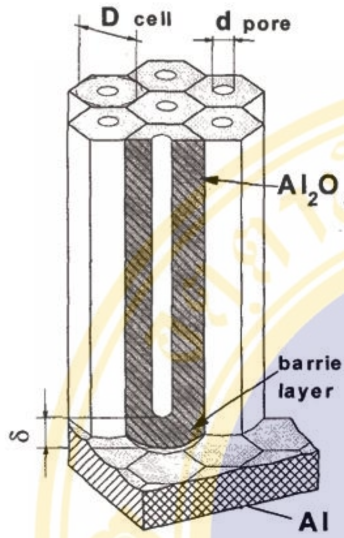


Figure 1.1 Hexagonal structure of porous anodic alumina [14].

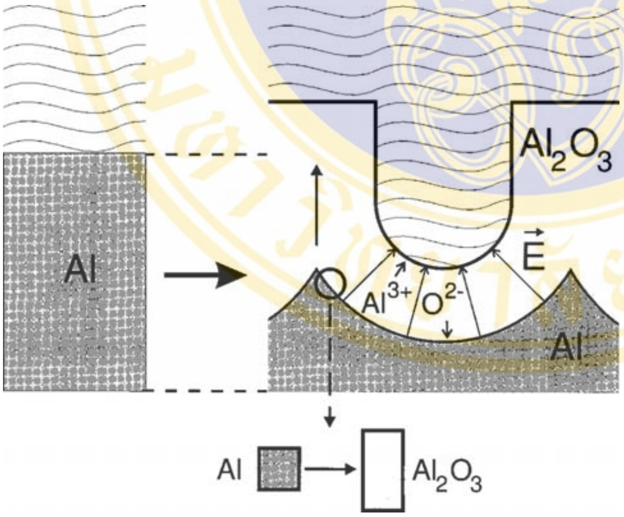


Figure 1.2 Hemisphere bottom of a pore [15].

The reaction that occurs at the oxide/electrolyte interface is an electrical field enhanced chemical dissolution. Metal dissolution at the metal/oxide interface is due to charge transfer (an electrochemical reaction). The drift of ions such as Al^{3+}, OH^-, and O^{2-} in the oxide layer plays an essential role for the formation of nanopores. Two opposite reactions of formation (due to the arrival of OH^- and O^{2-} ions) and dissolution (due to the emission of Al^{3+} ions) of the aluminum oxide take place at the interfaces between the oxide/electrolyte and metal/oxide layer, respectively. Those two processes are balanced by the steady growth of the nanopores so that the thickness of the oxide layer at the bottom of nanopores is maintained as constant. The thickness of barrier oxide layer at the bottom of the nanopores depends on the voltage.

During the first anodization, step nanopores are not highly ordered (especially within the first minute). After awhile the nanopores tried to adjust itself by self-organized to form the ordered array.

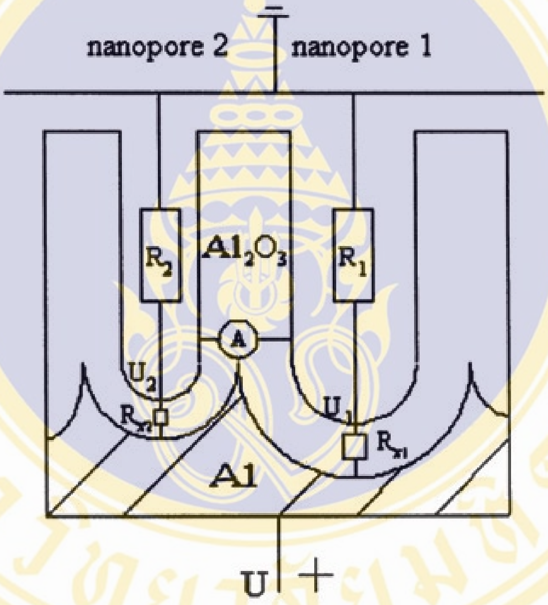


Figure 1.3 Schematic of the adjacent nano hole shows the potential at the bottom

We look at how the nanopores arrange themselves into an ordered pattern. We first consider what happens if adjacent pores are of different sizes. We assume that at the bottom of the nanopore, potentials are different as seen in figure 1.3. Nanopore 1 will have a potential U1 and nanopore 2, a potential U2. The barrier oxide layers at the bottom of the pores will have different resistance, i.e. Rx1 and Rx2.

In addition the electrolytes in each pore will also have a resistance, i.e.R1 and R2 which assume to be equal. We also now apply potential U between anode and cathode. If (U-U1) is large than (U-U2) or U1<U2, Rx1 is larger than Rx2. Thus, the

thickness of oxide layer (h) at the bottom of nanopore 1 is thicker than that of the bottom layer of nanopore 2 (h1>h2). The voltage difference between the two sides of the oxide layer determines the sizes of nanopore and cell. If the sizes of nanopore are different, the voltage drops in the oxide layers at the bottom of the pore will be different. The smaller voltage drop between the sides of the two nanopores will cause a small Al^{3+} current to flow in the sidewalls between the two nanopopres.

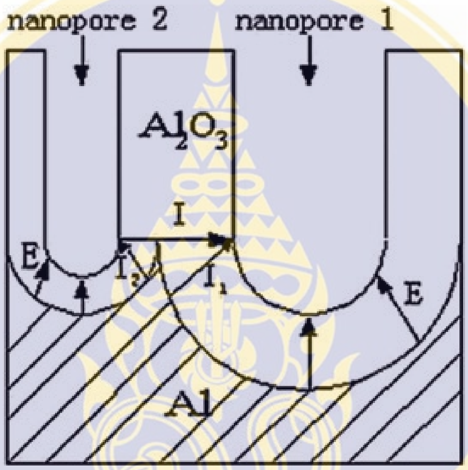


Figure1.4 Schematic of the adjacent nano hole shows the current.

Since U1<U2, there will be a current (I) across the bridge as show in figure 1.4. O^{2-} will migrate from the electrolyte in the larger pore into the small nanopore, leaving a lesser amount of O^{2-} ions to migrate through the bottom oxide barrier which are needed to oxidizing the aluminum metal. The formation of Al_2O_3 at the oxide-metal would be lesser. Combine this with the constant dissolution of Al_2O_3 at the oxide-electrolyte interface, the barrier would become thinner. Having more O^{2-} in the smaller pore increases the formation of bottom barrier layer. Nanopore 2 expands and nanopore 1 shrinks [16].

This bridge plays a role feedback. If the size of nanopore 2 is larger than nanopore 1, the current direction will reverse. The difference of diameter nanopore 1 and nanopore 2 will decrease by the self-feedback via the electrical bridge which nanopore1 and nanopore 2 reach self-adjustment. In the real system of the aluminum anodization, every nanopore is surrounded by six neighbors, which are the network of electrical bridges. Therefore all of them are correlated and lead to the self-organization of order nanopores.

1.4 Objective

The objectives of this thesis are to investigate influences of varying the current and temperature on anodizing of the aluminum when solution 0.3M of oxalic acid with the voltage is 40 volts in a two-step anodizing process. The first step is to anodize the aluminum to leave a texture of hexagonal pattern at the bottom of alumina. After removing the alumina, the hexagonal ridge on the top of aluminum is used seed pattern from which a highly ordered nano hole array can be grown during the second anodizing step.

CHAPTER II

EXPERIMENTAL DESCRIPTION

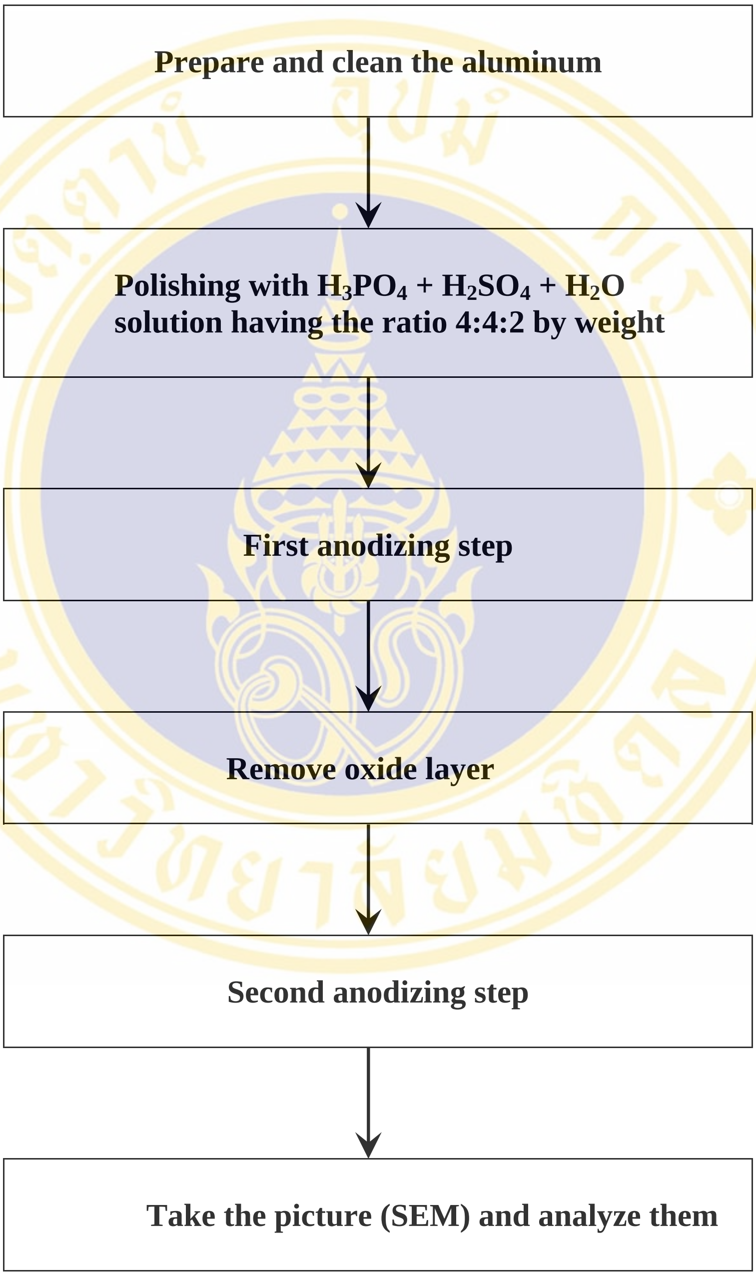
2.1 Materials and instruments

1. Aluminum sheet 99.999% with the thickness 0.4 mm. bought from Grikin Advanced Materials Company.
2. Graphite rods of diameter 0.5 cm.
3. Chiller to control the temperature of the solution.
4. Power supply.
5. Amp meter.
6. Interface sets.
7. Scanning Electron Microscope, HITACHI S-2500, JAPAN.
8. Annealing machine.
9. Ultrasonic cleaner.
10. Magnetic stirrers.

2.2 Chemicals

1. Phosphoric acid 85%.
2. Chromic acid.
3. Oxalic acid.
4. Sulfuric acid 96% and sulfuric acid 98%.
5. Ethyl alcohol 99.7%.
6. Sodium hydroxide, acetone, methyl alcohol.
7. Water that is used in this thesis is 3A water.

The flowchart of steps in anodizing aluminum oxide



2.3 Preparing and cleaning the aluminum

1. Cut the aluminum sheet 99.999% into discs of 2.5 cm. diameter.

2. Clean the aluminum discs with acetone and methanol.
3. Anneal the discs at temperature = 500°C (heated at the rate 10°C/min) for 5 hours.
4. Clean the aluminum discs in an ultrasonic cleaner with 3A water for 1 hour and then with ethyl alcohol 99.7% for 1 hour.
5. Wash in 3A water.
6. Immerse in NaOH 1M for 3-4 minutes
7. Wash in 3A water.

2.4 Polishing of aluminum

Electropolishing can be defined as a process in which the topography of a conductive surface is smoothed by polishing anodically in curtain electrolytes that are suitable for such application [17]. In this thesis, the chemical of electropolishing are as follow [18]. Aluminum 99% is use to find the optimum condition because its cost is not expensive.

The mixture of solution H_3PO_4 85% 70.31ml, H_2SO_4 98% 88.73ml, H_2O 51.11ml are prepared. The polishing is done under the various voltage, current and temperature in order to find the optimum conditions as show in the table below.

Table 2.1: Finding the optimum condition for polishing

NO.	Temp. (°C)	Time (min)	Current (A)	Voltage (V)
1)	0	10	0.5	1, 2, 5, 10, 15, 20, 25, 30
2)	0	30	0.5	2, 20
3)	Room temp.	10	0.5	20, 25
4)	48	10	0.5	2, 20, 25, 30
5)	45-60	10	1	10, 15, 20
6)	57	10	1.432	20, 25, 30
7)	55	10	1.432	10, 15, 20, 25
8)	55	15, 20	1.432	25

All these condition is done and the condition NO.8 is use to polish all samples before anodizing.

Set the experiment as shown in the picture by using the clean aluminum as the both cathode and anode.

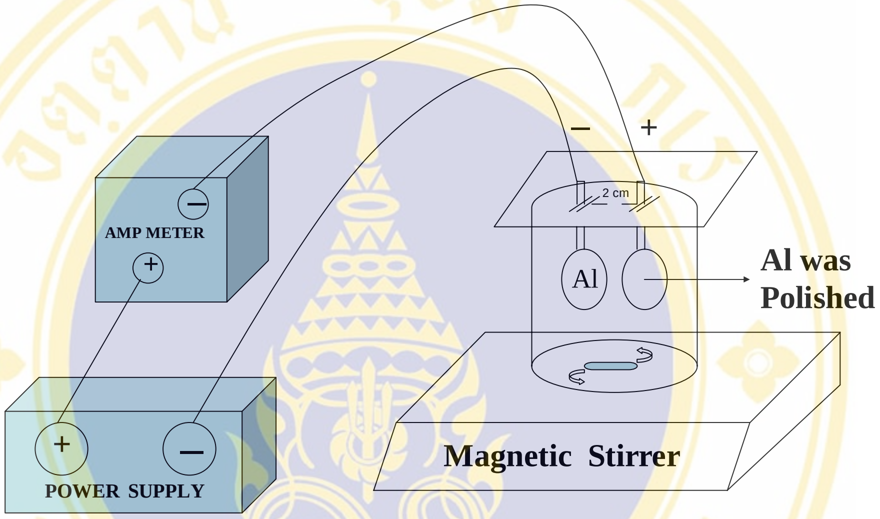


Figure 2.1: Schematic of polishing set up

2.5 Anodizing of aluminum

There are many methods to fabricate the aluminum oxide nano channel. In this thesis, the method for anodizing aluminum follows that of Masuda et al., [8]. They use the two step anodizing method using solutions of 0.3M of oxalic acid with the voltage of 40 volts.

The schematic of the experimental set up is the picture show below.

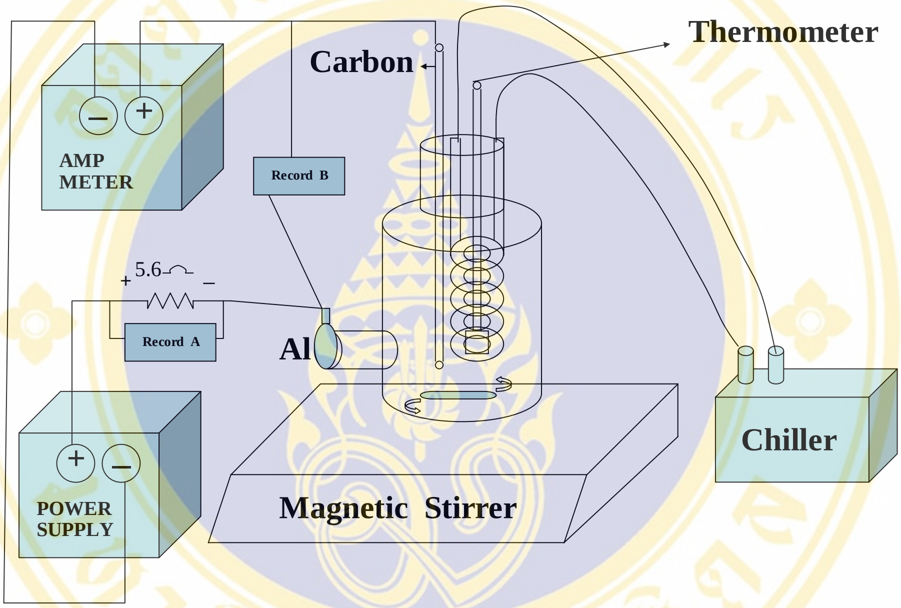


Figure 2.2: Schematic of anodization set up

In the picture above, the graphite rod acts as a cathode and the polished aluminum acts as an anode. Use oxalic acids 0.3M approximate 200ml as the electrolyte under the voltage 40 volts between the cathode and anode. The computer collected all the data: voltage and current at the same given times for all 6 hours in the first anodization. The cooler controls the temperature in the cell. Varying currents and temperatures showed in the table 2.2.

Table 2.2: Show currents and temperature that use in fabricate anodic alumina

Current(mA)	Temperature(°C)
50	16
	21
	26
70	16
	21
	26
90	16
	21
	26
110	16
	21
	26

After completing the first anodization, using solutions of 0.3M of oxalic acid operating at a voltage of 40V at all temperatures and currents, the aluminum discs were cleaned with 3A water. Afterwards, the oxide layer is dissolved away in the mixture of the chemical H_3PO_4 85% 2.7ml, chromic acid 1.8g and 3A water 91.84ml at 80°C for 40 minutes. The second anodizing (six hours) was done under the same condition as the first anodizing step. The discs were then washed and dried again. The surfaces of samples were coated with a palladium-platinum film before the SEM images were recorded.

The voltage and current was collected by the computer and the interface sets with the data studio program. The V-T graph and I-T graph was plot by the Microsoft Excel. The SEM image was pictured by “HITACHI S-2500”. The SEM film was scan by a scanner “CanoScan 9950F”. The Image Pro Program was used to cut the size of the SEM films. This program was used to collect the diameters and the areas of each hole. The data from Image Pro Program was use to plot the distribution diagram by Origin program. Mean and standard deviation was calculated by SPSS Program.

CHAPTER III
EXPERIMENTAL RESULTS

3.1. The result of polishing

The polishing of aluminum is done with a mixture of H_3PO_4 85% 70.31ml, H_2SO_4 98% 88.73ml and H_2O 51.11ml. To find the suitable voltage, current, temperature and time, we perform conditions 3.1.1 to 3.1.8 and see how good the mirror is.

Since we did not know the values of many parameters such as the temperature, the time, the current, the voltage and the distance between cathode – anode. We tried many combinations. We however, eliminate the distance between cathode and anode as a variable. We set the distance with 2 cm. Then we vary the voltage first by keep other parameters constant.

3.1.1. Condition: Temperature = 0 ºC
Time = 10 minuets
Current = 0.501 A

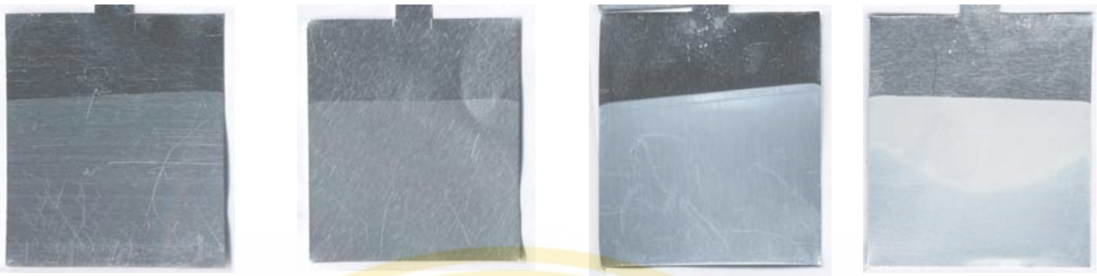
We fixed the value of voltage on the separate aluminum sheets as given in figure below. The current used at first was 0.501 A (from the power supply).


voltage = 1V


voltage = 2V


voltage = 5V


voltage = 10V



voltage = 15V voltage = 20V voltage = 25V voltage = 30V

Figure 3.1: The polished aluminum at T = 0 ºC, I = 0.501A, t = 10min.

We show that the current was not stable. It went up and down all the time. The surface of all the aluminum sheets was covered by an oxide layer. From this experiment, we determined that the amount of oxide form was occurred proportional to the voltage. We then changed time to 30 minutes.

