

## Gas permeation properties and characterization of asymmetric carbon membranes prepared by pyrolyzing asymmetric polyimide hollow fiber membrane

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Received 20 February 1997; received in revised form 29 April 1997; accepted 1 May 1997

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### Abstract

Carbon membranes were continuously prepared by pyrolyzing an asymmetric polyimide hollow fiber membrane at temperatures ranging from 600 to 1000°C under nitrogen for 3.6 min. The asymmetric polyimide hollow fiber membrane was treated under atmospheric air at 400°C before pyrolysis. By scanning electron microscopy, the carbon membranes were observed to have an asymmetric structure of which a skin layer consisted of nodule aggregates. The asymmetric carbon membranes displayed high performance of gas permeability and selectivity. For example, the membranes prepared by pyrolyzing at over 700°C had permeation rates of hydrogen ranging from  $10^{-4}$  to  $10^{-3}$  cm<sup>3</sup> (STP)/(cm<sup>2</sup> s cmHg) and ratios of the permeation rate of hydrogen to that of methane ranging from 100 to 630 at a feed gas composition of 50% hydrogen in methane and at 80°C.

**Keywords:** Carbon membranes; Polyimide; Hollow fibers; Gas and vapor permeation; Pyrolysis

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### 1. Introduction

Recently, inorganic membranes have attracted much attention for their potential uses in gas and vapor separation and in pervaporation. It has been reported that some of the inorganic films and membranes composed of carbon, silica, or a zeolite displayed higher permeabilities and selectivities than organic ones [1–18].

The gas permeabilities and selectivities on molecular sieve carbon membranes prepared by pyrolyzing

polymer hollow fibers have been reported by Koresh and Soffer [1,2]. From 1990, Kusuki and co-workers have applied for four patents covering carbon hollow fiber membranes prepared by pyrolysis of asymmetric polyimide hollow fiber membranes under nitrogen [3–6]. The carbon hollow fiber membranes have much higher permeation rates and selectivities of gases than commercial polyimide hollow fiber membranes. Hatori et al. [7] and Haraya et al. [8–10] have reported gas permeation properties on carbon films prepared by a carbonization of a Kapton polyimide film. Haraya et al. have reported that the carbon films prepared at 1273 K had high permselectivities of gases such as a

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permeability ratio of hydrogen over nitrogen of 900 [9]. Studies of carbon membranes displaying high membrane performance concentrate on the development of the membranes prepared by pyrolyzing thermostable polymers such as polyimides [1–16].

In this study, asymmetric carbon membranes were continuously prepared by pyrolyzing an asymmetric polyimide hollow fiber membrane, and their gas permeation properties and characterization were investigated.

## 2. Experimental

### 2.1. Membrane preparation

Asymmetric carbon hollow fiber membranes described in this study were prepared by pyrolyzing an asymmetric polyimide hollow fiber membrane in an electric tube furnace at temperatures ranging from 600 to 1000°C.

The asymmetric polyimide hollow fiber membrane, that is, a precursor of the asymmetric carbon hollow fiber membrane, was made from a *p*-chlorophenol solution of a polyimide prepared by 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and aromatic diamines [3–6], using a dry-jet and wet spinning method followed by coagulation in aqueous ethanol solution, solvent exchange, and drying under a nitrogen atmosphere at 270°C, as in previous papers [3–6,19]. It had an asymmetric structure consisting of a thin skin layer on the outside surface and a porous supporting layer on the other part. The outside and inside diameter of the fiber were 395 and 115 µm, respectively.

Fig. 1 shows a scheme of a pyrolyzation apparatus. The carbon membranes were continuously prepared by passing the precursor through the inside of a quartz glass pipe set in the furnace. The length of the furnace was 80 cm. The inner diameter of the pipe was 4 cm. The inside of the pipe was controlled in the atmosphere of nitrogen with the flow rate of 2 l/min. The precursor rolled around a bobbin equipped with a constant velocity motor was fed into the furnace, and the resulting carbon hollow fiber went out from the furnace and was wound by another bobbin. Both bobbins were 11 cm in diameter and were driven at 0.64 revolutions per minute by the motors; that is, the

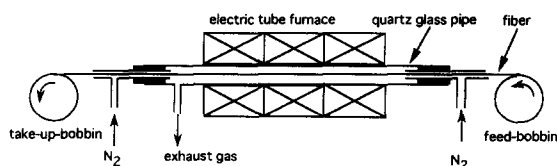


Fig. 1. Scheme of pyrolyzation apparatus.

residence time of the fiber in the furnace was about 3.6 min.

