Study on the Influence of Porous Anodic Alumina Membrane on Separation of Hydrogen and Methane

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Abstract. Hydrogen and methane have been regarded as the main energy for future. In recent years, membrane technology has developed to be an attractive technology to separate them. In this paper, porous anodic alumina membranes at different thickness were prepared for separation of hydrogen and methane. The thickness varied from about 77 to 250 \textmu m, moreover, the SEM (Scanning Electron Microscopy) images show a good linear relationship between the thickness (y) and anodizing time (x), with the fitting being $y = 22.56x - 36.082$. Gas permeance and separation index for hydrogen and methane were measured at different conditions, such as thickness and temperature. With the thickness increased, the permeances of two gases were decreased quickly but separation index vice versa. In this research, the actual separation index changed from 1.9 to 3.2.

Introduction

With the rapid development of industry, excessive consumption of energy and the greenhouse gases emission have been taken center stage in the world. How to make full use of clean energy, such as hydrogen, have risen to be an urgent problem. Hydrogen has been regarded as the future energy because of its high calorific value (62.8KJ/Kg). It is well known that China is the world's largest coke production. In 2010, the production of coke was four hundred million tons which was accounting for two-third of the world's total production. Coke gases produced during the coke processing are comprised of lots of hydrogen (55%, v/v) and methane (26%, v/v), but they are not utilized sufficiently. In 2010, the storage volume was 85 billion cubic meters, thus the full use of hydrogen and methane is related to energy saving and emissions reduction. In recent years, membrane technology has developed to be an attractive technology to separate them. The main advantage of membrane technology lies on its separation without the addition of chemicals, relatively low energy consumption and well-arranged process conductions. For the last few decades, porous anodic alumina membrane (PAAM) has been the focus of research. Due to its highly ordered porous structure, consisting of column form cells with uniformly sized pores, and could be controlled by changing anodizing parameters, such as electrolytes, anodizing voltage and temperature, so it could be used in gas separation systems, optoelectronics [1], magnetic recording [2] and as templates for the synthesis of various membrane such as metal organic framework membrane [3]. A number of recent studies have focused on the development of membranes; however the few researchers pay attentions to the separation of hydrogen and methane with porous
anodic alumina membrane\[4,5\]. In this study, the permeance and separation index were measured to discuss the influence of different thickness of porous anodic alumina membrane on separation of hydrogen and methane. It is hoped to be contributed to promote the wide usage of this technology and provide useful information for future experimental research.

**Experimental section**

**Membrane preparation**

PAAMs were prepared by electrochemical anodization of pure aluminium foil (99.999\%). This experimental procedure was the fabrication of PAAM and characterization of their structure by the scanning electron microscopy (SEM).

First, the aluminium foil was annealed at 400°C under nitrogen protection to remove mechanical stresses\[6\]. This foil was etched in 5% NaOH solution and then sonicated with a lot of distilled water. Subsequently, aluminium foil was electro polished in a (4/1, v/v) mixture of ethanol and perchloric acid. A platinum foil worked as a cathode. The values of the voltage and current were controlled via power supply. After anodization process, the remaining aluminum substrates along with barrier layers were chemically etched out in a CuCl$_2$/HCl solution and the pore bottoms were subsequently opened by chemical etching in 6 wt% phosphoric acid. Different conditions are shown in Table 1.

| Number | Electrolyte       | Temperature (voltage)                |
|--------|-------------------|--------------------------------------|
| 1      | phosphate acid    | room temperature/ ice bath (20V)     |
| 2      | oxalic acid       | room temperature/ ice bath (20V)     |
| 3      | sulfuric acid     | room temperature/ ice bath (20V)     |
| 4      | sulfuric acid     | ice bath(10V, 20V, 25V)              |

The determination of gas transmission rate was in accordance with ISO 15105-1 and the equipment is shown in Fig. 1. All gases were 99.999\% of purity purchased from Heli company.