3.1.2. Condition: Temperature = 0 ºC
Time = 30 minuets
Current = 0.501 A

We consider two voltages, 2V and 20V. We were able to see a trend in the amount of surface covered by the oxide. At the lower voltage, none of surface was covered with oxide. At 20V, there was coverage of the surface as show in the picture.

voltage = 2V voltage = 20V

Figure 3.2: The polished aluminum at T = 0 ºC, I = 0.501A, t = 30min.

From the experiment we find that the oxide was formed on the surface at the high voltage but not at the low voltage. This lead us to believe that no polishing occurs at 0 ºC. We therefore raised the temperature that of room temperature. We try 20V at first.

3.1.3. Condition: Temperature = the room temperature
Time = 10 minuets
Current = 0.501 A

We apply the voltage of 20V. Suddenly that we put the electrode to the solution, the voltage dropped. After 10 minutes, the voltage decrease to 17.3V. The surface develops the thick oxide layer.

We apply the voltage of 25V. Suddenly that we put the electrode to the solution, the voltage dropped. After 10 minutes, the voltage decrease to 13.5V. The surface has a thinner oxide layer. The picture was show below.

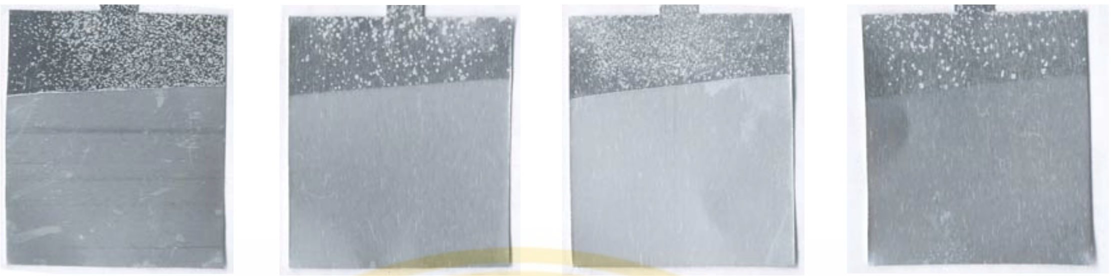
voltage = 20V

voltage = 25V

Figure 3.3: The polished aluminum at room temperature, I = 0.501A, t = 10min.

We the oxide cover on the surface. It appears that the polishing is not being done at this temperature or the current is not sufficient. So we have increased the temperature and current.

3.1.4. Condition: Temperature = 48 ºC
Time = 10 minuets
Current = 0.56 A



voltage = 2V voltage = 20V voltage = 25V voltage = 30V

Figure 3.4: The polished aluminum at T = 48 ºC, I = 0.56A, t = 10min.

There is some oxide at this temperature. If we look what happening at the higher voltage when different temperatures are used, we see that at the high voltage using the high temperatures has less oxide than the high voltage using the low temperatures. If we look at the effects of lower voltage at the different temperature, we see that the surface hasn't change much. Both high voltage and high temperature are required for polishing.

While we know the trend of two parameters, we do not know the exact value of them nor do know how the current affects the polishing. Now look at the effects of using the higher current.

3.1.5. Condition: Temperature = 45-60 ºC
Time = 10 minuets
Current = 1 A

When we apply the voltage of 10V (T = 46 ºC), the voltage drops to 7.7V after 10 minuets. The surface changes a little bit and it is not smooth and mirror like.

When we apply the voltage of 15V (T = 53 ºC), the voltage drops to 7.3V after 10 minuets. The surface is same as the sheet obtained with 10V. There is only a trace of oxide on the surface.

When we apply the voltage of 20V (T = 55 ºC), the voltage drops to 7.0V after 10 minuets. The surface remains same. It also has more oxide.

voltage = 10V (T = 46 ºC)
voltage = 15V (T = 53 ºC)
voltage = 20V (T = 55 ºC)

Figure 3.5: The polished aluminum at T = 45-60 ºC, I = 1A, t = 10min.

Now look at the effects of the current flow we should apply at the high voltage first because we want to see the oxide. We first apply a current flow 0.1 mA/cm^2.

3.1.6. Condition: Temperature = 57 ºC
Time = 10 minuets
Current = 1.432A.

Again, when we apply the voltage of 20V, the voltage suddenly drops to around 7.9V and after 10 minuets the voltage is 9V. The surface still has oxide cover but is a little bit more mirror like.

When we apply the voltage of 25V, the voltage suddenly drops to around 7.5V and after 10 minuets the voltage increase to 8.9V. The surface appears not have any oxide cover. The surface is more mirrors like and smooth.

When we apply the voltage of 30V, the voltage suddenly drops to around 5V and after 10 minuets the voltage increase to 6.9V. The surface is covered with more oxide layer. It remains mirror like and smooth.

voltage = 20V
voltage = 25V
voltage = 30V

Figure 3.6: The polished aluminum at T = 57 ºC, I = 1.432A, t = 10min.

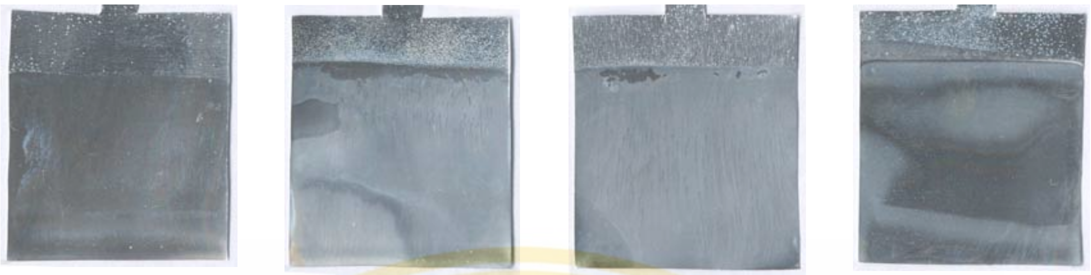
Thus the voltage of 25V appears to be the best condition, We then tried to confirm this result. We repeated 20V and 25V experiment. Both sheets have the oxide too much cover on them. Duration may not have been enough to achieve good polishing. We repeated the 25V experiment again but for 30 minutes. The voltage dropped to 15V after 30 minuets. The surface is mirror like and has more smoothen. (I can see the changes by my eyes). The picture was shown in figure 3.7.

Figure 3.7: The polished aluminum at voltage = 25V,
t = 30 min, T = 57 ºC, I = 1.432A.

It appears that a voltage around 25V, I = 0.1A/cm^2 and high temperature (40-60 ºC) are required. The surface seems to be good with a longer time of polishing. We noticed one important factor is the oxide in the air. We notice that so many times the oxide layer occurred when the sheet were dried in air. We repeated the experiment but now we dried it before washing with water.

3.1.7. Condition: Temperature = 55 ºC
Time = 10 minuets
Current = 1.432A.

As we said, the sample was first dry before washing with water. The pictures are shown in figure 3.8.



voltage = 10V voltage = 15V voltage = 20V voltage = 25V

Figure 3.8: The polished aluminum at T = 55 ºC, I = 1.432A, t = 10min.

The first sheet used an applied voltage of 10V. The surface shown a little oxide cover and is not quite mirror like and smooth.

The second sheet used an applied voltage of 15V. The surface has oxide cover and is mirror-like and smooth.

The third sheet used an applied voltage of 20V. The surface has more oxide cover and it is mirror like and smooth.

The forth sheet used an applied voltage of 25V. The surface shows also a little oxide cover. It is mirror like and smooth.

The forth sheet is better than others. Once we determine these three parameters, repeat the experiment but varied the time.

3.1.8. Condition: Temperature = 55 ºC
Voltage = 25 V
Current = 1.432 A.

time = 10 min time = 15 min time = 20 min

Figure 3.9: The polished aluminum at T = 57 ºC, I = 1.432A, voltage = 25V.

From the picture, we see that if we polish the aluminum 99% for 20 minutes, the surface appears to be better than others.

When we already know the optimum condition for polishing, we use these conditions to polish the 99.999% of aluminum. We notice that the high purity aluminum is more mirrored than the low purity aluminum. It becomes shinny faster than the low purity aluminum. We use a time of 15 minutes to polish the high purity aluminum. If we use the time more than 15 minutes, the surface becomes rough but remains shininess. Thus the time required to polish aluminum 99.999% is 15 minutes.

3.2 The result of anodization

3.2.1. Description of anodized aluminum oxide

The two-step anodization is the method to fabricate the aluminum oxide template. The first anodization step bring about the pattern of hexagonal on the surface. This pattern will be used as pre-texture form for the second anodization step.

In order to assure that removing the alumina on the first anodization step creates the ordered pattern on the surface. We took the photo of aluminum after removing alumina by SEM. The image present in the figure 3.10.

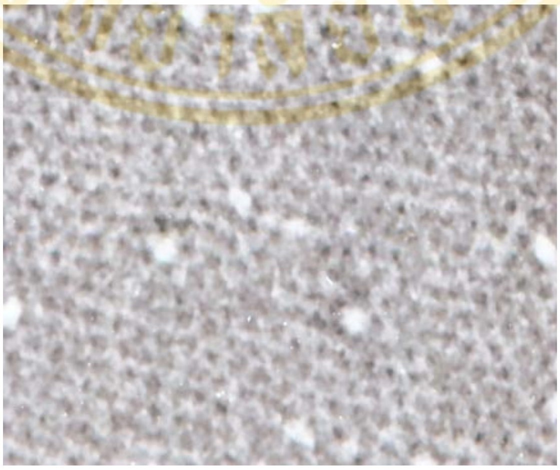


Figure 3.10: The ordered pattern on Al after removing Al_2O_3

(Condition:0.3M Oxalic acid, V = 40V, room temperature)

This morphology shows the ordered pattern on the aluminum surface after removing out alumina. The image identifies the ordered pattern leaving on the aluminum and it will lead to the growth of holes on the second anodization step.

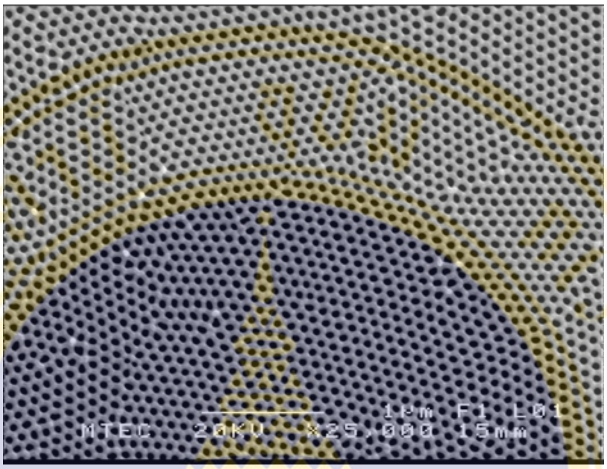


Figure 3.11: Top view after finishing the second anodization step
(Condition:0.3M Oxalic acid, V = 40V)

Figure 3.11 is taken on top of the alumina after finishing the second anodization step. The picture showed two dimensions representing the hexagonal pattern domain. These domains were separated to many boundaries hence we can observe some defects on the image.

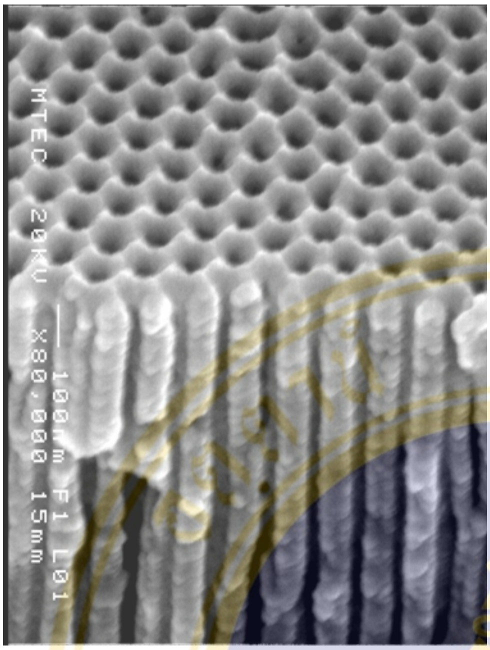


Figure 3.12: Side view of Al_2O_3 shows the parallel channel.
(Condition:0.3M Oxalic acid, V = 40V)

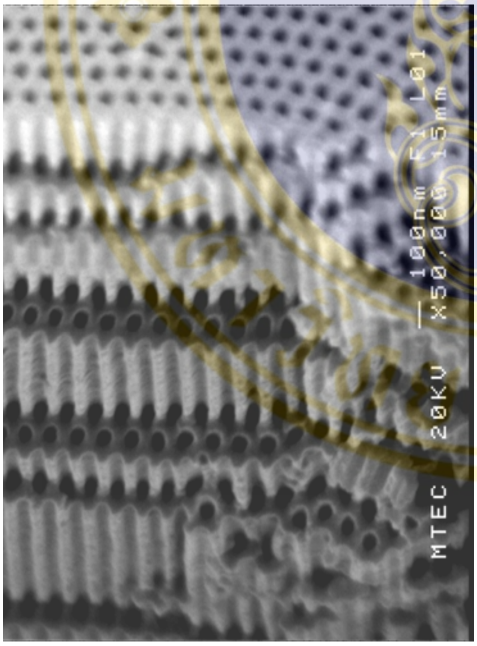


Figure 3.13: Side view of Al_2O_3 shows the fragment.
(Condition:0.3M Oxalic acid, V = 40V)

Figures 3.12 and 3.13 are the side view of alumina after finishing the second anodization step. We were notified the parallel channel which means that the alumina in the second anodization step grown perpendicular to the surface.

3.2.2. The results for all twelve conditions

The anodizing was done under twelve conditions. The common parameters in all the anodizing are the concentration of the acid in the electrolyte and the voltage across the cell. The parameters which were varied were the current and the temperatures. Once the SEM images were taken, a program called “Image Pro” was used to measure the size of each pore. The SPSS package was used to calculate the distribution of the data generated by “Image Pro”. The results of the anodizing under the twelve different conditions are each represented by five figures.

Figures A show the current versus voltage during the first anodizing step.
Figures B show the current versus voltage during the second anodizing step**.**
Figures C show the morphology of alumina obtained by the SEM.
Figures D show the distribution of holes’ diameter.
Figures E show the fraction of total number of holes having a given diameter.

The common parameters used during the anodizing of high purity aluminum are concentration of the acid (0.3M oxalic acid) and the voltage applied across the cell (40 volts).

The temperatures and currents used are

Condition 1) Temperature 26°C. Current 110 mA.
Condition 2) Temperature 26°C. Current 90 mA.
Condition 3) Temperature 26°C. Current 70 mA.
Condition 4) Temperature 26°C. Current 50 mA.
Condition 5) Temperature 21°C. Current 110 mA.
Condition 6) Temperature 21°C. Current 90 mA.
Condition 7) Temperature 21°C. Current 70 mA.
Condition 8) Temperature 21°C. Current 50 mA.
Condition 9) Temperature 16°C. Current 110 mA.
Condition 10) Temperature 16°C.Current 90 mA.
Condition 11) Temperature 16°C.Current 70 mA.
Condition 12) Temperature 16°C.Current 50 mA.

After the images of the anodizing under the twelve conditions were obtained, the analyses of the pore size were done. The results were then plotted together to determine whether there was any correlation of the pore size distribution with either the currents or temperature used.

These sets of graph show the current versus time and the voltage versus time in the same axis of time. Figures 3.A1-3.A12 are the twelve graphs for first anodization step and figures 3.B1-3.B12 are the twelve graphs for second anodization step. We collect current and voltage by the computer because we would like to know the behavior of them. We notice that they are changed during first time period. These changes occur quickly so only the computer could collect the data. The computer recorded the data every 0.5 second. . These graphs were plotted on a graph having a logarithm time axis. The temperature used in every condition had an error ± 0.5 ºC.

3.2.2.1 The current and voltage graph of first anodizing for twelve conditions.

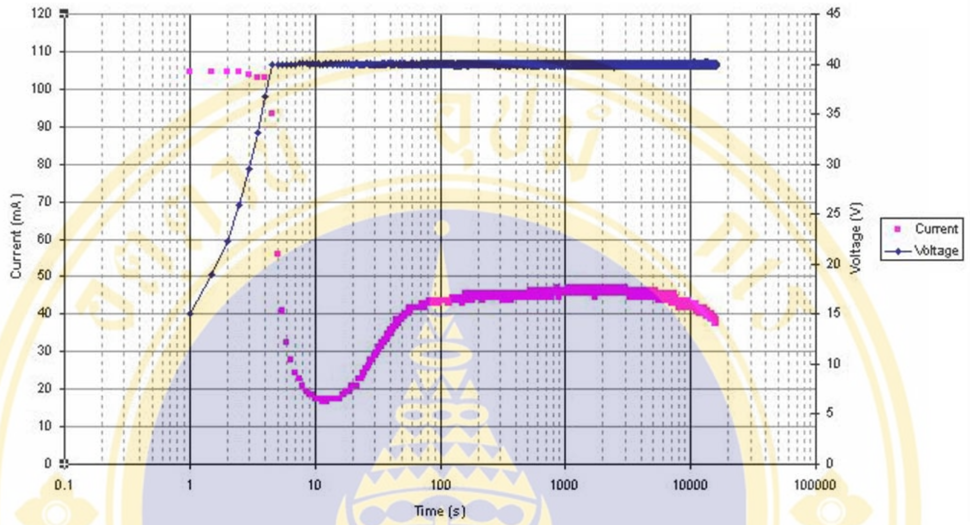


Figure 3.A1: Condition 1) 1st anodization at temperature of 26°C. Current is 110 mA.

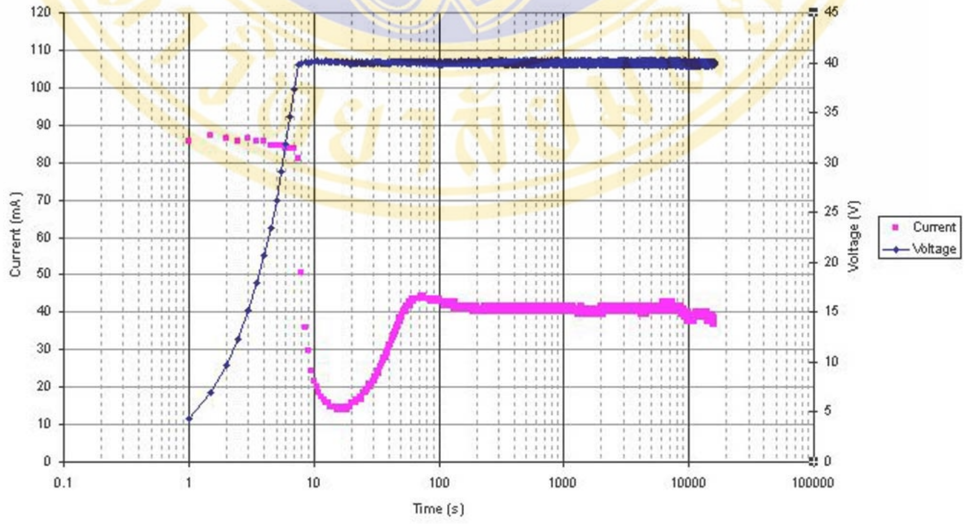


Figure 3.A2: Condition 2) 1st anodization at temperature of 26°C. Current is 90 mA.

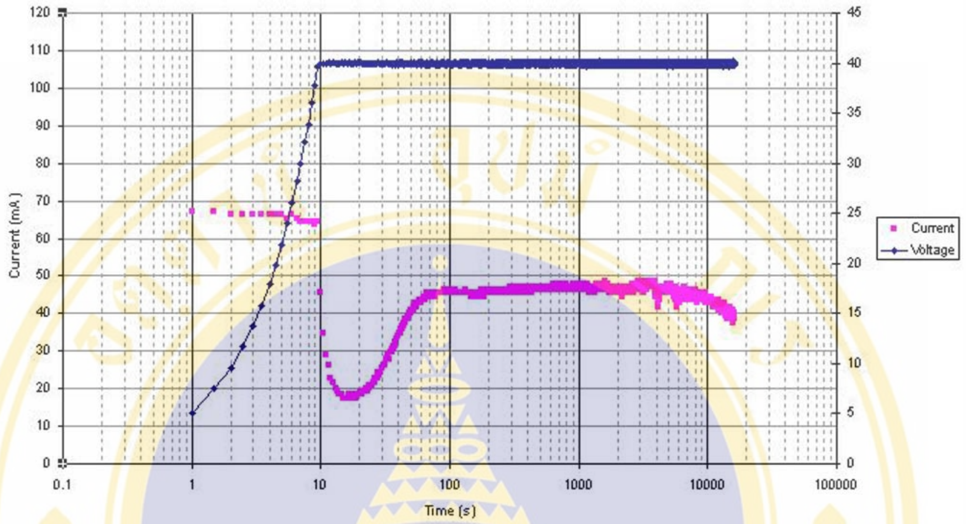


Figure 3.A3: Condition 3) 1st anodization at temperature of 26°C. Current is 70 mA.

