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Characteristics of Gas Permeation using Two-layered Alumina Membrane Prepared by Anodic Oxidation

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Abstract—The microporous alumina membrane with asymmetrical structure, having upper layer with pore diameter of 10 nm under and lower layer with pore diameter of 36 nm, was prepared by anodic oxidation using DC power supply of constant current mode in an aqueous H_2SO_4 solution as a electrolyte. The aluminum plate was pretreated with thermal oxidation, chemical polishing and electrochemical polishing before anodic oxidation. The membranes were prepared by controlling the current density such as a very low current density for upper layer and a high current density for lower layer of membrane. By controlling the cumulative charge density, the thickness of upper layer of membranes was about 6 μm and the total thickness of membranes was about 80-90 μm. We found from gas permeation experiments with the membranes prepared by above method that the mechanism of gas permeation of the all membranes prepared under each condition complied with model of the Knudsen diffusion.

Key words: Microporous Alumina Membrane, Anodic Oxidation, Asymmetrical Structure, Gas Permeation

INTRODUCTION

Processes of membrane separation have the advantages such as simple operation, low energy consumption, and high separation efficiency compared with the traditional separation processes like distillation, adsorption as well as extraction. So, processes of membrane separation are to be had application to wide processes such as the preparation of condensed nitrogen and oxygen, catalytic gas reaction and separation, hydrogen production and scavenging, and purification of various gases including waste gases [Hwang and Kammermeyer, 1984]. Among them, application range of membrane separation equipment in N_2 incubation processes has been extended recently to the whole industries including inert gases to protect against explosion in tankers, metallic treatment without oxidation, pack-use with N_2 for long time preservation of food, and CA (controlled atmosphere) storage for fresh fruit maintenance on account of more convenient processes in N_2 generation than N_2 supply by N_2 tank in which N_2 was prepared as by-product by separating air into N_2 and O_2 with the aim of O_2 incubation [The Korean Institute of Membrane, 1996].

On the other hand, sintering, sol-gel coating, extrusion and casting, dynamic deposition, and anodic oxidation methods have been the main manufacture methods of inorganic membranes that take on mechanical, thermal, chemical and biochemical stability, long lifetime, and feasibility of cleaning and regeneration [Ma et al., 1991]. Particularly, pore diameter and thickness of membrane can be controlled easily and treatment methods are simple in the case of anodic oxidation method that have been wide application to the field of industry [Itoh et al., 1996; Kobayashi et al., 1996; Dalvie and Baltus, 1992; Amith 1973].

Up to now, there has not been any report about alumina membrane with pore diameter of several nm prepared by anodic oxidation. But alumina membranes with 20-200 nm pore diameter have ever been reported. Pore diameter formed by anodic oxidation with DC power supply of constant current mode will be varied with electrolyte and concentration, temperature, and current density [Lee et al., 1998a]. Although the upper layer of membrane with pore diameter of several nm can be prepared by maintaining low current density, its proper thickness that is determined by coulomic amount needs lots of time to have mechanical strength. Moreover, if the membrane is exposed to soluble electrolyte for a long time, chemical dissolution effects on it will take place to reach its limit thickness quickly [Lee et al., 1998b, 2000].

Therefore, in this study, microporous alumina membranes with asymmetric structure composed of upper and lower layer are prepared by anodic oxidation process using DC power supply of constant current mode that was carried out under high current density after very low and definite current density to reduce the reaction time and achieve the proper mechanical strength, which have enough pore diameter of several nm on the surface to be applied to gas separation. And then gas permeation experiments were performed with those alumina membranes prepared in this way and its characteristics were observed.

EXPERIMENTAL

The whole flow chart that presents the procedures for preparation of microporous alumina membrane used in gas permeation experiments showed in Fig. 1. After preparation of microporous alumina membranes through pretreatment, anodic oxidation, and dissolution of aluminum substrate plate and barrier layer, the gas permeation experiments were performed with above membranes.