**Results and discussions**

**Surface morphology**

In this experiment, Fig. 2 is the SEM images of the PAAMs prepared under different conditions. Black spots indicate the presence of straight cylindrical pore. Fig. 2(A) shows that PAAM formed in oxalic acid consists of an array of 60 nm diameter pores with a density of $1.96 \times 10^{10}$ pores/cm$^2$. From this image we can see that parts of the pores are collapsed or dissolved causing the uncontinuous top surface. In this research, nothing is observed on the surface of membrane prepared...
in phosphate acid. According to literature[3], high anodization voltage should be used for preparing porous anodic alumina in phosphate acid. In case of dilute sulfuric acid at the room temperature, there is not porous anodic alumina membrane integrated successfully. The reason is that the temperature of electrolyte is so high that parts of the aluminum substrate dissolved. During the experiment, lots of gas bubbles were produced on electrode. Fig. 2(B) shows the pore diameters and density of PAAM prepared in ice water bath using oxalic acid solution at 20 V. Contrast to Fig. 2(A), pore diameter and pore density of PAAM are reduced to 10nm and $1.96 \times 10^{10}$ pores/cm$^2$, respectively. Interestingly, at this temperature, we obtained porous anodic alumina membrane using sulfuric acid, of which pore diameter being 25 nm and interpore distance of 80-100 nm. In O'Sullivan and Wood’s study [7], the pore diameter is usually proportional to the applied voltage and a ratio is equal to 1.29. The pores are very regular as Fig. 2(C) shown. Using sulfuric acids solution in ice water bath, the effects of anodizing voltage on the pore diameter were investigated. At 25 V, the phenomenon was dramatic and the temperature of solution rises quickly accompanying with a lot of gas bubbles. At 10 V, as Fig. 2(D) shown, the pore diameter is about 10 nm.

Fig. 2 SEM images of PAAMs. A: oxalic acid(RT) B: oxalic acid(ice water) C: sulfuric acid(20V) D: sulfuric acid(10V)

The SEM images of PAAM at different anodisation time are shown in Fig. 3. The thickness varies from 77 to 250 µm. Experimental results show that the thickness is proportional to anodization time. The thickest of membrane prepared at an anodisation of 20 V for 13 hours was 250 µm approximately. The cross-sectional image of all PAAMs shows clear, straight and cylindrical “pipeline” with the diameter of about 25 nm. The thickness of PAAM versus anodizing time is shown a linear relationship, which indicates that the thickness increased with the increasing anodizing time. The fitting formula is $y = 22.56x - 36.082$.

Fig. 3 Thickness of PAAMs at different anodisation time (A-D:5h-8h, E:10h, F:11h, G:13h, H: cross-sectional image, I:linear relationship between thickness and anodiasation time)
Gas separation
Single gas

The PAAM was investigated for the structure and its application by Smith in 1973 [8]. Table 2 shows the flux of hydrogen and methane through the PAAM at room temperature. For the experiment of 5h, the permeance of hydrogen and methane are highest among the other membranes. The permeance of hydrogen and methane are $5.607 \times 10^{-5}$ mol/Pa m$^2$ s and $2.385 \times 10^{-5}$ mol/Pa m$^2$ s respectively. The separation index is 2.35. With the thickness increased, the permeances of two gases are decreased quickly. For 6h condition, the permeance of hydrogen is $1.140 \times 10^{-5}$ mol/Pa m$^2$ s which is 3.98 times lower than that of 5h. The thickness of membrane for 6h is only 1.29 times higher than that of 5h. Similar to hydrogen, the permeance of methane is $0.562 \times 10^{-5}$ mol/Pa m$^2$ s, 4.24 times lower than that of 5h. With the thickness up to 224 µm, the permeances of hydrogen and methane are decreased to be $0.133 \times 10^{-7}$ mol/Pa m$^2$ s and $0.400 \times 10^{-8}$ mol/Pa m$^2$ s. The separation index is 3.33. Generally the permeance of membrane is inversely proportional to the square root of the molecular weight of the target gases, however the thickness of membranes plays an important role. In this research, the separation index changes from 2.35 to 3.47.