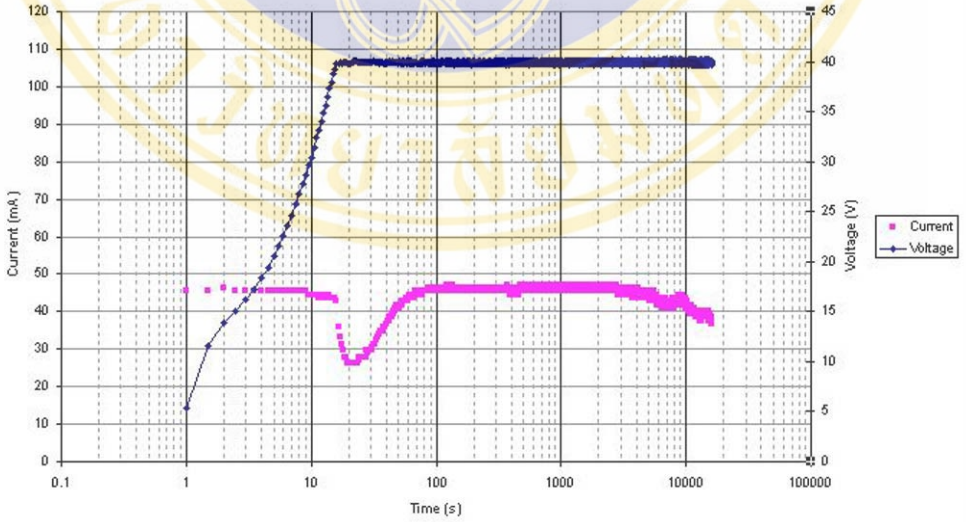


Figure 3.A4: Condition 4) 1st anodization at temperature of 26°C. Current is 50 mA.

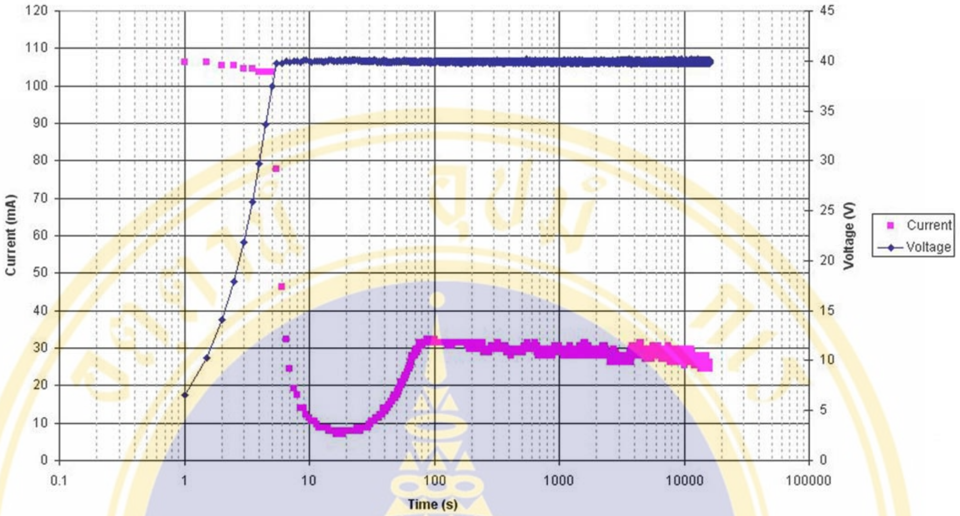


Figure 3.A5: Condition 5) 1st anodization at temperature of 21°C. Current is 110 mA.

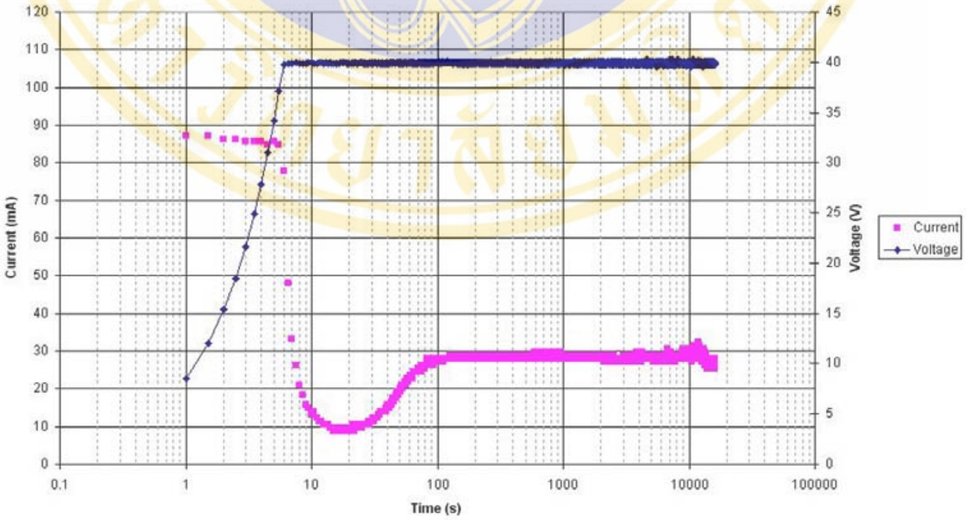


Figure 3.A6: Condition 6) 1st anodization at temperature of 21°C. Current is 90 mA.

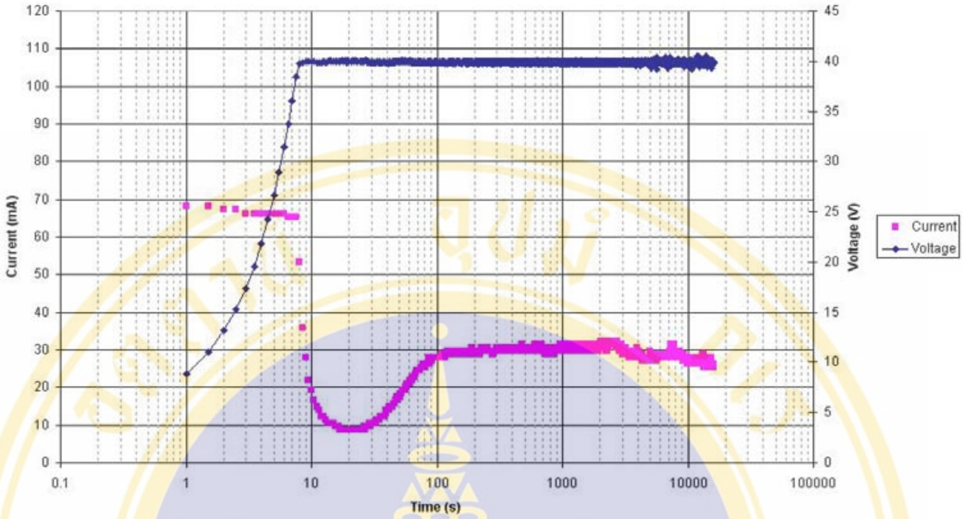


Figure 3.A7: Condition 7) 1st anodization at temperature of 21°C. Current is 70 mA.

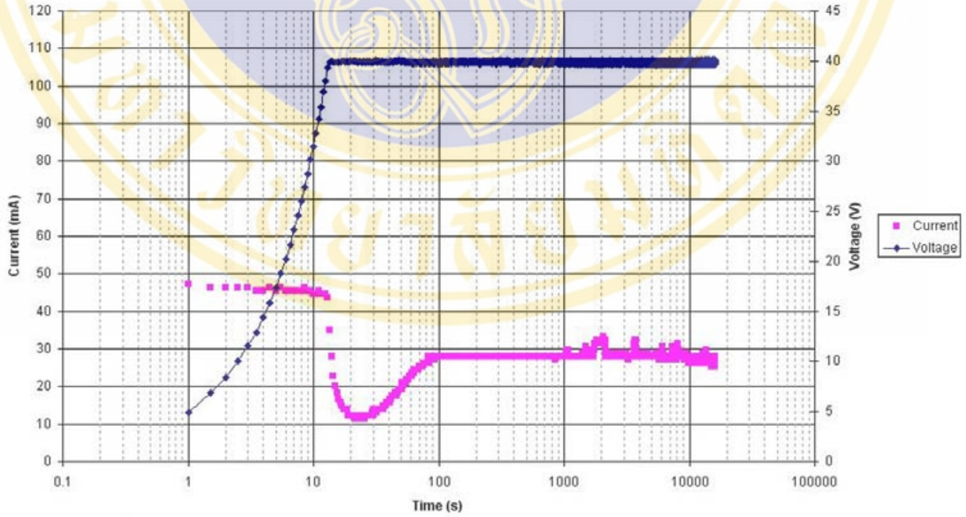


Figure 3.A8: Condition 8) 1st anodization at temperature of 21°C. Current is 50 mA.

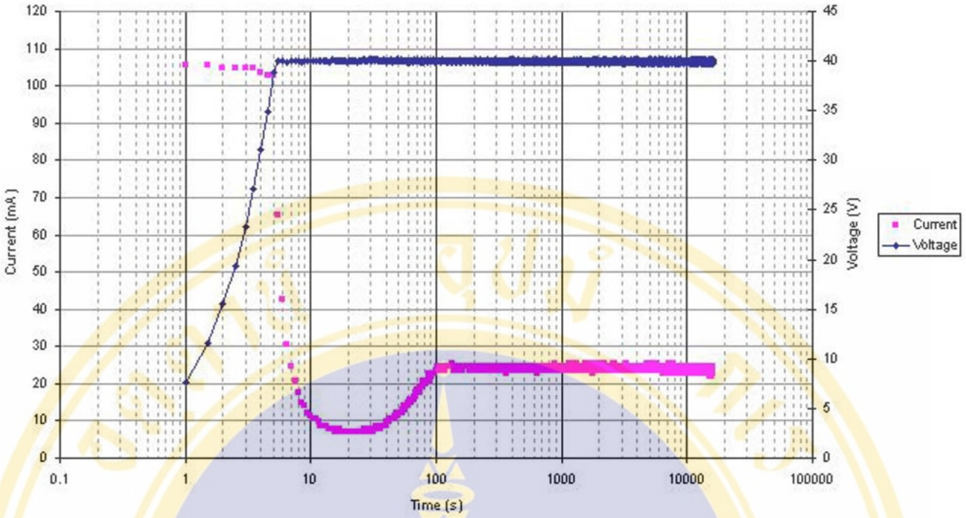


Figure 3.A9: Condition 9) 1st anodization at temperature of 16°C. Current is 110 mA.

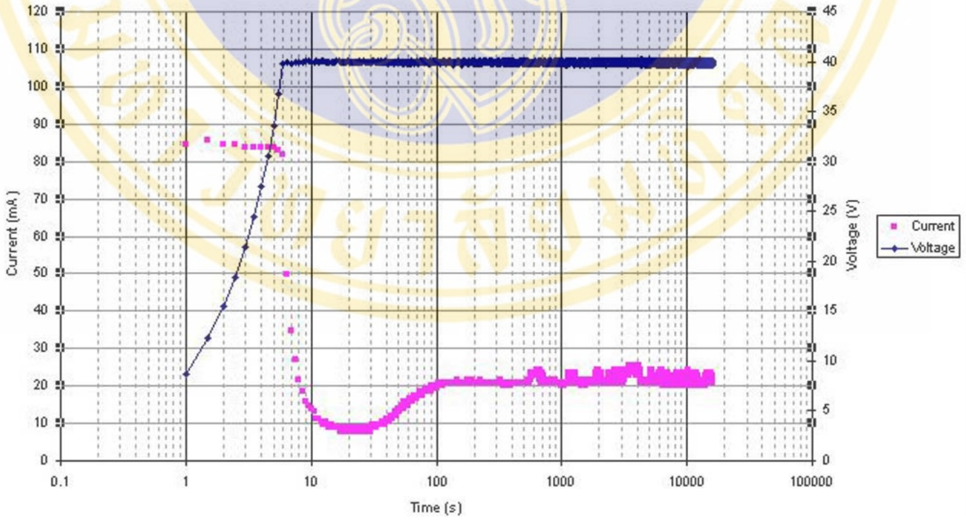


Figure 3.A10: Condition 10) 1st anodization at temperature of 16°C.
Current is 90 mA.

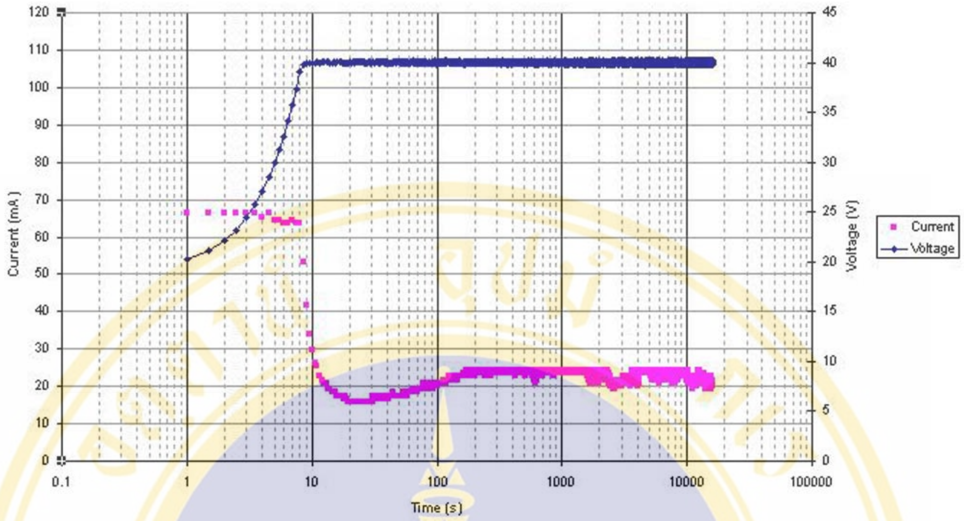


Figure 3.A11: Condition 11) 1st anodization at temperature of 16°C.
Current is 70 mA.

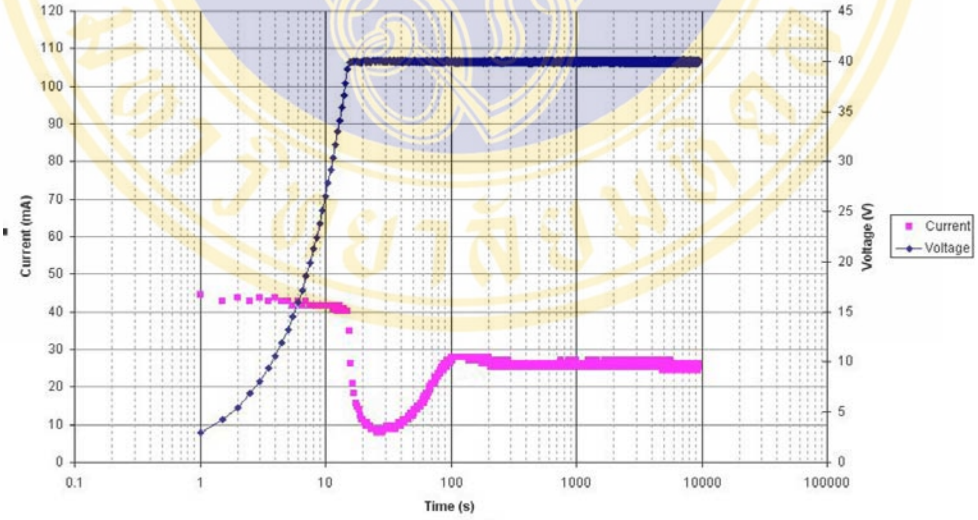


Figure 3.A12: Condition 12) 1st anodization at temperature of 16°C.
Current is 50 mA.

3.2.2.2 The current and voltage graph of second anodizing under the twelve conditions.

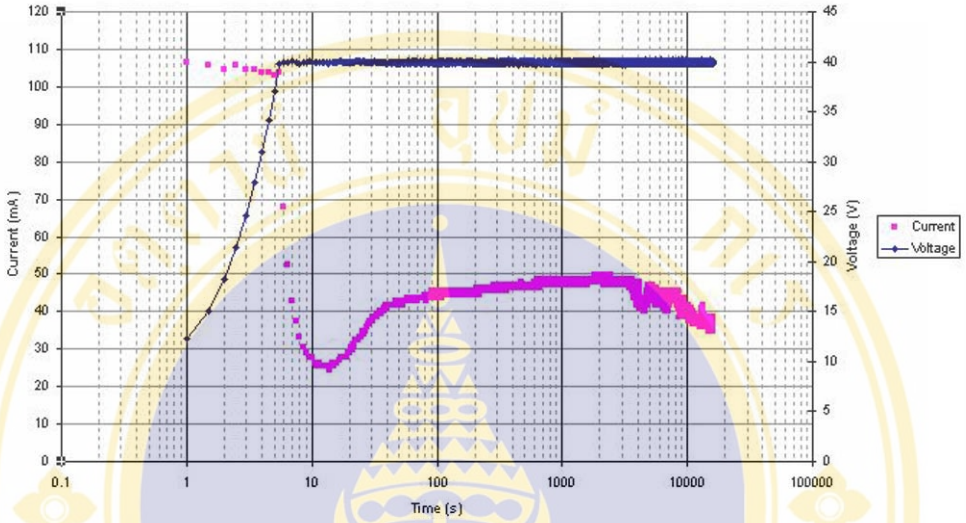


Figure 3.B1: Condition 1) 2st anodization at Temperature of 26°C. Current is 110 mA.

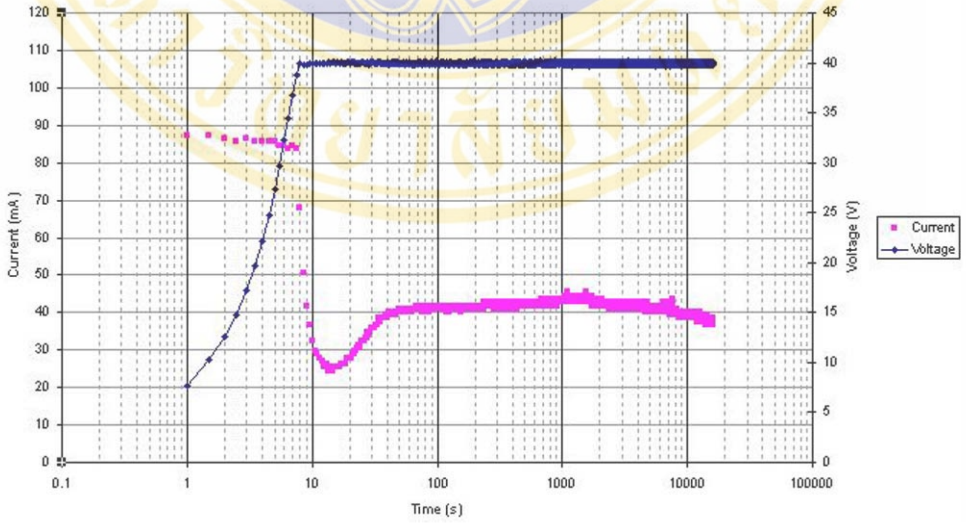


Figure 3.B2: Condition 2) 2st anodization at temperature of 26°C. Current is 90 mA.