1. Preparation of Microporous Alumina Membrane

1-1. Sample and Reagents

Aluminum plate with 99.8% and 0.6 mm thickness on the mar-

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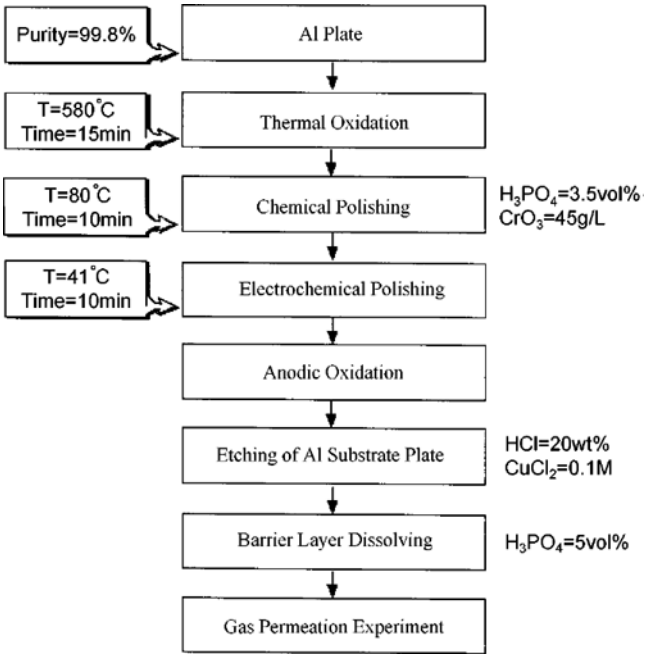


Fig. 1. Schematic diagram of experimental procedure.

kets was used by cutting to the 55×75 mm pieces and ultra pure water (resistivity=1-18 MΩ·cm) prepared by ultra pure water preparation equipment (Elga Stat Instrument, UHQ II) was used in both preparation of electrolyte solution and cleaning of sample. And various acids supplied by Junsei and Ducksan as a special grade were employed for a preparation of electrolyte and pre-treatment solution.

1-2. Pre-treatment Process

Before anodic oxidation, sample was washed by ultra pure water after eliminate the impurities on surface of them by acetone. After this procedure, thermal oxidation for 15 min at 580 °C was executed to make better pore and chemical polishing was carried out in aqueous solution of 3.5 vol% H_3PO_4 and 45 g/L CrO_3 for 10 min at 80 °C. Subsequently, electrolytic polishing was performed with a solution of H_3PO_4-H_2SO_4-H_2O (7 : 2 : 1) containing 35 g/L CrO_3 for 10 min at 41 °C under 200 mA/cm^2 current density in order to get rid of roughness and spontaneous oxidation film. Finally, in order to prepare alumina membrane in the form of disk type, the sample was sealed with silicon rubber except reaction site.

Table 1. Experimental condition for preparation of anodic alumina membrane

Electrolyte	Temp. [°C]	Current density [mA/cm^2]		Cumulative charge density [C/cm^2]	
		Low	High	Low	High
10 wt% H_2SO_4	0	0.5, 1.0	30	10.8	108

1-3. Anodic Oxidation Process

Fig. 2 showed experimental apparatus for anodic oxidation process with DC power supply of constant current mode. In anodic oxidation process, 10 wt% aqueous H_2SO_4 was used as electrolyte and reaction temperature was 0 °C. Circulator circulated aqueous C_2H_5-OH through jacket of reactor in order to maintain reaction temperature. At the time of anodic oxidation reaction, electrolyte was agitated by magnetic stirrer. And titanium plate was used as a counter electrode. The distance between electrodes was 5 cm. As the experimental condition to prepare microporous membrane with asymmetric structure that has both upper layer of several nm and lower layer of several tens nm pore diameter was shown in Table 1, first, anodic oxidation was carried out at 0.5 and 1.0 mA/cm^2 current density up to 10.8 C/cm^2 cumulative charge density and then at 30 mA/cm^2 current density up to 108 C/cm^2 cumulative charge density.

1-4. Etching of Aluminum Substrate Plate and Dissolution of Barrier Layer

After anodic oxidation, aluminum substrate plate was etched by putting in aqueous solution of 0.1 M $CuCl_2$ and 20 wt% HCl to separate alumina membrane from sample. Barrier layer that was formed at first stage of anodic oxidation on back of membrane was dissolved so as to observe the gas permeation properties through only membrane with asymmetric structure after that procedure.

