Contents lists available at ScienceDirect

Electrochimica Acta

The impact of viscosity of the electrolyte on the formation of nanoporous anodic aluminum oxide

Wojciech J. Stępniowski [a,*], Dominika Forbot [a,b], Małgorzata Norek [a], Marta Michalska-Domańska [a], Artur Król [c]

[a] Department of Advanced Materials and Technologies, Faculty of Advanced Technologies and Chemistry, Military University of Technology, Kaliskiego 2 Str. 00-908 Warszawa, Poland
[b] Institute of Chemistry, Faculty of Advanced Technologies and Chemistry, Military University of Technology, Kaliskiego 2 Str. 00-908 Warszawa, Poland
[c] Division of Tribology, Surface Engineering and Operating Fluids Logistics, Institute of Motor Vehicles and Transportation Faculty of Mechanical Engineering, Military University of Technology, Kaliskiego 2 Str. 00-908 Warszawa, Poland

ARTICLE INFO

ABSTRACT

Anodic aluminum oxide was formed in 0,3 M oxalic acid at various content of glycerol (from 0 to 100 vol. %), at voltage range from 20 to 60 V (30 °C, 1 h long steps). Due to the influence of viscosity on the ionic mobility, current density, as well as on the thickness of the grown oxide, current density and thickness of the grown oxide were found to be linear functions of the inversed viscosity. Quantitative FE-SEM images analyses revealed surprising relation: interpore distance increases with the viscosity (logarithmic function). Additionally, pore diameter, porosity and pores density were also influenced by viscosity of the electrolyte. We have found that viscosity of the electrolyte, one of the most important factors in electrochemistry, has significant influence on the anodic alumina formation.

1. Introduction

Self-organized anodization of aluminum provides hexagonally arranged anodic aluminum oxide (AAO). This ordered nanomaterial is well-known for its numerous applications in nanofabrication [1–8], energy harvesting and storage [9–11], sensors assembly [12,13], biomaterials development [14,15], surface enhanced Raman spectroscopy [16–18] etc.

Typically, it is formed in accordance to the two-step self-organized procedure: after the first step of anodization, chemical etching of the grown, poorly ordered AAO is done and bare aluminum with concaves, resulting from the first step of anodization, is re-anodized at the same set of the operating conditions [19,20]. The most commonly applied electrolytes are: sulfuric acid [21–23], oxalic acid [20,21,24–26] and phosphoric acid [21,27,28], at voltage range 15-25, 20-60 and 120-195 V, respectively. Additionally, there are numerous other electrolytes applied for AAO fabrication. For example anodizations in electrolytes like squaric [29], malic [30,31] citric [32], malonic [31,32], maleic [31], tartaric [31,32], tartronic [31], glutaric [31], lactic [33], propionic [33], glycolic [33] and succinic, [31,33] acids were successfully performed.

Electrolytes with additions of various modifiers are applied to form AAO in new conditions [34], to change the kinetics of growth [35], or to gain new properties [36]. Zaraska et al. formed AAO in phosphoric acid with addition of various alcohols to prevent anode from burning and to influence the kinetics of AAO growth [28]. In one of our previous papers, we have reported anodization in an ethylene glycol solution of sulfuric acid [37]. Nguyen et al. formed AAO in a glycerol solution of phosphoric acid at temperatures above the water boiling point [38]. Therefore, anodization even in non-aqueous electrolytes is possible.

According to the mechanism of AAO growth, changes of the viscosity occur at the anode/electrolyte interface [39]. Therefore, changing of the viscosity of the electrolyte may have an impact on the growth of AAO. Furthermore, Pashchanka and Schneider [39], taking into account viscosity and conductivity of the electrolyte, have postulated a criterion number, and ascribed to this number a major role in the AAO growth. Yet, a systematic study on the influence of electrolytes viscosity or conductivity on the growth of anodic aluminum oxide has not been reported.

There is a need for a wider range of pore distances and diameters of AAO obtained via self-ordering, due to the nanofabrication. Tailored geometric features of AAO in a much wider range,

* Corresponding author. Tel.: +48 22 683 94 46; fax: +48 22 683 94 45.
  E-mail address: wstepniowski@wat.edu.pl (W.J. Stępniowski).

resulting also from viscosity changes of the electrolyte can expand the fields of this material applications. Moreover, viscosity is one of the important factors in the electrochemistry, influencing i.e. ionic mobility, diffusion coefficient, or current density. Thus, influence of viscosity on the formation of AAO should be studied systematically. In this paper, the task is undertaken shedding some new light on the AAO growth mechanism. The systematic study of the influence of the viscosity on the AAO formation, including its influence on the current density as well as on the formed oxide thickness and nanopores geometry is carried out.

2. Experimental

A high purity, annealed 0,25 mm thick Al foil (99,9995%, Alfa Aesar) was cut into coupons (2,5 cm x 1,0 cm), degreased in acetone and ethanol and electropolished (1:4 volume mixture of $HClO_4$ and C_2H_5OH at constant current density of 500 mAcm^{-2} for 1 min at 10 °C, Pt grid as a cathode). Electropolishing was performed in 0,5 dm^3 double-walled cell, equipped in a thermostat with circulator (Lauda 105). After electropolishing a working surface area was limited to 1,0 cm^2 with the use of acid resistant paint. Also back and the edges of the samples were painted.

