Electrochemical Anodization of Aluminum at Room Temperature by Electronically Controlled Direct Current Circuit

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LIST OF ABBREVIATIONS

DC	Direct current
AC	Alternating current
AAO	Anodized aluminum oxide
FCC	Face center cubic
SEM	Scanning electron microscopy
PBR	Pilling Bedworth Ratio
DSSC	Dye sensitized solar cell
XRF	X-ray fluorescence
SEM	Scanning electron microscope
XRD	X-ray diffraction
LED	Light emitting diode
PhET	Physics Education Technology

LIST OF SYMBOLS

P	Power
V	Voltage
I	Current
R	Resistance
L	Length
R	Universal gas constant
T	Temperature
F	Faraday constant
J	Electron-contributing current density
E_{field}	Electric field
E_{B0}	Breakdown electric fields
ε	Dielectric constant
σ	Compressive stress
J	Current density
A	Cross sectional area
E_{redox}	Energy reduction/oxidation
Ri	Internal resistance
M_{Al2O3}	Molecular weight of alumina
M_{Al}	Molecular weight of aluminum
ρ_{Al2O3}	Density of alumina
ρ_{Al}	Density of aluminum
d_{cell}	Diameter of each cell
D_{int}	Interpore distance

D_B	Barrier layer thickness
E	Cell potential
E^o	Standard cell potential
Q	Reaction quotient
n	Number of electrons
k	Proportionality constant
K	Kelvin
V_f	Final voltage
V_a	Applied voltage
D	Average pore diameter
A	Area fractions of pores
P	Pore count
nm	Nanometer
ΔG	Gibbs free energy
ΔH	Enthalpy
ΔS	Entropy
^oC	Celsius

Penganodan Elektrokimia Aluminum Pada Suhu Bilik Oleh Litar Arus Terus Dikawal Secara Elektronik

ABSTRAK

Filem anodik aluminum oksida (AAO) telah dikaji dan digunakan dalam pelbagai bentuk produk lebih daripada 50 tahun. Morfologi filem AAO boleh dikelaskan kepada jenis halangan dan jenis berporos. Jenis halangan terdiri daripada alumina amorfus yang padat, manakala jenis poros terdiri daripada lapisan nipis jenis halangan di antara logam dan satu lapisan luar alumina berliang. Terdapat kekangan di dalam fabrikasi alumina nanoporos. Kekangan ini adalah pembekuan elektrolit dengan suhu rendaman terkawal, bezaupaya yang sangat tinggi dan masa penganodan yang lama telah digunakan semasa fabrikasi AAO. Isu terpenting adalah penggunaan dua langkah proses penganodan untuk menghasilkan filem AAO. Untuk mengatasi kekurangan yang dikaitkan dengan fabrikasi filem alumina berliang pada suhu bilik. Tujuan kajian ini adalah untuk mewujudkan satu proses fabrikasi filem alumina nanoporous yang novel dengan diameter liang yang dikawal secara luaran oleh litar arus terus. Langkah-langkah mengikut 'set-up" rekabentuk litar elektronik melibatkan spesifikasi, rekabentuk/ kos, pengesahan dan pengujian litar. Spesifikasi reka bentuk adalah untuk menangani isu suhu, keupayaan penganodan yang rendah dan nilai parameter proses yang paling kritikal (arus), dan parameter yang kurang kritikal (suhu dan kepekatan elektrolit). Langkah rekabentuk seterusnya ialah pengenalpastian komponen penting iaitu pemuat dan perintang yang kritikal semasa peringkat rekabentuk awal. Komponen-kompoenen ini adalah murah dan menyediakan satu bentuk litar yang stabil dan terkawal. Pengesahan dan ujian telah dilakukan oleh simulasi komputer (kit perisian PhET) dan ujian rekabentuk litar yang praktikal. Simulasi komputer telah menyediakan maklumat tentang rekabentuk litar yang paling sesuai di bawah keadaan simulasi yang berbeza.. Simulasi yang dikenalpasti adalah satu siri sambungan kapasitor nilai 60 V tunggal dan perintang 500 ohm untuk menjadi rekabentuk litar yang sesuai untuk menghadkan pengaruh parameter proses. Ujian praktikal menggunakan kepekatan elektrolit yang berbeza (0.7 M , 1.5 M, dan 2.2 M) , keupayaan rendah yang berbeza (10 hingga 50 V) yang beroperasi pada suhu bilik telah mengenalpasti nilai arus kritikal untuk menjadi kurang atau sama dengan 150 mA. Sebarang nilai arus di atas 150 mA ini gagal menyediakan satu struktur nanoporous alumina. Suatu ujian yang sama dijalankan pada suhu tinggi (50^oC) untuk memastikan kesesuaian litar untuk beroperasi pada suhu tinggi. Fungsi rekabentuk litar juga berasaskan persamaan yang dikawal oleh persamaan piawai di mana ia boleh dikendalikan melalui bekalan arus terus atau bekalan arus ulang-alik dan ini menjadikan keseluruhan proses adalah fleksibel , jitu dan tepat. Penganodan aluminium pada suhu bilik dan berkeupayaan rendah di dalam elektrolit yang berbeza selama 1 jam, 3 jam, dan 5 jam masing-masing. Keputusan mikroskop imbasan elektron (SEM) menunjukkan bahawa liang terbentuk pada keupayaan dan kepekatan elektrolit yang berbeza adalah dalam julat 10 - 200 nm. Liang tertabur secara rawak di seluruh permukaan aluminium. Keupayaan digunakan bertambah dengan masa menyebabkan diameter liang juga meningkatkan. Keputusan menunjukkan bahawa nanoporous alumina telah berjaya direka pada suhu bilik dan suhu yang tinggi dengan keupayaan rendah menggunakan teknik penganodan tunggal berbantukan sel elektrokimia yang diubahsuai dikawal oleh litar arus terus secara luaran.