2. Gas Permeation

Equipment for gas permeation experiment was shown in Fig. 3. Gas permeation experiments with the gases such as O_2, N_2, Ar, and H_2 was carried out by pressurized method. Gas was flowed into membrane from cylinder under controlling pressure and temperature. Constant pressure was maintained by dint of valve and pressure gauge. Gas flowed from high pressure was permeated through

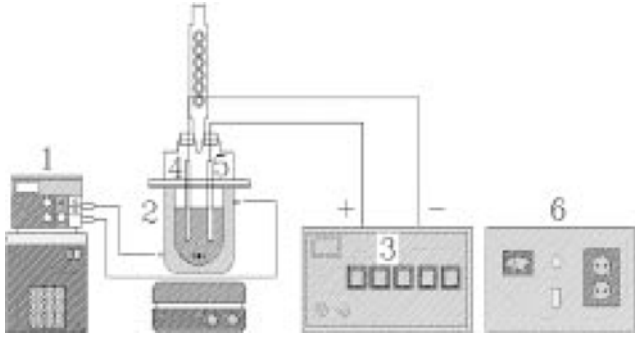


Fig. 2. Experimental apparatus for preparation of anodic alumina membrane.

1. Circulator
2. Reactor
3. DC power supply
4. Cathode(Titanium)
5. Anode(Aluminum)
6. A.V.R.

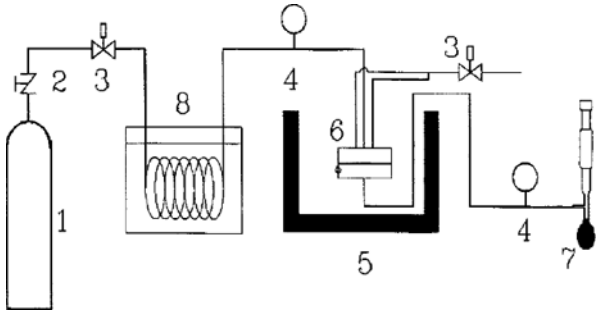


Fig. 3. Experimental apparatus for gas permeation.

1. Gas cylinder
2. Regulator
3. Valve
4. Pressure gauge
5. Water bath
6. Permeation cell
7. Bubble flow meter
8. Gas temp. controller

the membrane in permeation cell and then discharged above permeation section in atmospheric pressure state. The amount of gas permeated was measured using bubble flowmeter. In permeation cell, support plate was installed at the lower section of membrane and O-ring was attached to protect against gas efflux.

Gas permeation experiments were carried out under condition that available cell area was 5 cm^2, pressure difference was 0.25-2.0 kg_f/cm^2, and temperature was 25 °C. Permeated gases were measured after sufficient elapsed time to make steady state.

Permeability coefficient according to gas permeation experiment was calculated from following equation.

$$\mathbf{P} = \frac{V \cdot l}{A \cdot t \cdot \Delta P}$$

Where **P** is permeability coefficient [barrer, $\times 10^{-10}$ cm^3-cm/cm^2-sec-cmHg, STP], V is permeation volume [cm^3, STP], l is membrane thickness [cm], A is permeation area [cm^2], t is permeation time [sec], and ΔP is pressure difference [cm Hg].

Ideal separation factor ($\alpha_{1/2}$) was calculated from the ratio of each gas's square root of molecular weight, namely,

$$\alpha_{1/2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

3. Instrumental Analysis

3-1. Scanning Electron Microscope (SEM) Analysis

Pore diameter, membrane thickness, and geometric structure of microporous alumina membranes prepared by anodic oxidation were analyzed by SEM (JEOL Co., JSM-5800).

3-2. Measurement of Pore Diameter and Distribution

The analysis of pore diameter and distribution of the upper layer of membrane were measured by BET (Brunauer, Emmett and Teller) method using equipment of size distribution measurement. After sample was dried in dry oven for 24 h at 120 °C, about 0.2 g sample was put into sample tube and degassed completely at 350 °C under below 10 μm Hg pressure.

Adsorption isotherm was obtained according to adsorption and desorption of N_2 gas after moving sample tube to analysis port. Pore diameter was measured according to BJH (Barret-Joyner-Halenda) method during desorption process.

