



## High-field anodization of aluminum in concentrated acid solutions and at higher temperatures

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### ARTICLE INFO

#### Article history:

Received 16 January 2012

Received in revised form 23 March 2012

Accepted 26 March 2012

Available online 3 April 2012

#### Keywords:

Porous anodic alumina  
High-field anodization  
Self-ordering  
Barrier layer  
Avalanche breakdown

### ABSTRACT

Previous studies suggested that high-field anodization of aluminum could be realized only in relatively dilute acid at a low temperature to avoid the occurrence of undesired breakdown during anodization process. According to the model of avalanche breakdown, we proposed that the key to preventing the breakdown is to reduce the barrier-layer thickness of porous anodic alumina (PAA). Since the barrier-layer thickness of PAA decreases with increasing the acid concentration and temperature, the breakdown phenomenon during high-field anodization should not be occurred in concentrated acid solutions and at higher temperatures. Anodization behaviors of aluminum in concentrated oxalic acid solutions and at higher temperature were studied in detail. The results indicated that in the oxalic acid solutions of higher concentrations (>0.3 M) and at higher temperatures (16–40 °C), stable high-field anodization can be realized without the occurrence of breakdown and well-ordered PAA films can be available. Moreover, the well-ordered PAA film can be obtained even without stirring of the electrolyte. Our findings offer not only a simple and fast fabrication process of PAA templates but also an opportunity to fully understand the breakdown and the self-ordering mechanism during the growth of PAA.

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### 1. Introduction

Porous anodic alumina (PAA) films have received particular attention throughout the nanomanufacturing community over the last decade as popular templates for fabricating various functional nanostructures [1–5]. Considerable research efforts have been directed toward the fabrication of the PAA with long-range ordered nanoholes [5–16]. Several special methods have been developed to achieve this goal. For example, Masuda and other workers proposed a two-step anodization process and a pre-texturing process to successfully fabricate PAA films with perfect nanopore arrays [5–7]. Their fabrication techniques generally utilize a constant-voltage anodization mode. This conventional constant-voltage anodization is characterized by low current densities through the barrier layer of PAA ( $\sim 5 \text{ mA cm}^{-2}$ ) and narrow process windows for self-ordered PAA films [1,8–13]. Furthermore, these fabrication methods typically require tedious pretreatment procedures and long processing time (even up to a few days) due to the slow oxide growth rates (e.g.,  $2\text{--}6 \mu\text{m h}^{-1}$ ).

In order to realize the fast fabrication of highly ordered PAA films, Lee et al. later developed a so-called 'hard anodization' approach which is characterized by high current densities (or high electric field strength) and low electrolyte concentrations and

temperatures [14]. This hard anodization approach can achieve highly ordered PAA films with a high aspect ratio (>1000) of uniform nanopores and the growth rate of the PAA film is 25–35 times larger ( $>50 \mu\text{m h}^{-1}$ ) than that of the conventional anodization approach [14]. Other researchers also suggested that high electric field strength is a key controlling factor of self-ordering for PAA films [15–17]. Nevertheless, a phenomenon of electrical breakdown or burning is usually encountered during the hard anodization process owing to its high current density resulting in high electric field strength in the barrier layer of PAA. In order to suppress the breakdown effects or local burning phenomena, various techniques have been proposed. The method introduced by Lee et al. was to add a pre-anodization step, i.e., a thin uniform porous oxide layer on the aluminum surface was first formed by the conventional anodization process before the hard anodization process [14]. Chu et al. reported that the breakdown or burning voltage of PAA films would increase with the aging of the solution after a long period of anodization [16]. Hence, the aged solutions would exhibit higher breakdown voltages. Li et al. added ethanol into a phosphoric acid aqueous solution and obtained the highly ordered PAA films [18]. They claimed that stable high-field anodization ( $150\text{--}400 \text{ mA cm}^{-2}$ ) could be realized in the  $\text{H}_3\text{PO}_4\text{--H}_2\text{O--C}_2\text{H}_5\text{OH}$  system [18]. However, it is worth emphasizing that the electrolyte temperatures were required to be kept at a rather low value ( $\sim 0^\circ\text{C}$ ) during the whole high-field anodization process using a powerful cooling system for all these methods. We found that the effect of these

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methods on the suppression of breakdown was not evident when the temperatures were not sufficiently low ( $\sim 10^\circ\text{C}$ ) during anodizing. In reality, the low electrolyte temperature in these methods plays a more important role in suppressing the breakdown effects. For industrial applications, however, keeping a solution at low temperature is difficult to achieve and not cost-efficient since the high-field anodization process is accompanied by a large evolution of heat due to the high current densities.

Actually, the dielectric breakdown during anodizing of valve metals (Al, Ta, etc.) has been a subject of intensive research over the last decades due to its importance in the field of electrolytic capacitors [19–21]. Despite a tremendous amount of research has been carried out, the phenomenon of breakdown is still not well understood [22,23]. Especially for the phenomenon of breakdown during PAA growth process, there is relatively little work done although it is usually encountered in the fabrication of PAA films.

