

Study on the influence on the formation of highly ordered porous anodic alumina membrane

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Abstract: We have studied porous anodic alumina template through the second anodic oxidation of preparation. Observing the morphology of nanoscale AAO template using scanning electron microscope (SEM), the results indicate that the pores are orderly paralleled arranged with uniform pore diameter, perpendicular to the template surface.

A detailed study of the influence of different oxidation conditions, such as different type of electrolyte, concentration, voltage and temperature on the template of alumina and its electrochemical mechanism were performed.

By changing the oxidation voltage, electrolyte type, concentration, pore diameter and template thickness can be altered in a wide range such that we can obtain the desired aspect ratio.

Keywords: AAO, membrane, second anodic oxidation

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1. Introduction

Since anodic aluminium oxide membrane has a special nano-hole structure, it is the one of important materials in nano material technique.

The study on fabrication technique of aluminium oxide membrane has been performed recently by many researchers [1-3].

The structure of anodic aluminium oxide obtained by anodizing aluminium with high purity in electrolytic solution of sulfuric acid, oxalic acid, phosphoric acid and so on consists of a porous layer, barrier layer, and aluminium basis [4-6].

Different kinds of electrolyte, concentration, voltage, current density, electrolytic time, reaction temperature and so on affect the pore density, pore diameter, barrier layer thickness of AAO membrane and the voltage is approximately proportional to the size of pore diameter.

We have investigated the factors affecting the formation of highly ordered porous AAO membrane in this work.

2. Infulence of anodization voltage on the formation of nano pores of AAO membrane

Figure 1 shows the SEM photographs(JSM-6700F) of samples which were anodized with two steps at voltages of 30V, 40V, 50V and 60V, where the anode was

the aluminium plate in which the layers of oil and oxide were removed and the electrolyte was the solution of 0.3M oxalic acid.

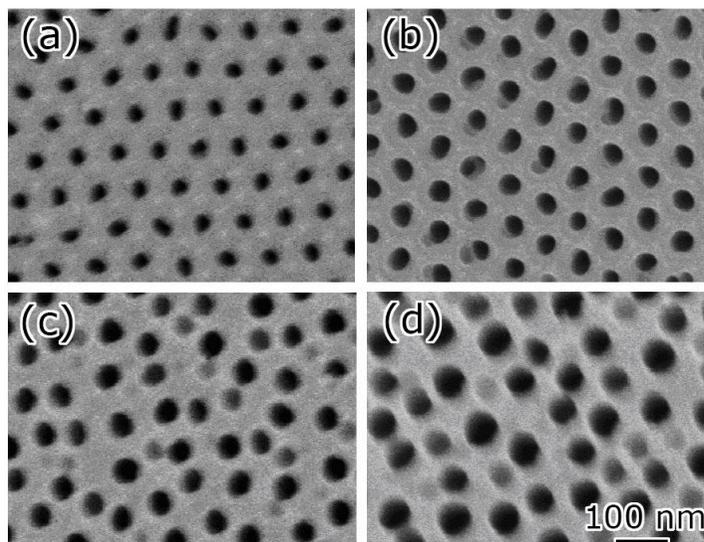


Fig.1 SEM photographs of AAO membrane obtained at various voltages in solution of 0.3M oxalic acid. ((a) 30V, (b) 40V, (c) 50V, (d) 60V)

As shown in this figure, in a case of comparative low voltage the pore diameter and the distance between the pores of AAO membrane are relatively small and the pore density is big and the distribution of nano pores is uniform. As the anodization voltage increases, the pore diameter and the distance between the pores increase and therefore the pore density decreases and the degree of order of pore distribution becomes low.

This is because the volume of aluminium oxide expands steadily in the course of pore formation and the internal stress occurs in the boundary surface. With a slightly low voltage of anodization, the rate of growth of aluminium oxide varies slowly and the nano hole obtained is small because the effect of expansion of volume, internal stress, rejection effect and so on are comparatively small. Increasing the voltage of anodization gradually, since the the effect of expansion of volume, internal stress, rejection effect becomes large, with rapid variation of the rate of growth of aluminium oxide, the diameter of pore obtained increases and therefore its degree of order decreases gradually. However, if the voltage of anodization increases, the reaction takes place strongly and the internal stress and rejection effect generated are so large and the degree of order of the pores obtained decrease such that the porous structure can't be obtained.

The relationships between the anodization voltage and pore diameter, inter-pore distance, and pore density are shown in the Figure 2 below.

