A Simple Method for Preparation of Through-Hole Porous Anodic Alumina Membrane

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Porous anodic alumina (PAA) has a packed array of columnar hexagonal cells with central, cylindrical uniformly sized holes ranging from 4 to 200 nm in diameter, pore density as high as 10^8-10^{11} pores/ cm^2 and the film thickness varying from 0.1 to 300 μm.[1−3] In addition, the above dimensions are adjustable. It has been reported that the pore density and pore size of the PAA can be controlled by the anodizing voltage and the solution composition, whereas the membrane thickness can be adjusted by the charge passed in the anodic electrolysis. The adjustable and ordered nanochannel-array material has been attracting extensive interest due to its important applications;[4−6] especially it can be used as a template for preparation of nanodots,[7] nanowires,[8] metal nanohole arrays,[9] and nanotubes.[10,11] Therefore, in the past 80 years, many methods have been developed to prepare or improve porous alumina membrane. Thompson gave a detailed review on the anodic alumina film formation from aluminum.[3] Masuda and co-workers advocated a two-step oxidation technology[7] and molding process[12] to prepare highly ordered pore arrays. Some special procedures for creating particular shapes and structures such as hexagonally ordered nanopore arrays with high aspect ratios,[5,6] tubular anodic aluminum oxide,[13,14] and PAA films having bone-shaped nanochannels[15] were developed for different applications. Recently, a triangle or polygon shape of alumina pores was observed.[16] However, three main factors should be born in mind for successful fabrication of perfect PAA. The first factor involves the pretreatment including annealing and polishing of the aluminum sheet, which is considered to be essential for the preparation of ordered pores.[12,17] These two processes make the fabrication procedure tedious and boring. The second factor influencing the quality of PAA is that multioxidation steps are usually required to obtain a highly ordered holes array,[5,7,12] but little detailed information about the process was presented.[5,7] The third factor is the removal of an oxide barrier layer between the porous alumina and the aluminum base to ensure the pores open-through. It was reported early that the barrier-layer thickness can be reduced by lowering the anodizing voltage.[1,18] Recently, Xu et al. have demonstrated that Ar^+ ion milling at grazing incidence could open the nanopores from the "closed side" in a controlled fashion, thus allowing the formation of hexagonally ordered periodic holes of diameter much smaller than that afforded by extended anodization in acid solution.[19] Up to now, although many efforts have been made to deal with these processes, the detaching and pore-opening processes are still beyond control. Xu et al. reported a method to prepare an ordered PAA membrane without the annealing process followed by traditional chemical etching for detaching the membrane from the barrier layer.[20] In fact, contamination of heavy metallic ions cannot yet be avoided, although nail polish was used for protection. Paterson and his co-worker advocated an interesting method for detaching the PAA from the barrier layer by using a short time voltage pulse.[21,22] However, these authors used a tedious pretreatment process for preparing the PAA membrane.

Here, we take advantage of the above two methods[20−22] to prepare free-standing PAA. In this method, annealing and polishing pretreatment processes of the aluminum bases are not necessary. Simple pretreatment including only degreasing and oxide removal is enough for obtaining clean and flat Al species which are essential for symmetrical distribution of the applied electric field on the aluminum surface in the followed anodizing process for achieving ordered pores. The mechanism for two-step oxidation was discussed. A schematic representation of the whole procedure is shown in Figure 1. In the first step, a clean aluminum sheet is anodically oxidized to form an alumina membrane (A). This preformed membrane is subsequently removed completely by a phosphocromic acid solution[7,15,19] to form a textured pattern of concave substrate (B) for the second anodic oxidation process. After another anodic oxidation of B,