RESULTS AND DISCUSSION

1. Preparation of Microporous Alumina Membrane

Microporous alumina membrane with asymmetric structure was prepared by anodic oxidation as following procedure. Lower layer with relatively large pore size was prepared at 30 mA/cm^2 current density up to 108 C/cm^2 cumulative charge density after upper layer with pore size of several nm was prepared at 0 °C reaction temperature, each 0.5 and 1.0 mA/cm^2 current density up to 10.8 C/cm^2 cumulative charge density, and 10 wt% H_2SO_4 electrolyte in order to reduce preparation time to protect pore size of several nm in upper layer of membrane against damage and also to increase flux of membrane. Because pore size of upper layer in membrane prepared at 0.5 mA/cm^2 current density was too small to measure exactly with SEM analysis. So, BET analysis kept pace with SEM analysis. Pore diameter distribution obtained from N_2 desorption using BJH method among results of BET analysis was presented

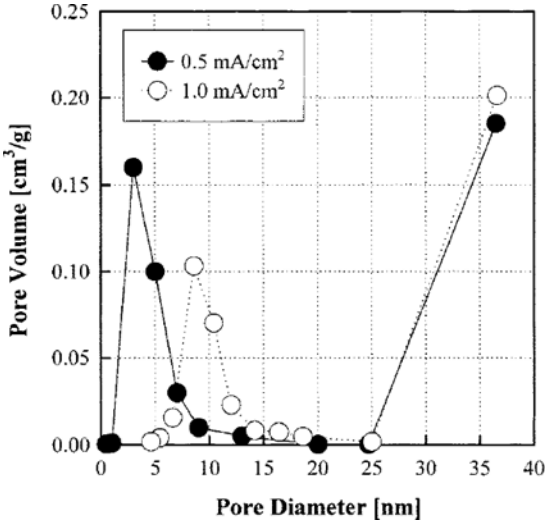


Fig. 4. Pore distribution of microporous alumina membrane.

in Fig. 4. As shown, pore diameter of upper layer of membrane prepared at 0.5 mA/cm^2 current density was 3 nm and that prepared at 1.0 mA/cm^2 current density was 9 nm. In addition, pore diameter of lower layer of membrane prepared under 30 mA/cm^2 current density was the range of 35-40 nm. These results corresponded to those of SEM analysis that analyzed pore diameter of the front and back of membrane. Besides, it was confirmed that the pore diameter of upper layer was increased as current density was high. This tendency that pore diameter was increased with current density occurred because ionic conduction effect increased with current density during anodic oxidation and because the solvency was increased due to increase in activity of electrolyte with electrolytic voltage. Microporous alumina membrane with pore diameter of several nm could be prepared according to current density.

Fig. 5 presented BET adsorption and desorption isotherm of membrane prepared at 1.0 mA/cm^2 current density and that pore structures were the two different bimodal micropore of which shape

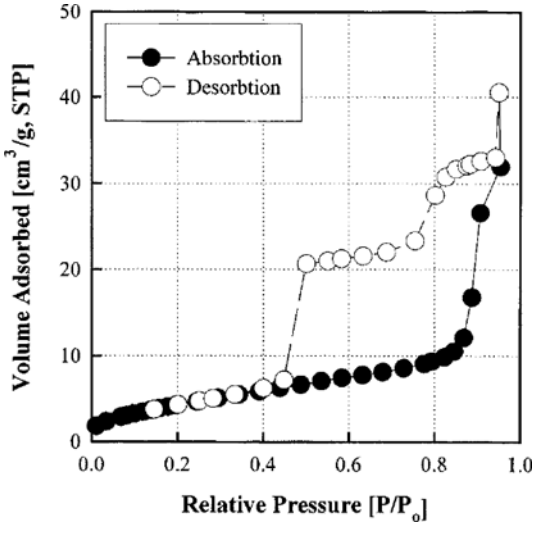
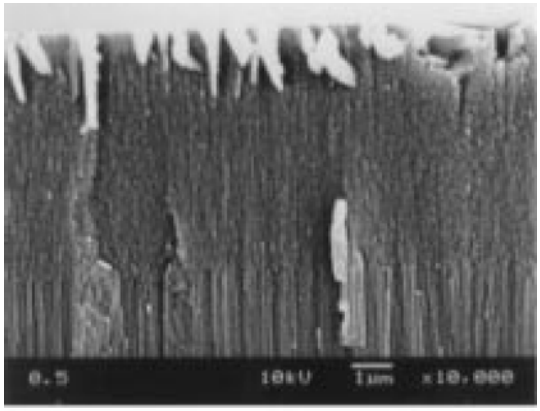
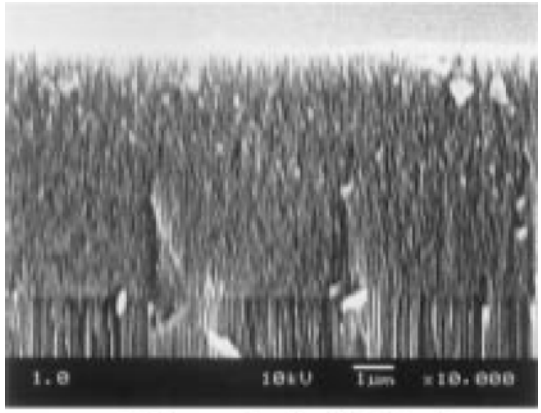


