JOURNAL OF MATERIALS SCIENCE 31 (1996) 6185–6187

Preparation of tubular alumina membrane with uniform straight channels by anodic oxidation process

Y. KOBAYASHI*, K. IWASAKI, T. KYOTANI, A. TOMITA
Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba, Sendai 980-77, Japan

We prepared alumina tubes by an anodic oxidation process. The tube obtained was mechanically tough against a pressure of about 1 MPa from the outside of the tube. The tube was characterized by scanning electron microscopy (SEM) and a gas permeability measurement. The SEM observations revealed that this has uniform straight channels penetrating through the tube wall. The channels are vertical to the tube surface and their diameter is about 150 nm. The permeability of gas was measured with H_2, He, N_2, O_2 and CO_2 in the range of 0–100 kPa. The gas flow was mainly governed by Knudsen flow. This indicates the absence of big cracks in the tube.

1. Introduction

A great deal of attention has been paid to gas separation systems using a membrane, because such systems do not need a phase change, and hence, the efficiency can be very high [1, 2]. Moreover, if the membrane has a catalytic function, it may be possible to separate a target product from the reactants simultaneously with the catalytic reaction. The membrane can thus be used as a membrane reactor [3–8]. Many kinds of membranes are now commercially available for various purposes [2, 9]. Polymeric membranes and inorganic ones are most frequently used. Only the latter can be used under high temperature conditions. In order to use the membrane in a practical application, it is necessary to make it as a module. Since inorganic membranes are not flexible, tubular membranes are more desirable than flat ones for fabrication into a module. Tubular alumina membranes are the most popular among the many inorganic ones. In general, alumina membranes are prepared by calcining α-alumina powder or by coating a thin layer of γ-alumina on an α-alumina support tube. The membranes prepared in this way usually have different pore shapes and a wide distribution in diameter. If the pore sizes and shapes are not uniform, it is difficult to control gas selectivity in gas separation because gas flow mainly depends on pore size and shape. Therefore, inorganic tubular membranes with the same shape and a uniform pore diameter are desirable for a separation material or membrane reactor. Alumina membranes prepared by anodic oxidation have uniform straight channels perpendicular to the surface with a diameter of 5–200 nm. Studies on anodic alumina are, however, concerned only with flat alumina films [10, 11]. In this study, we attempted to prepare tubular alumina membranes by the anodic oxidation technique and their channel structure was investigated by scanning electron microscopy (SEM). We also examined its gas permeability performance.

2. Experimental details

Aluminium tube (99.5% purity), with length of 50 mm, outer diameter of 2 mm and wall thickness of 0.2 mm, was used as a starting material. The tube was annealed for 2 h at 500 °C under air flow in order to reduce possible strain in the tube. Then, this tube was degreased with acetone and washed in distilled water. Fig. 1 shows the apparatus for anodic oxidation of the aluminium tube. One of the open ends of the alumina tube was closed by a silicon rubber cap in order to prevent the inside of the tube contacting with electrolyte solution. Thus, only the outer surface of the tube is anodically oxidized. The tube was set as the anode in a 4 wt % aqueous $H_2C_2O_4$ electrolyte. An aluminium tube with a diameter of 30 mm was set as the cathode around the anode. The cell current was controlled by a d.c. power supply. The current density was held constant at 20 mA cm^{-2} for 2 h at room temperature. During this period, the voltage changed from 50 to 90 V. Then, the voltage was maintained at 90 V for 30 h. After the anodic oxidation, the cap was removed and the tube was rinsed in distilled water. 10 wt % aqueous HCl was passed through the inside of the tube for 1.5 h in order to etch any unoxidized aluminium. Then, a barrier layer, which consists of the boundary between an oxide layer and unreacted aluminium, was etched similarly by passing 4 wt %

*To whom all correspondence should be addressed.