The precursor was treated thermally in atmospheric air at 400°C for 30 min before the pyrolysis. The treatment contributed to the stabilization of the asymmetric structure of the precursor to temperatures of the pyrolysis. In the case of the precursor without the treatment, the precursor softened during the pyrolysis and the resulting carbon membrane had a low membrane performance. In this paper, the treatment is called a thermostabilization and the precursor fiber that performed the treatment is called a thermostabilized fiber. Thus, the carbon membranes in this study were prepared in the following three steps of heat treatment. The first step is the drying of the polyimide hollow fiber at 270°C in a nitrogen atmosphere, the second is the thermostabilization at 400°C in atmospheric air, and the third is the pyrolysis at over 600°C in nitrogen.

Elemental analysis was performed on a Perkin-Elmer 240-C element analyzer. Thermogravimetry with gas chromatography and mass spectrometry (TG-GCMS) was measured with a Shimadzu TG-GCMS system at a heating rate of 15 K/min, in helium, and at temperatures ranging from room temperature to 1000°C. Observation of a cross section and a surface of the fibers was performed by scanning electron microscopy (SEM) and atomic force microscopy (AFM), using a Nihon Denshi JSM-840A and a Seiko Instrument SFA300, respectively.

### 2.2. Gas permeation

Hollow fiber membrane modules were one-end-opened types and consisted of about 6 pieces of the fiber of ca. 8 cm active length. One end of the fiber bundle was sealed with an epoxy resin and the other was potted in a stainless steel pipe of 5 cm length and 6 mm diameter with the epoxy. The effective membrane areas of the modules were ca. 6 cm<sup>2</sup>. Gas

permeation experiments were carried out at temperatures ranging from 30 to 120°C. The experiments for pure gases such as H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> and for a mixed gas of 50% H<sub>2</sub> in CH<sub>4</sub> were performed at a feed pressure of 1.08 MPa and those for pure C<sub>3</sub>H<sub>8</sub> at 0.74 MPa. The module was set in a stainless steel tube cell of 1 cm inside diameter with Swagelok fittings and ferrules. The cell was placed in a thermostated air bath. The feed gas was introduced to the outside of the hollow fiber membrane. A flow rate of a permeate gas that flowed from the bore of the fiber was measured with a bubble flow meter. Composition analysis of the mixed gases was performed on a Shimadzu GC-8A gas chromatograph equipped with a 2 m long column packed with Unibeads C 60/80 mesh using argon as a carrier gas.

### 3. Results and discussion

#### 3.1. Characterization of asymmetric carbon membranes

Table 1 shows results of the elemental analysis. The thermostabilized hollow fiber, that is, the polyimide hollow fiber treated in atmospheric air at 400°C, had a higher elemental ratio of oxygen to carbon than the polyimide hollow fiber. The thermostabilized hollow fiber did not dissolve in *p*-chlorophenol. These facts indicate that thermostabilization induces oxidization and crosslinking of the polyimide precursor. The analysis revealed the presence of 75.2 atomic% carbon for the carbon hollow fiber prepared at 600°C and the presence of 85.7 atomic% carbon for the carbon

hollow fiber at 800°C. The carbon content of the carbon hollow fiber in this study was lower compared with the carbon membranes reported in the other literature [9–14]. With an increase in the temperature of the pyrolysis, the carbon content increased and the elemental ratio of hydrogen, oxygen, and sulfur to carbon decreased.

Fig. 2 shows the outside and inside diameter of the fibers with the heat treatment temperature. The outside and inside diameter decreased with an increase in the heat treatment temperature. The length of the fiber

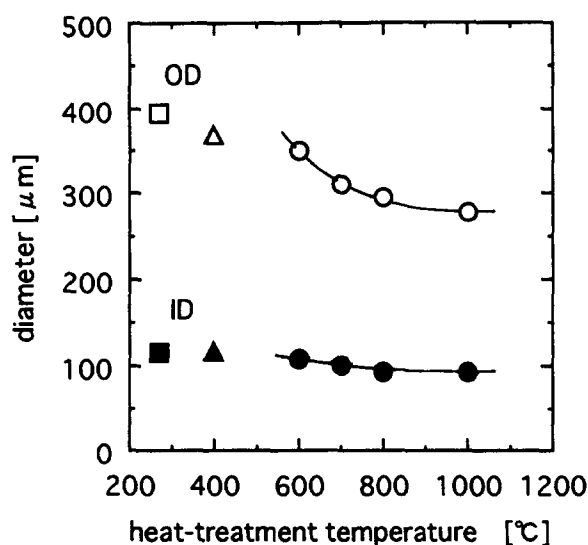


Fig. 2. Plots of outside and inside diameter of fibers against heat treatment temperature. (□) Asymmetric polyimide hollow fiber, (△) thermostabilized hollow fiber and (○) carbon hollow fiber.

