



Effect of ethanol on the fabrication of porous anodic alumina in sulfuric acid



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ABSTRACT

Porous anodic alumina (PAA) films with small pore diameters and interpore distances are significantly important in many practical applications such as isolation of pathogens, catalysis and molecular sieving. This kind of PAA films is generally prepared in diluted sulfuric acid, and the film growth is very slow due to the low anodizing potential and current density. Many efforts were done to enhance the PAA formation, and the majorities focused on increasing growth rate by increasing the anodizing potential, which also increases the pore diameter and interpore distance of the obtained PAA. In our paper, the influence of ethanol addition in electrolyte of sulfuric acid was studied in details. Results show that the addition of ethanol can maintain the low self-ordering potentials in sulfuric acid and at the same time significantly increase the growth rate of PAA. With a series of ethanol addition, it was found that with the 10% ethanol addition, the growth rate increases by 5 times from 1.6 $\mu\text{m}/\text{h}$ to 8 $\mu\text{m}/\text{h}$ at 2 °C and 25 V, and there is a nonlinear relationship between ethanol addition amount and PAA growth rate. These findings are of great significance for further investigation on PAAs with ultrasmall nanopores, as well as for PAA commercialization.

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1. Introduction

Porous anodic alumina (PAA) with self-organized hexagonal arrays of uniform parallel nanochannels has been intensively utilized as a template for fabricating various functional nanostructures in areas such as renewable energy, photonic devices, molecular sieving, pathogen isolation, and so on [1–7]. The increasing attraction of PAA template is mainly due to its relatively easy and low-cost preparation process. What's more, the structural features such as pore diameter, interpore distance and film thickness can be easily controlled by adjusting the anodizing conditions, such as electrolyte components, applied voltage, temperature and anodizing duration. For example, the most popular applied electrolytes for self-organized two-step anodization are sulfuric acid, oxalic acid and phosphoric acid, and the corresponding anodizing potentials are different from each other [8]. Combination of the electrolytes and potential regimes with anodizing time, people can prepare PAA templates with pore diameters ranging from 10 to 500 nm, interpore distances from 50 to 1100 nm, and film thicknesses from 0.1 to 150 μm [9–11], which can meet the needs in the fabrication of different nanostructures with controllable parameters.

PAA fabricated in sulfuric acid is particularly interesting because the anodizing potentials of 20–27 V in sulfuric acid are much lower than that in oxalic acid and phosphoric acid, and thus the realized PAA has smaller pore diameter/interpore distance. Smaller pore diameter is often required in the preparation of some nanostructures such as efficient thermoelectric generators, filtration, isolation of pathogens, catalysis, molecular sieving, and so on [12–15]. In addition, sulfuric acid electrolyte is commonly used in industry due to their low cost and ease of handling for circumstance. However, the anodization in sulfuric acid has its disadvantage of very slow film growth [16]. Our experimental data indicated that the growth rate is only 0.5 to 1.5 $\mu\text{m}/\text{h}$ with the voltage from 20 to 25 V under 0 °C and 0.3 M sulfuric acid, which means that 40–120 h is needed for fabricating a free-standing 60 μm PAA film (60 μm thickness is required for filtration). Furthermore, such long time anodization may destroy the surface due to the dissolution of alumina in sulfuric acid.

In recent years, various attempts to increase the growth rate in sulfuric acid have been reported. Chu et al. [17] successfully fabricated highly ordered PAA films in aged sulfuric acid with high growth rate under 40–70 V. Kathrin et al. [18] investigated the hard anodization of aluminum in sulfuric acid through multiple-step anodization through the voltage change and electrolyte change. Although these works have improved the growth rate, the applied voltages have been increased to 40–80 V, and the corresponding PAAs have a larger pore diameter

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and interpore distance compared with 20–27 V anodization in pure sulfuric acid. We noticed that Li et al. [19] fabricated highly ordered PAA films in phosphoric acid electrolyte with ethanol addition and improved growth rate while maintaining self-ordering potentials unchanged. Some organic materials were also reported to protect PAA pore walls from the dissolution in an acidic electrolyte [20]. So in this letter, we studied the oxidation process of PAAs in sulfuric acid with various ethanol additions under low voltages from 20 to 30 V. The main objective is to increase the growth rate while maintaining the low anodizing potentials, i.e. to fast fabricate PAAs with small pore diameter and interpore distance. Results indicate that addition of small amount of ethanol (5 and 10%) can speed up the anodizing growth. Especially, 10% ethanol addition can bring about 5 times growth rate. With more ethanol addition, the growth rate goes down. The nonlinear effect of ethanol was discussed from the view of PAA formation. This work is very important for fast growth of PAA with smaller nanopores and interpore distance.

2. Experimental details

Prior to anodization, Al sheets (99.99% purity, 0.25 mm thickness) were first annealed at 500 °C under vacuum ambient for 2 h to remove mechanical stress and then electropolished in a mixed solution of HClO₄ and C₂H₅OH (1:4, volume ratio) to obtain a smooth surface. PAAs were fabricated using a typical two-step anodization process in sulfuric acid with various ethanol additions. The concentration of sulfuric acid was 0.3 M and the volume proportions of ethanol, P_E, were chosen as 0, 5, 10, 20, 30, 40 and 50%. The anodizing potentials varied from 20 to 30 V, and the temperature of the electrolyte was controlled at 2 °C throughout the whole duration of the anodization. The first anodization step lasted for 5 h and the formed oxide layer was removed by immersing it in a mixture of 6.0 wt.% H₃PO₄ and 1.8 wt.% H₂CrO₄ at 60 °C for 2 h and the second anodization was carried out under the same condition as the first one.