0022–2461

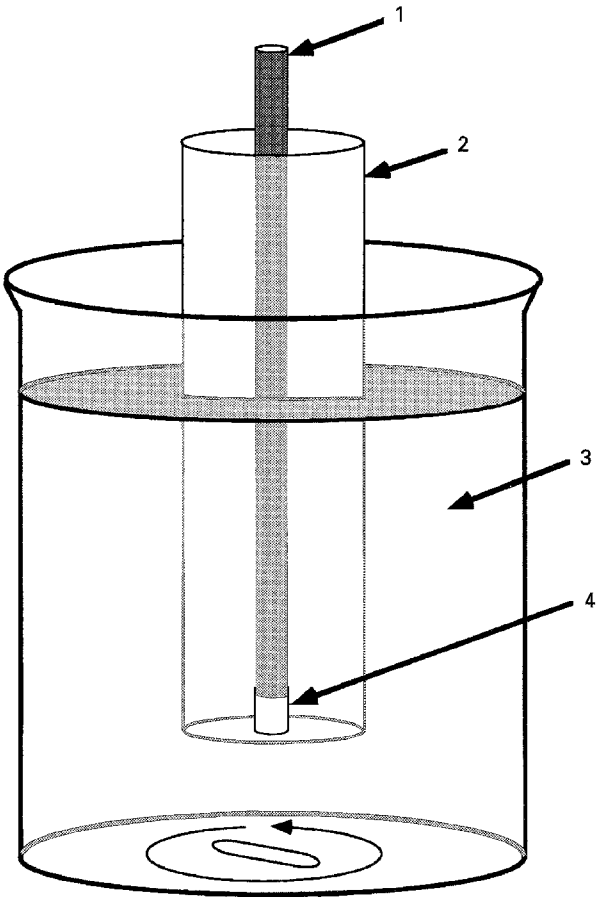

Figure 1 Apparatus for anodic oxidation of aluminium tube. Key: (1) aluminium tube (anode); (2) aluminium tube (cathode); (3) electrolyte; (4) silicon rubber cap.

aqueous H_3PO_4 through the tube for 2 h. After these etchings, the tube was washed with distilled water and dried in air. In this procedure, there are two important points to be mentioned. One is the use of aqueous $H_2C_2O_4$ as the electrolyte. Other acids such as aqueous H_2SO_4 etch not only the aluminium metal but also the produced oxide more quickly and thus the tube becomes more brittle during the oxidation process. The other important point is the control of the current density and voltage during the oxidation. In general, anode dissolution occurs under a high voltage. In our case, the alumina tube prepared above 90 V was mechanically weak due to anode dissolution. Therefore, after arriving at 90 V, the voltage was kept at 90 V to prevent the anode from dissolving under higher voltage.

3. Results

The resultant alumina tube was observed by SEM. Fig. 2a and b show the SEM microphotographs of the cross-section of the tube wall near the outer and inner surfaces, respectively. The outer surface is uneven and the cross-section of the tube wall is rough up to about 10 μm in depth from the outer surface. It is thought that aqueous $H_2C_2O_4$ etched some of the aluminium oxide layer which had been prepared by the oxidation process. Conversely the cross-section of tube wall near the inner surface is more smooth than the outer surface, since the inner surface does not come into contact with the aqueous $H_2C_2O_4$. Fig. 2c shows the higher magnification SEM microphotograph of the