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(1) Keller, F.; Hunter, M. S.; Robinson, D. L. *J. Electrochem. Soc.* **1953**, *100*, 411.
(2) Diggle, J. W.; Downie, T. C.; Goulding, C. W. *Chem. Rev.* **1969**, *69*, 365.
(3) Thompson, G. E. *Thin Solid Films* **1997**, *297*, 192.
(4) Martin, C. R. *Science* **1994**, *266*, 1961.
(5) Li, A.-P.; Müller, F.; Birner, A.; Nielsch, K.; Gösele, U. *Adv. Mater.* **1999**, *11*, 483.
(6) Müller, F.; Birner, A.; Schilling, J.; Li, A.-P.; Nielsch, K.; Gösele, U.; Lihmann, V. *Microsyst. Technol.* **2002**, *8*, 7.
(7) Masuda, H.; Satoh, M. *Jpn. J. Appl. Phys.* **1996**, *35*, L126.
(8) Shingubara, S.; Okino, O.; Sayama, Y.; Sakaue, H.; Takahagi, T. *Jpn, J. Appl. Phys.* **1997**, *36*, 7791.
(9) Masuda, H.; Fukuda, K. *Science* **1995**, *268*, 1466.
(10) Brumlik, C. J.; Martin, C. R. *J. Am. Chem. Soc.* **1991**, *113*, 3174.
(11) Bao, J. C.; Tie, C. Y.; Xu, Z.; Zhou, Q. F.; Shen, D.; Ma, Q. *Adv. Mater.* **2001**, *13*, 1631.
(12) Masuda, H.; Yamada, H.; Satoh, M.; Asoh, H.; Nakao, M.; Tamamura, T. *Appl. Phys. Lett.* **1997**, *71*, 2770.
(13) Itoh, N.; Kato, K.; Tsuji, T.; Hongo, M. *J. Membr. Sci.* **1996**, *117*, 189.
(14) Itoh, N.; Tomura, N.; Tsuji, T.; Hongo, M. *Microporous Mesoporous Mater.* **1998**, *20*, 333.
(15) Xu, T. T.; Fisher, F. T.; Brinson, L. C.; Ruoff, R. S. *Nano Lett.* **2003**, *3*, 1135.
(16) Nielsch, K.; Choi, J.; Schwirn, K.; Wehrspohn, R. B.; Gösele, U. *Nano Lett.* **2002**, *2*, 677.
(17) Jessensky, O.; Müller, F.; Gösele, U. *Appl. Phys. Lett.* **1998**, *72*, 1173.
(18) Furneaux, R. C.; Rigby, W. R.; Davidson, A. P. *Nature* **1989**, *337*, 147.
(19) Xu, T.; Zangari, G.; Metzger, R. M. *Nano Lett.* **2002**, *2*, 37.
(20) Xu, T. T.; Piner, R. D.; Ruoff, R. S. *Langmuir* **2003**, *19*, 1443.
(21) Mardilovich, P. P.; Govyadinov, A. N.; Mukhurov, N. I.; Rzhevskii, A. M.; Paterson, R. *J. Membr. Sci.* **1995**, *98*, 131
(22) Lira, H. de L.; Paterson, R. *J. Membr. Sci.* **2002**, *206*, 375.

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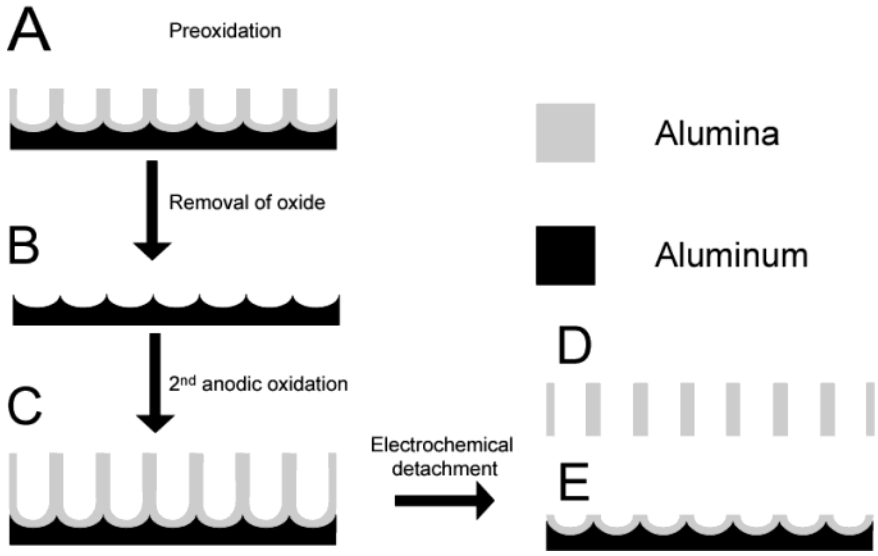

Figure 1. Schematic representation of the fabrication procedure for the formation of ordered and through-hole porous alumina membrane. (A) Formation of the porous alumina layer after the first anodic oxidation process; (B) removal of the porous alumina layer; (C) formation of the ordered porous alumina layer after the second anodic oxidation process; (D) free-standing PAA; and (E) the barrier layer structure on aluminum base after electrical detachment of the PAA.

a well-ordered PAA membrane (C) with ordered pores is formed. This final film is then detached from the barrier layer by a short time voltage pulse about 5 V higher than that for anodic oxidation to form a free-standing PAA membrane (D) and an alumina barrier layer covered aluminum substrate (E).

