



The influence of electrolyte composition on the growth of nanoporous anodic alumina



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ARTICLE INFO

Article history:

Received 19 April 2016

Received in revised form 20 May 2016

Accepted 15 June 2016

Available online 16 June 2016

Keywords:

Anodization

Self-organization

Alumina

Nanopores

Ionic mobility

ABSTRACT

Aluminum was anodized in mixtures of aqueous sulfuric and chromic acid in different ratios, with overall concentration of 1.0M. It was found that the logarithm of current density (and consequently, oxide growth rate) is a square function of the anodizing voltage. Moreover, the barrier layer thickness at the pores bottom was found to increase exponentially with the voltage, and increased as well with the fraction of chromic acid in the electrolyte. Additionally, interpore distance of anodic aluminum oxide, formed at the same voltage, was found to increase exponentially with the molar fraction of the chromic acid. Altogether, the high impact of the composition of the electrolyte on the morphological features of the nanoporous arrays is revealed.

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1. Introduction

Anodization of aluminum gives numerous opportunities to researchers in the field of nanofabrication. Recently, several advances in catalysis [1], optics [2], fuels cells assembly [3,4], energy storage [5], sensors performance [6,7], surface enhanced Raman spectroscopy (SERS) [8,9], magnetic materials engineering [10,11], biomaterials engineering [12], drug-releasing platforms [13,14], structural color generation [15–17] and fabrication of hierarchical 3D nanostructures [18], were achieved with the use of anodic aluminum oxide (AAO).

To form nanoporous AAO, aluminum is oxidized in acidic electrolytes at relevant voltage range, determined by the type of the electrolyte. Geometrical features of AAO, like pore diameter, interpore distance and thickness of the formed anodic oxide are controlled by the operating conditions like type, concentration and temperature of the electrolyte [19–24], applied voltage [19–24] and duration of the second step of anodization [19–24].

Recently, to widen the area of experimental conditions, new, organic and inorganic, electrolytes are being applied [15,17,25,26], as well as new approaches like pulse anodizing [16] or sinusoidal anodizing [27]. Moreover, various additives are being introduced to the electrolyte to form AAO at lower voltages [28], or with higher oxide growth rate [29]. Additionally, anodization in non-aqueous electrolytes is also performed [30,31]. It was found that the higher the viscosity of the electrolyte the larger the interpore distance and the lower the oxide growth rate [32]. It was found that ionic mobility plays important role in the AAO growth [32]. For the same reason, anodizations in mixed electrolytes are being performed, e.g. sulfuric acid with oxalic acid [33–36], oxalic acid with phosphoric acid [37], and phosphoric acid with citric acid and ethylene glycol [38]. All these anodization strategies mentioned above allowed to form AAO with nanopores significantly varied in size: from about 10 nm in diameter up to micron scale [38].

Despite the anodization in mixed electrolytes has been already reported, until now no in-depth study of the influence of the mixed electrolyte composition on the AAO growth has been presented. Moreover, it is suspected that various compositions of the electrolyte may have similar impact on the anodic oxide growth,

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in terms of current density, oxide growth rate and morphological features, as viscosity, while both viscosity and average hydrodynamic radius of the electrolyte are inversely proportional to the ionic mobility, and linked with current density [32]. In this work, the influence of electrolyte composition on the anodic oxide growth phenomena is systematically researched in detail. Sulfuric acid and chromic acid mixtures with various molar ratio were chosen to anodized aluminum. Both electrolytes are applied in industrial practice and fundamental research as well.

2. Experimental

High purity (99.9995%), 0.25 mm thick Al foil (Alfa-Aesar, Puratronic) was cut into samples (25 mm × 10 mm), degreased (in acetone and ethanol subsequently) and electropolished (in a mixture of perchloric acid and ethanol, HClO₄:C₂H₅OH 1:4 vol., at 0 °C and 20 V for 2 min). The so-prepared samples were protected with acid-resistant non-conductive paint at back and edges, such that the working surface area was limited to ~1.0 cm². The samples were then anodized for 12 h at 0 °C in aqueous electrolytes containing sulfuric and/or chromic acid of various molar proportions, accordingly to Table 1. To prevent aluminum samples anodized in sulfuric acid from “burning”, temperature equal 0 °C was applied [39,40]. The samples were anodized at voltage ranging from 15 to 60 V with 5 V steps. The upper voltage according to a set limitation against too high current densities *j*, occurring for the most aggressive electrolyte compositions, which would otherwise cause “burning” of the anode [39,40]. After anodization, the formed oxide was chemically removed in a mixture of 6 wt.% H₃PO₄ and 1.8 wt.% H₂CrO₄ at 60 °C for 90 min. Subsequently, the samples were re-anodized at the same operating conditions as during the first anodization, to obtain highly-ordered nanoporous AAO.