The morphology of the PAA films was investigated by field-emission scanning electron microscope (JSM 7500F) under 5 kV or 6 kV after sputtering a sub-10 nm layer of Pt. The current density during anodization was recorded at an interval of 1 s.

3. Results and discussion

Under the experimental conditions described above, the self-ordered potentials in pure sulfuric acid ranges from 20 to 25 V, and

the corresponding top-view SEM images of PAAs fabricated under 20 and 25 V are shown in Fig. 1a and b, respectively. When anodizing potentials are lower than 20 V, the arrangement of the cell became irregular although the current density is steady. And if the potential exceeds 25 V, the current density goes too high, and the anodization becomes unstable with sample burning. After addition of ethanol, the self-ordered potential regimes are broadened slightly. As shown in Fig. 1c and d, the upper limit potentials increase to 27 V for P_E = 5% and 30 V for P_E = 50% from 25 V for pure sulfuric acid while the lower limit of potential is unchanged, i.e. 20 V. Fig. 1e–g show the barrier side (bottom view) topographic images of PAA films anodized in P_E = 50% at different potentials in self-ordering regime scope. The highly ordered, hexagonal patterns of hemispherical cells are achieved. As a representative, Fig. 1h gives the cross section view of PAA prepared at P_E = 50% under 30 V, and it is clear that the nanopores are straight and parallel to each other.

The addition of ethanol does not impact the pore diameters and interpore distances due to the unchanged low potentials. As an example, Fig. 2 shows the top surfaces and cross-section of PAA films anodized at the same anodizing potential, 25 V, in mixed electrolytes with different additive amount of ethanol. The average pore diameters are 15 nm, 15 nm, and 17 nm when the ratios of ethanol are P_E = 0%, 5% and 50% respectively. At the same time the average interpore distances of PAA films are 68 nm, 65 nm, and 65 nm in three conditions. These data confirm that at the same anodizing potential, the addition of ethanol does not change these two important factors of PAAs.

The most interesting result is the PAA growth rate change due to the ethanol addition. Fig. 3 shows the cross sectional view of the PAAs fabricated at 25 V under 2 °C for 5 h with P_E = 0%, 5%, 10%, 20%, 30%, 40% and 50%, respectively. These SEM images directly present the pore depth, i.e., PAA film thickness, of 7.98, 24.1, 40.2, 22.5, 18.0, 14.0 and 5.41 μm, respectively. In order to show the complete lengths of the PAA films, the images were not taken at identical magnification and the thickness were measured with SEM software in accordance with every magnification. The enlarged cross sectional images, as well as the top and bottom view SEM images (not shown here), of these PAAs also confirm the ordered nanopore arrangements. The current density during anodizing is very helpful for understanding anodizing behavior. Fig. 4a shows the current density-anodizing time curves with various ethanol additions. It is clear that the ethanol in the electrolyte is a critical factor for the current density. However, the current density goes up with 5% and 10% ethanol additions, while it goes down with more

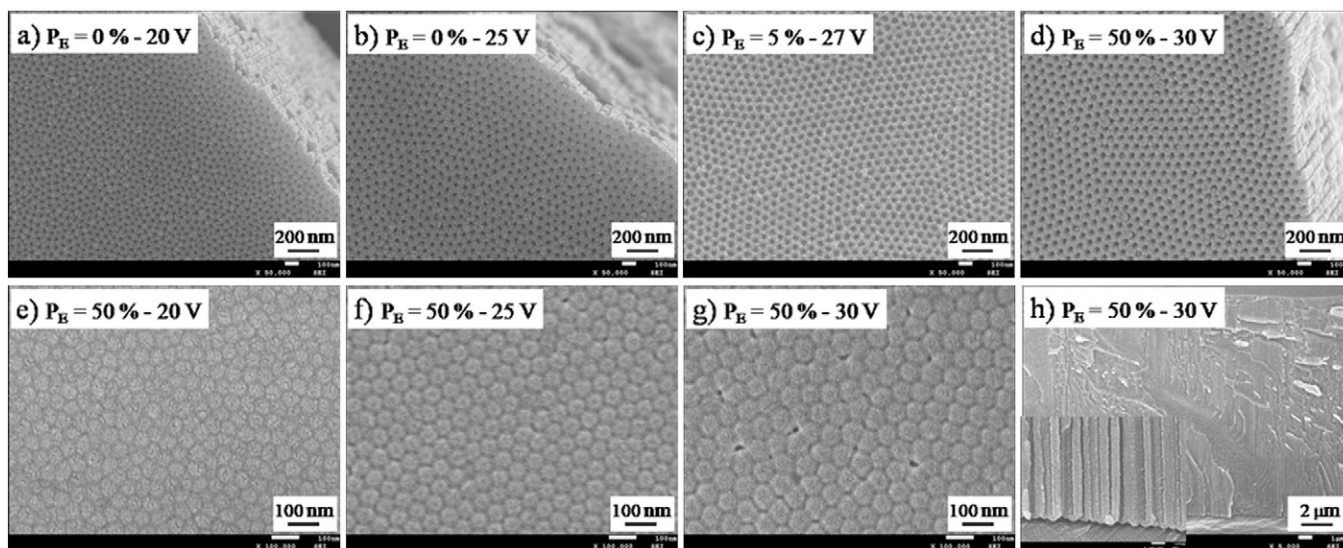


Fig. 1. a)–d) top surface images of PAAs prepared in a) P_E = 0%, 20 V; b) P_E = 0%, 25 V; c) P_E = 5%, 27 V; and d) P_E = 50%, 30 V. e)–g). Bottom surfaces of PAA films after remove of residual aluminum anodized in P_E = 50% at 20 V, 25 V and 30 V. h) Cross-sectional SEM image of PAA prepared at P_E = 50% under 30 V and the enlarged bottom part are also shown in the inset.

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