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Stability of anodic aluminum oxide membranes with nanopores

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Abstract

The anodic aluminum oxide membranes (AAOMs) with nanopores, produced by electrochemical etching method in oxalic/sulphuric/phosphoric acid, were transformed from amorphous phase to crystalline phase by annealing. Differential thermal analysis and X-ray diffraction were performed for the phase transformation studies. Scanning electron microscopy studies show that the crystalline AAOMs keep the nanopore morphology and become very stable in the violent acid and violent alkali solutions.

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Keywords: Anodic aluminum oxide membrane; Nanopore; Stability

Nanoscale materials have being widely studied because of their peculiar properties and potential applications. One-dimensional nanoscale materials, nanowires and nanotubes, have attracted much attention in recent years [1–3]. One of the most important method for the preparation of the one-dimensional nanoscale materials is the template method, which use the membranes with nanopore channels as the template. In the template method, anodic aluminum oxide membranes (AAOMs), prepared by electrochemical etching aluminum foil in oxalic/sulphuric/phosphoric acid solution are the most popular membranes used in the experiments. For example, the AAOMs have been used in the fabrication of ordered carbon nanotube arrays [4], wide gap semiconductor nanowires [5–8] and superconductor nanowire arrays [9]. The magnetic nanowire arrays prepared by electrodepositing the corresponding materials into the nanopores of the AAOMs are regarded as a potential media in high density magnetic storage [10–12]. In all these experiments, the synthesis environmental condition is vapor or nearly neutral solutions. Many experiments have shown that the AAOMs are unstable and can be dissolved in the violent acid or alkali solutions. This property confines the application areas of the AAOMs. In the previous studies, thermal treatment and solubility of the AAOMs have been performed carefully in the view point of chemistry [17]. In this Letter, in

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the view point of one-dimensional nanoscale materials synthesis, we studied the stability difference of the AAOMs before and after calcinations.

The AAOMs can be formed in oxalic acid, sulphuric acid or phosphoric acid solutions [13]. By using high purity (99.999%) aluminum foil as the starting material, three groups of AAOMs were prepared in oxalic acid/sulphuric acid/phosphoric acid solution separately with all the acid concentration of 0.4 mol/l. The electrochemical etching time was 20 hours for all the samples. The environmental condition was ice/water which kept the acid solution temperature with 0 °C in the whole process. The anodic voltages used in the experiments were 60, 28 and 140 V for oxalic acid, sulphuric acid and phosphoric acid, respectively. The distance between the neighboring pore centers was fixed after the electrochemical etching, they were about 150, 65 and 400 nm, respectively. The diameter of the nanopores can be adjusted by phosphoric acid solution. After removal of the remaining aluminum, the AAOMs were put into a 30 °C phosphoric acid with 10 wt% concentration for 40 minutes to adjust the nanopore diameters. The diameters of the nanopores were about 70, 35 and 120 nm for the three groups of prepared AAOMs. These results will be shown in the following scanning electron microscopy (SEM) studies. These AAOMs were used as the prepared materials for further studies in this Letter. For simplicity, the AAOMs prepared in the oxalic acid were used as an example. The properties of the AAOMs prepared in sulphuric acid and phosphoric acid are similar with that of the AAOMs prepared in the oxalic acid.

In the stability studies of the AAOMs, a sulphuric acid with 1 mol/l concentration and a sodium hydroxide solution with 1 mol/l were used as the testing solution. The temperature of the testing solution was fixed at 50 °C with water bath. These two solutions are typical for violent acid and violent alkali. Generally speaking, if the AAOMs are stable in these testing solutions, they will be stable in other violent acid or violent alkali solutions.

Two pieces of prepared AAOMs were put into the testing solutions separately. The AAOMs will be decomposed within 3 minutes in the sodium hydroxide testing solution and 2 hours in the sulphuric acid testing solution. This shows the instability of the AAOMs when used in the violent acid and alkali environments. In order to show the etching effect of the testing solutions, two pieces of AAOMs were used in the SEM studies. One AAOM was draw out from the sodium hydroxide solution after 100 seconds immersing, and another AAOM was draw out from the sulphuric acid solution after 20 minutes immersing. Both of the two pieces of AAOMs were washed many times immediately by distilled water after they were draw out from the testing solution.