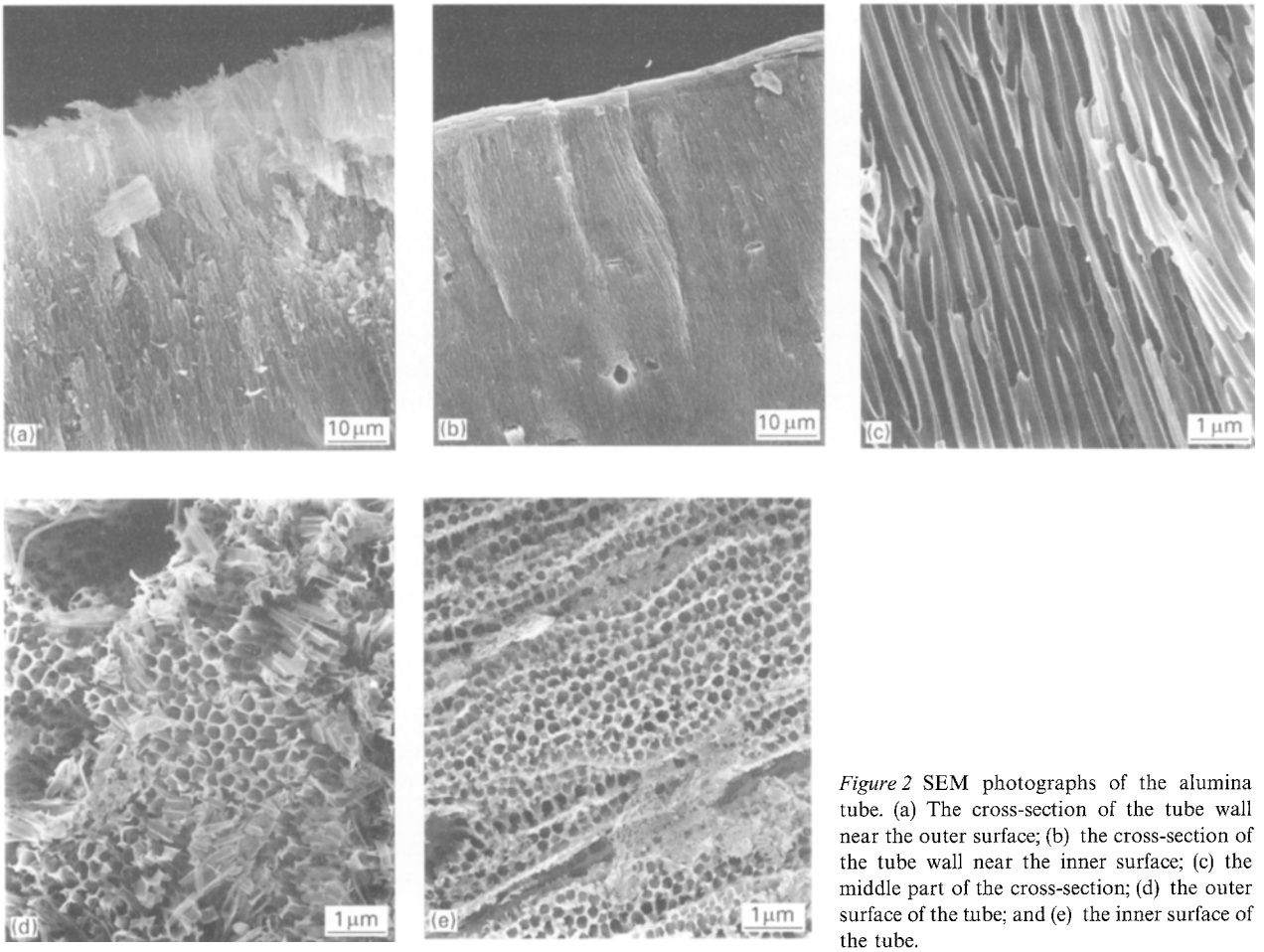

Figure 2 SEM photographs of the alumina tube. (a) The cross-section of the tube wall near the outer surface; (b) the cross-section of the tube wall near the inner surface; (c) the middle part of the cross-section; (d) the outer surface of the tube; and (e) the inner surface of the tube.

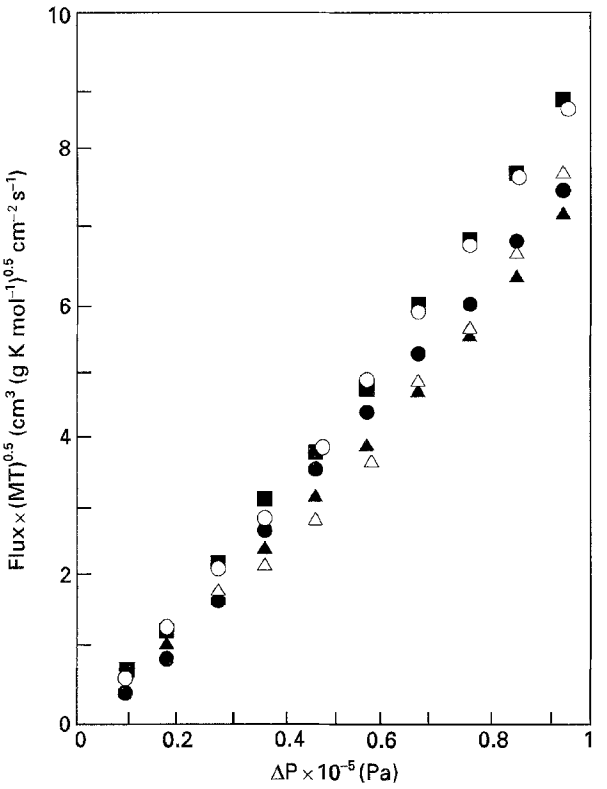

Figure 3 Pressure dependence of gas flux at 303 K. ●, H_2; ▲, He; ■, N_2; ○, O_2; △, CO_2, ΔP stands for the pressure difference between the outside and inside of the alumina tube.

cross-section of the tube wall. The channels penetrate through the tube wall vertically to the tube surface and they are approximately straight. The channel diameter is about 150 nm. Fig. 2d shows the SEM microphotographs of the outer surface of the tube. The surface is rather rough. Compared to the outer surface, channel mouths were more uniformly distributed on the inner surface (Fig. 2e). The diameter of channel mouths at the outer surface is somewhat larger than those at the inner surface, since the outer channel mouths are etched by aqueous $H_2C_2O_4$.