Table 1  
Results of elemental analysis of fibers

Hollow fiber	<i>t</i> <sup>a</sup> [°C]	Presence of element [wt%]					Ratio [–]		
		C	H	N	O	S	H/C	O/C	S/C
Polyimide hollow fiber	270	66.9	3.1	4.8	14.2	5.2	0.046	0.212	0.078
Thermostabilized fiber	400	66.4	2.9	4.9	15.5	4.6	0.044	0.233	0.069
Carbon fiber	600	75.2	2.9	5.7	9.6	1.9	0.039	0.128	0.025
	650	81.2	2.8	5.5	5.9	2.1	0.034	0.073	0.026
	700	85.1	2.3	4.5	2.9	2.0	0.027	0.034	0.024
	800	85.7	1.1	3.8	1.8	1.0	0.013	0.021	0.012
	900	88.3	0.7	3.8	1.2	2.1	0.008	0.014	0.024

<sup>a</sup> *t* is temperature at each step of heat treatment.

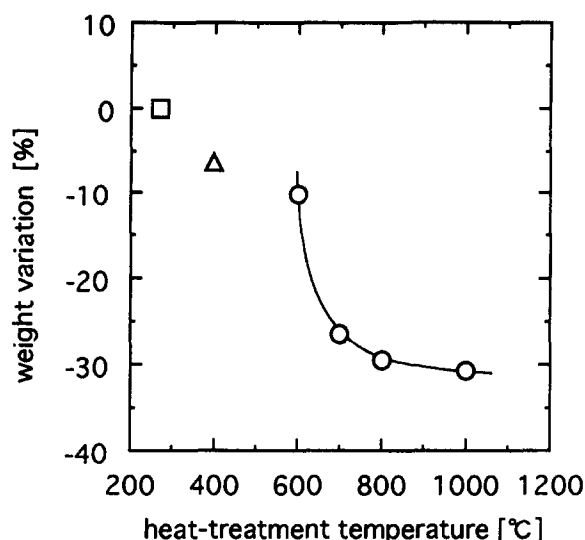


Fig. 3. Plots of percentage of weight variation on fibers against heat treatment temperature. The keys are the same as Fig. 2.

decreased about 7% by thermostabilization. By pyrolyzation, the length remained unchanged because the take-up-bobbin and the feed-bobbin were driven at the same speed. Fig. 3 shows the percentage of weight variation on the fibers from the weight of the polyimide hollow fiber treated at 270°C with the heat treatment temperature. The weight decreased with an increase in the heat treatment temperature. The TG-GCMS analysis of the polyimide hollow fiber and the thermostabilized hollow fiber revealed evolution of CO<sub>2</sub>, O<sub>2</sub>, and CO from around 500°C and sulfur dioxide and aliphatic and aromatic compounds such as aliphatic hydrocarbons, acetonitrile, benzene, biphenyl, benzonitrile from around 600°C. The decrease in the weight of the fibers with pyrolysis was attributed to evolution of the compounds from the precursor.

Figs. 4 and 5 show SEM photographs of the cross section (fractured section) from the skin layer side of the asymmetric polyimide hollow fiber, the thermostabilized hollow fiber, and the carbon hollow fiber, and AFM images of the surface of those fibers respectively. The skin layers of the asymmetric polyimide hollow fiber and the thermostabilized fiber were observed to be composed of dense aggregation of nodules of ca. 100 nm diameter. The skin layers of the carbon fibers were also observed to be composed of the nodule aggregates, but the diameter of the

nodules was smaller than 50 nm. A surface roughness measured by AFM was 1.21, 1.09, and 0.906 nm for the polyimide hollow fiber, the thermostabilized fiber, and the carbon fiber pyrolyzed at 800°C, respectively. The nodule size and the surface roughness decreased with an increase in the heat treatment temperature.