Electrochemical Anodization of Aluminum at Room Temperature by Electronically Controlled Direct Current Circuit

ABSTRACT

Anodic aluminum oxide (AAO) films have been investigated and used in numerous products for more than 50 years. The morphologies of the AAO films can be classified into barrier-type and porous-type. Barrier-type films consist of compact amorphous alumina, while porous-type films comprise of a thin barrier layer next to the metal and an outer layer of porous alumina. There are limitations in the way nanoporous alumina has been fabricated. The limitations are the freezing of the electrolyte with a temperature controlled bath, very high potential and prolong anodizing time have also been used during AAO fabrication. In order to overcome these shortcomings associated with the fabrication of this porous alumina film at room temperature, this study aim to create a novel process to fabricate nanoporous alumina film with controlled pore diameters that is externally controlled by direct current circuit. The steps followed during the electronic circuit design set-up involved specification, design/cost, verification and testing of the circuit. The specification of the design is to address the issue of temperature, low potential anodization and the value of the most critical process parameter which is current, and the less critical parameters which are temperature and concentration of electrolyte. The next step of the design was the identification of important components i.e. capacitors and resistors that are crucial during the preliminary design stage. The components are cheap and provide a form of stability and control of the circuit. The verification and testing was done by computer simulation (PhET software kit) and practical testing of the circuit design. The computer simulations provided the information about the most suitable circuit design under different simulated conditions. The simulation identified a series connection of a single 60 V rated capacitor and a 500 ohms resistor to be the most suitable circuit design to limit the influence of the process parameters. The practical testing using different electrolyte concentration (i.e. 0.7 M, 1.5 M, and 2.2 M), different low potentials (i.e. 10 to 50 V) operating at room temperature identified the most critical current value to be less or equal to 150 mA. Any current value above this failed to produce a nanoporous alumina structure. A similar testing was also performed at higher temperature (50^{o}C) to confirm the suitability of the circuit to operate at higher temperatures. The functionality of the circuit design is also equation based controlled by standard equations which can be operated via a direct circuit supply or alternating current supply, making the entire process flexible, accurate and precise. The room temperature and low potential anodization of aluminum were anodized under different electrolyte conditions for 1 hour, 3 hours, and 5 hours respectively. The scanning electron microscope (SEM) results show that the pores formed at different potentials and concentrations of electrolytes is within the range of 10 – 200 nm. The pores are randomly distributed all over the surface of the aluminum. As the applied voltage is increased with time subsequently the pores also increase in diameter. This results show that with the aid of the upgraded electrochemical cell controlled by the external dc circuit, nanoporous alumina were successfully fabricated at room temperature and high temperature with low potentials using a single step anodization technique which was suitable for AAO fabrication.

CHAPTER 1

INTRODUCTION

1.1 Background

Metals and alloys still constitute the most important group among engineering materials, and the demand for metallic materials with higher strength and special properties is on the increase with the advancement of technology. With annual consumption of 35 million metric tons, aluminum is the worlds most commonly used metals (Christian, 2004). Aluminum is the third most abundant element in the earth's crust and constitutes 7.3% by mass. In nature however it only exists in very stable combinations with other materials (particularly as silicates and oxides) (Christian, 2004). The use of aluminum and its alloys in industry has increased due to its exceptional properties (low-specific mass, good thermal and electrical conductivities, good corrosion resistance, etc.) (Choo and Devereux, 1976; Li et al., 2005).