Experimental Section. *Pretreatment.* The aluminum sheets (thickness: 0.1 mm; purity: 99.99%) were obtained from Xingjiang Zhonghe limited Corporation (Xingjiang, China). Before anodizing experiments were performed, the aluminum foils (35 × 40 mm) were degreased in acetone (CH_3COCH_3) for 12 h and followed by 180 s of ultrasonic cleaning. Then the samples were rinsed with distilled water and etched in 3.0 mol/L NaOH until bubbles over the surface occurred and finally the sample was rinsed ultrasonically with distilled water.

Anodic Oxidization of the Aluminum Electrode. A house-made power supplier was used for the preparation of PAA via anodic oxidation of the aluminum. For obtaining pores on a single side, experiments were carried out using a two-electrode configuration at constant voltages in the range of 20−80 V (dc) from a vigorously stirred solution of 0.5 mol/L $H_2C_2O_4$ under thermostatic conditions. The cleaned aluminum sheet was used as the anode and Al foil as the cathode. The aluminum sheet was first anodized at 15.0 °C for 1 h, and then it was immersed in a phosphocromic acid solution (6% H_3PO_4 + 1.8% H_2CrO_4 aqueous solution) at 60 °C under ultrasonic conditions for 30 min to remove the preformed PAA film only, leaving the Al base intact, followed by multiple distilled water rinsings. After the alumina film was stripped off, the sample was oxidized again under the same conditions as described in the first step for 4 h.

One-Step Detaching Porous Alumina Film from Barrier Layer. To obtain a through-hole membrane, the sample was anodically oxidized in a solution of $HClO_4$ (72% w/w) and $(CH_3CO)_2$ (98%) (v/v = 1:1) at a voltage of 5 V higher than the oxide formation voltage for 3 s. After this process, the porous alumina film separated from the barrier layer immediately. The free-standing PAA membrane was then rinsed in acetone and double-distilled water. A scanning electron microscope (HITACHI X-650, Hitachi, Japan) and atomic force microscopy (SPA-300 HV, Seiko, Japan) were used to characterize the quality of the PAA film.

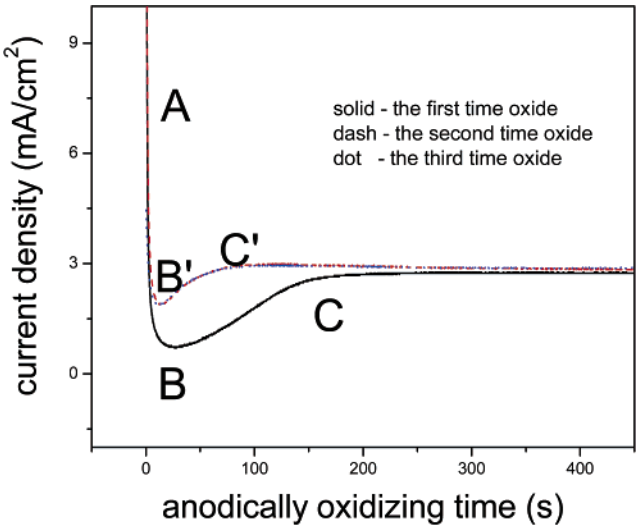

Figure 2. Current densities as a function of time during the anodic oxidation processes at 30 V in a solution of 0.5 mol/L $H_2C_2O_4$ at 15 °C. The solid, dashed, and dotted curves are for the first, second, and fourth anodic oxidation processes, respectively.