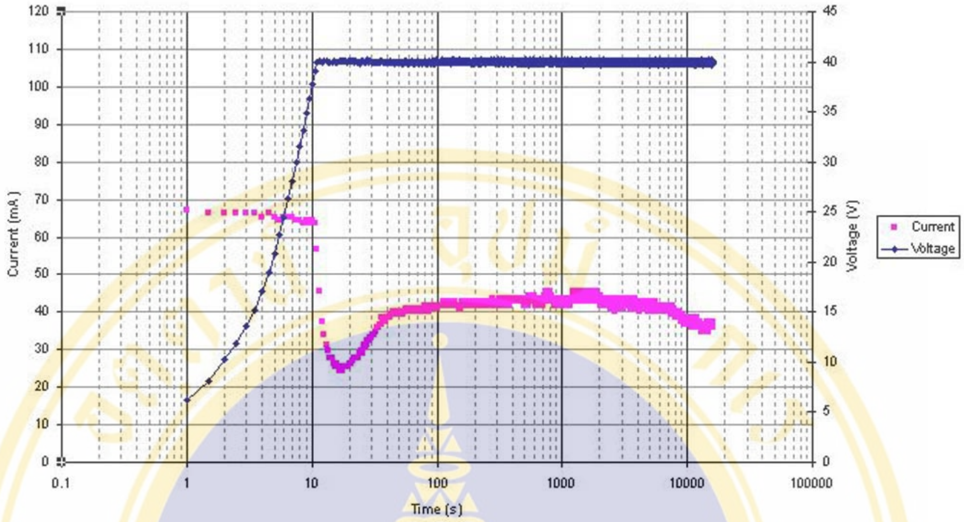


Figure 3.B3: Condition 3) 2st anodization at temperature of 26°C. Current is 70 mA.

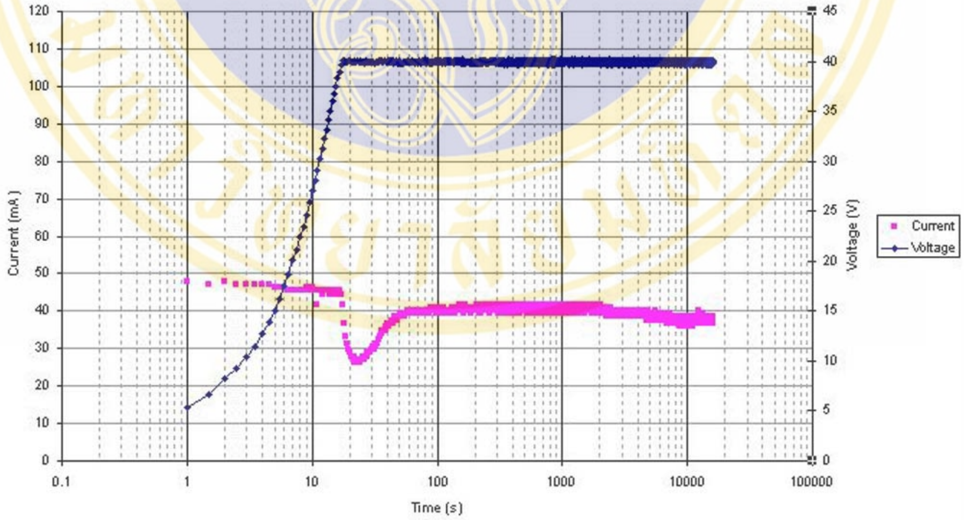


Figure 3.B4: Condition 4) 2st anodization at temperature of 26°C. Current is 50 mA.

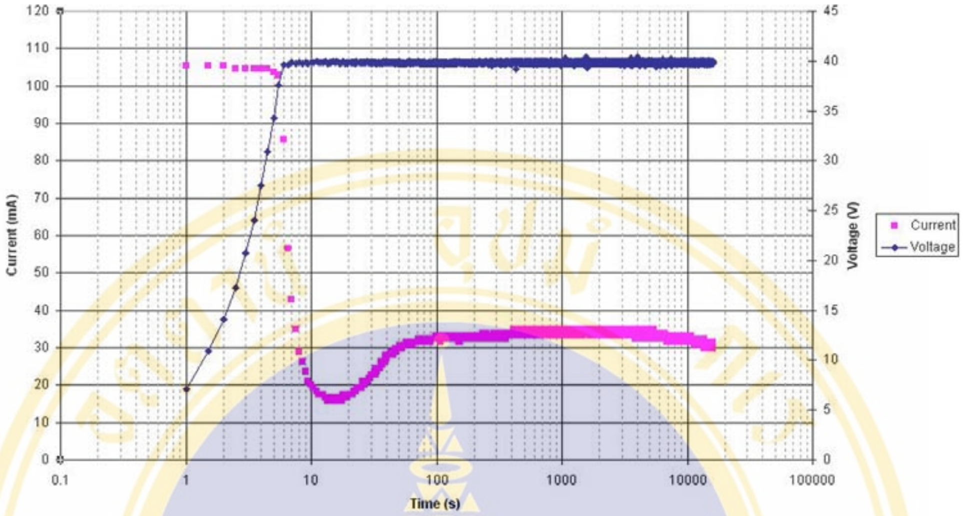


Figure 3.B5: Condition 5) 2st anodization at temperature of 21°C. Current is 110 mA.

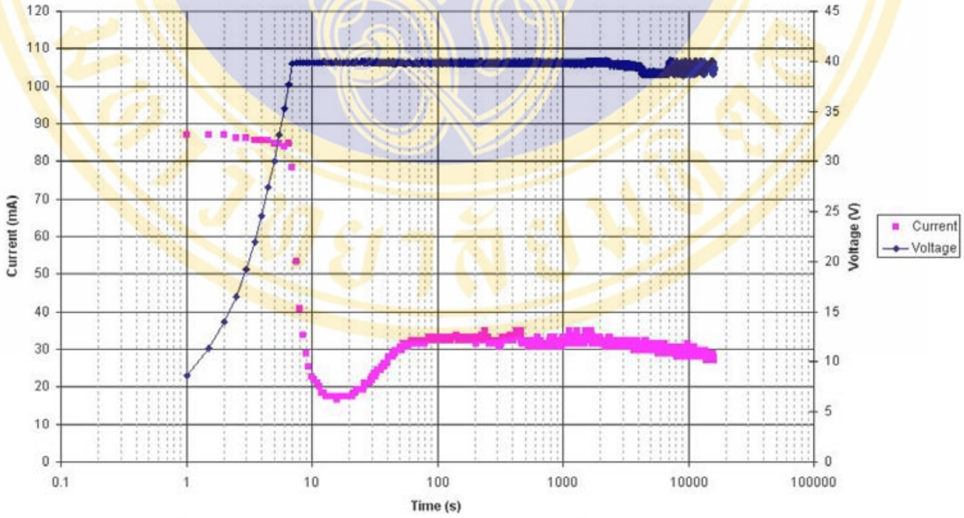


Figure 3.B6: Condition 6) 2st anodization at temperature of 21°C. Current is 90 mA.

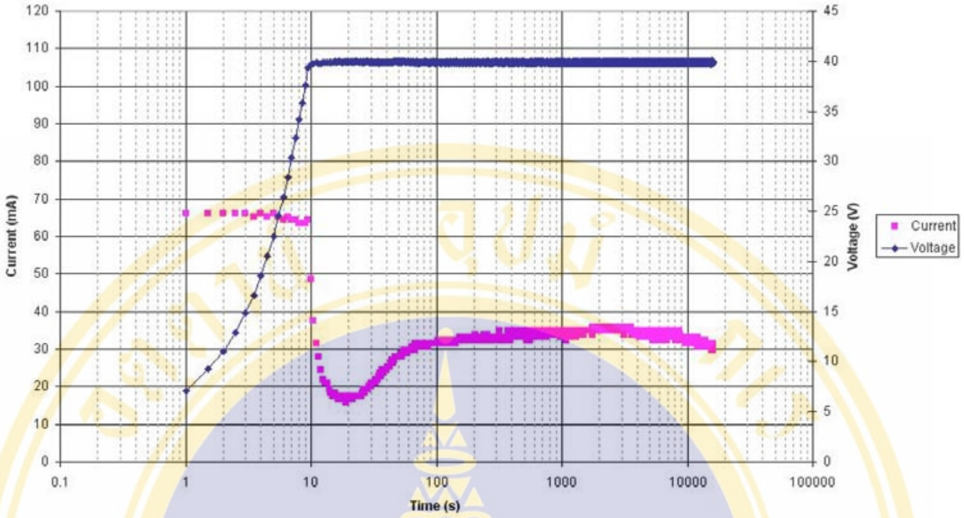


Figure 3.B7: Condition 7): 2st anodization at temperature of 21°C. Current is 70 mA.

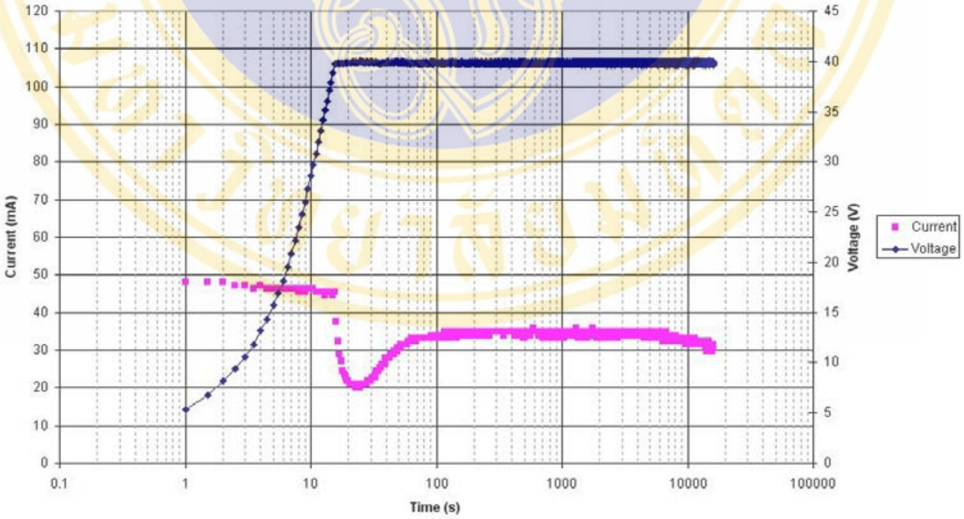


Figure 3.B8: Condition 8) 2st anodization at temperature of 21°C. Current is 50 mA.

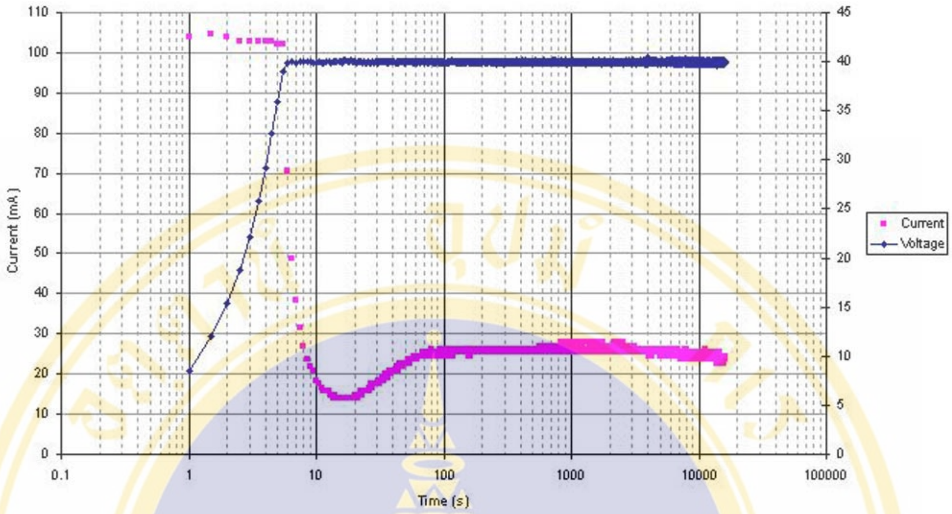


Figure 3.B9: Condition 9) 2st anodization at temperature of 16°C. Current is 110 mA.

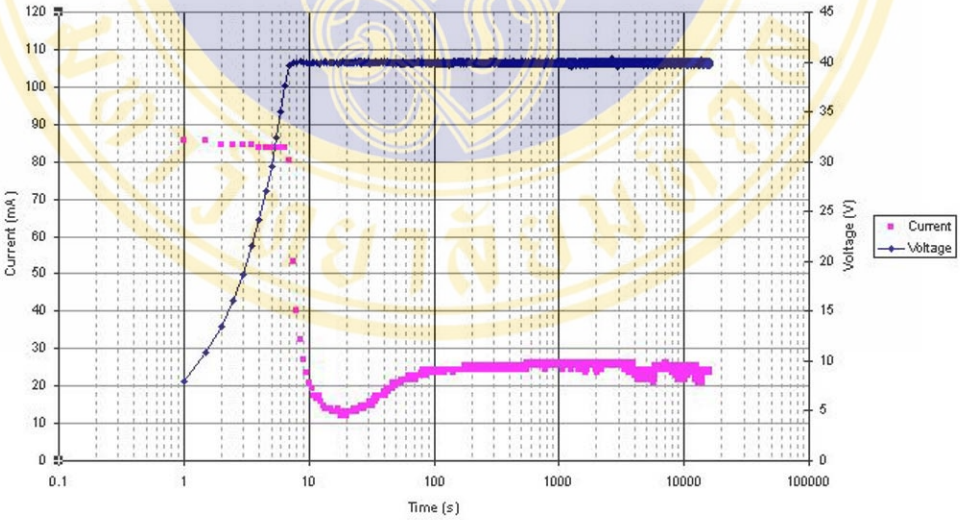


Figure 3.B10: Condition 10) 2st anodization at temperature of 16°C.
Current is 90 mA.

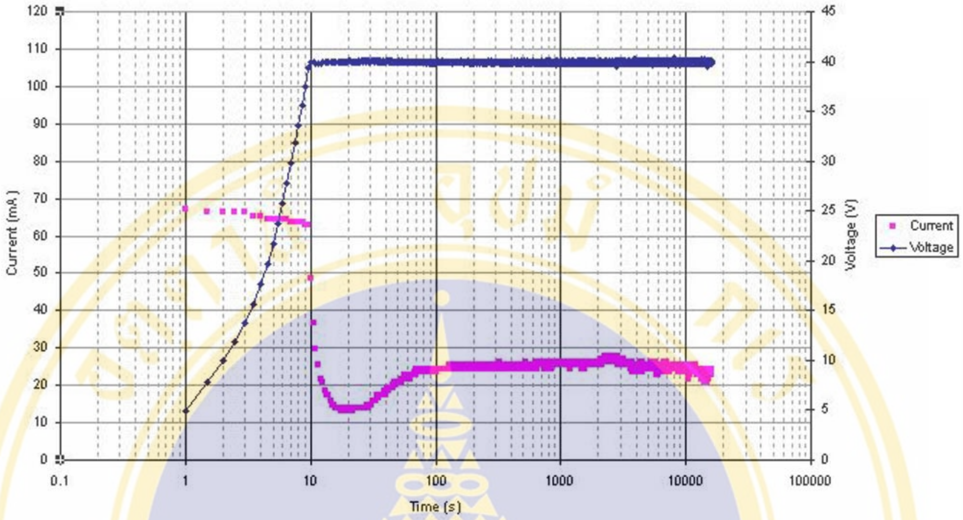


Figure 3.B11: Condition 11) 2st anodization at temperature of 16°C.
Current is 70 mA.

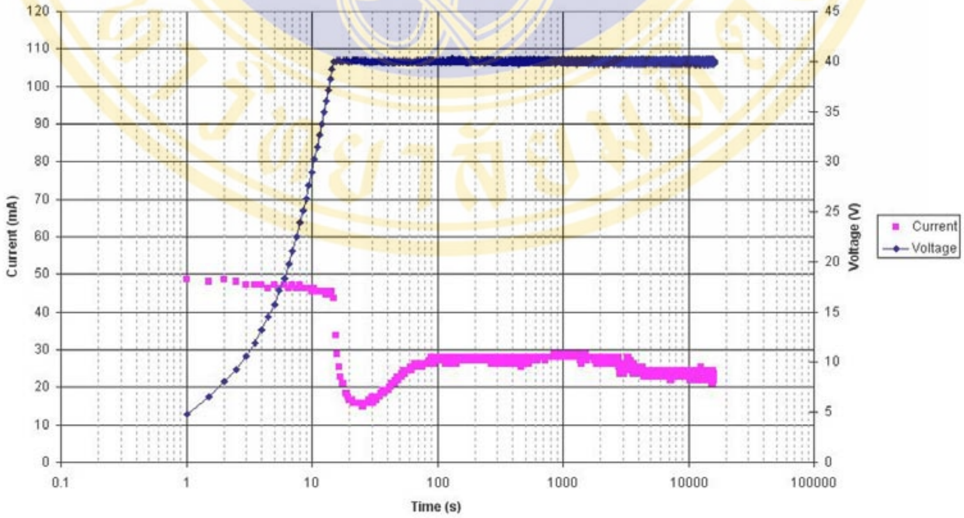


Figure 3.B12: Condition 12) 2st anodization at temperature of 16°C.
Current is 50 mA.

In the figures of current above, we have separated the current into four parts as shown in the picture below

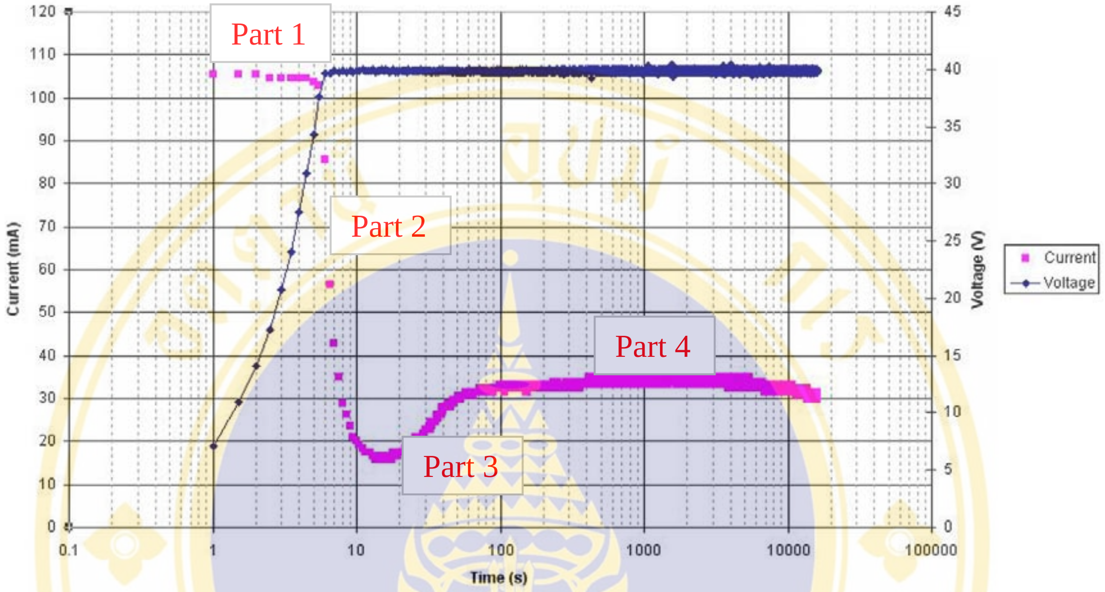


Figure 3.14: The four parts of current density.

In the above figure 3.14, the current during part 1 is seen to decrease slightly. This correlates with the increase in the voltage. When the voltage reaches 40 volts, the current decrease quickly to its lowest point. The current then begins to increase. This increase occurs in a relatively short period. After the process reaches its equilibrium condition, the current will remain constant for quite a while. After a long time, the current will decrease slightly as seen in part 4.

In part 2, the Al_2O_3 grows into a thick layer very fast. Since it is the non conductive layer, the current will drop quickly. After awhile the current reach the lowest point which Al_2O_3 begin to form pits in the layer. Then Al_2O_3 begin to dissolve at the Al_2O_3 - electrolyte interface. The current increase. When the oxidation of aluminum and the dissolving of Al_2O_3 are in equilibrium, therefore the current will be constant. Over long period of time, part 4, the pore becomes deeper and the Al_2O_3 layer becomes thicker layer. This causes the current decrease slightly because the O^{2-} in electrolyte takes time to travel to the bottom of the pore to form new Al_2O_3. The rate of growth Al_2O_3 therefore decreases.

3.2.2.3 The morphology of alumina with SEM image for twelve conditions

The morphology of the alumina is recorded by the SEM having a magnification power of 25,000 times. The picture was print on a photo film. Then that photo was scanned by a scanner with the resolution of 2,500 dots/pixel. The picture of Al_2O_3 is observed in two dimensions. Every region of ordered array of pores are separated by boundaries. Some regions are big, some regions are small and the regions may have the different orientation. We see some defects at the boundaries of the regions and some defects (white spot) occur within the region. All the SEM pictures were investigated by Image Pro program. This program calculates area and diameter of each hole. This data was used to analyze the average size of hole diameter for every condition.