The aluminum samples were anodized in 0,3 M oxalic acid at constant temperature of 30 °C for 1 h at various voltages (20–60 V with a step of 10 V) and under various viscosity of the electrolyte, tuned by addition of the glycerol (0, 20, 40, 60, 80, 100 vol. % of the glycerol). After the first step of anodization, formed oxide was chemically removed in a stirred mixture of 6 wt % H_3PO_4 and 1.8 wt % H_2CrO_4 at 60 °C, for 1 h. Next, the samples were re-anodized at the same set of the experimental conditions.

Conductivity of the electrolytes was measured in a thermostated cell, with Elmetron CC 505 conductivity meter. At the end, average values from five measurements are given.

Viscosity of the electrolytes was measured according to the ASTM D445 standard.

Geometrical features of AAO and microanalysis of chemical composition were performed using field-emission scanning electron microscope FE-SEM (FEI, Quanta) equipped with energy dispersive X-ray spectrometer (EDS). The quantitative image analyses were done with freeware software: WSxM [40,41] and ImageJ [42]. For every quantitative image analysis, three images of sample from various zones were done at the magnification of 50,000x and averaged values were taken into account for further calculations.

Oxide layer thickness was evaluated from the cross sections of AAO. At least five cross section images were taken for a sample at given set of operating conditions.

3. Results and discussion

3.1. Influence of the viscosity of the electrolyte on the current density during anodization

Viscosity of the electrolyte is related to the ionic mobility (u) through the following equation (1) [43]:

$$u = \frac{ze}{6\pi\eta a} \tag{1}$$

where z is ion's charge, e is elemental charge, η is the viscosity and a is a hydrodynamic radius of the ion including solvent particles associated with the ion. Moreover, according to the empirical Walden's principle, electrical conductivity of the electrolyte (σ) is inversely proportional to the viscosity (2) [43]:
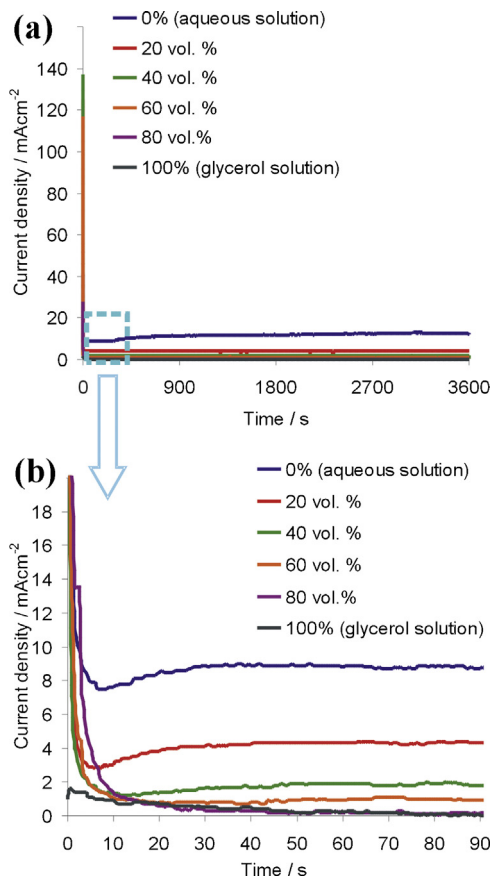
$$\eta \cdot \sigma = const. \tag{2}$$

Fig. 1. Current density vs. time recorded for the second step of anodization in 0,3 M $(COOH)_2$ at 40 V.

The current density during the electrochemical processes is described according to the following equation (3) [44]:

$$j = \alpha c_0 e (z_+ u_+ + z_- u_-) E \tag{3}$$

where j–current density, α–dissociation fraction, c_0–concentration, $z_{+,-}$–ions charge coefficient, e–elemental charge, $u_{+, -}$ - ionic mobility of cation and anion respectively, E–electric field intensity.

In liquid solutions the reactions are often controlled by diffusion, and therefore, the diffusion coefficient of the ions during anodization may strongly regulate the occurring phenomena. According to the Einstein's equation, diffusion coefficient (D) depends on the ionic mobility (u) (4) [43,44]:

$$D = kTu |z| \tag{4}$$

where: k–Boltzmann's constant, T–temperature, z–ions charge coefficient.

If the viscosity change influences the current density and the diffusion coefficient, one should expect repercussions on the AAO growth and new relations in this matter should be revealed.

In Fig. 1 current density vs. time graphs are presented for the second step of aluminum anodization at 40,0 V for various content of the glycerol in the electrolyte: from aqueous to pure glycerol 0,3 M solution of oxalic acid. As expected from the equations mentioned above, increased viscosity (Table 1) caused electrical conductivity and ionic mobility drop (Table 1) (1, 2), which, in turn, implied current density decrease (3) (Fig. 1a). For anodizations conducted in aqueous solution and with addition of 20 and 40 vol. % of the glycerol a typical anodization curves are observed consisted of three intervals: rapid decrease indicating formation of the barrier layer, slight increase indicating pores nucleation and a constant current density, indicating steady state pores growth (Fig. 1b). For greater