Results and Discussion. *Formation of Porous Alumina.* Figure 2 shows the apparent current densities (using geometric area of the aluminum exposed to solution) as a function of the anodic oxidation time at an anodic oxidation voltage of 30 V and solution temperature of 15 °C. The solid, dashed, and dotted curves are for the first, second, and fourth anodic oxidation processes, respectively. For all cases, three current regions can be distinguished for the formation of porous alumina, giving detailed information of the oxidation process for the preparation of ordered porous alumina membrane. In the first region, a barrier layer of isolated

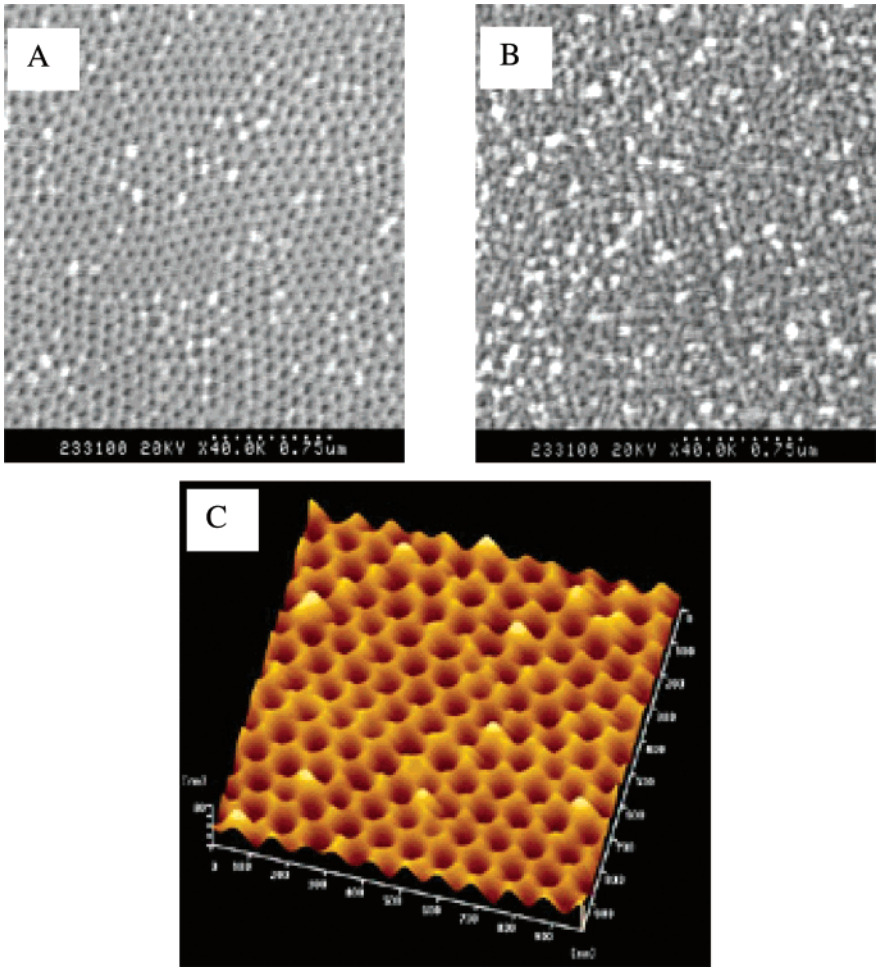

Figure 3. SEM images of the anodic alumina layer. (A) Top surface; (B) bottom surface. AFM image of the top view of the barrier layer on the Al base (C).

nonporous oxide forms quickly as the anodic potential was applied to the aluminum base. With the fast growth of the oxide barrier layer, resistance of the electrode increases considerably, resulting in a sharp decrease in current (A → B or A → B′). As the thickness of the oxide barrier film reaches a certain value (point B or point B′), the surface resistance of the electrode increases considerably. The local heat resulted from the resistance and the field-assisted effect promotes local dissolution of the insulated barrier layer,[1,2,23,24] resulting in pore nuclei formation. Both the localized pore growth and the local dissolution process result in a slow increase in real surface area, which is reflected by a slow increase in current (B → C or B′ → C′). Up to a certain growth time of pores, the real surface area reaches a constant value; accordingly, the apparent current reaches a constant value (points C and C′). At this point, the formation rate of the oxide due to anodic electrolysis is equal to the local dissolution rate of the oxide barrier layer at the bottom of the pores. The present observation demonstrates a localized pore formation and dissolution process in the region of points B and C (also the region between points B′ and C′), which is in good agreement with that obtained in the same process of anodic oxidation of aluminum base with annealing and polishing pretreatment.[24,25]