### 3.2. Permeation properties

Fig. 6 shows the effects of heat treatment temperature on a permeation rate,  $P'$ , of H<sub>2</sub> and a ratio of the permeation rate of H<sub>2</sub> to that of CH<sub>4</sub>,  $P'(\text{H}_2)/P'(\text{CH}_4)$ , for the feed gas mixture of 50% H<sub>2</sub> in CH<sub>4</sub> at 80°C. The thermostabilized membrane treated at 400°C had lower  $P'(\text{H}_2)$  and higher  $P'(\text{H}_2)/P'(\text{CH}_4)$  than the asymmetric polyimide hollow fiber membrane treated at 270°C.  $P'(\text{H}_2)/P'(\text{CH}_4)$  increased with an increase in the temperature of the pyrolysis in the range of 600 to 850°C. On the other hand,  $P'(\text{H}_2)$  decreased with an increase in the temperature of the pyrolysis. The pyrolysis changed the membrane performance remarkably. Those are because, by pyrolysis, the asymmetric structure of the membrane became dense due to a physical shrinking of the membrane with a decomposition and chemical condensation of the precursor and the evolution of the compounds. The asymmetric carbon membrane prepared at 700°C displayed  $P'(\text{H}_2)=1.0 \times 10^{-3} \text{ cm}^3 (\text{STP})/(\text{cm}^2 \text{ s cmHg})$  and  $P'(\text{H}_2)/P'(\text{CH}_4)=132$  and at 850°C displayed  $1.8 \times 10^{-4} \text{ cm}^3 (\text{STP})/(\text{cm}^2 \text{ s cmHg})$  and  $P'(\text{H}_2)/P'(\text{CH}_4)=631$ . The asymmetric carbon membranes obtained in this study had high membrane performance for separation of hydrogen and methane.

Fig. 7 shows plots of  $P'$  at 120°C against kinetic diameters of the gas molecules for the pure gases [16,20]. The asymmetric carbon membrane pyrolyzed at 700°C displayed higher permeability than the asymmetric polyimide hollow fiber membrane of all gases measured in this study. The asymmetric carbon membrane pyrolyzed at 850°C had lower permeability than the membrane pyrolyzed at 700°C, but had higher selectivity. Rough linear relations between the logarithm of the permeation rates and the kinetic diameters were observed for the asymmetric polyimide hollow fiber membrane and the asymmetric carbon membranes. These facts suggest that permeability selectivity is mainly attributed to diffusivity selectivity for those membranes. The slopes of the linear relations

