



Trade Science Inc.

Research & Reviews In Electrochemistry

Full Paper

RREC, 4(1), 2013 [1-6]

Development of high energetic nano porous electrode by controlled anodization of aluminium

Subir Paul*, Rakib Baidya

Department of Metallurgical and Material Engineering, Jadavpur University, Kolkata-700032, (INDIA)

ABSTRACT

Pure Al (99.99%) was electropolished in a solution of Perchloric acid and Ethanol and anodized in galvanostatic circuit using Al cathode in sulphuric acid and oxalic acid solutions at different concentrations and temperatures, in order to form nanoporous alumina template. Anodization process was found to be strongly dependent on potential, type of acid, its concentration and temperature. Single anodization produces poorly ordered structure. The concave texture of the Al surface, which was formed by selective removal of the film after the first anodizing step, is used to induce the ordered formation of pores even at the initial stage of anodization in the second step. Much ordered nano porous template was fabricated. Pore size was found to be strongly dependent on the concentration and type with type of acids, concentration and potential. Anodizing in sulphuric acid produced smaller pore size compared to that in oxalic acid. Scanning electron microscopy revealed pore diameter in the range 30-150 nm in general. Average pore size was estimated from X-ray diffraction pattern, using Scherer's formula and nano pores as below 15 nm was achieved. Polarization study of the electrode was carried out. Both exchange current density and limiting current density were found to be influenced by pore size. The smaller the nano pore, higher is the current density.

© 2013 Trade Science Inc. - INDIA

KEYWORDS

Anodization;
Nano porous electrode;
Exchange current density;
Limiting current density.

INTRODUCTION

Nanostructured materials produced by the template method, entails synthesizing desired material within the pores of nanoporous membrane. In this case the size and shape of the nano-structures are controlled by the size and shape of the template. The template method has number of interesting and useful feature. This method can be used to produce conductive polymers, metals,

semiconductors, carbon tube. The pores have the dimensions ranging from sub micrometer to nanometer range, which can be used as template to fabricate nanowire or nanotubes, as nanodevices in electronic, optoelectronic and micromechanical systems^[1-3]. But for fabrication of these devices, highly ordered pore arrangement, controllable pore diameter and channel length are very much essential. There are problems in achieving total control of nanopore dimensions^[4].

Full Paper

Anodization of aluminum produces porous oxide layer. By controlling external conditions such as acid concentrations and applied potential, nanostructures with extraordinary small diameter can be prepared and the diameter of the hole can be controlled.

Anodized aluminum is electrically insulating (10^{18} ohm/cm), optically transparent over a wide energy band, chemically stable^[5]. Porous aluminum oxide is most commonly grown in dilute sulfuric acid. But there are also processes available using phosphoric acid, chromic acid, oxalic acid and mixture of inorganic acid and organic acid. Studies of formation of nanoporous anodized alumina as template are being carried out for some years. Masuda et al produced in oxalic acid^[6] and sulfuric acid^[7]. Gosele's group studied alumina nano template using sulfuric, oxalic and phosphoric acids^[8-10]. They reported that periodic arrangements were observed when the volume expansion from aluminum to alumina was 1.4 times, irrespective of any electrolyte. Studies of nanoporous alumina was originally initiated on pure aluminum foil. Das and McGinnis^[5] fabricated alumina template on silicon substrate by anodizing vacuum processed alumina in sulfuric acid. Liu et al^[11] used a focused ion beam pre-patterned aluminum surface to fabricate alumina nanotemplate. Sun and Kim^[12] used holographically patterned aluminum films to form alumina nanotemplate.

In the present work endeavors were made to fabricate porous alumina in nano range by two steps anodization of aluminum in oxalic acid and sulfuric acid, using pure Al. Polarization study of the porous electrode was carried to observe its performance as fuel cell electrodes fabricated by biomass^[13,14].

EXPERIMENTAL PROCEDURE

Highly pure Al (99.99%) of 1cm by 1cm with 2mm thickness was degreased, annealed at 400 C in nitrogen atmosphere and electropolished in a solution of Perchloric acid and Ethanol (1:5 in volume). Leaving one square surface, all the faces of the samples were covered with insulating coating. The sample was anodized in galvanostatic circuit using Al cathode in sulphuric acid and oxalic acid solutions at different concentrations temperatures. Anodization of aluminum was carried out by a two stage process. The first anodized

alumina layer was then selectively removed by immersing in 4 vol. % CrO₃ + 10 vol. % H₃PO₄ for 12 h at 25C.