Several mechanisms have been proposed to explain the breakdown phenomenon [19–24]. The first attempt to develop a quantitative theory of the breakdown was made in 1977 by Ikonopisov [19]. By assuming a process of avalanche multiplication of electrons injected into the oxide conduction band by the Schottky mechanism, Ikonopisov has correctly predicted the dependence of breakdown voltage on electrolyte resistivity. Later, Albella et al. have extended the Ikonopisov model to explain the details of the breakdown phenomenon [21,22]. They reported evidence that electrolyte species incorporated into oxides act as a source of avalanching electrons [21]. It is known that the avalanche electron multiplication process by an impact ionization leads to an exponential increase of the electronic current with film thickness [22,25]. Hence, the breakdown would occur after the film has reached a given thickness ( $d_c$ ) sufficient to cause an increase of the electronic current up to a critical value [20]. This is why there is a limited thickness instead of an unlimited one when barrier-type anodic film is formed in neutral solutions. This is also why the breakdown is more easily encountered in phosphoric acid where the thicker barrier-layer is formed than that in sulfuric acid or oxalic acid for the conventional anodization. Consequently, the key to preventing the breakdown is to control the barrier-layer thickness of PAA. Previous researches have shown that the barrier-layer thickness of PAA decreases as the acid concentration and temperature increase [8]. Therefore, stable high-field anodization can be kept without breakdown by means of increasing the acid concentration and/or temperature. From this point of view, stable high-field anodization process may be performed in concentrated acid solutions and at higher temperatures.

In this work, we focused on anodization behaviors of aluminum in concentrated oxalic acid solutions and at higher temperature. The influences of the electrolyte concentration, temperature and current density on anodization behaviors were investigated systematically. The morphology and microstructure of the as-fabricated PAA films were also examined. This study was aimed at developing a simple but fast approach to fabricate well-ordered PAA films in concentrated oxalic acid solutions at room temperature. The well-ordered PAA films prepared in the present study should exhibit a homogeneous morphology of parallel pores which grow perpendicular to the surface with a narrow distribution of diameters and interpore distances ( $D_{int}$ ).

## 2. Experimental

High-purity ( $\geq 99.99\%$ ) aluminum sheets of 0.2 mm thickness were employed without the annealing step. The aluminum sheets were dipped into 2 wt.% sodium hydroxide solution at  $70^\circ\text{C}$  for chemical polishing for 2 min and then electropolished at a constant current density of  $120\text{ mA cm}^{-2}$  for about 1.5 min in an electrolyte

composed of phosphoric acid (80 wt.%), chromium trioxide (12 wt.%) and deionized water (8 wt.%) at  $75^\circ\text{C}$ . The electropolished aluminum sheet was used as the anode, another aluminum sheet with the same purity and larger surface areas was used as a cathode. Since the current density (or, the electric field strength) is an important parameter governing the structural parameters and growth rate of PAA, galvanostatic anodization was performed in the present work. Unlike the high-field anodization of constant voltage, galvanostatic anodization has a linear growth rate of PAA instead of a nonlinear growth rate, which is favorable for the control of film thickness. The applied current densities were in the range from  $25\text{ mA cm}^{-2}$  to  $100\text{ mA cm}^{-2}$ . The oxalic acid concentrations were examined in the range of 0.05–0.75 M. During the anodization process, the electrolyte was vigorously stirred in all experiments unless indicated otherwise. The electrolyte temperatures were not measured directly, but controlled by the water-bath temperatures preset in the range of  $6\text{--}60^\circ\text{C}$ . The electrolyte temperatures were typically less than  $1^\circ\text{C}$  and ca.  $5^\circ\text{C}$  higher than the preset water-bath temperatures with and without stirring of electrolyte, respectively.

The voltage–time responses during anodizing were recorded automatically by a computer measurement system described elsewhere [26]. The morphology of the PAA film was characterized by field-emission scanning electron microscope (FE-SEM, Hitachi S-4800). To facilitate the observation of cells arrangement, the as-prepared PAA films were dipped into a 5 wt.% phosphoric acid solution at  $30^\circ\text{C}$  for pore-widening treatment after the anodization.

## 3. Results and discussion

### 3.1. Influence of the electrolyte concentration

Fig. 1 shows the voltage–time curves for galvanostatic anodization of aluminum at  $50\text{ mA cm}^{-2}$  in oxalic acid solutions with different concentrations. In the initial period of anodization (Fig. 1, bottom panel), the resultant curves display a typical voltage–time

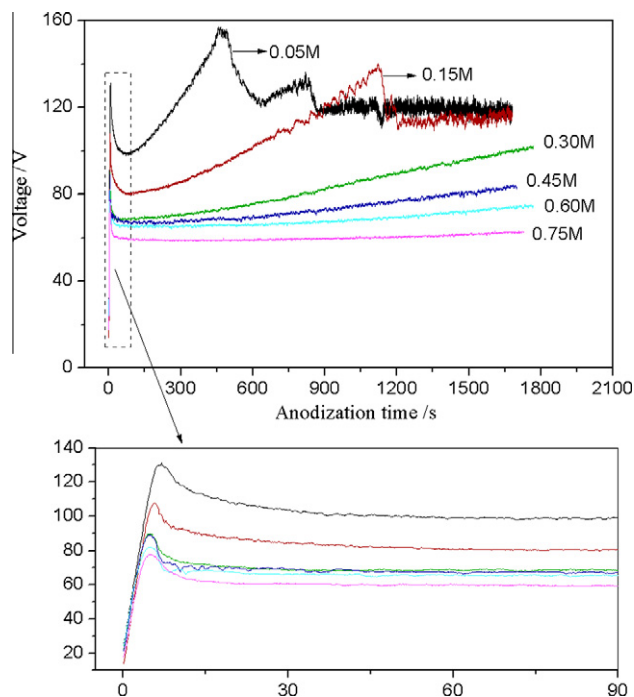


Fig. 1. Voltage–time transients for aluminum anodization at  $50\text{ mA cm}^{-2}$  in oxalic acid solutions with different concentrations at a water-bath temperature of  $25^\circ\text{C}$ . Bottom panel shows the voltage–time transients in the initial period of anodization.

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