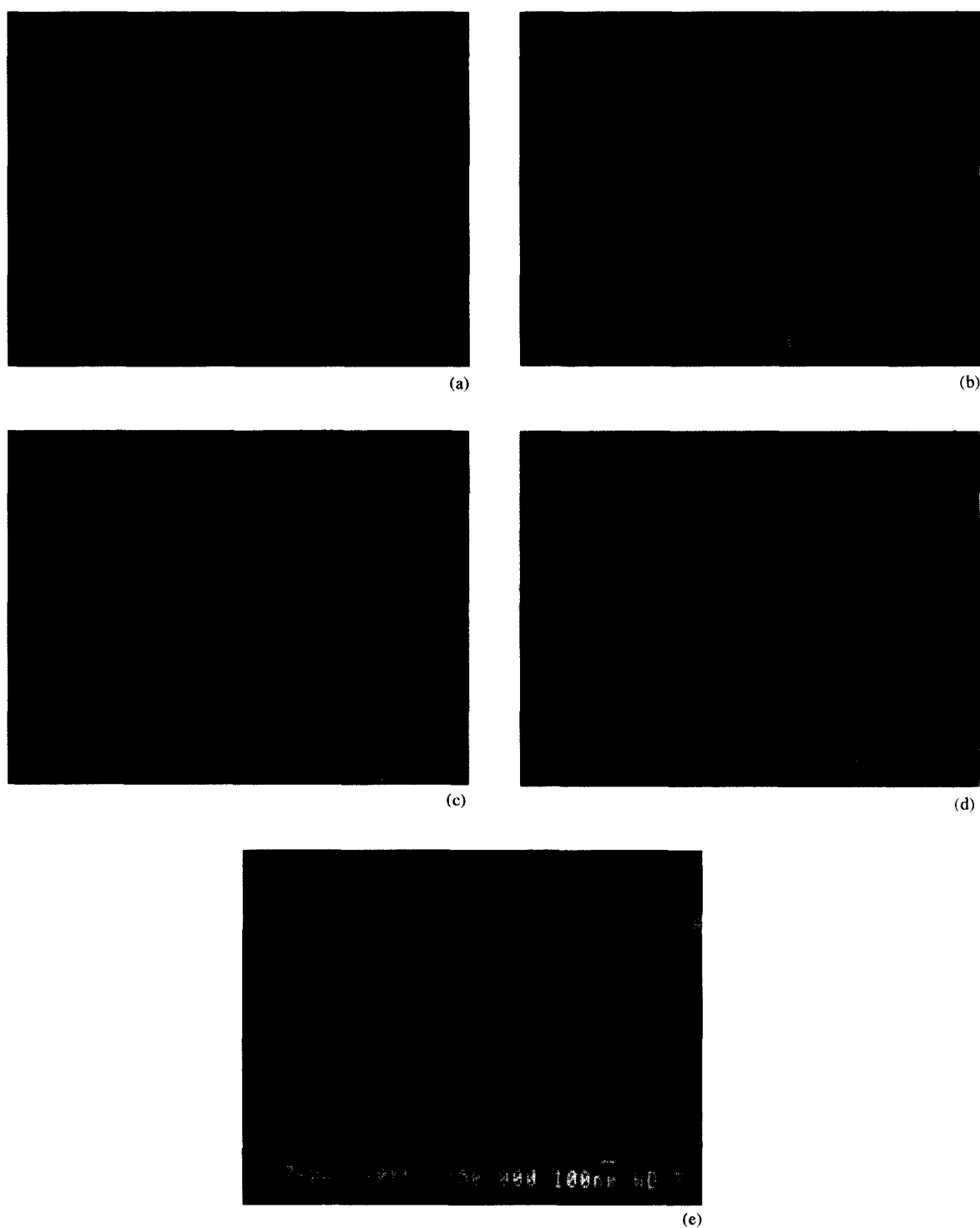


Fig. 4. SEM photographs of a cross section (fractured section) from the skin layer side of (a) asymmetric polyimide hollow fiber membrane, (b) thermostabilized membrane, and (c) carbon membrane pyrolyzed at 700°C, (d) at 800°C, and (e) at 900°C, respectively.

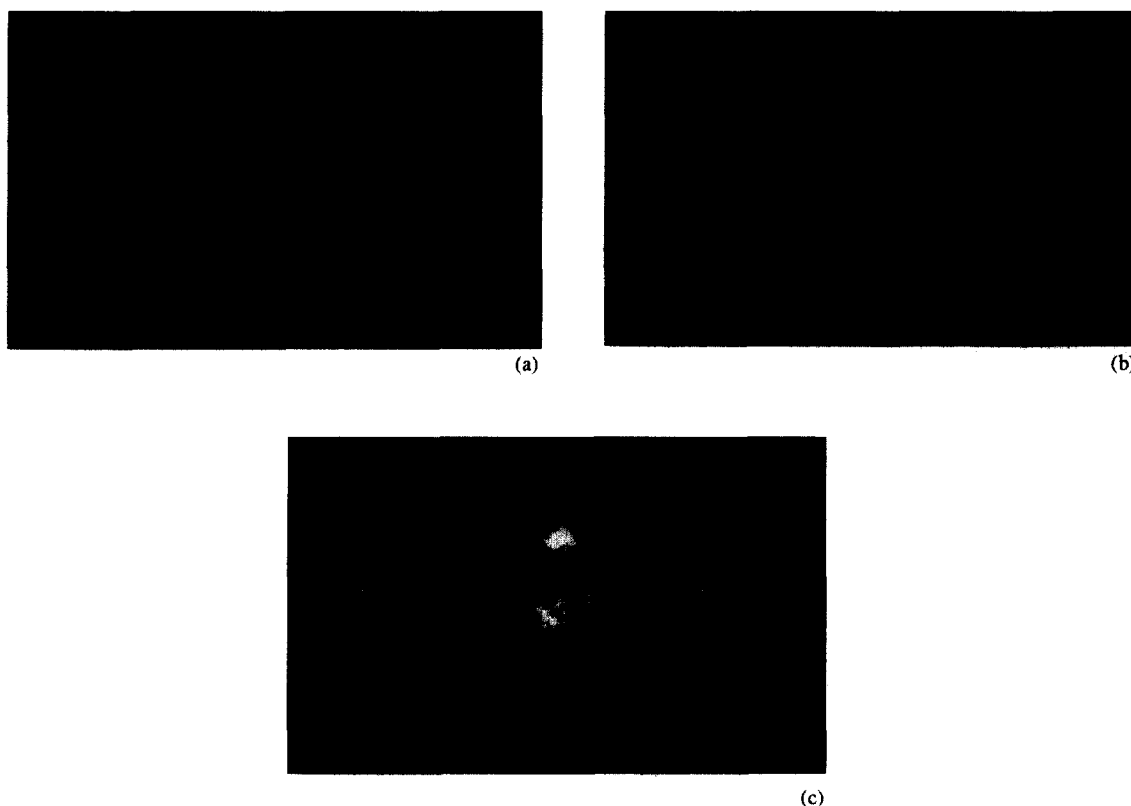


Fig. 5. AFM images of surface of (a) asymmetric polyimide hollow fiber membrane, (b) thermostabilized membrane, and (c) carbon membrane pyrolyzed at 800°C, respectively.