Over the last decade, there has been an ever increasing interest and research effort in the synthesis, characterization, functionalization, molecular modeling and design of nanoporous materials. Porous materials are of scientific and technological importance because of the presence of voids of controllable dimensions at the atomic, molecular, and nanometer scales (Lu and Zhao, 2004). Generally, porous materials have porosity (volume ratio of pore space to the total volume of the material) between 0.2 - 0.95 (Lu and Zhao, 2004). Pores are classified into two types: open pores which connect to the surface of the material, and closed pores which are isolated from the outside. In functional applications such as adsorption, catalysis and sensing, closed pores are not of any use. In separation, catalysis, filtration or membranes, often penetrating open pores are required. Materials with closed pores are useful in sonic and thermal insulation, or lightweight structural applications. Pores have various shapes and morphology such as cylindrical, spherical and slit types. There are also pores taking more complex shapes such as hexagonal shapes can be straight or curved or with many turns and twists. International Union of Pure and Applied Chemistry (IUPAC) classifies porous materials into three categories; micropores less than 2 nm in diameter, mesopores between 2 and 50 nm, and macropores greater than 50 nm (Lu and Zhao, 2004).

Nanoporous materials have specifically a high surface to volume ratio, with a high surface area, large porosity, and very ordered, uniform pore structure. It has very versatile and rich surface composition, surface properties, which can be used for functional applications such as catalysis, chromatography, separation, and sensing. A lot of inorganic nanoporous materials are made of oxides often non-toxic, inert, and chemically and thermally stable, although in certain applications the thermal stability requirement is very stringent (Lu and Zhao, 2004). An example of these nanoporous materials is porous alumina. The fabrication of porous alumina film by electrochemical process consists of converting aluminum into its oxide by appropriate selection of the electrolyte and the anodizing conditions, such as current density, voltage, temperature, and concentration. The porous alumina structure has good mechanical properties and is chemically and thermally stable. The application of this porous structure currently being tested include defined pore sizes, catalysts, high density storage media, functional nanomaterials exhibiting quantum size effects, highly sensitive chemical sensors, nanoelectronic devices and functional biochemical membranes (Shingubara, 2003).

1.2 Electrochemical Anodization

Electrochemical anodization is an electrochemical process that converts the metal surface into a decorative, durable, corrosion-resistant, anodic oxide finish. Aluminum is ideally suited to anodization, although other nonferrous metals, such as magnesium and titanium, also can be anodized. For the anodization process to be accomplished the conducting piece (i.e. aluminum) undergoing this process is connected to the positive terminal of a direct current power supply and placed in a suitable electrolytic bath where it serves as the anode. The cathode is commonly a plate or rod of platinum, although materials such as carbon are sometimes used. When power is applied electrons are forced from the electrolyte to the positive anode, this process expose the surface metal to oxygen ions within the electrolyte that leads to the formation of the oxide layer. The electrons travel through the power source and return to the cathode where, if an appropriate electrolyte pH is present, it reacts with the hydrogen ions and the combination bubbles off as hydrogen gas. Since the metal oxide partially dissolves in any electrolyte, it is necessary to use only those electrolytes for which the oxide forms more rapidly than it dissolves. The electrolyte composition is also the primary determinant of whether the oxide film is porous or if it forms a barrier layer. Oxide barrier layers grow in those neutral or slightly alkaline solutions, while porous oxide layers grow in acidic electrolytes (Grimes and Mor, 2009).

1.3 Electronics

The computers, televisions, telephones and all other electronic systems rely on circuits, which are the paths that electricity takes through various electrical components in order to perform some kind of useful tasks. Electronics by modern definition is that part of electrical science which deals with semiconductors. As such the history of electronics is really a continuation of the history of electrical knowledge. From its first development in the late 19^{th} century to the coming of age of digital computers, the field of electronics and electronic design was well defined and occupied many thousands of engineers, technicians and others in closely related specialties (David and Joseph, 2007). For every new problem, the design engineers would dive into search for a solution and usually would come up with a hard wired design. The electronic circuits and systems tended to be inflexible, accommodating only the range of application that was design into the circuits. This electronic circuit design can be considered an art based on the fundamental concept of electrical and electronic engineering. Passive components such as resistors, capacitors, inductors, transformers need to be mixed effectively and optimally with semiconductor components in building a particular circuit (Nihal, 2008). A simple circuit, for example might consist of a battery with its positive terminal connected by a wire to one end of a light bulb filament, then a wire leading from the filaments other end back to the battery (David and Joseph, 2007).