Fig. 5. BET isotherm of microporous alumina membrane [current density=1.0 mA/cm^2].



(a) Current density = 0.5mA/cm^2



(b) Current density = 1.0mA/cm^2

Fig. 6. SEM photographs of cross-section of microporous alumina membrane.

was cylindrical and straight with different pore diameter, which was proved from hysteresis loop shown in Fig. 5 [Allen 1990]. These facts coincided with results confirmed in Fig. 4.

The SEM photographs of cross section of the upper layers of microporous alumina membranes prepared under the condition that anodic oxidation was carried out at 30 mA/cm^2 current density up to 108 C/cm^2 cumulative charge density after performed at 0.5 and 1.0 mA/cm^2 each current density up to 10.8 C/cm^2 cumulative charge density was presented in Fig. 6. It is shown in Fig. 6 that pore with straight and cylindrical shape made progress in membrane and that membranes were asymmetric structures of asymmetry which consist of upper and lower layer with different pore diameter. These results coincided with those of above BET analysis. Besides, pore diameter could be controlled more easily with current density, in this study, than P. Hoyer's method that for the purpose of preparation of membrane with 20 and 50 nm pore diameter, membrane with 20 nm pore diameter was obtained through anodic oxidation executed in 0.3 M aqueous oxalic acid using constant voltage method after this membrane was etched in 5% phosphoric acid to widen pore diameter up to 50 nm and then anodic oxidation with this membrane was carried out under the same under the same above condition [Hoyer et al., 1996].

The results obtained from SEM and BET analyses of microporous alumina membranes prepared by anodic oxidation were presented in Table 2. As shown in Table 2, the upper layer thickness

Table 2. Pore diameter and thickness of microporous alumina membrane prepared by anodic oxidation

Current density [mA/cm^2]		0.5	1.0
Pore diameter of upper layer [nm]		3	9
Thickness [μm]	Upper layer	6.1	6.1
	Total	82.3	87.9

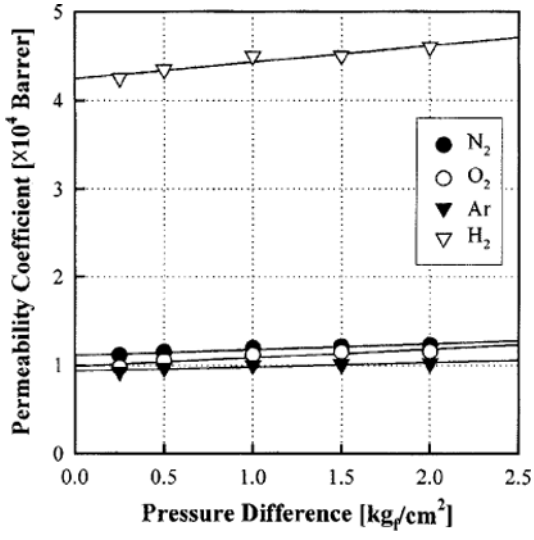


Fig. 7. Permeability coefficient for porous alumina membrane [D_p=9 nm].

of membranes prepared at each 0.5 and 1.0 mA/cm^2 current density was the interior and exterior of 6 μm respectively and their pore diameters were the range of 3-10 nm. Therefore there was no big difference in thickness. In addition, it was possible to prepare the microporous alumina membrane of asymmetric structure with 80-90 μm total thickness of upper and lower layer.

The most important point was that microporous alumina membrane that had pore diameter of several nm and asymmetric structure to improve flux could be prepared by anodic oxidation by controlling current density.

2. Gas Permeation Characteristics

The results of gas permeation experiment with microporous anodic alumina membrane showed in Fig. 7 through 9. The experiment, using O_2, N_2, Ar, and H_2, was carried out at 25 °C using pressurized method.