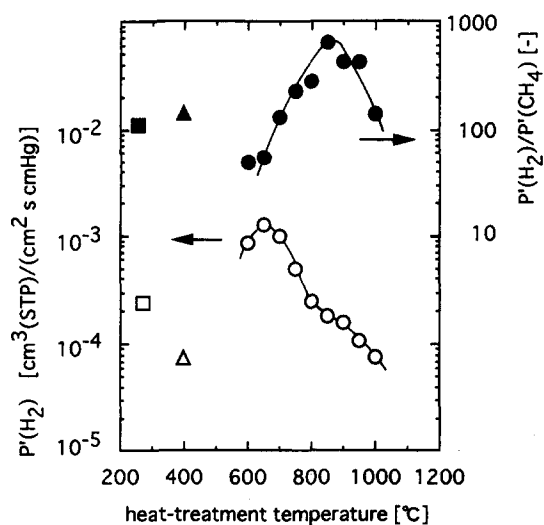


Fig. 6. Plots of  $P'(\text{H}_2)$  and  $P'(\text{H}_2)/P'(\text{CH}_4)$  for feed gas mixture of 50%  $\text{H}_2$  in  $\text{CH}_4$  at 80°C against heat treatment temperature. Open and closed plots show  $P'(\text{H}_2)$  and  $P'(\text{H}_2)/P'(\text{CH}_4)$ , respectively.

increased with an increase in the heat treatment temperature. By pyrolysis, the membranes began to have larger dependence of the permeability rate on the molecular size of the penetrant. Matsuda et al. [10] have reported that gas permeability, diffusivity and solubility are discussed in detail for carbon films formed by pyrolysis of the Kapton polyimide film, and that the extremely high permselectivity of the carbon films is suggested to originate from molecular sieving effects. It is considered to make little difference in the phenomenon of gas permeation between the films in the literature and the hollow fiber membranes in this study.

Fig. 8 shows temperature dependences of  $P'$  of the pure gases on the asymmetric polyimide hollow fiber membrane and the asymmetric carbon membranes pyrolyzed at 700 and 850°C. Table 2 shows activation energies of the permeation rates. Differences between the activation energies for each of the gases on the carbon membranes were smaller than those on the

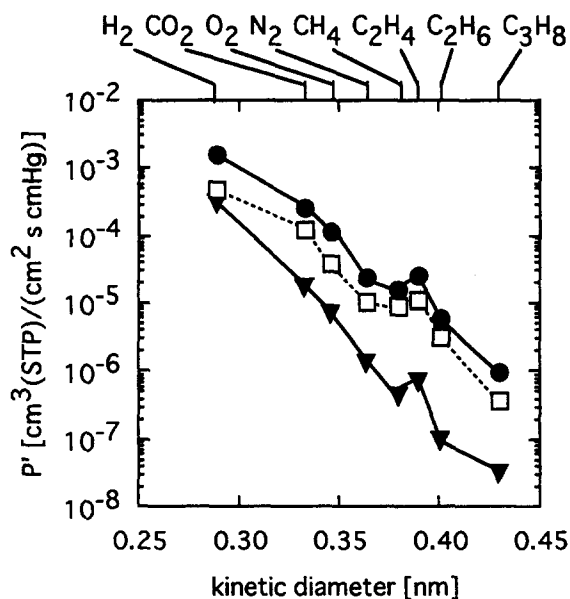


Fig. 7. Plots of permeation rates at 120°C against kinetic diameter for pure gases. (□) Asymmetric polyimide hollow fiber membrane, (●) carbon membrane pyrolyzed at 700°C, and (▼) carbon membrane pyrolyzed at 850°C.

asymmetric polyimide hollow fiber membrane. It is surmised that the diffusion of the gases on the asymmetric carbon membranes occurs in holes that existed originally. On the other hand, it is guessed that the diffusion on the asymmetric polyimide hollow fiber membranes occurs in free space holes made by thermal motion of the polyimide chains and those that existed originally because the polyimide is the glassy polymer, and that the larger size of gas molecules, the larger the active energy needed for thermal motion is. From the above-mentioned suppositions, it is considered that the activation energies of the diffusion on the asymmetric carbon membranes are smaller than those on the asymmetric polyimide hollow fiber membrane for the gases especially having larger molecular size. This is considered as the reason that the differences between the activation energies of the permeation rate on the former membranes were smaller than those on the latter membranes. Consequently, with an increase in the temperature measured, permselectivities for the gas pairs such as  $H_2$ /hydrocarbons,  $CO_2$ /hydrocarbons,  $O_2/N_2$ , on the asymmetric polyimide membrane decreased remarkably, but those on the asymmetric carbon membrane decreased slightly.