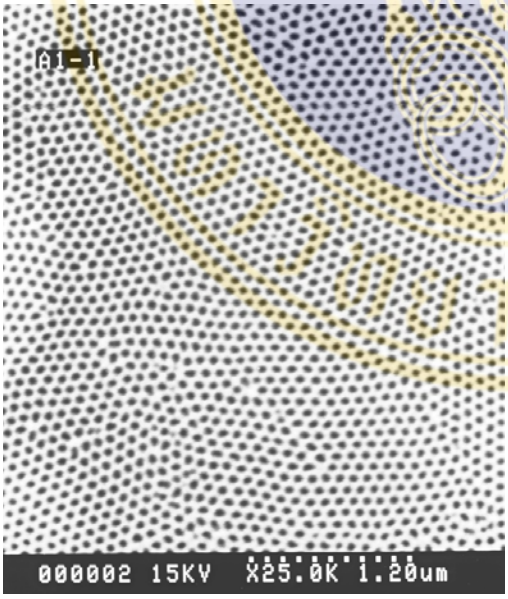


Figure 3.C1: Condition 1) Morphology at temperature of 26°C. Current is 110 mA.

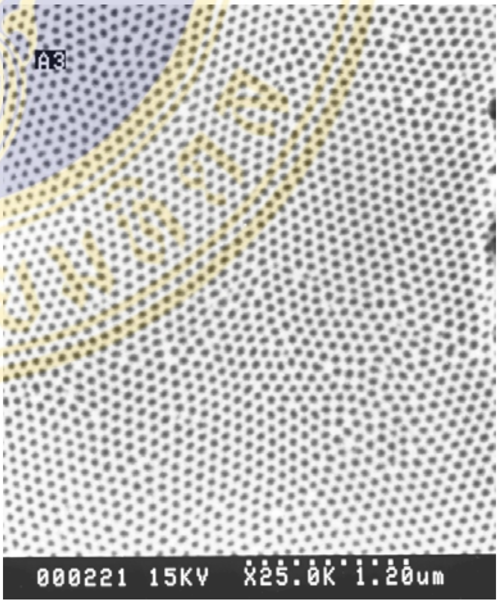


Figure 3.C2: Condition 2) Temperature is 26°C. Current is 90 mA.

Figure 3.C3: Condition 3) Temperature is 26°C. Current is 70 mA.

Figure 3.C4: Condition 4) Temperature is 26°C. Current is 50 mA.

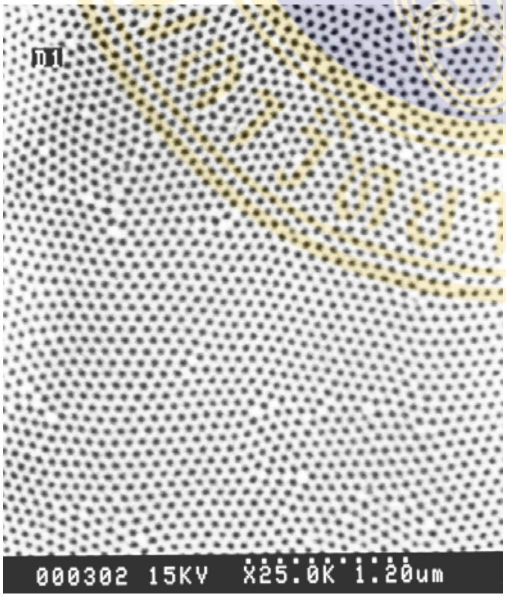


Figure 3.C5: Condition 5) Temperature is 21°C. Current is 110 mA

Figure 3.C6: Condition 6) Temperature is 21°C. Current is 90 mA

Figure 3.C7: Condition 7) Temperature is 21°C. Current is 70 mA

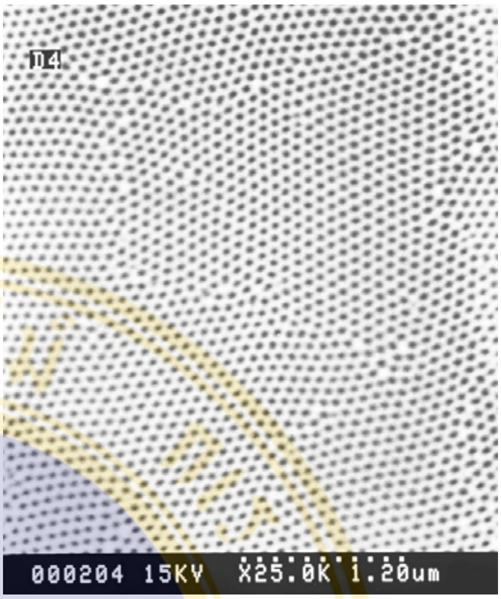


Figure 3.C8: Condition 8) Temperature is 21°C. Current is 50 mA

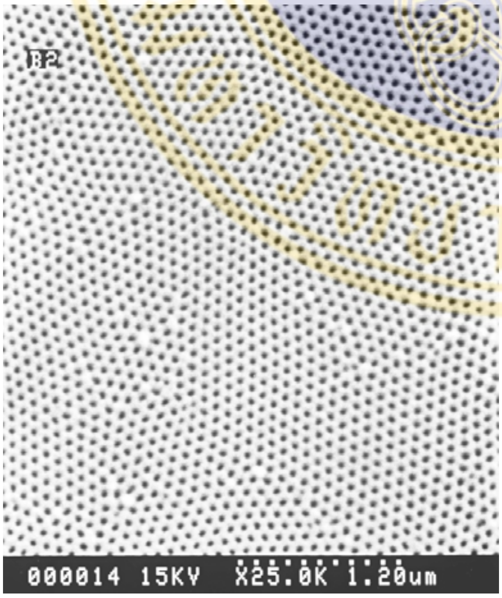


Figure 3.C9: Condition 9) Temperature is 16°C. Current is 110 mA

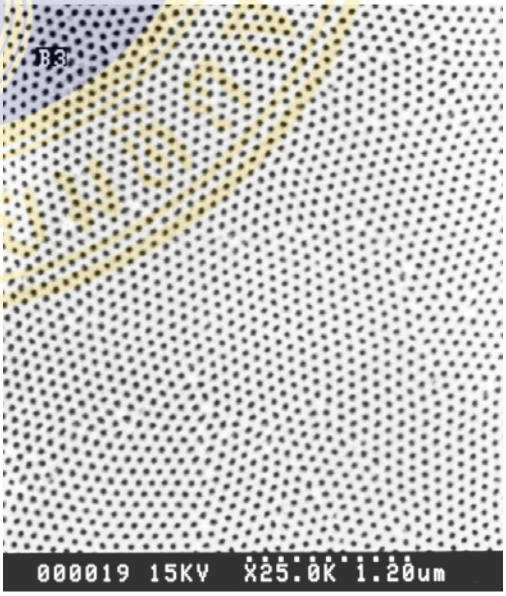


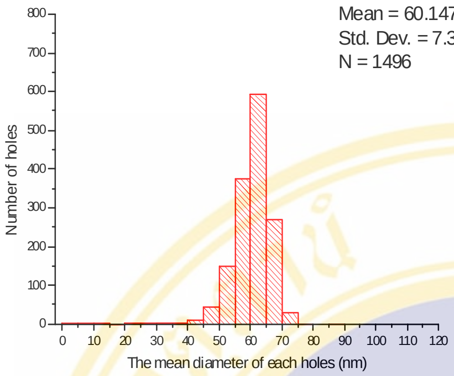
Figure 3.C10: Condition 10) Temperature is 16°C. Current is 90 mA

Figure 3.C11: Condition 11) Temperature is 16°C. Current is 70 mA

Figure 3.C12: Condition 12) Temperature is 16°C. Current is 50 mA

3.2.2.4. The distribution of holes' diameter for the twelve anodizing conditions.

The data from the Image Pro program was use to calculate the average size of hole diameter and standard deviation by using a SPSS program. The mean diameter and standard deviation was plotted versus in both current and temperature which are shown in next section. The Origin program was used to plot histograms where we notice that the anodizing done 16 ºC produced pores having sharper distribution in pore size than those produced at higher temperatures.



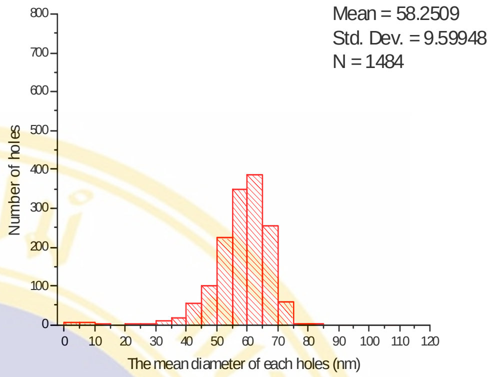
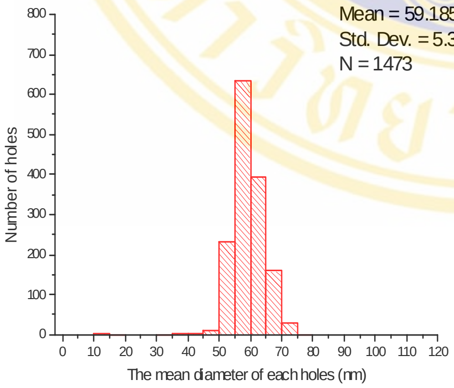


Figure 3.D1: Condition 1) Distribution of holes at temperature of 26°C. Current is 110 mA.

Figure 3.D2: Condition 2) Temperature is 26°C. Current is 90 mA.



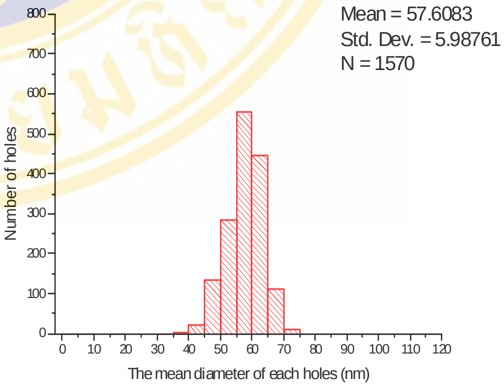


Figure 3.D3: Condition 3) Temperature is 26°C. Current is 70 mA.

Figure 3.D4: Condition 4) Temperature is 26°C. Current is 50 mA.

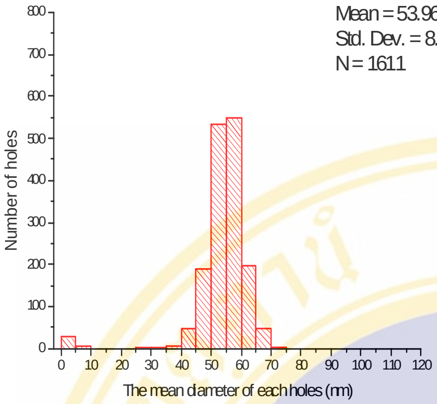


Figure 3.D5: Condition 5) Temperature is 21°C. Current is 110 mA

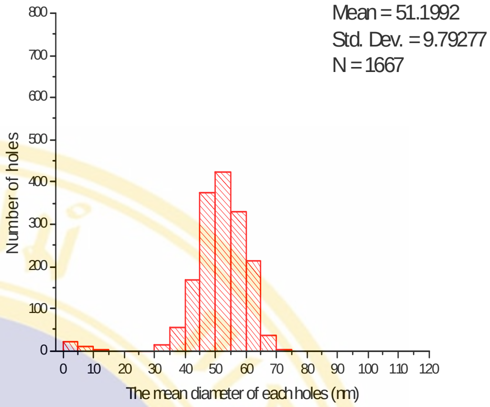


Figure 3.D6: Condition 6) Temperature is 21°C. Current is 90 mA

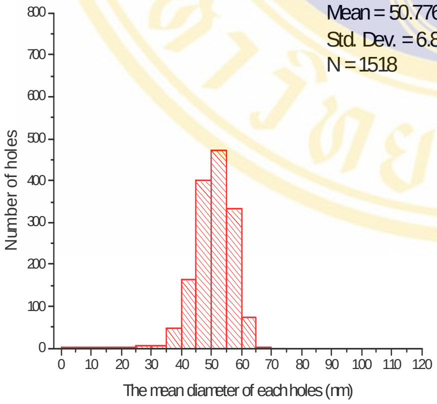


Figure 3.D7: Condition 7) Temperature is 21°C. Current is 70 mA

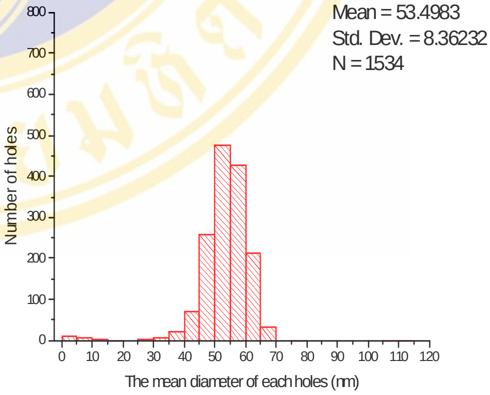


Figure 3.D8: Condition 8) Temperature is 21°C. Current is 50 mA

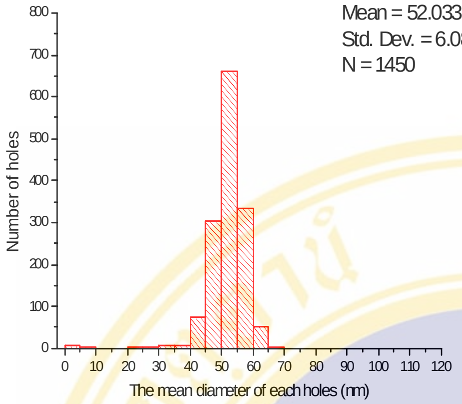


Figure 3.D9: Condition 9) Temperature is 16°C. Current is 110 mA

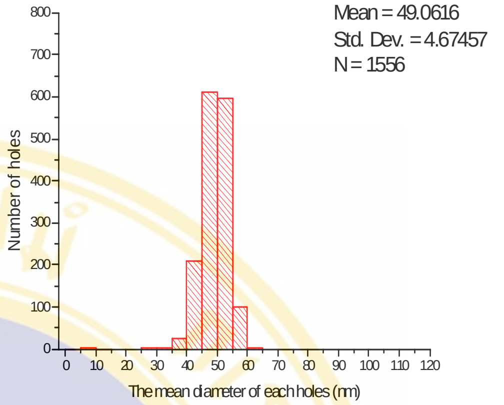


Figure 3.D10: Condition 10)Temperature is 16°C. Current is 90 mA

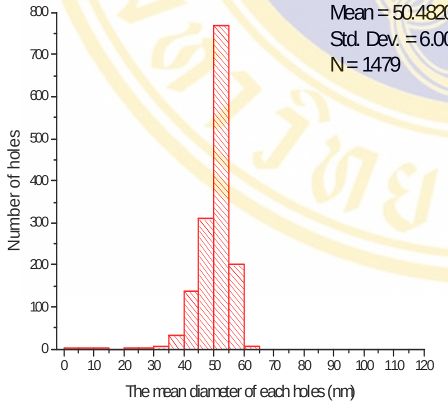


Figure 3.D11: Condition 11)Temperature is 16°C. Current is 70 mA

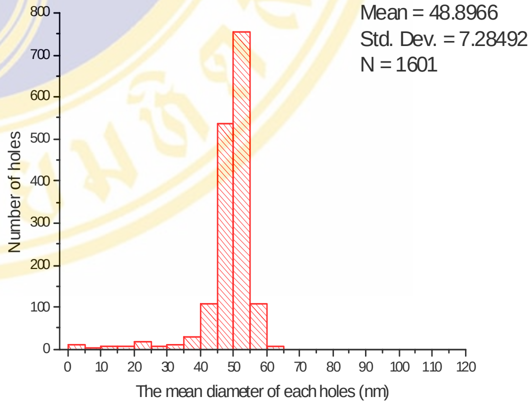
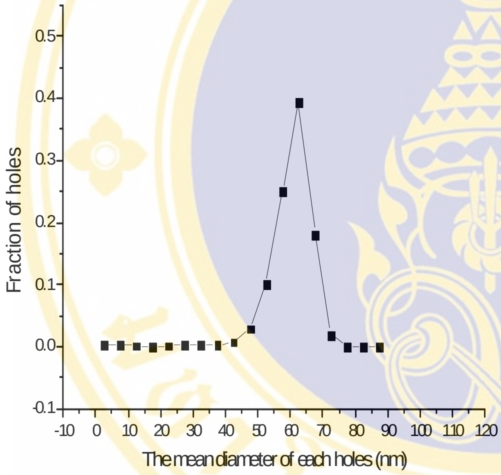


Figure 3.D12: Condition 12)Temperature is 16°C. Current is 50 mA

3.2.2.5 The fraction of holes having different sizes for the twelve conditions.

Since the number of holes are not the same in every picture, we normalize the histogram graph by divide every column with the total hole number for each picture. Doing this, we got the fraction of holes of each size. We plotted graph again with Y-axis normalized. We see that, the temperature 16 ºC, the top of the normalized graph is close to 0.5. It means that half of the total holes have the same size.



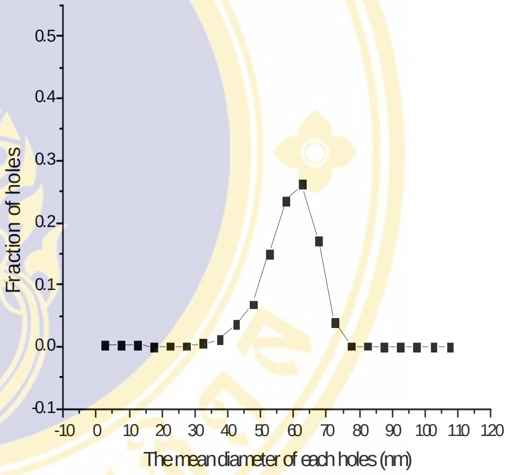


Figure 3.E1: Condition 1) Temperature is 26°C. Current is 110 mA.

Figure 3.E2: Condition 2) Temperature is 26°C. Current is 90 mA.

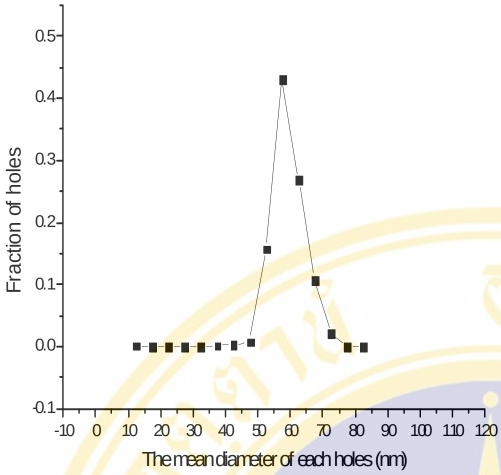


Figure 3.E3: Condition 3) Temperature is 26°C. Current is 70 mA.

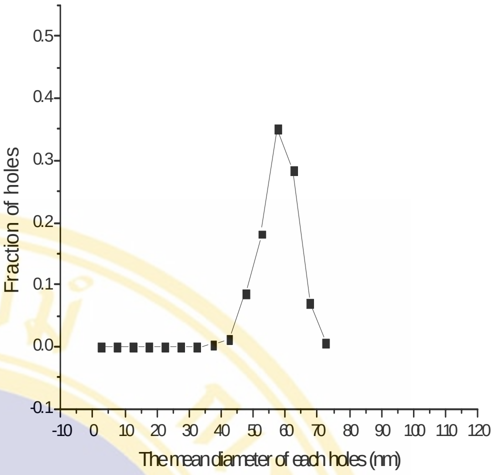


Figure 3.E4: Condition 4) Temperature is 26°C. Current is 50 mA.

