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A new self-ordering regime for fast production of long-range ordered porous anodic aluminum oxide films

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ABSTRACT

Porous anodic aluminum oxide (AAO) films with large interpore distance (D_{int}, 307–415 nm) have been fabricated by using a new self-ordering regime in oxalic acid based electrolyte systems. The new regime corresponds to the stage with a stable voltage during constant-current anodization process, accompanied by high anodization voltage (U_a, 135–183 V) and current density (J_a, 300–500 A m^{-2}) which facilitate the high speed growth of long-range ordered porous AAO films. In addition, the formation mechanism of the self-ordering regime, together with the influence of anodization conditions on the microstructural parameters of AAO films have been investigated in detail. Experimental results showed that the value of the stable U_a during constant-current anodization can be adjusted by varying the anodization conditions. Accordingly, the self-ordering window of the as-prepared porous AAO films can be modulated, widening the regulating range of D_{int} to a large extent.

1. Introduction

Since the first report of carbon nanotubes by Lijima [1], many investigations have focused on production of nano- or submicron materials which have many desirable properties due to their unique structures [2,3]. Over the last decade, electrochemical methods toward this kind of materials have become a hot topic because of their significant applications in various fields, *e.g.*, bioanalysis, environmental protection, and industry [4–9]. Therefore, finding proper methods for production of these materials has attracted considerable attention, and will continue to prosper in the next few years. Porous anodic aluminum oxide (AAO) films formed by electrochemical anodization process of aluminum have been investigated for more than a century [10–24]. It has been known that porous AAO films with highly ordered pores (*i.e.*, the honeycomb structure) can be obtained when anodization is performed under a self-ordering regime [15,16]. In addition, the interpore distance (D_{int}), pore size (D_p), and thickness of the films can easily be regulated by varying the anodization conditions and chemical etching process [15,16,23,24]. Based on these unique characteristics, they have become one of the most commonly used porous templates for the synthesis of diverse nano or submicron materials which can be widely applied in various fields [25–36]. Moreover, they can also be used as porous functional materials for numerous applications, *e.g.*, photonics, sensors, biotechnology [37–41].

It is worth mentioning that the 'two-step anodization' process is the most commonly used method to obtain highly ordered porous AAO films [15–18,23,24,30,31]. Therefore, finding proper conditions of the first anodization for achieving long-range ordered structural cell arrangement at the barrier layer surface of AAO films is significant. Until now, most of the production processes are based on the conventional so-called 'mild anodization (MA)' which always requires quite a long processing time to obtain a satisfactory ordering of the structural cells, limiting their applications in industrial processes so far. Moreover, the self-ordering occurs only in narrow windows, resulting in a relatively smaller regulating range of D_{int}. It has been known that D_{int} and D_p will directly determine the spacing interval and external diameter of target nanoarrays, respectively. Considering that D_p can be controllably adjusted by a further chemical etching process, and the maximum D_p is dependent on D_{int}, developing appropriate methods for obtaining porous AAO films with large D_{int} has attracted much attention. Accordingly, the so-called 'hard anodization (HA)' has been applied in aluminum anodization processes [42–47]. Compared with MA, the HA processes need shorter anodization time for achieving highly ordered cells, and a wider self-ordering window can be obtained. However, the anodization current density (J_a) during constant voltage HA processes are usually unstable,

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e.g., exponentially decreasing with time. Considering that both the anodization voltage (U_a) and J_a are main influencing factors of D_{int}, it is difficult to fabricate porous AAO films with constant D_{int} along the pore growth direction. It has been known from the previous reports that ideally ordered porous AAO films can often be fabricated under two anodization stages: constant voltage anodization with a stable current (CVSC) or constant-current anodization with a stable voltage (CCSV) [15–18,24]. In addition, high U_a and J_a during anodization usually correspond to AAO films with large D_{int} and fast film growth rate, respectively. Therefore, finding new self-ordering regimes of porous AAO films in CVSC or CCSV anodization modes with high U_a and J_a is significant from the view point of both fundamental science and commercial applications.

In the present work, a simple, fast, and effective anodization process has been proposed for the production of long-range ordered porous AAO films with a large-range tunable D_{int} in oxalic acid based electrolyte systems, which corresponds to a new self-ordering regime. The self-ordering window of the porous AAO films can be easily regulated by varying anodization conditions in different CCSV modes. In addition, related mechanisms of the anodization processes have also been investigated. The findings in this work may widen the application of porous AAO films in diverse industrial processes.

2. Experimental

2.1. Materials and reagents

High-purity (99.999%) aluminum sheets with a thickness of 0.3 mm and a size of 1.5 cm × 1.5 cm were used as starting materials (Research Institute of Nonferrous Metals and Rare Earth Applications, Beijing, China). Analytically pure reagents were produced by Guangzhou Chemical Reagent Factory (China), including oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$, 99.5 wt%), perchloric acid ($HClO_4$, 70–72 wt%), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99 wt%), ethanol (CH_3CH_2OH, 99.7 wt%). The de-ionized water was produced by a pure water system (Ultra pure, Hitech, Shanghai, China).