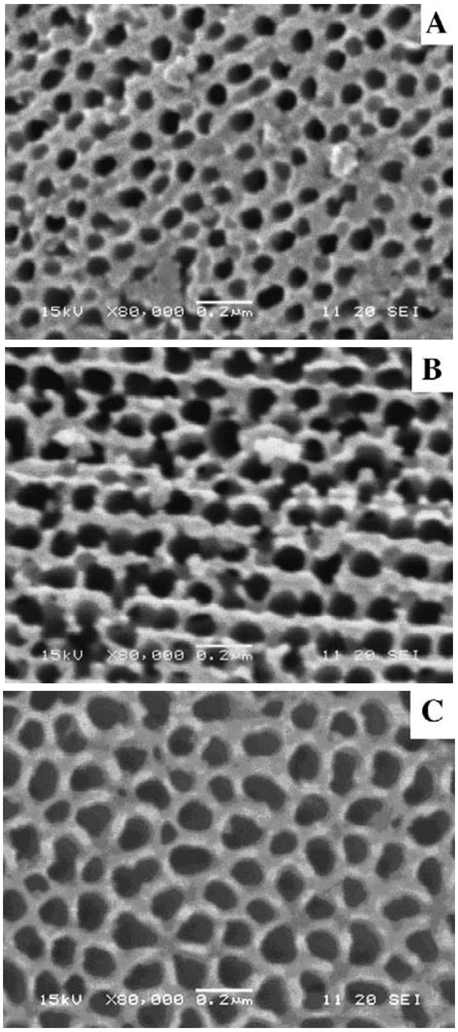

Fig. 1. The unstability of the as-prepared AAOMs in testing solutions. (A) as-prepared AAOM, (B) after 100 seconds etched in alkali solution, (C) after 20 minutes etched in acid solution.

The morphology of the AAOMs was performed by a scanning electron microscopy (SEM, JEOL, JSM-5900). Fig. 1 shows the top view of the AAOMs as-

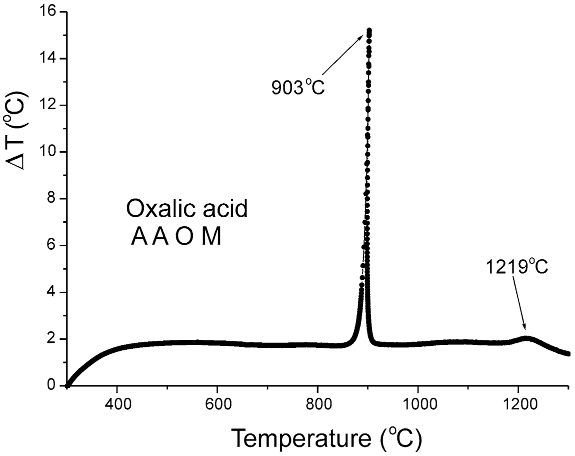

Fig. 2. DTA curve of the AAOM prepared in oxalic acid solution.

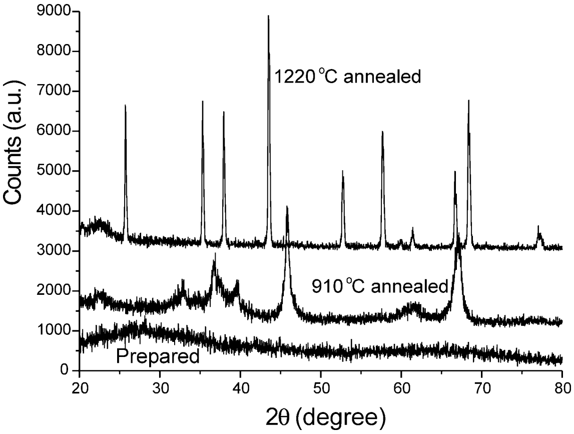

Fig. 3. The XRD patterns of the AAOMs.

prepared (A) and etched for 100 seconds in the alkali (B) and for 20 minutes in the sulphuric acid (C). The diameters of the nanopores were 70, 90 and 120 nm, respectively. These results reveal that the AAOMs will be dissolved in the sodium hydroxide and sulphuric acid solution. When the time is short for immersing in the testing solutions, the nanopores will be widened, and the diameter will increase. When the time is long enough for the membrane immersing in the testing solutions, the membrane will be decomposed totally.

As shown in the following, the as-prepared AAOMs are in amorphous phase. Some researches showed that there are many voids in the membrane, which is formed in the preparation of the AAOMs [14]. The voids distributed all over the AAOMs make it easy to occur for the chemical reaction between the AAOM body and the testing solutions. This property has been used in the preparation of alumina nanotubes [15,16]. Perhaps it is the reason why the AAOMs can be dissolved in the testing solutions. This reveals us a way, crystallization, may be used to get more stable membrane. Annealing is the general method for the crystallization of amorphous materials. In order to find the crystallization temperature, differential thermal analysis (DTA) was employed in the study of the thermal property of the AAOMs. Fig. 2 shows a typical DTA curve of the oxalic prepared membrane. From the DTA results, two peaks can be observed at 903 °C and 1219 °C, which correspond to the crystallization temperature of amorphous phase to γ-Al_2O_3 phase and the transition temperature from γ-Al_2O_3 phase to α-Al_2O_3, respectively.