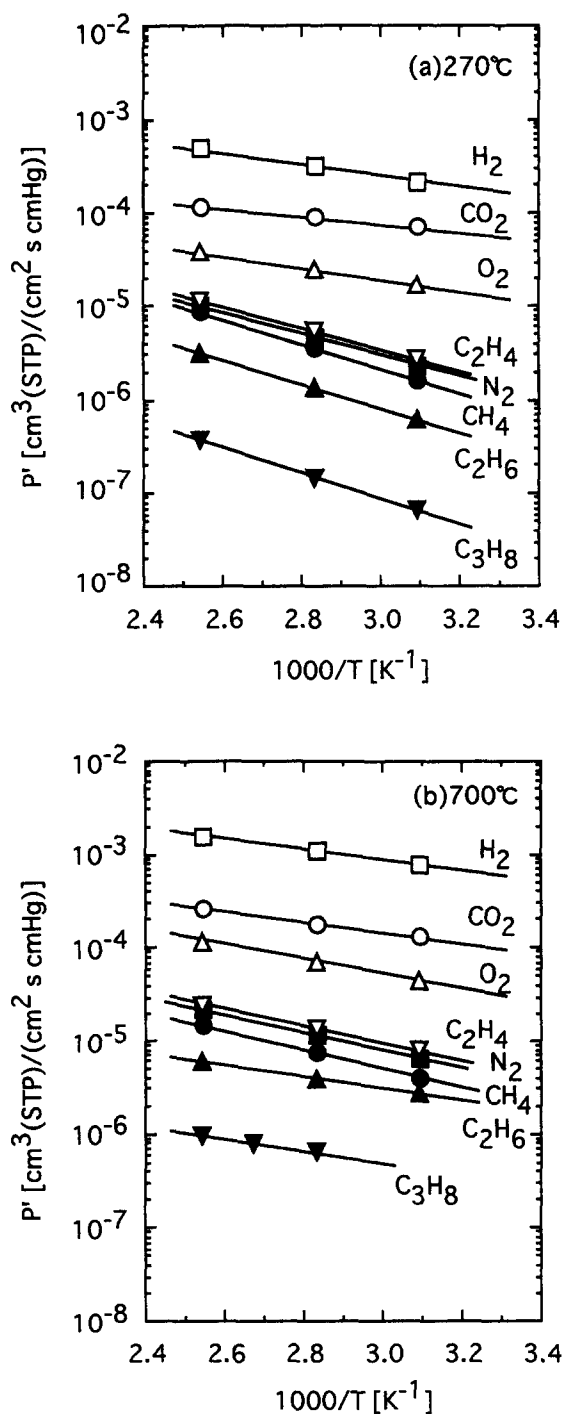


Fig. 8. Temperature dependence of permeation rates for pure gases on (a) asymmetric polyimide hollow fiber membrane, (b) carbon membrane pyrolyzed at 700°C, and (c) carbon membrane pyrolyzed at 850°C, respectively.

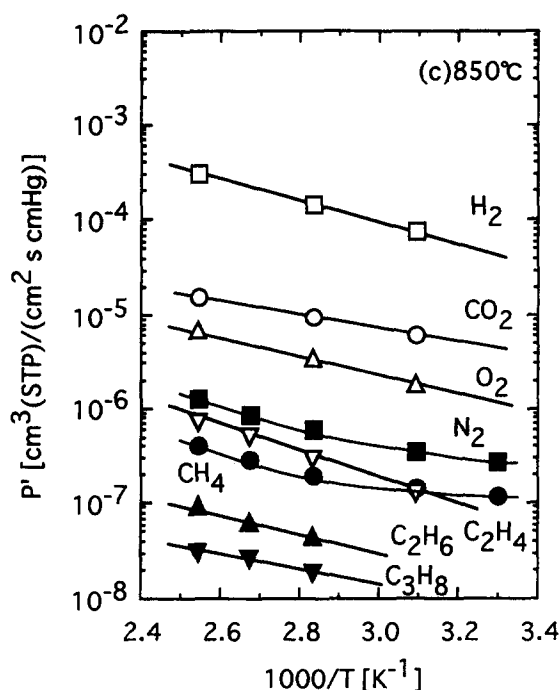


Fig. 8. (continued)

The asymmetric carbon membranes in this study had high permeation rates for the smaller gas molecules and high permselectivities for separation of the smaller ones from the bigger ones.

#### 4. Conclusion

The carbon membranes were continuously prepared by pyrolyzing the thermostabilized asymmetric polyimide hollow fiber membrane. The carbon membranes had the asymmetric structure of which the skin layer consisted of a dense aggregation of the nodule of about

50 nm diameter. The asymmetric carbon membranes displayed high membrane performance for the gas separation of H<sub>2</sub>/CH<sub>4</sub>.