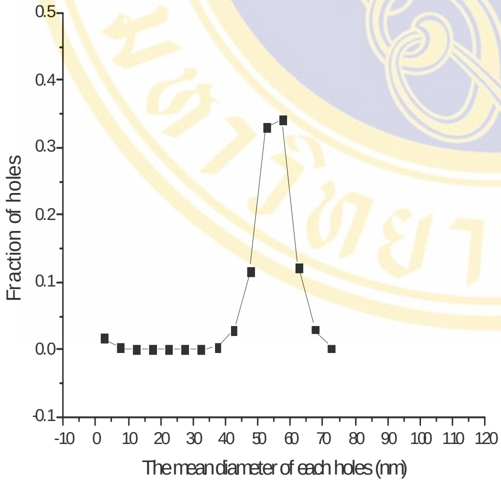


Figure 3.E5: Condition 5) Temperature is 21°C. Current is 110 mA

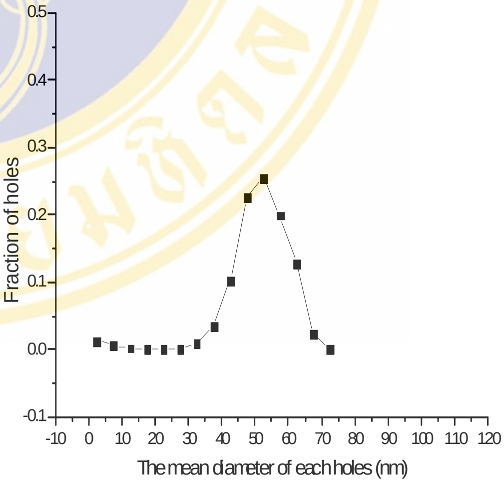


Figure 3.E6: Condition 6) Temperature is 21°C. Current is 90 mA

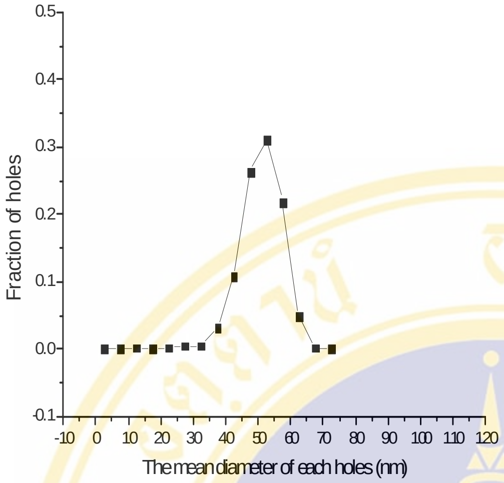


Figure 3.E7: Condition 7) Temperature is 21°C. Current is 70 mA

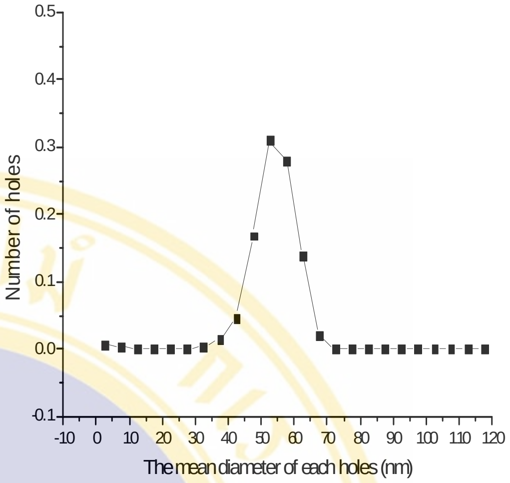


Figure 3.E8: Condition 8) Temperature is 21°C. Current is 50 mA

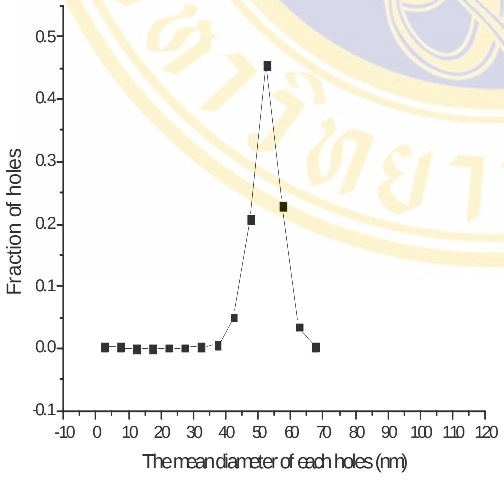


Figure 3.E9: Condition 9) Temperature is 16°C. Current is 110 mA

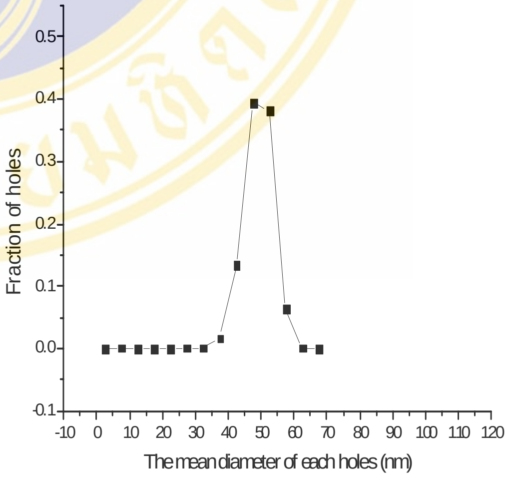


Figure 3.E10: Condition 10) Temperature is 16°C. Current is 90 mA

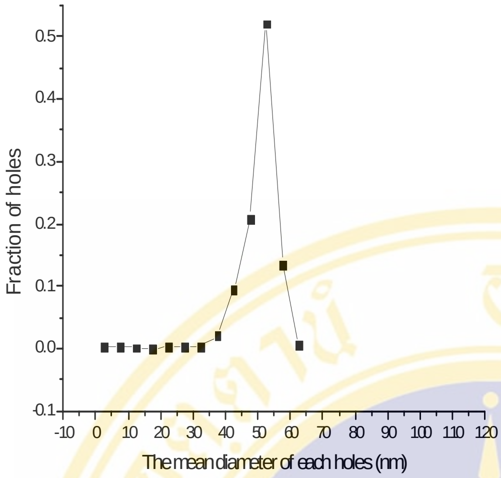


Figure 3.D11: Condition 11)Temperature is 16°C. Current is 70 mA

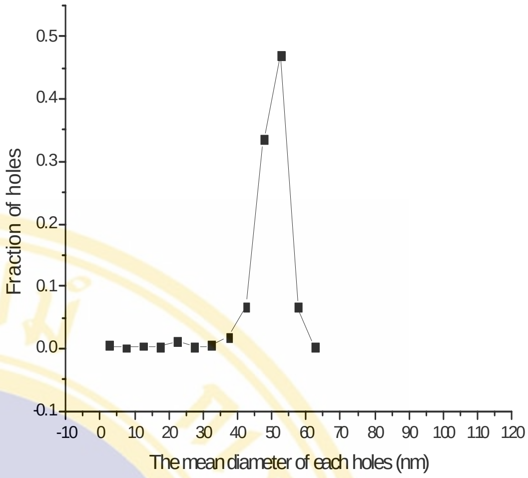
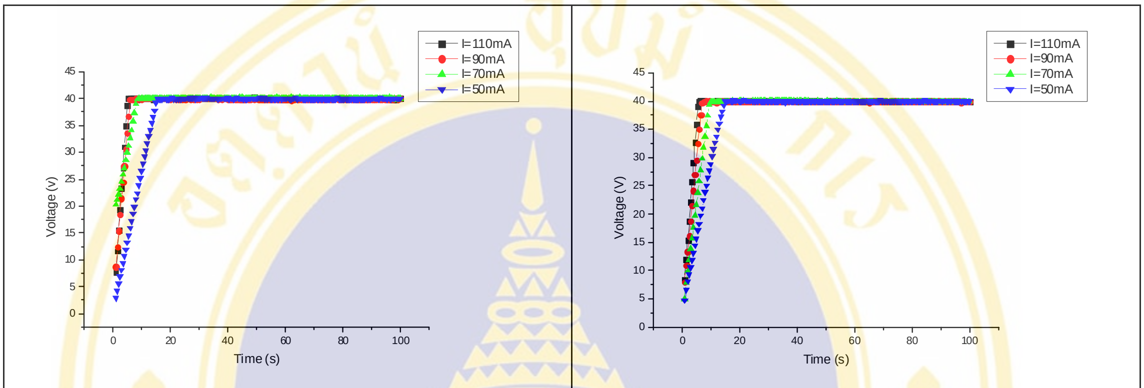


Figure 3.E12: Condition 12) Temperature is 16°C. Current is 50 mA

3.2.3 The analysis of the processes

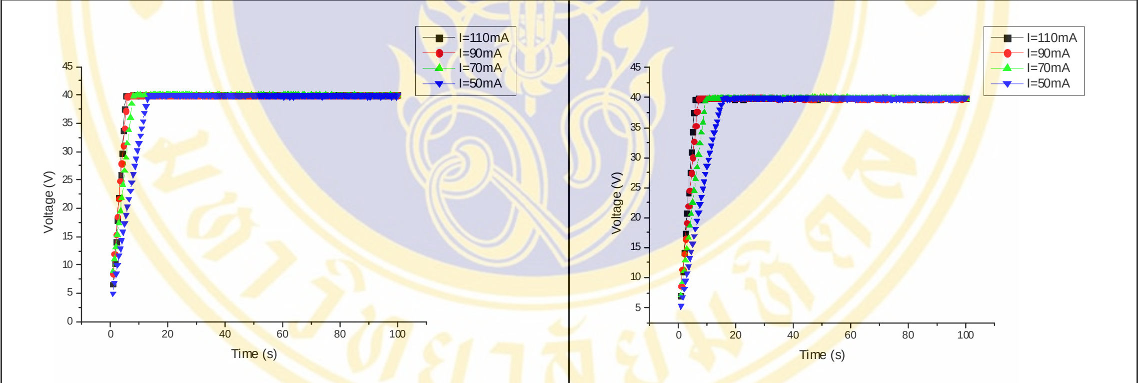
The analysis of the data such as current, voltage, diameter and stand deviation for each was done.

3.2.3.1 Analysis of voltage



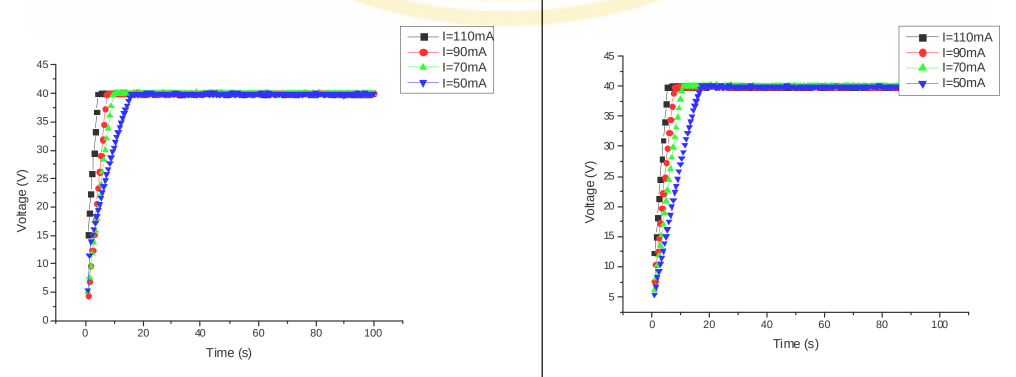
First anodizing step at T =16°C

Second anodizing step at T =16°C



First anodizing step at T =21°C

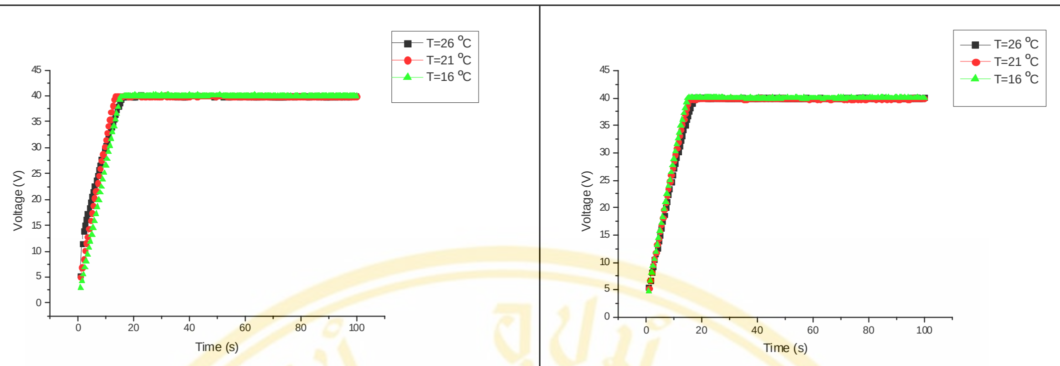
Second anodizing step at T =21°C



First anodizing step at T =26°C

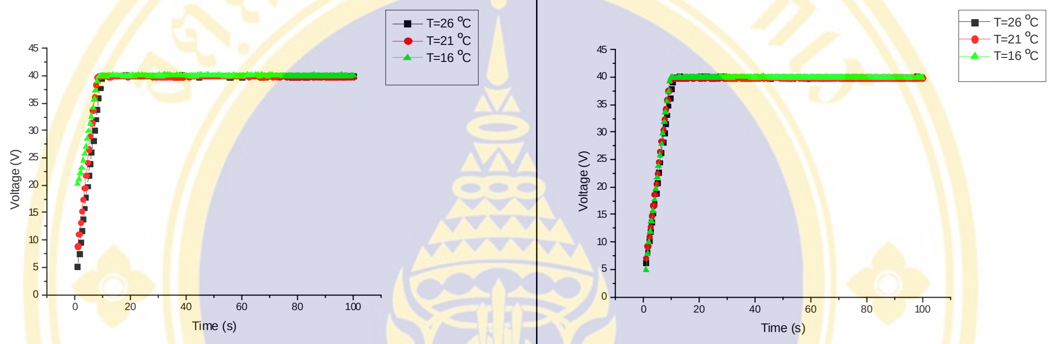
Second anodizing step at T =26°C

Figure 3.15: Time evolution of the voltages at for different currents during the first and second anodizing steps when different temperatures are used.



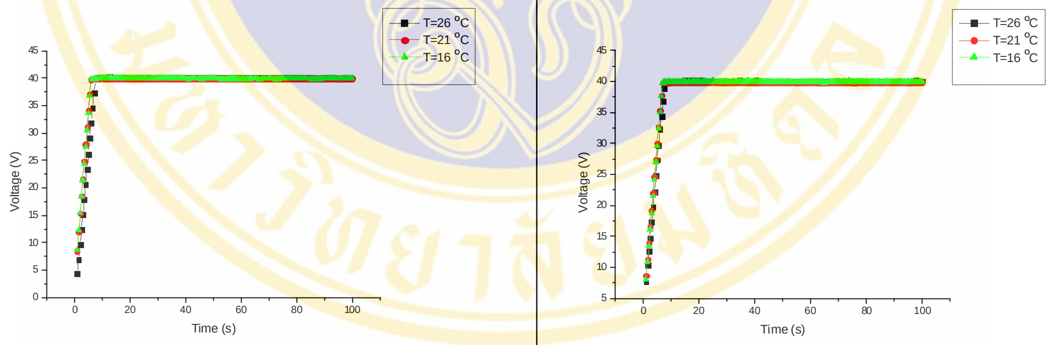
First anodizing step with I = 50mA

Second anodizing step with I = 50mA



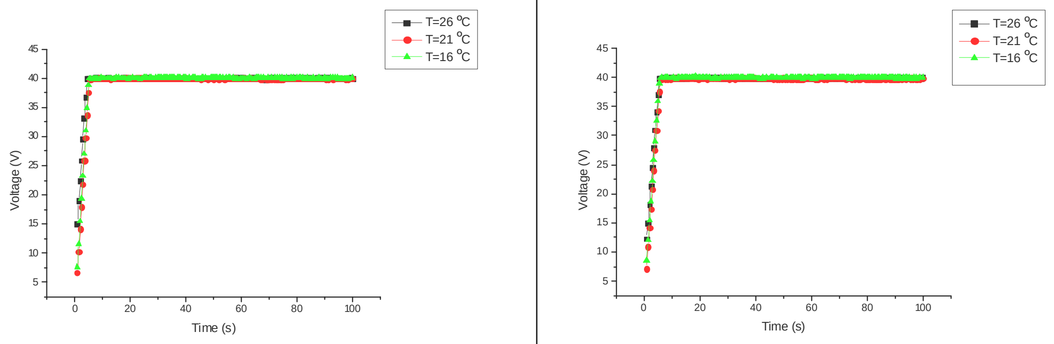
First anodizing step with I = 70mA

Second anodizing step with I = 70mA



First anodizing step with I = 90mA

Second anodizing step at I = 90mA

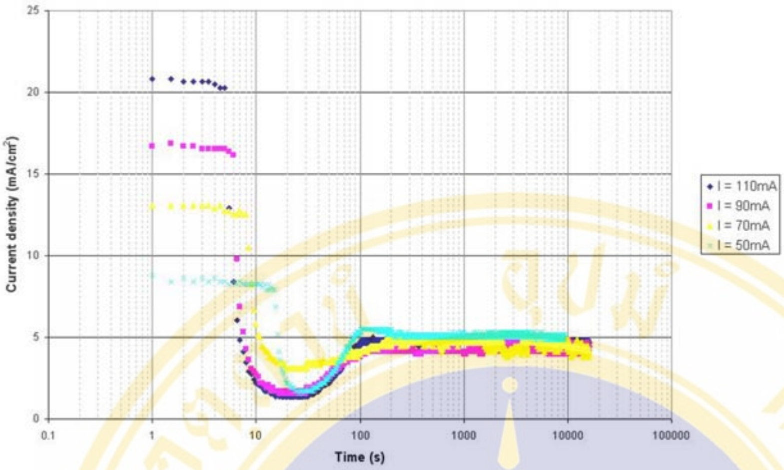


First anodizing step with I = 110mA

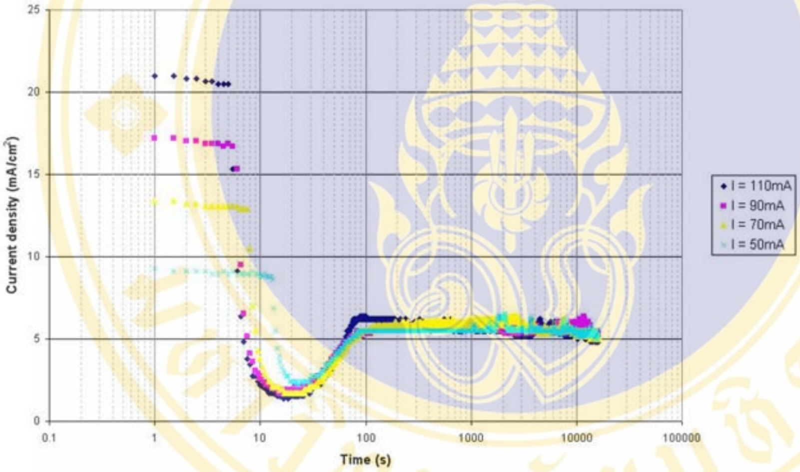
Second anodizing step with I = 110mA

Figure 3.16: Time evolution of the voltages at different temperatures during the first and second anodizing steps.