In order to get crystalline phase of the AAOMs, the AAOMs were annealed at different temperatures for about 10 hours in the atmosphere ambient. The crystalline structure was performed by X-ray diffraction (XRD). Fig. 3 shows the XRD patterns of the AAOMs. An amorphous curve is observed for the as-prepared AAOM. The AAOMs after 500 °C annealing also shows amorphous outline in the XRD pattern. The AAOM annealed at 910 °C shows crystalline peaks in the XRD pattern. The XRD peaks belong to the γ-Al_2O_3. All the peaks in XRD pattern of the 1220 °C annealed AAOM belong to α-Al_2O_3. This reveals that after 910 °C and 1220 °C annealing, the AAOMs prepared in oxalic acid crystallize to crystalline phases γ-Al_2O_3 and α-Al_2O_3, respectively. The similar results have been observed in the AAOMs prepared in sulphuric acid and phosphoric acid.

There is a possibility that the nanopore microstructure of the AAOMs can be destroyed when annealing. For illustrating the stability of the annealed AAOMs, SEM studies were performed for the annealed samples. Fig. 4 is the top view of the AAOMs annealed at 910 °C and 1220 °C. Compared with Fig. 1(A), no apparent changes of the nanostructure can be observed.

In order to study the stability of the annealed AAOMs in alkali solution, the annealed AAOMs were put into the sodium hydroxide testing solution for 120 minutes. The experimental time is 150 minutes for the stability study in sulphuric acid testing solution. After washed in distilled water for several times,

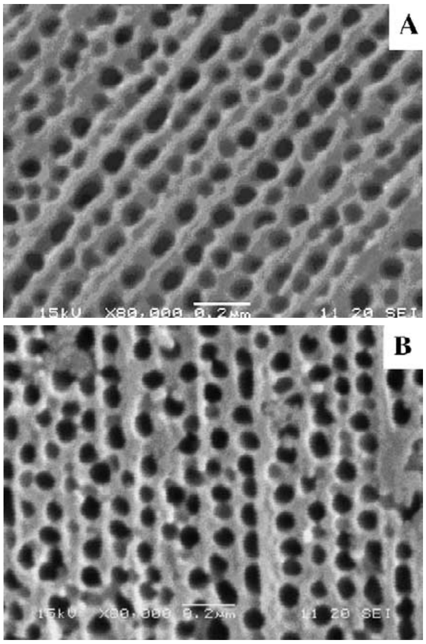

Fig. 4. Top view of the AAOMs annealed at (A) 910 °C, (B) 1220 °C.

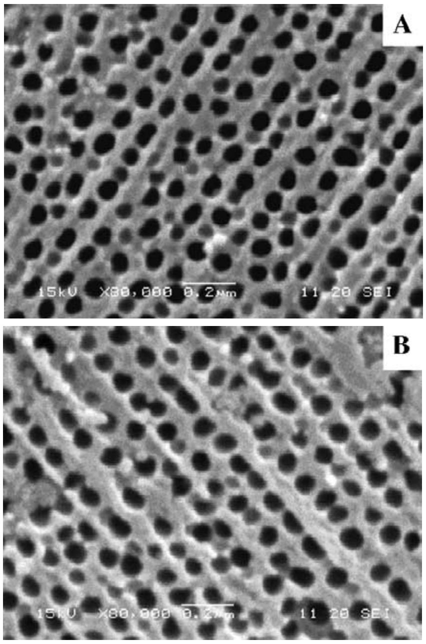

Fig. 5. SEM images of the AAOMs annealed at 910 °C etched (A) in sodium hydroxide testing solution, (B) in sulphuric acid testing solution.

the morphologies of the AAOMs were performed by SEM. Fig. 5 is the top view of the AAOMs annealed at 910 °C and etched in testing solutions. In these figures no apparent changes of the nanostructure is observed after etching in the testing solutions. The diameters of all these membranes are almost the same with the as-prepared AAOMs. The same results have been observed for the samples annealed at 1220 °C. This result reveals that the crystallized AAOMs are stable in sulphuric acid and sodium hydroxide solutions.

Comparing the SEM images in Figs. 1, 4 and 5, for the AAOMs prepared in oxalic acid solution, the diameter of the AAOMs is almost the same before and after annealing. This shows that the annealing treatment will not change the nanopore structure of the membranes below 1220 °C. The diameter of the AAOMs annealed above 910 °C cannot be widened in the sulphuric acid or sodium hydroxide testing solution. In other words, the annealed AAOMs are stable in alkali and acid solutions.

The AAOMs prepared by sulphuric acid and phosphoric acid have the similar properties. The as-prepared AAOMs will decompose in the testing solution. Otherwise, they will become very stable after crystallization by annealing. SEM studies have illustrated the stability of these AAOMs.

In summary, the as-prepared AAOMs are amorphous, which can be decomposed in violent acid and alkali solutions. This amorphous aluminum oxide can be transformed to crystalline phase when annealing above 910 °C. The annealed AAOMs keep the nanopore microstructures as they were prepared. The crystalline phase of the AAOMs is very stable in either sulphuric acid solution or sodium hydroxide solution. This result reveals that the annealed AAOMs can be used in a more widely condition, including violent acid solutions and violent alkali solutions.

Acknowledgements

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