1.4 Problem Statement

1.4.1 The Anodization Process

The electrochemical process of anodizing aluminum has been limited to three main acidic electrolytes sulphuric acid, phosphoric acid and oxalic acid. These acidic electrolytes have been in use since the early 19^{th} century to fabricate nanoporous alumina.

The limitations associated with the previous methods of preparation of nanoporous alumina films include:

(a) The freezing of the electrolyte with the use of temperature controlled water bath is a limiting factor which is required to provide low temperatures (2 ^oC, 5 ^oC, 11 ^oC), and in some cases extremely low freezing temperatures (-8 ^oC, -3 ^oC, 0 ^oC) for the anodization process (Leszek et al., 2010; Jia et al., 2014; Marta et al., 2013; Song et al., 2013; Byeol and Jin, 2014; Belwalkar et al., 2008; Zhaojian and Kelong, 2007; Ghafar et al., 2010; Kun et al., 2002; Sulka et al., 2002; YuCheng and Jose, 2001; Daniel et al., 2009; Jung et al., 2009; Nasirpouri et al., 2009; Dongdong et al., 2008; Jian et al., 2008; Fernandez et al., 2008; Stojadinovic et al., 2008a; Bensalah et al., 2008; Hui et al., 2008; Ho et al., 2007; Zhou et al., 2007; Seonghyun et al., 2006; Abel et al., 2011; Liu et al., 2011).

Most industries are in businesses to make more profits by lowering their investment cost as much as possible. Low freezing temperature controlled baths are expensive and could cost even more if the inclusion of the operating cost, servicing and maintenance cost is also considered. If there is a way with which all these expenses/costs can be reduced by producing the porous alumina structure at room temperature, it will definitely be accepted not only by the industries but also the research institutes and the academicians.

(b) Increasing the size of alumina nanopores in some cases are attributed to high voltage and/or prolong anodization time which are two limiting factors, because it is energy and time consuming (Ghafar et al., 2010; Leszek et al., 2010; Yanchun et al., 2005; Yan et al., 2006; Proenca et al., 2008; Ya et al., 2008; Su et al., 2008; Sulka and Parkola, 2007; Wen et al., 2006; Younghyun et al., 2014; Beomgyun et al., 2013; Hendrik et al., 2013; Tatsuya et al., 2014).

The anodization of aluminum at very high voltages (e.g. 195 V) is not safe, and would require a very good laboratory practice to avoid hazards or accidents. Anodizing the aluminum for a long period of time (e.g. 24 hours) is both energy, and time consuming. Since the more time you spend during the anodization process the more current is being used and therefore the operating cost goes up. The possibility of producing alumina nanoporous structure with same pore size but at a lower voltage (e.g. 10 V, 30 V, and 50V) and shorter time of 1, 3 or 5 hours will be acceptable because the overall power consumption and operating cost will be reduced.

1.4.2 The Circuit Set-up

The electronic circuit set-up takes into consideration the flaws associated with previously used electrochemical cell for aluminum anodization, in which the most critical parameter is current, followed by two other critical parameters namely temperature and concentration of electrolyte. The role or influence of these critical parameters current, temperature and concentration of electrolyte as severely restricted the improvement in the performance and further understanding of the electrochemical cell used in aluminum anodization. If these process parameters are not properly controlled, anodizing aluminum foil at room temperature leads to a rapid dissolution and etching of the alumina surface, and thereby preventing the propagation and growth of the nanoporous alumina structure. The fabrication of the electronic circuit is to provide a complete control of the current and at the same time limits the influence of the other critical parameters by identifying there critical values. The best parameters that can be used to control the new electrochemical cell are power and resistance; its values can be calculated from standard equations.

1.5 Research Objective

(a) To fabricate a low cost electronic circuit set-up for the electrochemical cell to produce nanoporous alumina foils at room temperature.

(b) To analyze the suitability of the electronically controlled cell to sustain a low potential fabrication and controlled pore formation of nanoporous alumina structure.

1.6 Scope of Research

(a) The electronic circuit design:

For the electronic circuit design it is important to know how the process parameters influence the anodization process to aid in the circuit design by providing a form of control over the process parameters. The verification and testing of the circuit by both computer aided theoretical simulations and practical testing is to identify the most critical values and limits of the parameters that strongly influence how the aluminum foil will respond to the external circuit control. The electrochemical anodization process should be able to function at a convenient temperature (room temperature) making the process cost effective and does not require the use of expensive thermostatic bath. An increased overall efficiency since the operation of the electrochemical cell is equation based.

(b) The fabrication of the porous alumina foils:

The AAO foils should have large pores to increase the surface area; the fabrication of the porous structure should be repeatable; the porous structure should not be prone to corrosion and should be able to withstand fairly high heat treatment process (<680 ^{o}C); The