Two-Step Oxidation To Achieve Highly Ordered Array Holes. After performance of the first anodic oxidation of the aluminum base for 1 h (solid curve, Figure 2), the porous and the barrier oxide layers were removed completely, leaving a concave textured pattern on the surface of the aluminum substrate.[7] This aluminum substrate was anodically oxidized for another 1 h under the same conditions as in the case of the first oxidation process. The recorded apparent current density (the total current divided the apparent area) is shown in Figure 2, dashed curve. Although the same current behaviors for these two anodic processes are similar, there are several important differences between the results observed in the first and second anodic oxidation. For the second anodic oxidation, the times for reaching the lowest and constant current are significantly shorter than those for the first oxidation. In addition, the lowest apparent current density is higher for the second oxidation than for the first oxidation. The longer time for reaching the steady-state condition in the first curve is simply due to the fact that at the beginning the porous structure is not yet formed; accordingly, the time for pores nucleation and growth for the first time (Figure 2, points B and C) is longer than those in the second or third oxidation process (points B′ and C′) in which the pore patterning was already formed. Obviously, the time for reaching the lowest current in the second oxidation

(23) Li, A.-P.; Müller, F.; Birner, A.; Nielsch, K.; Gösele, U. *J. Appl. Phys.* **1998**, *84*, 6023.
(24) Hoar, T. P.; Yahalom, J. *J. Electrochem. Soc.* **1963**, *6*, 614.
(25) Huang, G. S.; Wu, X. L.; Mei, Y. F.; Shao, X. F. *J. Appl. Phys.* **2003**, *93*, 582.

process is also shorter. On the other hand, the thermal effect, high electric field and the change of the diffusion mechanism from planar diffusion to spherical diffusion, accelerate diffusion rate of protons to the oxide/solution interface, which results in great acceleration of both the barrier layer dissolution and the growth of pores, namely, the time for reaching a stead state is shorter. Under constant potential conditions, the observed larger apparent current density in the second oxidation step is owing to the larger surface area left by the dissolution of previous porous structure (see Figure 1B). Further anodic oxidation experimental results showed that the apparent current density−time curves for the anodic oxidation were the same as that for the second anodic oxidation process (Figure 2, dotted curve for the fourth anodic oxidation). This coincidence in current−time curves for the second and third anodic oxidation processes is due to the fact that the starting surface structures (i.e., same concave patterns) were the same. Our results demonstrate that two-step oxidation of the aluminum base is enough for preparation of well-ordered pores structure.

Achievement of Open-Through Pores by Voltage Pulse. After the formation of an ordered PAA in the second time anodic oxidation of the aluminum electrode, a 3-s anodic voltage pulse with 5 V higher than the oxide forming voltage was applied to this electrode in a solution of 70% $HClO_4$ + $(CH_3CO)_2$ at 15 °C, resulting in a complete separation of the membrane from the barrier layer immediately.[21,22] Scanning electron microscopic characterization of the top surface (Figure 3A) and bottom surface (Figure 3B) of the membrane shows that nearly all pores are open-through. In addition, the AFM image of the top view of the barrier layer (Figure 3C) on the Al base confirms that open-through ordered porous alumina was really achieved. Further understanding of the detaching mechanism is undergoing.

There were three advantages in the membrane electrical detachment process. First, the pore size can be fully controlled, while previously reported chemical methods usually result in enlarged pores due to partial dissolution of pore walls inevitably. Second, the used solution of $HClO_4$ and $(CH_3CO)_2$ is environmental friendly and free of heavy metallic ions. Consequently, the problems caused by residues of metal ions do not exist. Finally, the present method is more simple and rapid than the one reported previously.[20]

In conclusion, through-hole porous anodic alumina membranes can be simply and rapidly fabricated from aluminum foil without any special pretreatment (e.g., annealing and electropolishing) with the present method. Results showed that a two-step oxidation process is enough for preparation of well-ordered pores. The present pore-opening process using short time electrical oxidation for detaching the PAA film was used to improve the fabrication of anodic alumina with an array of nanopores. Pore diameter of 30−60 nm, interpore distance of 80−100 nm, and film thickness of 25 μm can be achieved easily using the present fabrication procedure. The pore density can be as high as 1.34×10^{10}/cm^2. The fabricated pore-through PAA films can then be used as templates for growth of nanowires and nanotubes while the barrier oxide covered base for preparation of nanodots.

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