Anodized templates were observed under scanning electron microscope.

X-ray diffraction analysis was carried out in a Rigaku Ultima-3 X-ray diffractometer with Cu K_α (1.5406Å) radiation at 40 kV and 30 mA. The scanning rate was kept at 5°-2θ / min, from 2θ = 40° to 100°. Polarization studies of Nano porous electrodes were carryout in anodic and Cathodic solutions by Gamry Potentiostat. Anodic solution was ethyl alcohol, required for directs alcohol fuel cell. The cathode compartment was filled with phosphate buffer and 0.02 M potassium hexacyanoferrate in a volumetric ratio of 4:1 and continuously purged with air for Cathodic Oxygen reduction reaction.

RESULTS AND DISCUSSION

To determine the required potential and current density to form nanoporous layer of anodizing film, I-E characteristics of aluminum anodization is carried out galvanostatically in oxalic and sulphuric acids, as illustrated in Figure 1. The anodization rate and stability of anodic process are found to be strongly influenced by type of electrolyte and its composition. In general, the potential (voltage) initially increased slowly with an increase in applied current densities, followed by a rapid increase in the current density without significant change in voltage. At a given applied current density, the measured voltage in oxalic acid was higher than in sulfuric acid solutions. The measured voltages decreased with increasing sulfuric acid concentration.

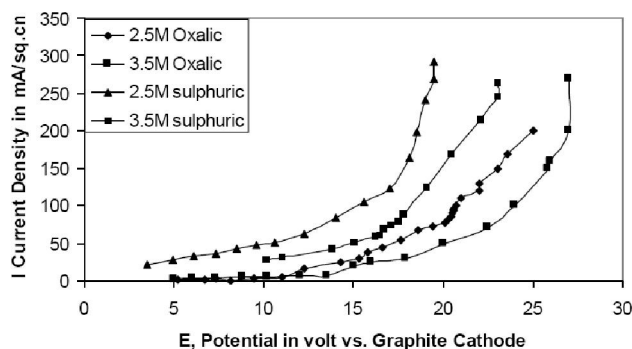


Figure 1 : Galvanostatic polarization curve of anodization of Al in sulphuric and oxalic acid

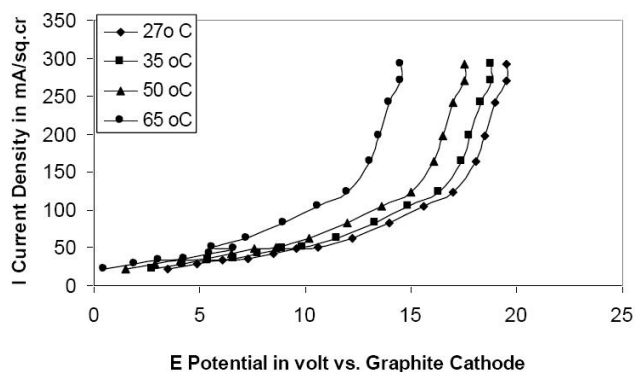


Figure 2 : Galvanostatic study of anodization of Al in 1.5 M sulphuric acid solution with variation of electrolyte temperature

Figure 2 illustrates the effect of temperature on I-E characteristic. Here the potential is found to decrease with increasing temperature at fixed current density.

Anodization of aluminum was carried out by a two stage process. Because single anodization produces poorly ordered structure (SEM micrograph figure 3). The concave texture of the Al surface, which was formed by selective removal of the film after the first anodizing step, is used to induce the ordered formation of pores even at the initial stage of anodization in the second step. Much ordered nano porous template was fabricated (Figure 4). with a two stage anodization.

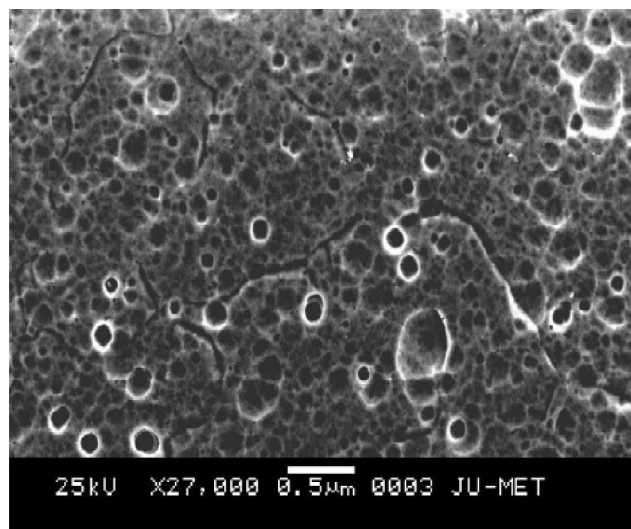


Figure 3 : Single stage anodizing in 1M sulphuric acid at fixed current density of 120 mA /cm²