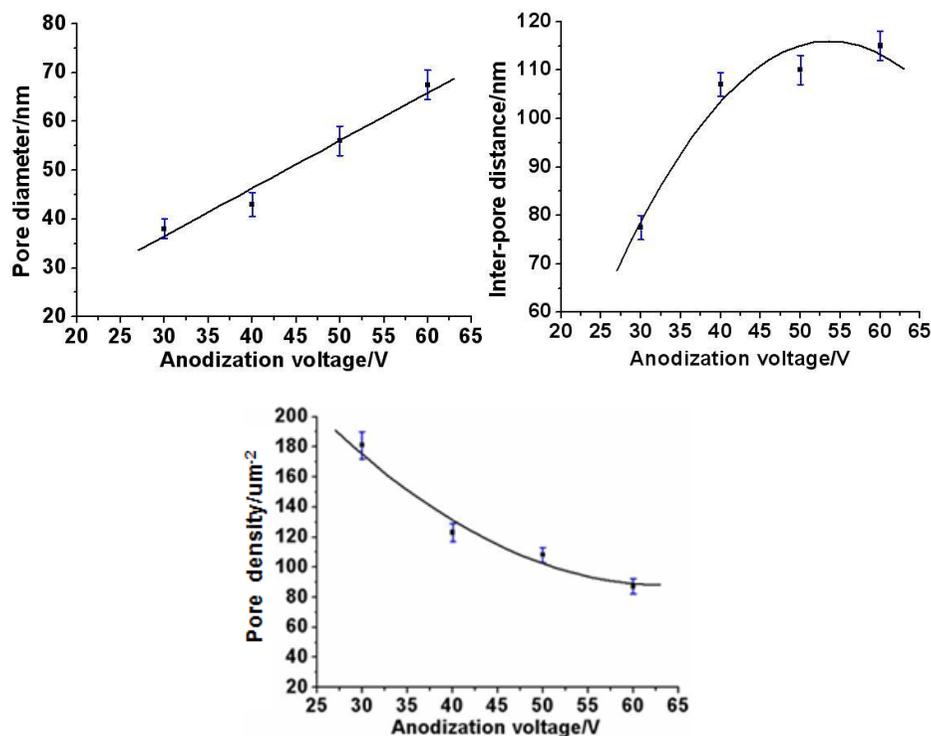


Fig.2 Relationships between the anodization voltage and pore diameter, inter-pore distance, and pore density of AAO fabricated in an electrolytic solution of 0.3M oxalic acid

As we can see in this figure, the linear increasing relationship is basically satisfied between the pore diameter and anodization voltage. The inter-pore distance increases and the pore density decreases with anodization voltage.

The degree of order of AAO membrane obtained in comparative high voltage is low and the quality of membrane decreases but the relatively large inter-pore distance is able to increase the distance between the nanowires in nanowire arrangement and adjust the extent of relatively large pore diameter at the step of pore extension of phosphoric acid of the fabrication process of AAO membrane.

According to the experiment in the electrolytic solution of oxalic acid, the degree of order of AAO membrane obtained at an anodization voltage of 40V is relatively high and has a hexagonal close-packed structure. The pore diameter is about 45nm and it has the range of 55~60nm on extending the hole using phosphoric acid.

3. Effect of electrolyte concentration on the formation of aluminium oxide membrane

Figure 3 shows the SEM photographs of AAO membrane, with SEM

JSM-6700F, which was obtained by anodizing secondly in sulfuric acid solutions of different concentration and figure 4 shows the variations of pore diameter,

interpore distance, and pore density with electrolyte concentration.

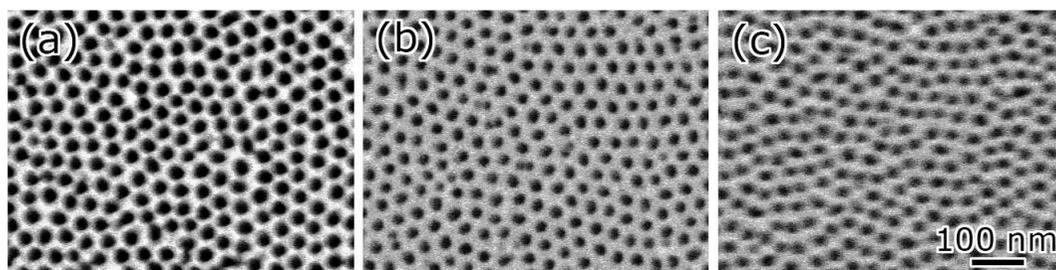


Fig.3 SEM photographs of AAO membranes obtained at 20V in sulfuric acid solutions of different concentration: (a) 0.5m, (b) 0.6M, (c) 0.8M