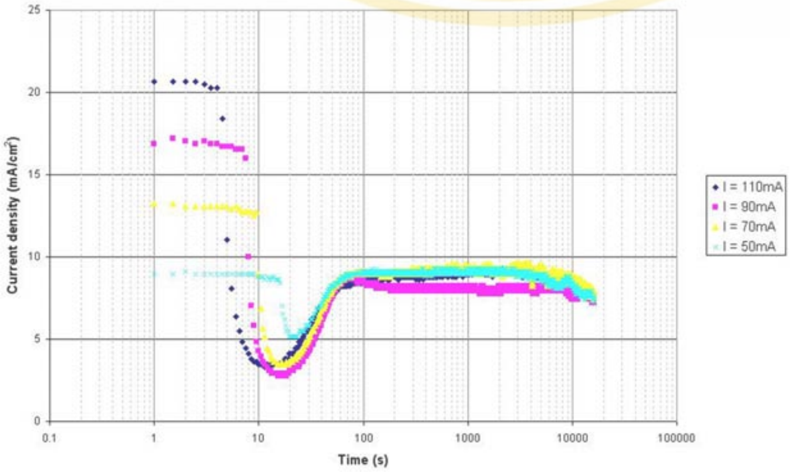
3.2.3.2 Analysis of current density



First anodizing step with T=16°C

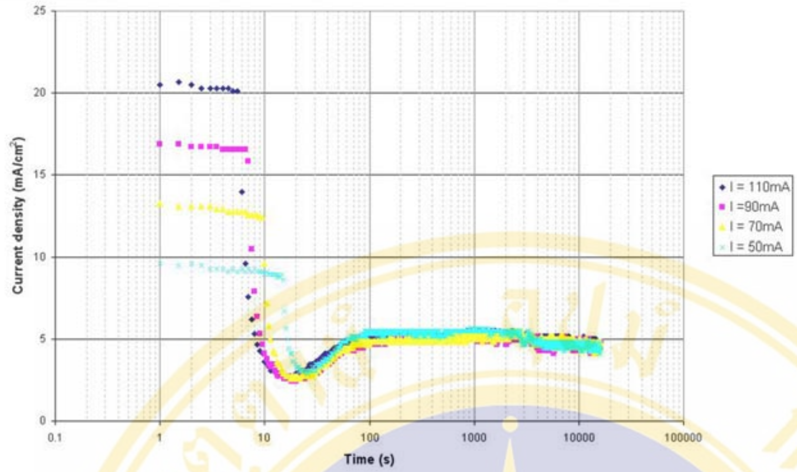


First anodizing step with T=21°C

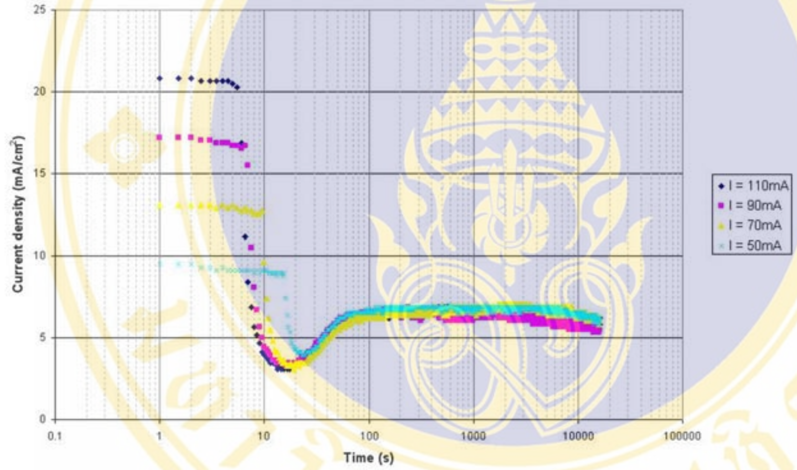


First anodizing at T=26°C

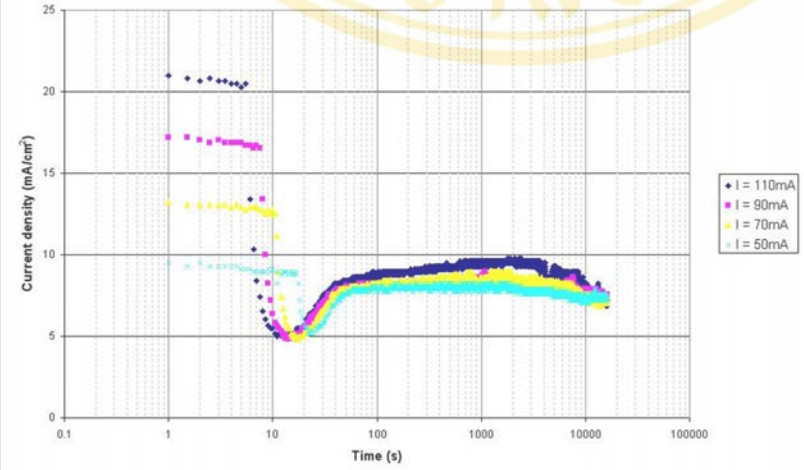
Figure 3.17: Current density as a function of time during the first anodizing step.



Second anodizing step with T=16°C

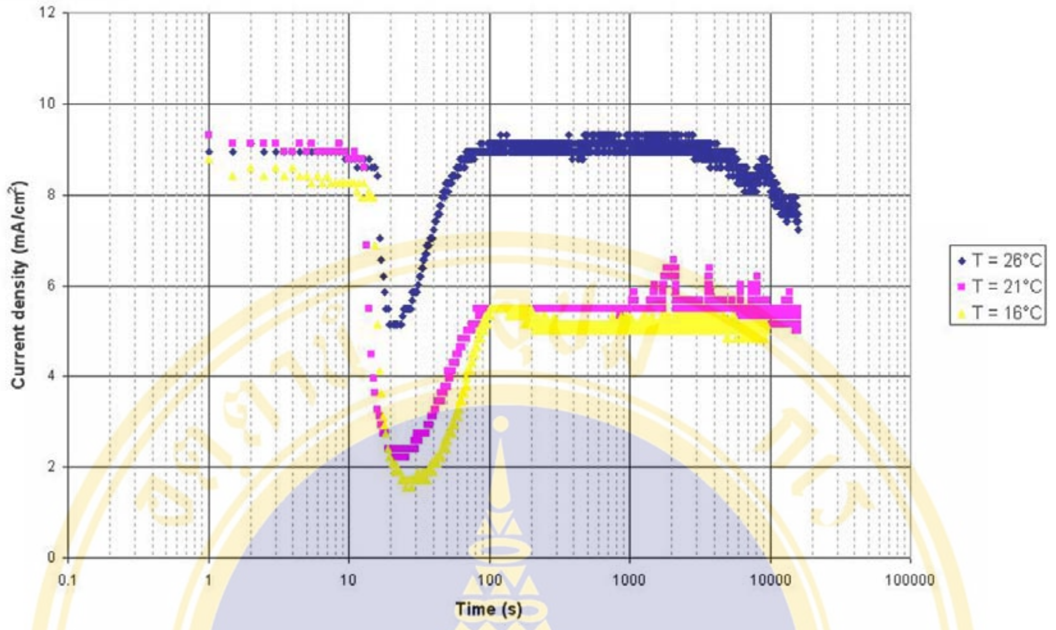


Second anodizing step with T=21°C

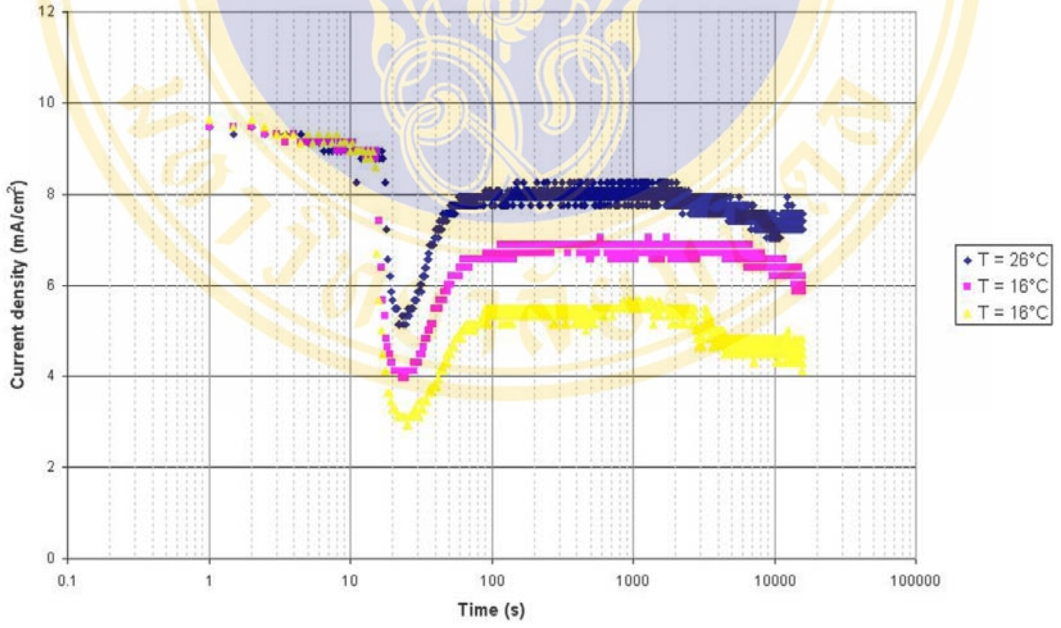


Second anodizing step with T=26°C

Figure 3.18: Current density as a function of time during the second anodizing step.

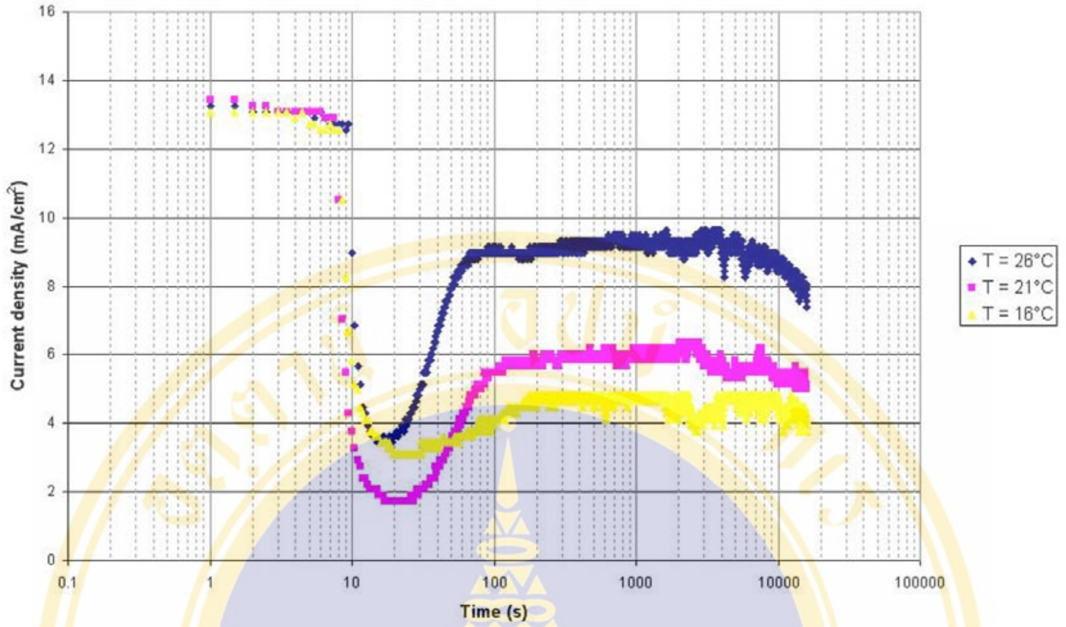


First anodizing step

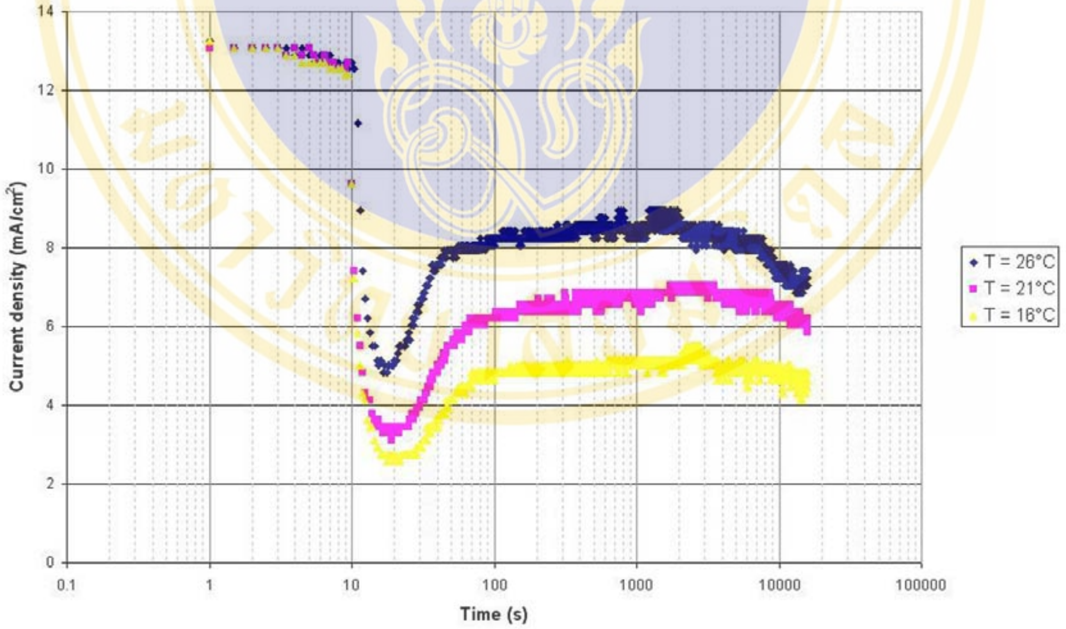


Second anodizing step

Figure 3.19: Time evolution of the current density (I=50mA) when different temperatures are used.

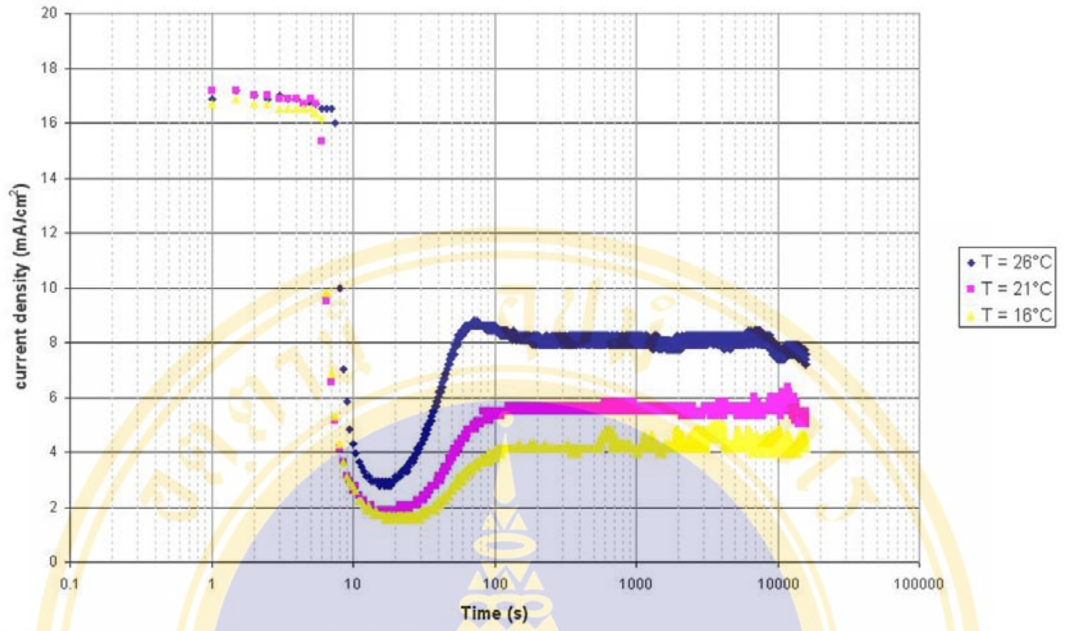


First anodizing step

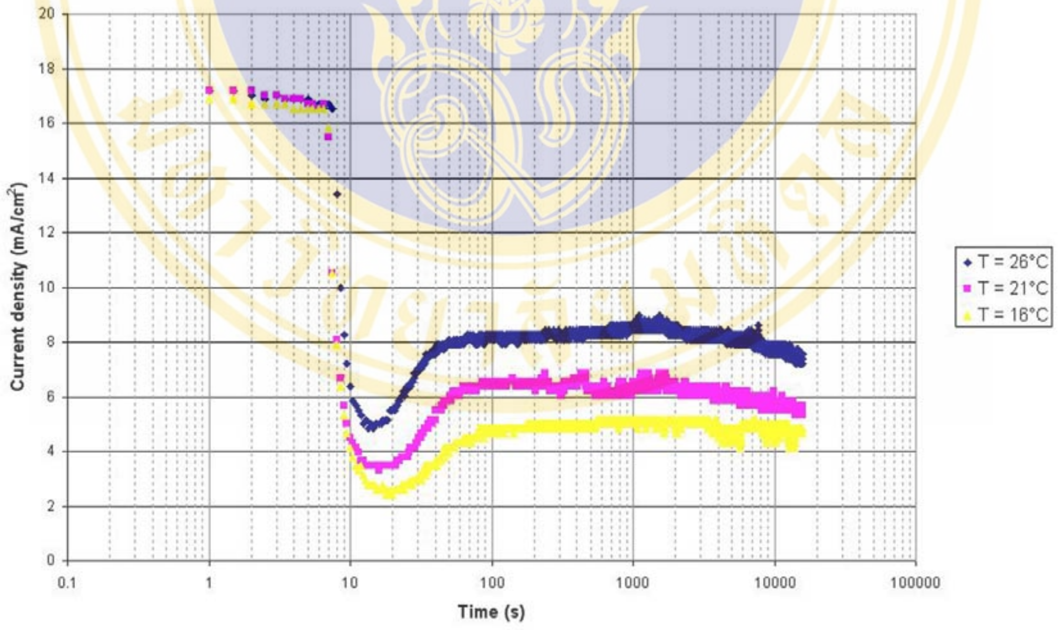


Second anodizing step

Figure 3.20: Time evolution of the current density (I=70mA) when different temperatures are used.

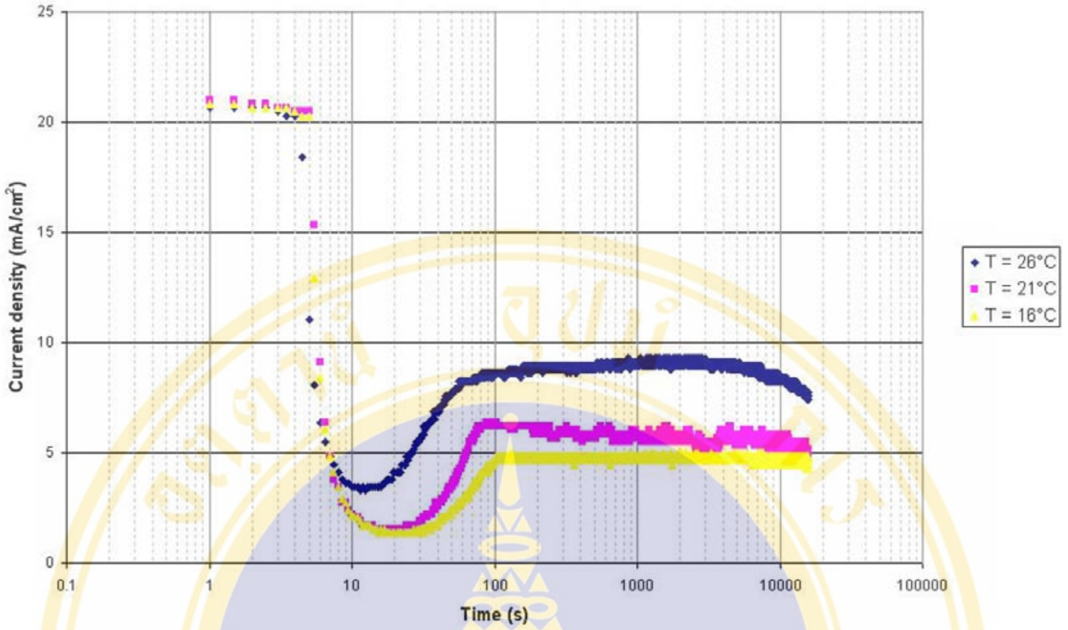


First anodization

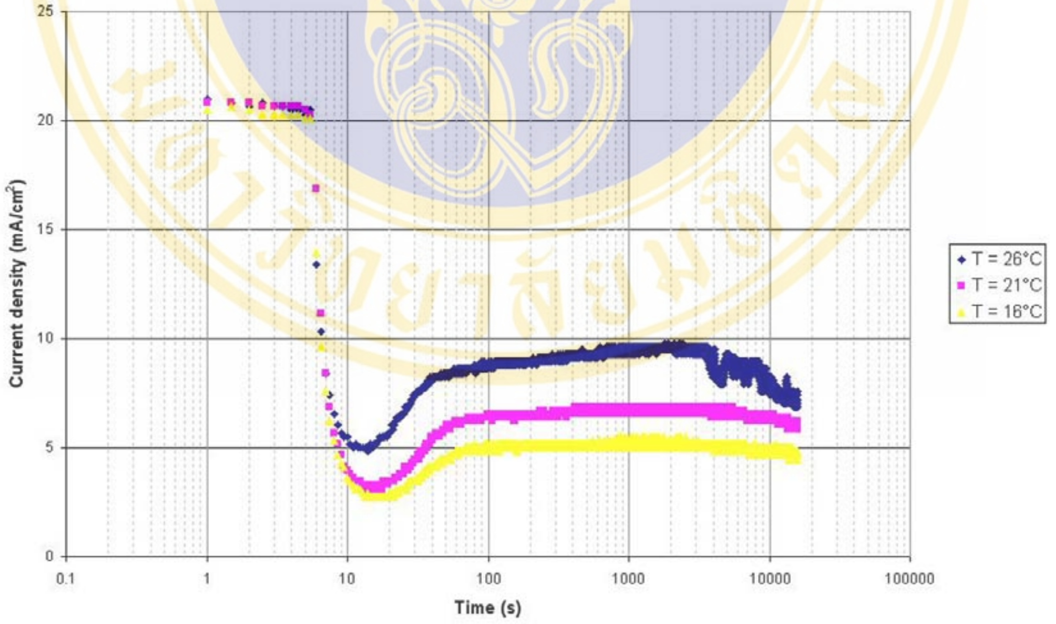


Second anodization

Figure 3.21: Time evolution of the current density (I=90mA) when different temperatures are used.