It is seen that an alumina nano template with controlled pore dimensions can be achieved by altering the solution composition and operating temperature at fixed current density. At fixed current density of 120 mA/cm², if the concentration of sulphuric acid is increased,

the pore sizes decreases as reflected from X ray diffraction data as well as SEM images.. Figure 4 and 5 displays the SEM micrograph of anodized aluminum at 1 M and 2.5 M sulphuric acid at 120 mA/cm² cd. and 27 °C. Unlike the alumina nanotemplates from sulphuric acid baths, the same from oxalic acid baths produced less ordered alumina nanotemplates with larger pore diameter distribution. The average particle size was estimated from X-ray diffraction peak and width pattern, using Scherer's formula as follows.

$$t = \frac{0.09\lambda}{B \cos \theta_B} \text{ nm}$$

where, t = average particle size, Å; B = spread at half the intensity (width of peak at half the peak height), radians; λ = wavelength of X-Ray; θ_B = Bragg angle.

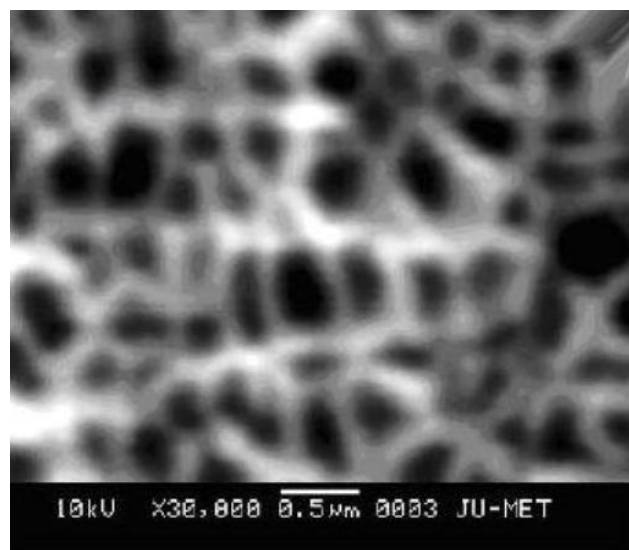


Figure 4 : Two stage anodizing in 1M sulphuric acid at fixed current density of 120 mA /cm²

Spread at half the intensity (B) is found out by determining the peak height and then finding the width of the at half the peak height. This value is multiplied by $\pi/180$ to get the value of B in radians. The data and the details of determination of pore diameter is depicted in TABLE 1. The effect of increasing acid concentration on reduction of pore size is also very well reflected here. For anodization in sulphuric acid, the average pore size decreases from 37 nm to 12 nm as acid concentration is increased from 1M to 3.5 at same current density of 120mA/cm² and temperature 27 °C. It is also to be noted here that for oxalic acid, while pore size decreases with increase in

Full Paper

acid concentration, pores are larger in size compared to that with sulphuric acid.

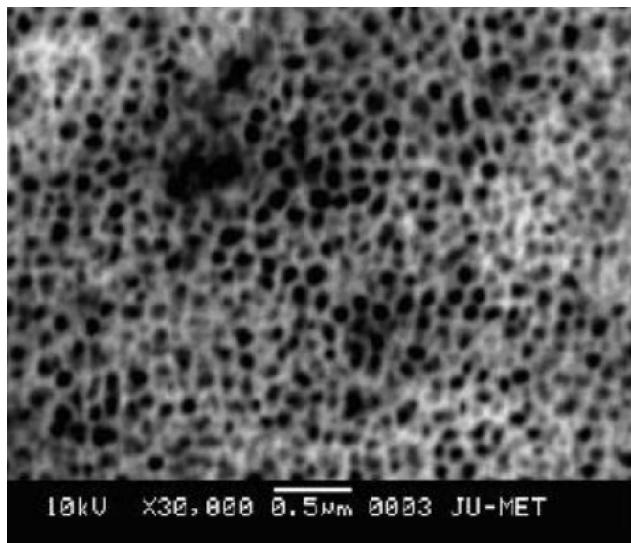


Figure 5 : Two stage anodizing 2,5M sulphuric higher at fixed current density of 120 mA/cm²