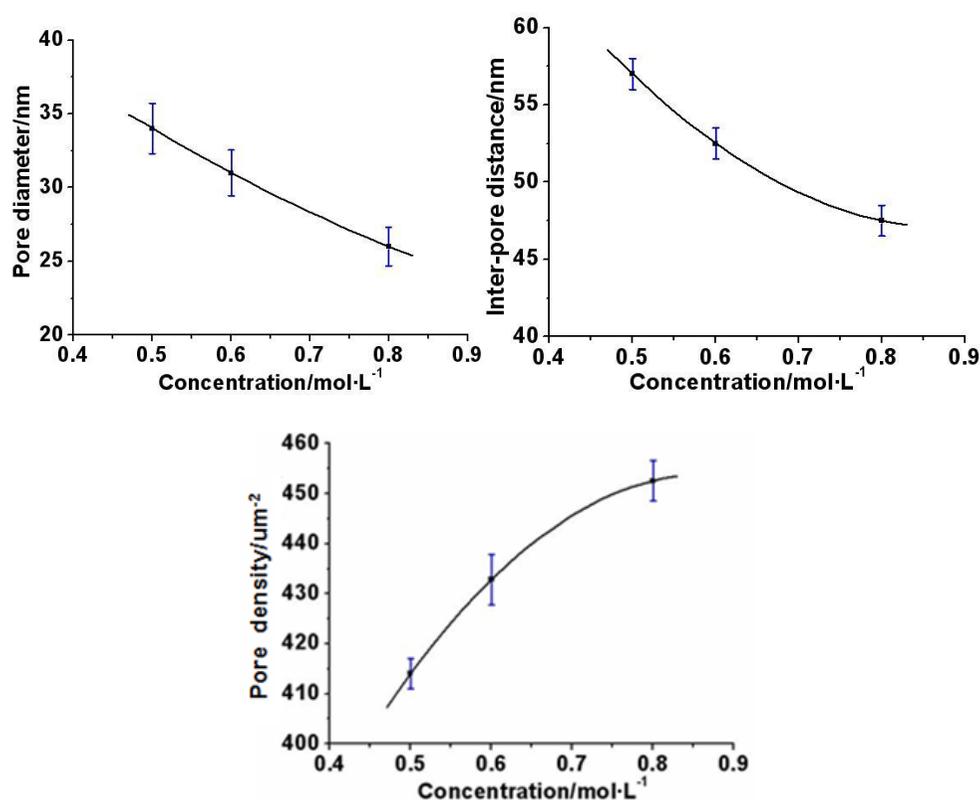


Fig.4 Variations of pore diameter, interpore distance, and pore density with concentration of sulfuric acid solution.

As shown in figure 4 above, pore diameter and interpore distance of nano pore membrane decrease gradually with the increase of concentration of sulfuric acid solution and the pore density therefore increases and the degree of order of pores becomes low.

PH of solution affects reasonably the formation of AAO membrane under the constant anodization voltage and in the same acid electrolyte.

As the concentration of H^+ ion increases, the solution velocity in a nano pore path and partial field becomes fast. This time, the longitudinal growth speed of nano pore path is greater than transversial one.

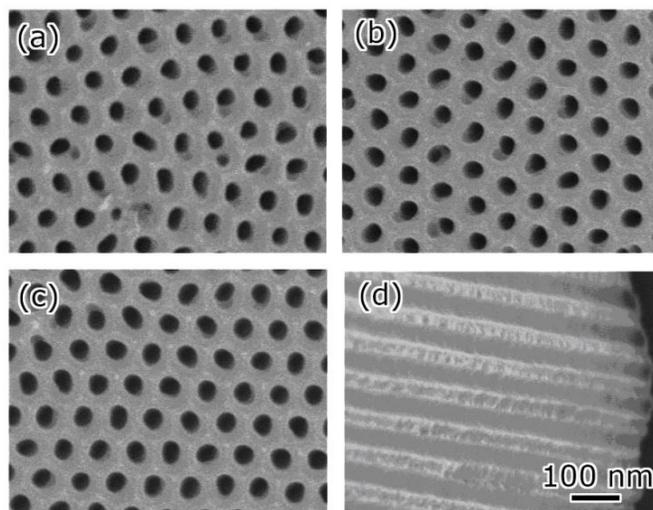


Fig.5. SEM photographs of AAO at 40V with electrolyte concentration of oxalic acid: (a) 0.2M, (b) 0.3M, (c) 0.6M, (d) side of AAO membrane.