First anodization



Second anodization

Figure 3.22: Time evolution of the current density (I=110mA) when different temperatures are used.

The voltage versus time for different currents and temperatures are plotted together in Figure 3.15 and Figure 3.16, respectively. Figure 3.15 show the different initial currents lead to give different slope when the temperatures were the same. This figure shows the results both the first and second anodization steps. A higher initial current lead to the higher slope and a decreasing slope follow the decreasing of initial current. The higher initial current will take less time to reach 40V too. Figure 3.16 show that if we apply the same current in any temperature, the slope will be same. This means that the slopes depend on the initial current only. They do not depend on the temperature used. This will occur during both the first and second anodization steps.

The cross section area where we anodized the aluminum was circular shape and the diameter of the circles was constant for all the samples. The diameter is 1 inch so the anodized cross section area is 5.067 cm^2. The current that we recorded by computer was divide by that area so we obtained the value of current density (unit: mA/ cm^2). We plot graphs of current density versus time the different currents (Figure 3.17 and Figure 3.18) and the different temperature (Figure 3.19 – Figure 3.22). Figure 3.17 and Figure 3.18 show the current density at first anodization and second anodization, respectively. We see that the current density at the equilibrium state is not different for the same temperature, although we apply the different initial currents. The higher current density takes less time to drop down to the lowest point than the lower current density. Figure 3.19 to Figure 3.22 show the current densities at different temperatures. We see that the higher temperature produces the higher current density. The sequence of current densities is same as the sequence of temperatures for both the first and second anodization steps. The lowest current densities decrease when the temperature decreased, except for first anodization at the condition I = 70 mA. Figure 3.20 shows the lowest current density for 16 ºC is higher than the lowest current density 21 ºC.

3.3 Analysis of size distribution

The effects of the currents and temperatures on the diameters of holes formed in the anodic aluminum oxide are seen in the changes in the mean diameters of the holes are seen in the Table 3.1.

Table3.1: Mean diameters and standard deviation for various currents and temperatures

Temperature Current	T = **26°C**	**T = 21°C**	**T = 16°C**
I = 110 mA	Mean = 60.1472 Std. Dev. = 7.30154	Mean = 53.9600 Std. Dev. = 8.9059	Mean = 52.0334 Std. Dev. = 6.08613
I = 90 mA	Mean = 58.2509 Std. Dev. = 9.59948	Mean = 51.1992 Std. Dev. = 9.79277	Mean = 49.0616 Std. Dev. = 4.67457
I = 70 mA	Mean = 59.1850 Std. Dev. = 5.31865	Mean = 50.7761 Std. Dev. = 6.88351	Mean = 50.4820 Std. Dev. = 6.00121
I = 50 mA	Mean = 57.6083 Std. Dev. = 5.98761	Mean = 53.4983 Std. Dev. = 8.36232	Mean = 48.8966 Std. Dev. = 7.28492

From Table 3.1, we see that the mean diameter decreased when lower temperatures are used. However, there is no correlation between the sizes and the current used. We have plotted graphs of temperatures versus diameters and currents versus diameters below. The figure 3.23 shows the plot of the diameter versus the temperature used. As we see that there is no correlation of diameters with the temperature used when the same current is used. In figure 3.24 we plot the current versus the diameters of the holes produced. The figure shows that the diameters at T = 26 °C is larger than the diameter at T = 21 °C which in turn is larger than the diameter at T = 16 °C. These points to the mean diameter becoming smaller when lower temperatures are used. Others have reported that the diameter not only depends on the temperature used, but also on the concentration of the acid and on the types of acid used [19, 20].

In figure 3.25 and figure 3.26, we have plotted the values of the lowest current density versus the current during the first and second anodizing steps. The graphs show the lowest current densities decrease when the anodizing is done at lower temperatures. Figures 3.27 and 3.28 show the lowest current density when the anodizing is done at different temperatures. We see that the lowest current increases when the anodizing is done at higher temperatures in both anodizing steps.

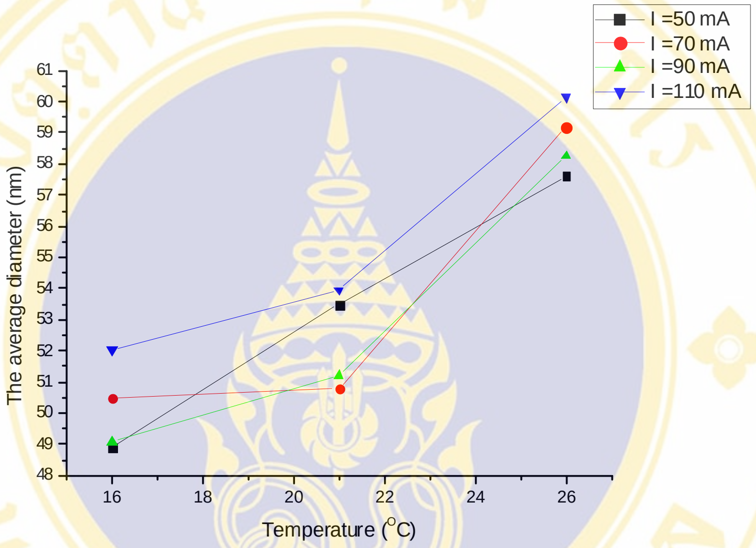


Figure 3.23: Plot of the diameters of the holes obtained when different temperatures were used.

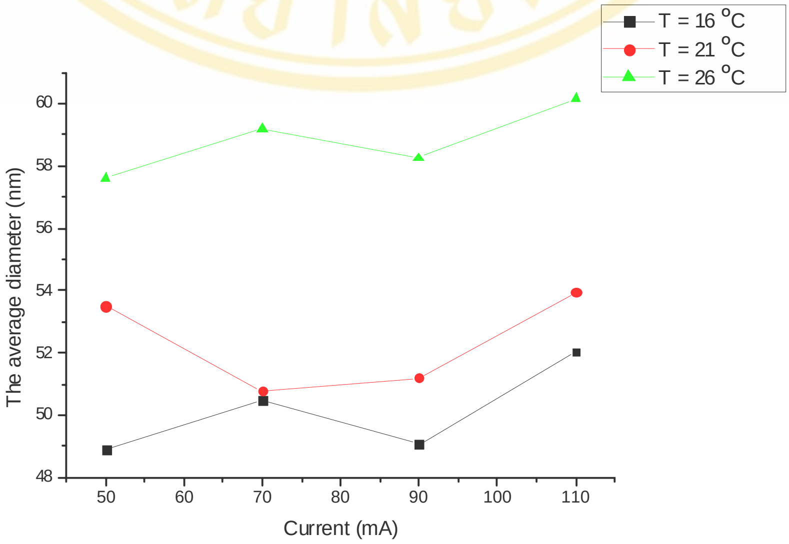


Figure 3.24: Plot of the diameters of the holes obtained when different currents were used.

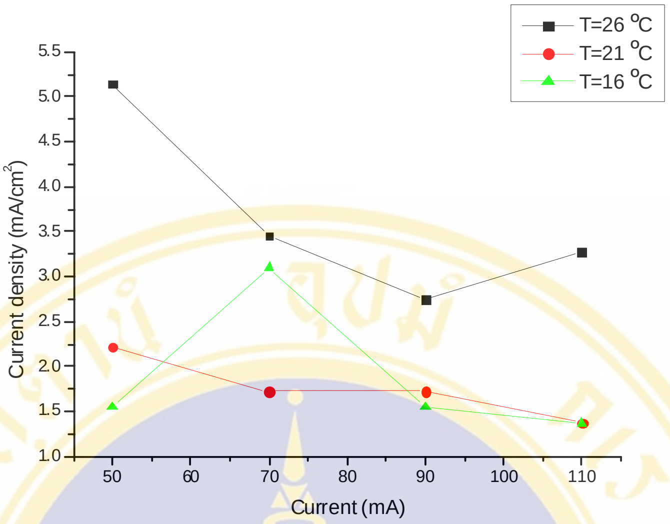


Figure 3.25: Plot of the lowest current density versus current during the first anodizing step done at different temperatures

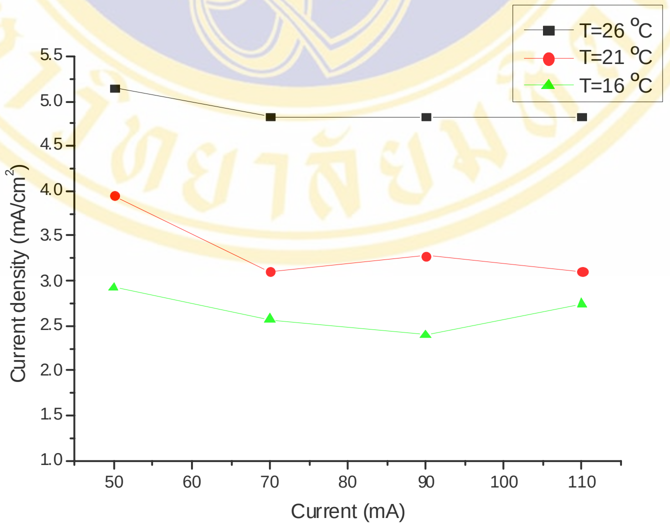


Figure 3.26: Plot of the lowest current density versus current during the second anodizing step done at different temperatures

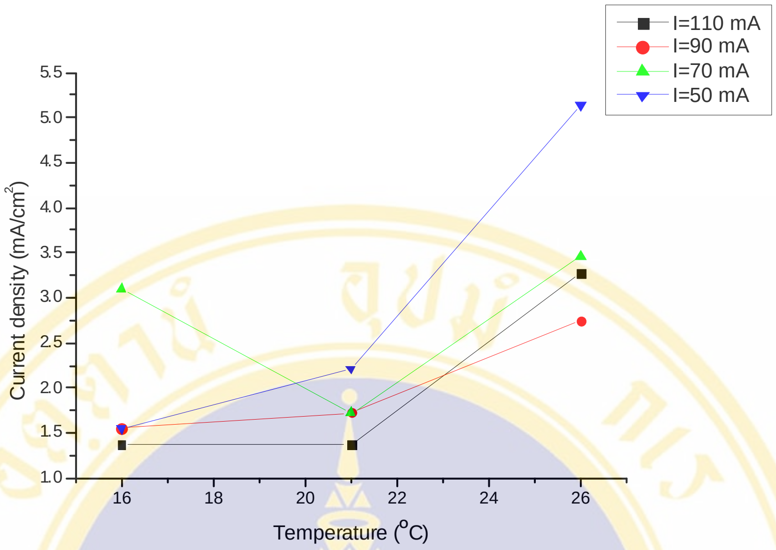


Figure 3.27: Plot of the lowest current density during the first anodizing step versus temperature done at different currents.

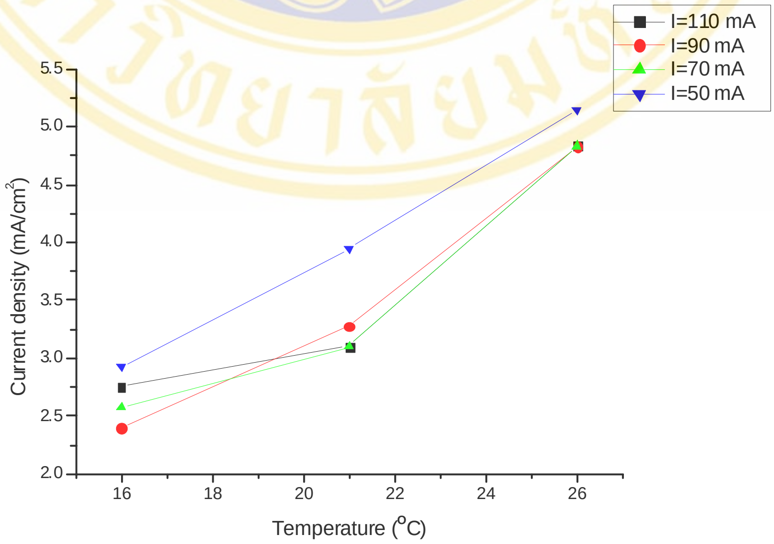


Figure 3.28: Plot of the lowest current density during the second anodizing step versus temperature done at different currents.

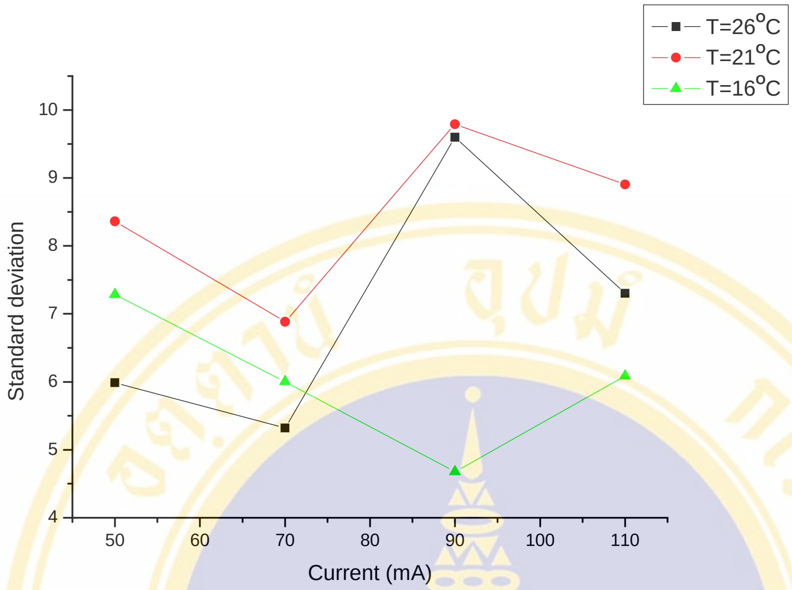


Figure 3.29: Plot of the standard deviation of the pore size versus the current used.

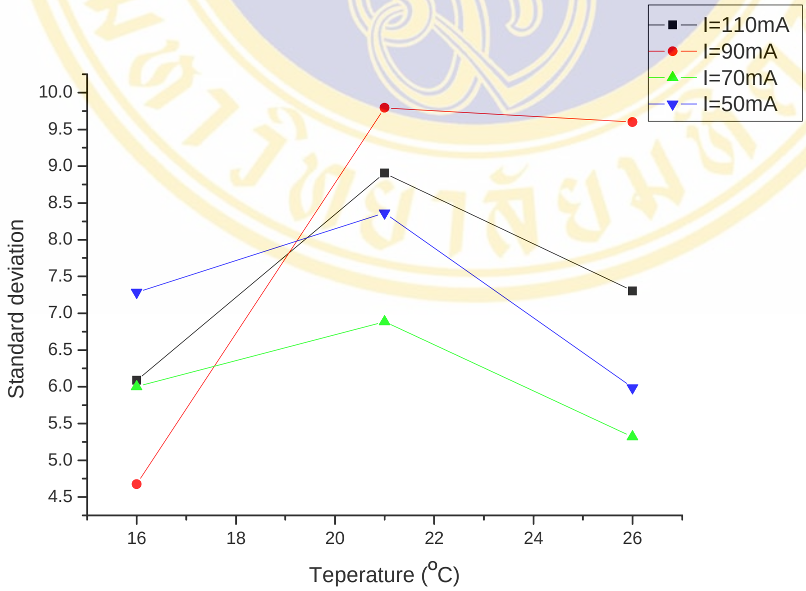


Figure 3.30: Plot of the standard deviation of pore sizes versus the temperature used.

As we see, figure 3.29 and figure 3.30, does not indicated that the standard deviations do not show any correlation with either the current or temperatures used during the anodizing.

CHAPTER IV

CONCLUSION

In the beginning of anodization process, the voltages increase to 40 volts. The voltages increase with the same slope when the same current is used. There is no correlation between the values of the slope and the temperature at which the anodizing is done at. For the currents used in the experiments (110mA, 90mA, 70mA, 50mA) the voltages increase at different rates. The higher currents give the higher slopes. This occurs in during both anodizing steps. The current densities decreased when the temperature is decreased. The current densities at the equilibrium points are the same when the same temperature is used. We can therefore say that the current densities change when different temperatures and that it does not depend on the initial current flows.

Temperatures had the effect on the diameters of holes which formed in the anodic aluminum oxide. The mean diameter of holes decreased when lower temperatures are used. However, there is no correlation between the sizes and the current used. There is no correlation of diameters with the temperature used when the same current is used. The diameters at T = 26 °C is larger than the diameter at T = 21 °C which in turn is larger than the diameter at T = 16 °C. These points to the mean diameter becoming smaller when lower temperatures are used.

REFERENCES

1. Keith B. Oldham, Jan C. Myland, “Fundamentals of Electrochemical Science”, 99 (1994).
2. J.B. Mohler, “Electroplating and Related Process”, 78 (1969).
3. H. Toftlund, Ionics 7 (2001) 161-164.
4. Donal T. Sawyer, Andrzej Sobkowiak, Julian L. Roberts, “Electrochemistry for chemists’, second edition, 1-2 (1995).
5. Rolf H. Muller, “Anodic Films”, 1983.
6. J. I. Goldstein and H. Yakowitz, “Practical Scanning Electron Microscope”, Plenum Press, New York, 1975.
7. F. Keller, M. S. Hunter, D. L. Robinson, *J. Electrochem*, Soc. **100**, 411 (1953).
8. H. Masuda, K, Fukuda, Science, 268 (1995) 1466.
9. S.G. Yang, H. Zhu, G. Ni, D.L. Yu, S.L. Tang, Y. W. Du, *Appl. Phys*., **33** (2000) 2388-2390.
10. D.H. Qin, M. Lu, H.L. Li, *Chemical Physics Letters*, 350 (2001) 51-56.
11. Shaoguang Yang, Hao Zhu, Dongliang Yu, Zhiqiang Jin,Shaolong Tang, Youwei Du, *J. Magn. Magn. Mater*. 222 (2000) 97-100.
12. M. Zheng, L. Menon, H. Zeng, Y. Liu, S. Bandyopadhyay, R. D. Kirby, D. J. Sellmyer, *Physical Review B*, Volume 62, Number 18, 2000, 12282-12286.
13. Yi=Kun Su, Dong-Huan Qin, Hao-Li Zhang, Hua Li, Hu-Lin Li, *Chem. Phys. Lett*., 388 (2004) 406-410.
14. Alexander N. Govyadinov, Sergej A. Zakhvitcevich, Technical Digest of IVMC’97 Kyongju, Korea 1997 (735).
15. O. Jassensky, F. Muller, and U. Gosele, *Appl. Phys. Lett.* 72 (1998) 1173.
16. Hui Pan, Jianyi Lin, Yuanping Feng, amd Han Gao, IEEE TRANSACTIONS ON NANOTECHNOLOGY, vol.3, 2004.
17. D. Padhi, J. Yahalom, S. Gandikota, G Dixit, *Journal of The Electrochemical Society*, **150** (1) G10-G14 (2003).

18. S.W. Lin, S.C. Chang, R.S. Liu, S.F. Hu, N.T. Jan, *J. Magn. Magn. Mater.* 282 (2004) 28-31.
19. M. Almasi Kashi, A. Ramazani, , *Appl. Phys.*, **38** (2005) 2396-2399.
20. A. P. Li, F. Muller, A. Birner, K. Nielsch, U. Gosele, , *J. Appl. Phys.*,Vol, **84** (1999), 6023-6026.

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