TABLE 1: Pore size determination

λ of Cu Kα radiation =1.54 Å ⁰					
Sl. No.	Anodized aluminium sample	'd'-value	Spread at half the intensity, radians (B)	2θ	Pore Size nm
1.	by 0.2M oxalic acid	1.2214	0.01268	78.2	140.86
2.	by 0.5M oxalic acid	1.2214	0.001484	78.2	120.373
3.	by 1M H ₂ SO ₄	1.2214	0.00479	78.2	37.28
4.	by 2.5M H ₂ SO ₄	1.2214	0.00609	78.2	29.28
5.	by 3.5M H ₂ SO ₄	1.2214	0.01457	78.2	12.249

Anodization of aluminum is a process of following electrochemical reactions

Anodic dissolution at the metal | Oxide Interface



At Oxide | Electrolyte Interface



Cathodic reaction



Pores are created by the reaction (1), while growth of oxide occurs due to reaction (2). By controlling the rates of these two reactions, Percentage porosity as well as pore size can be retrained. Al³⁺ ions are generated and

accumulated at the metal | Oxide Interface, while O²⁻ ions from the solution specifically adsorb at the Oxide| electrolyte Interface, giving rise to layer of opposite charges across the two faces of the oxide layer, producing an electrical field. Application of external potential (anodization voltage) control the field and mobilization of oppositely charged ions towards the opposite direction, causing porous anodized oxide. Since under a minimum electrical field strength, ions initiate to move, a minimum potential is to produce the porous anodization. This is well reflected in Figure 1 and 2, which show the potential (voltage) initially increased slowly with an increase in applied current densities, followed by a rapid increase. This change of inflection of the curve is functions of electrolyte type, its concentration and temperature, which influence concentrations of ions and mobility of ions. It is interesting to observe from Figure 1, at fixed current density, higher electrical field (potential) is required to mobilize more ions to move and generate uniform distribution nano pores with smaller pore size, with increasing acid concentration.. Higher current density enhances the kinetics of the anodic reaction(1), while higher electrical field force the ions to move out to generate pores, penetrating the oxide layer.

Polarization studies of the nano porous anodized aluminum was carried out in cathodic and anodic electrolytes to find its behavior as electrode material. Figure 6 depicts the anodic and cathodic polarization behavior of the electrodes anodized by 1M oxalic acid and 1M sulphuric acid. The Tafel lines have been produced backwards to cut the horizontal lines of reversible potential of anodic and cathodic reactions to estimate and compare exchange current density. It is seen that anodic exchange current density I_{0a} for the electrode produced by anodization in sulphuric is few hundred times more than that of one produced in oxalic acid. It was found from the foregoing results and discussions much smaller size nano pores was produced with anodization in sulphuric acid. The cathodic exchange current density I_{0c} is also found to be much higher for the electrode produced in sulphuric acid compared to one in oxalic acid, where its I_{0c} value is in the much lower order (point of intersection not seen in the Figure 6). Assuming the electrolyte resistance is negligible, maximum current drawing capacity of the fuel cell I_{max}, is found 30-40 times higher for electrode produced in sulphuric acid compared to one in oxalic acid.

Limiting current density I_L has also been illustrated in the Figure 6. Diffusional rate is also found to be dependent on pore size. One with narrower pore (with sulphuric acid) is giving higher limiting current density. Figure 7 illustrates and compares similar polarization behavior of the electrodes anodized in higher (SulCa2 & SulAn2) and lower (SulCa1 & SulAn1) concentrations of sulphuric acid. It was already found in the foregoing paragraphs that higher the acid concentration, smaller is the nano pore size. It is clearly seen here all the properties of the electrode, viz. exchange current density I_0 , limiting current density I_L and maximum current delivering capacity I_{max} are much greater with the electrode produced with anodization in higher concentration of acid (3.5M). Thus it produces a high energetic material that can be used in fuel cell with much less polarization and more current and energy delivering capacity.