#### References

- [1] J.E. Koresch and A. Soffer, Molecular sieve carbon permselective membrane. Part I. Presentation of a new device for gas mixture separation, *Sep. Sci. Technol.*, 18 (1983) 723.
- [2] J.E. Koresch and A. Soffer, The carbon molecular sieve membranes. General properties and the permeability of CH<sub>4</sub>/H<sub>2</sub> mixture, *Sep. Sci. Technol.*, 22 (1987) 973.
- [3] T. Yoshinaga, H. Shimazaki and Y. Kusuki (Ube Industries Ltd.), *Jpn. Pat. Appln.*, 90-110157 (1990).
- [4] Y. Sumiyama and Y. Kusuki (Ube Industries Ltd.), *Jpn. Pat. Appln.*, 90-320958 (1990).
- [5] H. Shimazaki, N. Maru and Y. Kusuki (Ube Industries Ltd.), *Jpn. Pat. Appln.*, 92-66558 (1992).
- [6] T. Yoshinaga, H. Shimazaki, Y. Kusuki and Y. Sumiyama (Ube Industries Ltd.), Asymmetric hollow filamentary carbon membrane and process for producing same, *Eur. Pat.*, 0 459 623 B1 (1994).
- [7] H. Hatori, Y. Yamada, M. Shiraishi, H. Nakata and S. Yoshitomi, Carbon molecular sieve films from polyimide, *Carbon*, 30 (1992) 305.
- [8] K. Haraya and N. Ito, Gas permselectivities of carbonized Kapton polyimide, Abstract of the 1993 International Congress of Membranes and Membrane Processes (ICOM 1993), Heidelberg, Germany, 1993, p. 2.5.
- [9] H. Suda and K. Haraya, Molecular sieving effect of carbonized Kapton polyimide membrane, *J. Chem. Soc., Chem. Commun.*, (1995) 1179.
- [10] M. Matsuda, H. Suda, H. Yanagishita, N. Itoh, K. Haraya and T. Hakuta, Gas separation properties of carbon membranes formed by pyrolysis of polyimide, *J. Nat. Inst. Mater. Chem. Res. Jpn.*, 4 (1996) 223.
- [11] C.W. Jones and W.J. Koros, Carbon molecular sieve gas separation membranes - I. Preparation and characterization based on polyimide precursors, *Carbon*, 32 (1994) 1419.
- [12] C.W. Jones and W.J. Koros, Carbon molecular sieve gas separation membranes - II. Regeneration following organic exposure, *Carbon*, 32 (1994) 1427.

Table 2

Activation energy of permeation rate for pure gas

Membrane	<i>t</i> <sup>a</sup> [°C]	Activation energy [kJ/mol]							
		H <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	N <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
Polyimide hollow fiber membrane	270	13	7.6	13	22	22	25	25	26
Carbon membrane	700	11	11	15	17	19	20	12	11
	850	21	14	20	26	(21)	(19)	21	14

<sup>a</sup> *t* is temperature on each step of heat treatment.



- [13] C.W. Jones and W.J. Koros, Characterization of ultramicro-porous carbon membranes with humidified feeds, *Ind. Eng. Chem. Res.*, 34 (1995) 158.
- [14] C.W. Jones and W.J. Koros, Carbon composite membranes: A solution to adverse humidity effects, *Ind. Eng. Chem. Res.*, 34 (1995) 164.
- [15] J. Hayashi, M. Yamamoto, K. Kusakabe and S. Morooka, Simultaneous improvement of permeance and permselectivity of 3,3',4,4'-biphenyltetracarboxylic dianhydride-4,4'-oxydianiline polyimide membrane by carbonization, *Ind. Eng. Chem. Res.*, 34 (1995) 4364.
- [16] J. Hayashi, H. Mizuta, M. Yamamoto, K. Kusakabe, S. Morooka and S.-H. Suh, Separation of ethane/ethylene and propane/propylene systems with a carbonized BPDA-pp'O-DA polyimide membrane, *Ind. Eng. Chem. Res.*, 35 (1996) 4176.
- [17] S. Kitao, H. Kameda and M. Asaeda, Gas separation by thin porous silica membrane of ultra fine pores at high temperature, *Mak. (Membrane)*, 15 (1990) 222.
- [18] H. Kita, H. Horii, Y. Ohtoshi, K. Tanaka and K. Okamoto, Synthesis of a zeolite NaA membrane for pervaporation of water/organic liquid mixtures, *J. Mater. Sci. Lett.*, 206 (1995) 14.
- [19] K. Nakagawa, Y. Asakura, S. Nakanishi, H. Hoshino, H. Kouda and Y. Kusuki, Separation of vapor mixtures of water and alcohol by aromatic polyimide hollow fibers, *Koubunshi Ronbunshu*, 46 (1989) 405.
- [20] D.W. Breck, *Zeolite Molecular Sieves*, John Wiley and Sons, New York, 1974, p. 636.