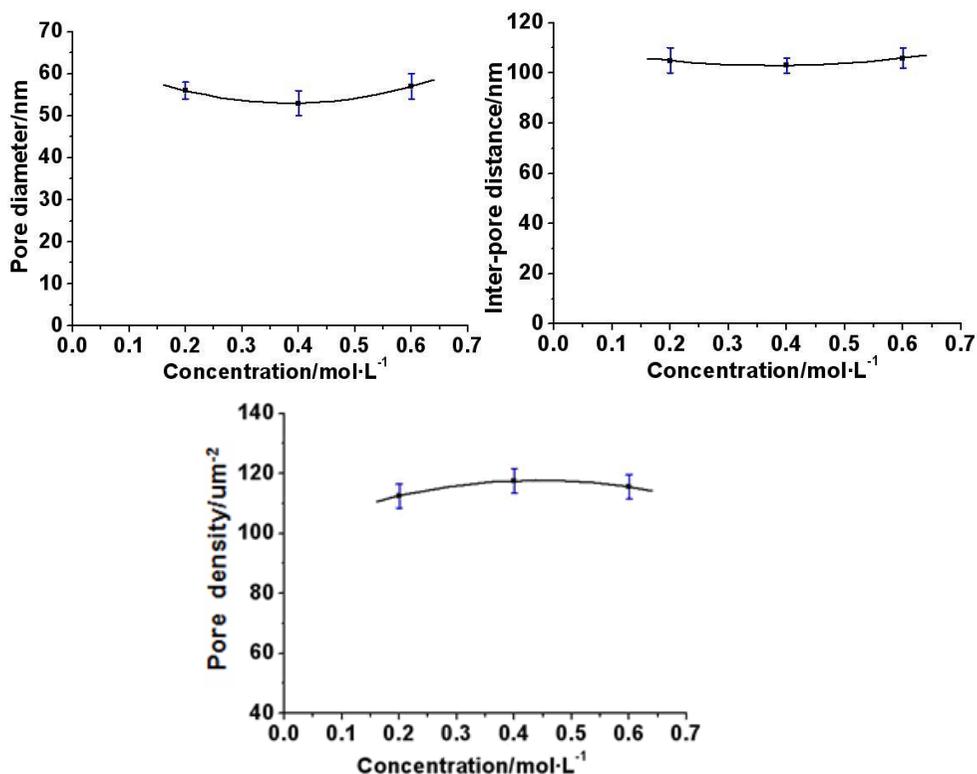


Fig.6. Variation of pore diameter, inter-pore distance, and pore density at 40V with electrolyte concentration of oxalic acid.

SEM photographs of AAO membrane fabricated in oxalic acid solutions of different concentration are shown in figure 5 and the variations of pore diameter, inter pore distance, and pore density with concentration in figure 6.

As shown in the above figure, variation of nano pore diameter and interpore distance are not great and degree of order of pore distribution is consistent. The electrolyte concentration of oxalic acid does not affect the growth of AAO membrane much and therefore we can see that this experiment is completely different from the variation rule of pore path parameter of nanowire membrane with electrolyte concentration of sulfuric acid.

This is because oxalic acid is weak one and the variation in concentration changes pH value very slightly and therefore H^+ ions of first ionized oxalic acid become remained in stable concentration and the variation in size of nano pore diameter and inter-pore distance are small with increase of oxalic acid concentration. Thus, nano pore diameter and inter-pore distance are generally conserved without variation as electrolyte concentration of oxalic acid increases. In addition, when the anodization is performed in acid solution, H^+ ions are vanished continually. In case of oxalic acid electrolyte, decrease of H^+ ions reduces the control of ionization of oxalic acid and oxalic acid is further ionized and compensates H^+ ions vanished in solution.

That is, when the ionization speed of oxalic acid is equal to the decrease speed of H^+ ions, H^+ ions of solution keep steady state and this is advantageous to the ordered growth of nano pore of AAO membrane.

AAO membrane of particular pore dimension can be obtained by controlling pore extension time. But in case of so long extension time nano pore wall thins out and membrane can be destroyed.

4. Conclusions

In this paper we have investigated and analysed the fabrication technique of porous AAO membrane, the effect on formation of porous aluminium oxide membrane and growth mechanism.

First, pore diameter and inter-pore distance increase linearly and pore density decreases with the increase of anodization voltage.

If pH of solution is increased, longitudinal growth speed of pore path becomes greater than transversal one and pore diameter is decreased. Because of concentration of first ionized H^+ ion in oxalic acid solution stable concentration is remained and since pH variation is so small, the effect on growth of pore path can be neglected.

Next, according to the present experiment, temperature affects greatly the degree of order of pore arrangement, that is, degree of order of AAO membrane becomes higher. AAO membrane with pore diameter required can be obtained by controlling pore extension time in phosphoric acid solution.

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