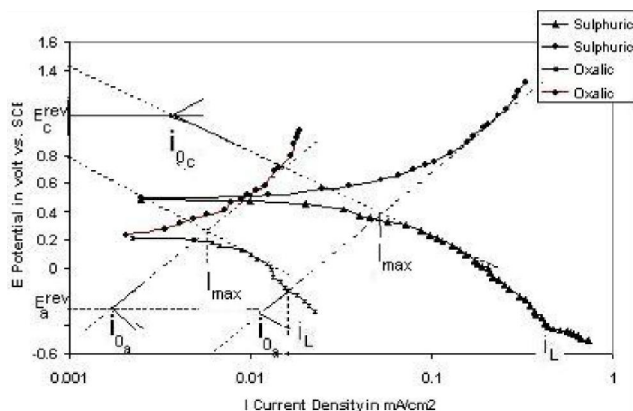


Figure 6 : Comparison of polarization curves of nano porous electrode produced by anodization in 1M oxalic acid and sulphuric acid

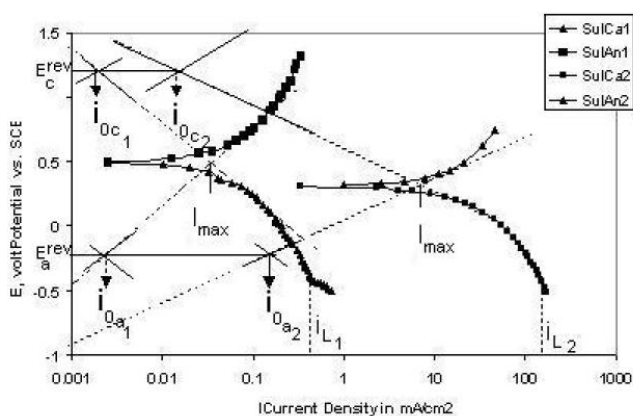


Figure 7 : Comparison of polarization curves of nano porous electrodes produced by anodization in 1M and 3.5M sulphuric acids. The curves illustrate higher anodic and cathodic current density for smaller nano pores sizes

A planer electrode having a 2D geometry, will draw smaller current per geometric unit area, whereas a porous electrode is of 3D geometry and having much higher specific surface area. Porous electrode containing catalytic material into the pores help to enhance the kinetic of the electrode reactions. Nano porous pores of the electrode, also influence the limiting current density I_L . Since diffusion boundary layer δ gets reduced by many times due to formation of 3-phase boundary of gas, electrolyte and solid electrode^[15]. This increases the limiting current density by many folds.

CONCLUSION

Nanoporous alumina template could be formed by anodization in acids at some fixed current density and temperature. Two stage anodization process produces more ordered and uniformly distributed nano pores. It is seen from scanning micrographs and X ray diffraction analysis that pore size decreases with increase in concentration of acid. The pore diameter in the order of 12-3 nm was achieved by anodization in 3.5M sulphuric acid at 120mA/cm² current density. Polarization studies revealed high exchange current density and limiting current density for the fabricated nano porous electrodes in both Cathodic and anodic solutions. Electrodes developed are well suited for high energetic electrode material for Bioelectrochemical fuel cells.

ACKNOWLEDGEMENT

The work was performed with financial support from Nano Science & Technology, Jadavpur University, Kolkata.

REFERENCES

- [1] R.E.Ricker, A.E.Miller, et al.; J.Electron Mater., **25**, 1585 (1996).
- [2] H.Masuda, et al.; J.Appl.Phys., **40**, L1217 (2001).
- [3] M.Sun, et al.; Appl.Phys.Lett., **78**, 2268 (2001).
- [4] Nano Lett., **2**, 677 (2002).
- [5] B.Das, S.P.McGinnis; Appl.Phys.A.Matter., **71**, 681-8 (2000).
- [6] H.Masuda, K.Fukuda; Science, **268**, 1466-8 (1995).
- [7] H.Masuda, et al.; J.Electrochem.Soc., **144**, L127-30 (1997).

Full Paper

- [8] A.P.Li, F.Muller, A.Bimer, K.Niensch, U.Gosele; J.Appl.Phys., **84**, 6023-6 (1998).
- [9] O.Jessensky, F.Muller, U.Gosele; J.Electrochem. Soc., **145**, 37735-40 (1998).
- [10] M.V.Myung, et al; Nanotechnology, **15**, 833-838 (2004).
- [11] C.Y.Liu, A.Datta, Y.L.Wang; Appl.Phys.Lett., **78**, 120-2 (2001).
- [12] Z.Sun, H.K.Kim; Appl.Phys.Lett., **81**, 3458-60 (2002).
- [13] S.Paul, A.Jana; Study on bioelectrochemical fuel cell with algae, Journal Institution of Engineers, Interdisciplinary, **88**, May (2007).
- [14] Fabrication and characterization of bioelectrochemical fuel cell with pyrolysed produced bio oil and hydrolysed biomass by fermentation subir paul and prakash mondal, Journal Institution of Engineers, Interdisciplinary, (2010).
- [15] J.O.M.Bocris, A.K.Reddy; Modern Electrochemistry, McGraw-Hill Book Company, **1**, 1812.