Table 2 Flux and ideal separation index of hydrogen and methane

| anodisation time | hydrogen($10^{-5}$ mol/Pa m$^2$ s) | methane($10^{-5}$ mol/Pa m$^2$ s) | Idea separation |
|------------------|-------------------------------|-------------------------------|-----------------|
| 5                | 5.607                         | 2.385                         | 2.35            |
| 6                | 1.410                         | 0.562                         | 2.51            |
| 7                | 0.796                         | 0.262                         | 3.03            |
| 8                | 0.133                         | 0.040                         | 3.33            |
| 10               | 0.016                         | 0.0046                        | 3.47            |

Fig. 4(A) confirms a relationship between permeances of the two gases and different feed pressure. The results show that the permeance is constant. Under 0.1-0.3MPa, the permeances of hydrogen and methane are $5.6 \times 10^{-5}$ mol/Pa m$^2$ s and $2.3 \times 10^{-5}$ mol/Pa m$^2$ s approximately for 5h case, and the ideal separation index is 2.35. For 6h case, the separation index is 2.77. Fig. 4(B) shows the temperature dependence of hydrogen and methane permeances through PAAM. The permeances of hydrogen and methane decrease with temperature, and the ideal separation rate is also decreased slightly. The permeances of hydrogen is decreased from $6.321 \times 10^{-5}$ mol/Pa m$^2$ s (0°C) to $4.380 \times 10^{-5}$ mol/Pa m$^2$ s (100°C) in 5h study, and the separation index is changed from 2.37 to 2.29. For 6h case, the permeances of hydrogen and methane are $1.578 \times 10^{-5}$ mol/Pa m$^2$ s and $0.564 \times 10^{-5}$ mol/Pa m$^2$ s (0°C) to $1.335 \times 10^{-5}$ mol/Pa m$^2$ s and $0.501 \times 10^{-5}$ mol/Pa m$^2$ s (100°C). Meanwhile, the separation index is varied from 2.80 to 2.66.

Fig. 4 Flux of H$_2$ and CH$_4$ (A: under different feed pressure. B: at different temperature)
Mixture gases

Fig. 5 shows the thickness dependence of hydrogen and methane permeances through PAAM (1/1, v/v,). Compared to single gas experiment, the actual separation index is lower than ideal separation index. For example, the actual separation index of hydrogen and methane is 1.90 under 0.3MPa feed pressure at room temperature, which is 0.81 times lower than that of ideal separation index in 5h. The permeance decrease with the thickness increased, but the actual separation index of hydrogen and methane is increase from 1.9(5h) to 3.2(8h). If initial concentration ratio of hydrogen and methane is 2, the separation index is increased from 3.9(5h) to 6.7(8h). In ice water bath, the separation index is up to 7(6h).

![Chromatographic analysis of separation of hydrogen and methane (A:5H, B:7H, C:8H)](image)

**Conclusions**

In this work, the PAAMs of different thickness were successfully prepared, of which pore diameters were changed from 10 nm to 60 nm and thickness ranges from 77 µm to 250 µm. The gas-permeation performances of the membranes are evaluated. With the thickness increased, the permeances of hydrogen and methane are decreased. The results show that the thickness of membrane plays an important role on separation index. The actual separation index of hydrogen and methane varies from 1.9 to 3.2 in mixtures of hydrogen and methane.

**References**

[1] Huang Y., Duan X., Gui Y., Lieber: Nano Lett, vol. 2(2002), p. 101–104.
[2] Nielsch K., Muller F., Li A.P., Gosele, U: Adv. Mater, vol. 12(2002), p. 582–586.
[3] Xiaolong Cao, Yongli Che, Wei Wang, Qingshan Li, Fuquan Wu: Laser Technology, vol. 30(2006), p. 415-417.
[4] Helio de L. Lira, Russell Paterson: Journal of Membrane Science, vol.206(2002), p. 375-387.
[5] Meizhen Qu, Yijun Chen, Weizhu An, Shendu Guo: Chinese Journal of Synthetic Chemistry, vol. 3(1992), p. 32-39.
[6] Ali G., Ahmad M., Akhter J.I., Maaz K., Karim S: Nanotechnol, vol. 9(1998), p. 223–228.
[7] J.P. O'Sullivan, G.C. Wood: Proc. R. Soc. Lond.A, vol. 317 (1970), p. 511-543.
[8] A. W. smith: J. Electrochem. SOC, vol. 120 (1973), p. 1068-1069.