Gas permeation experiments were carried out as follows using H_2, He, N_2, O_2 and CO_2. One end of the tube was sealed with epoxy resin and the other remained open. The alumina tube was set in a stainless steel tube with an inner diameter of 8 mm: the space between the stainless steel tube and the alumina tube edge with the open end was sealed with epoxy resin. The gas flowed from outside to inside of the alumina tube. The flux of gas was measured at 303 K. Fig. 3 shows pressure dependence of flux for each gas at 303 K. The ordinate is the flux multiplied by $(MT)^{0.5}$, where M and T are molecular weight and temperature, respectively. The normalized fluxes are approximately proportional to the pressure difference between the outside and inside of the tube. Moreover, the slopes are almost the same for all the gases examined. This indicates that the permeation is mainly governed by Knudsen flow [1, 12]. This also indicates that there are no big cracks in the tube. However, these lines do not go through the origin completely. Moreover, a small difference in the gas flows appeared as the pressure difference increased. It seems that other flows such as viscous flow are also contained partially in the total gas flow. For practical purposes, it is necessary that the tube can endure a high pressure difference. No leaks were observed even at a pressure difference of about 1 MPa. From the results mentioned above, it can be judged that this tubular alumina membrane can be applied to gas separation or as a membrane reactor.

4. Conclusion

In conclusion, we succeeded in preparing a tubular alumina membrane by the anodic oxidation process. The tube obtained has uniform straight channels penetrating vertically to the tube surface with a diameter of about 150 nm. It was found that the gas flow is governed by Knudsen flow. The alumina tube can be expected to be used as a gas separation membrane or a membrane reactor. However, since the pore diameter is rather large, the alumina tubular membranes may be more suitable for ultrafiltration rather than for gaseous separations. Controlling the pore size is important for several applications and is currently being studied.

References

1. S.-T. HWANG and K. KAMMERMEYER "Membrane in Separations" (John Wiley & Sons, 1975).
2. W. S. W. HO and K. K. SIRKAR (eds) "Membrane Handbook" (Van Nostrand Reinhold, New York, 1992).
3. O. SHINJI, M. MISONO and Y. YONEDA, *Bull. Chem. Soc. Jpn.* **55** (1982) 2760.
4. N. ITO, Y. SHINDO, K. HARAYA and T. HAKUTA, *J. Chem. Eng. Jpn.* **21** (1988) 399.
5. Y.-M. SUN and S.-J. KHANG, *Ind. Eng. Chem. Res.* **27** (1988) 1136.
6. T. OKUBO, K. HARUTA, K. KUSAKABE, S. MOROOKA, H. ANZAI and S. AKIYAMA, *Ind. Eng. Chem. Res.* **30** (1991) 614.
7. V. T. ZASPALIS, W. VAN PRAAG, K. KEIZER, J. G. VAN OMMEN, J. R. H. ROSS and A. J. BURGGRAAF, *J. Appl. Catal.* **74** (1991) 205.
8. A. M. CHAMPAGNIE, T. T. TSOTSIS, R. G. MINET and E. WAGNER, *J. Catal.* **134** (1992) 713.
9. J. N. ARMOR, *Appl. Catal.* **49** (1989) 1
10. K. ITAYA, S. SUGAWARA, K. ARAI and S. SAITO, *J. Chem. Eng. Jpn.* **17** (1984) 514.
11. K. WADA, S. ONO, K. WADA, T. YOSHINO, N. BABA, K. KURODA, O. TAKAHASHI, Z. KAWAHARA and S. YABUSHITA, *Hyoumengijutu* **40** (1989) 1388.
12. S.-T. HWANG and K. KAMMERMEYER, *Can. J. Chem. Eng.* **44** (1966) 82.

Received 2 October 1995
and accepted 13 June 1996