Characterization of the AAO morphology was done with scanning electron microscope (SEM) imaging made with field-emission (FE) SEM instrument Quanta D FEG (FEI, USA). The oxide growth rate *d* was estimated from the FE-SEM cross sectional images of AAO.

To obtain average pore diameter, 3 FE-SEM images from each sample were taken and analyzed with NIS-Elements software. Depending on the operating conditions, approximately 2000 of pores per sample were analyzed and 3σ test was applied.

To estimate average interpore distance, 3 FE-SEM images from each sample were taken and analyzed with WSxM software [41,42]. Radial averages of fast Fourier transform of each image were calculated. The inverted value of the abscissa of the radial average maximum equals interpore distance.

3. Results and discussion

Fig. 1 shows the first 50 min of the second step of anodization at 25.0 V. It is clearly seen that the higher the molar fraction of chromic acid x_{Cr} the lower the current density *j*. This is caused by the decrease in the ionic mobility of the electrolyte with the

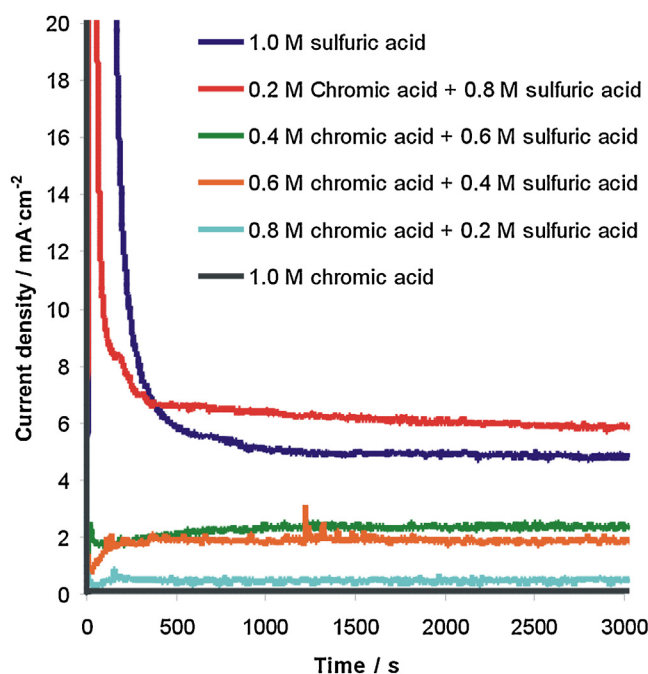


Fig. 1. First 3000 seconds of the second step anodization performed at 25.0 V in electrolytes with various values of the molar fraction of chromic acid.

increase of chromate content. In fact, the hydrodynamic radius *a* of the sulfate anion is smaller than that of the chromate anion, what has direct impact on their mobility *u*, according to [32,43]:

$$u = \frac{ze}{6\pi\eta a} \quad (1)$$

where *e* is elemental charge, *z* is the ion charge in *e* units, and η is electrolyte viscosity. Additionally, there is a linear relation between the ionic mobility *u* and the current density *j* [32,43]:

$$j = \alpha c_0 e (z_+ u_+ + z_- u_-) E \quad (2)$$

where α is the dissociation fraction, *c*₀ the concentration, *z*_± the ion charge coefficient, *u*_± the ionic mobility of cation and anion respectively, and *E* the electric field intensity. As can be seen in Eq. (2), not only the ionic mobility has a great impact on the current density, but also the dissociation fraction of the electrolyte has. H₂SO₄ is considered as strong acid, while H₂CrO₄ has a pK_{a1} of 0.74, which means a much lower dissociation fraction, and this is another reason for the decrease in current density *j* with the molar fraction x_{Cr} . Additionally, for mixed electrolytes, especially for those with lower pH, CrO₄²⁻ anions may transform into Cr₂O₇²⁻ anions (or in larger ones) with bigger hydrodynamic radius and lower mobility, what additionally decreases the current density for chromate-rich electrolytes.

Table 1
Chemical composition of the electrolytes and applied voltage range.

Concentration of sulfuric acid/M	Concentration of chromic acid/M	Molar fraction of chromic acid x_{Cr}	Applied voltage range/V
1.0	0	0.0	15-25
0.8	0.2	0.2	15-55
0.6	0.4	0.4	15-60
0.4	0.6	0.6	15-60
0.2	0.8	0.8	15-60
0	1.0	1.0	15-60

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