Fig. 7 was the results of gas permeation experiment with microporous membrane 9 nm pore diameter. As shown in Fig. 7 showed the permeability coefficient against difference in pressure, the permeability coefficient of membrane was about 10,000-50,000 Barrer for each gases, and little affected by pressure difference within the range of pressure difference applied to experiment. These gas permeation through membrane reflected Knudsen diffusion.

Fig. 8 showed the permeability coefficient according to $1/\sqrt{M}$. From the left side of x-axis, the permeation gases are argon, oxygen, nitrogen and hydrogen, respectively. For each membranes, 3 nm and 9 nm in pore diameter (D_p), the permeability coefficient against $1/\sqrt{M}$ was straight line as shown in Fig. 8, which complied with Knudsen diffusion.

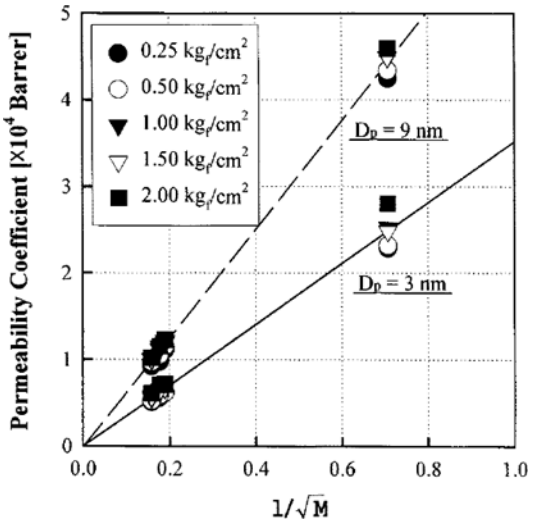


Fig. 8. Permeability coefficient against $1/\sqrt{M}$.

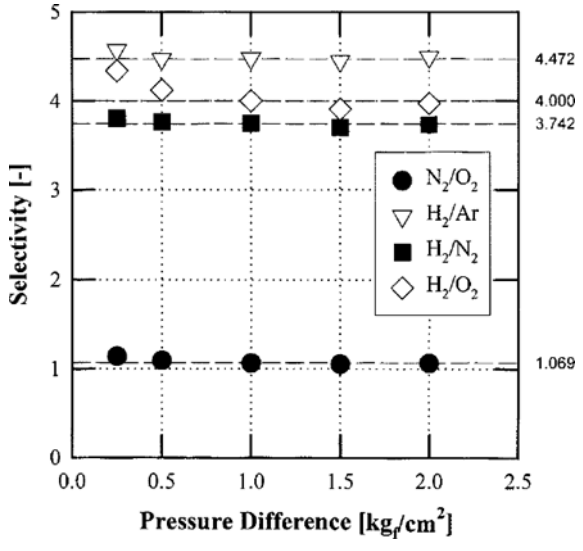


Fig. 9. Selectivity for microporous alumina membrane [D_p=9 nm].

Selectivity obtained from gas permeation experiment with microporous alumina membrane 9 nm pore diameter was compared with Knudsen theoretical selectivity that was calculated by the inverse of square root of molecular weight in Fig. 9. The results were that selectivity adjacent to Knudsen theoretical selectivity.

From above results of gas permeation experiments, the membranes used in this study complied with Knudsen diffusion very well, which is considered to apply to gas separation such as nitrogen condensation and hydrogen recovery.

CONCLUSION

We had following conclusion by investigating the properties of gas permeation with microporous alumina membranes prepared by anodic oxidation.

When anodic oxidation was performed in aqueous H_2SO_4 electrolyte at under 1.0 mA/cm^2 current density, microporous alumina membrane with pore diameter of several nm could be prepared and its pore diameter was increased with current density.

The asymmetric and microporous alumina membranes with asymmetric structure which is consecutive upper and lower layer having different pore diameter could be prepared by controlling current density during anodic oxidation. And from the results of gas permeation experiments with asymmetrical and microporous alumina membrane, gas permeation mechanism complied with Knudsen diffusion as well as selectivity was adjacent to Knudsen theoretical selectivity.

From above conclusions, these membranes are to be applied to gas separation such as nitrogen condensation and hydrogen recovery, which need Knudsen permeation selectivity.

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