2.2. Preparation of porous AAO films

The aluminum sheets were polished by using an electrochemical method at 5 °C and 21 V for 8 min in a mixed solution of perchloric acid and ethanol (1:4, V/V) to diminish the roughness of their surface. Then the sheet was carefully washed with de-ionized water and put into a holder which is made up of polymethyl methacrylate and aluminum nitride ceramic plates sealed by a silicone rubber gasket with a square area of 1 cm × 1 cm exposed to the electrolyte. The aluminum sheets worked as anode, and a graphite plate was used as cathode. The anodization were conducted in different electrolyte systems: Electrolyte I (0.3 M oxalic acid electrolyte), Electrolyte I with different addition ratios of ethanol (Electrolyte I: ethanol = 1: 0.2, 1: 0.33, 1: 0.5, 1: 0.75, 1: 2, V/V, respectively), with vigorous magnetic stirring (IKA RET basic, Germany) under 4–8 °C. A low temperature circulatory system (DFY-10L/10, YUHUA, Gongyi, China) and an electrolysis cell (1 L) were used in the anodization process. The heat generated during anodization was removed by using the aluminum nitride ceramic plate which was in thermal contact with the aluminum sheets. The anodization processes were performed as follows: (1) U_a was applied directly or increased linearly at a rate of 1 V s^{-1} until J_a reached the

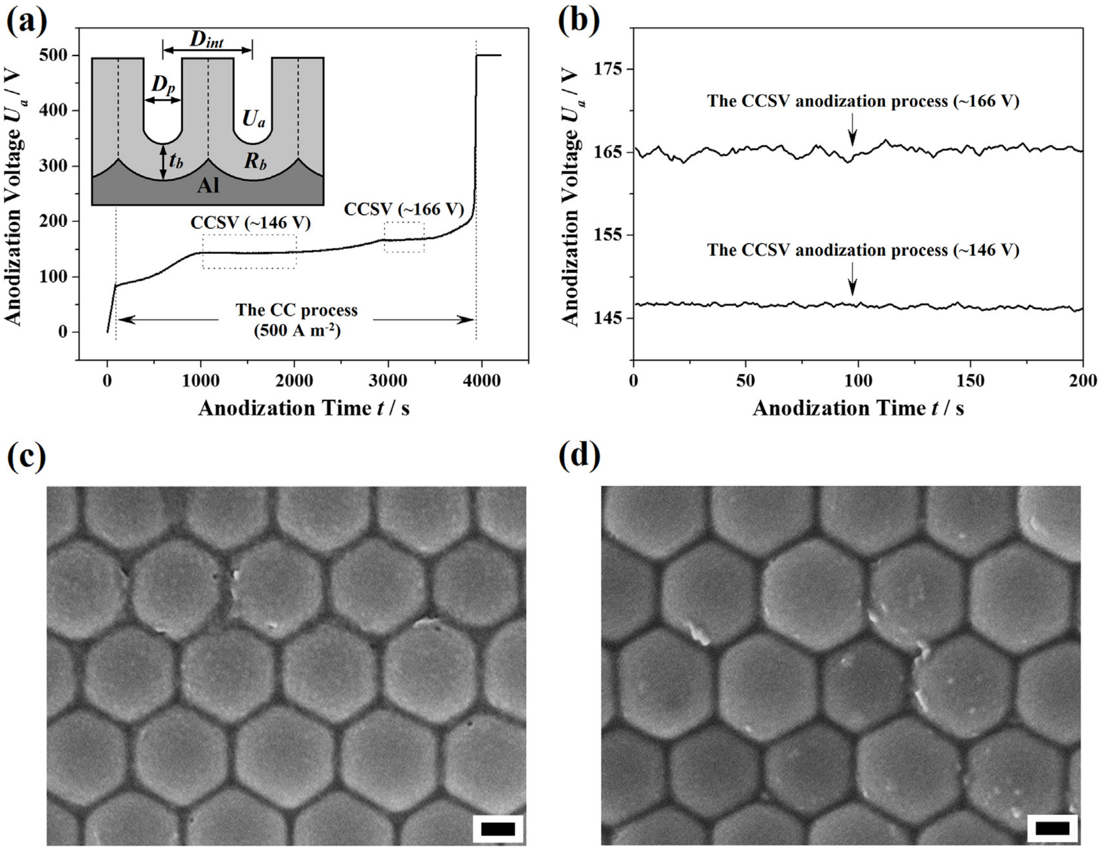

Fig. 1. The evolution of anodization voltage (U_a) as a function of anodization time (t) and corresponding barrier layer side SEM images of porous AAO films fabricated in Electrolyte I (8 °C): (a) the whole CC anodization process, and the structural model of porous AAO films; (b) the last 200 s of the production processes of porous AAO films under CCSV mode; (c) and (d) correspond to 146 V and 166 V, scale bars = 100 nm.