

High flux zirconia composite membrane for hydrogen separation at elevated temperature

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Abstract

Several $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--SiO}_2$ membranes of which, $(\text{ZrO}_2\text{--Y}_2\text{O}_3)$ content were in the range of 90–100%, were prepared via metal alkoxide method. The sintering temperature was increased with the increase of ZrO_2 contents from 1373 for 90% to 2073 K for 100%. On alumina (Tammann temperature=1500 K) support tubing, two membranes having ZrO_2 contents 90 and 92.5% show separation for 50–50% $\text{CH}_4\text{--CO}_2$ gas mixture. On zirconia (Tammann temperature=2100 K) support tubings, successful membranes were obtained on the smoothed surface with 40 coating times. Membranes coated with 20 times of $\text{ZrO}_2=92.5\%$ solution followed by 20 times of 90% shows separation factor $\alpha_{\text{CH}_4/\text{CO}_2}$ of 1.15 and that with 40 times of 90% 1.08.

The composite membranes of ZrO_2 content 90% on alumina tubing showed the high permeance for H_2 more than $10^{-6} \text{ mol}/(\text{m}^2 \text{ Pa s})$, and peculiarly high permeance for H_2O , by 1.7 times more than that expected by Knudsen permeation mechanism. This membrane was tested to separate H_2 from gaseous mixtures of H_2 , H_2O and HBr , product of thermochemical water decomposition processes, and found that the maximum separation factors for H_2 over H_2O and H_2 over HBr were 4.1 and 259, respectively.

From the correlation of the pure gas permeances against the reciprocal of square root of the quantity of the absolute temperature times molecular weight, the main permeation mechanism of all gases except H_2O are estimated as Knudsen diffusion and main H_2O permeation mechanism surface diffusion. It seems that, at higher temperature, permeation mechanism for all gases except H_2O shifts to the activated diffusion but for H_2O to Knudsen diffusion. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Inorganic composite membrane; Gas separation; Zirconia–silica composite membrane; Hydrogen; Conjugated membrane

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1. Introduction

Expectation for hydrogen has been increasing, as a clean, renewable and flexible carrier of energy particularly for the means of transport, rockets, vehicles, aeroplanes and so on. Conventional methods of hydrogen production are steam reforming of hydrocarbon, electrolysis of water, by-production of petroleum refining, petrol-chemistry and so on. Unconventional hydrogen production methods which will use unused or untapped energy resources such as nuclear heat, hydrogen sulfide etc., has been investigated; the decomposition of hydrogen sulfide [1], the thermochemical water decomposition (TCWD) and so on. Several attempts for TCWD process have been made but very few such as UT-3 cycle process [2] and IS process [3] are successful.

The UT-3 thermochemical hydrogen production cycle, developed at The University of Tokyo, is a four-step process; hydrolysis (endothermic reaction) and bromination (exothermic) of Ca and Fe compound [2]. In the process, only solid and gas reactant/products are used. The mole fraction of $H_2:H_2O:HBr$ in the product gas

mixture from the UT-3 cycle process was reported as 0.95:91.43:7.62 at 725.9 K [4]. If the produced hydrogen can be separated from the gaseous mixture of H_2 , H_2O and HBr by membrane process instead of condensation and evaporation, the thermal efficiency of the process would increase and the cost of hydrogen decrease. Exergy loss in H_2 separation by membrane was discussed by Kusakabe et al. [5]. A comparison of the relative costs of hydrogen produced by various approaches, including the high temperature gaseous reactor (HTGR) is made in Fig. 1.

The operating conditions of TCWD process are high temperature and highly corrosive environment. Therefore, novel membrane, which have high thermal resistivity and highly corrosive resistance, are required.

Zirconia is one of the most thermal resisting materials, showing melting point of 3043 K, and has highly corrosive resistance. Ohya and co-workers [6–9] successfully fabricated composite zirconia membrane on porous alumina tubing by a zirconia-silica alkoxide solution dip-coating and sintering method. The addition of tetraethoxysilane (TEOS) to zirconium-tetra-

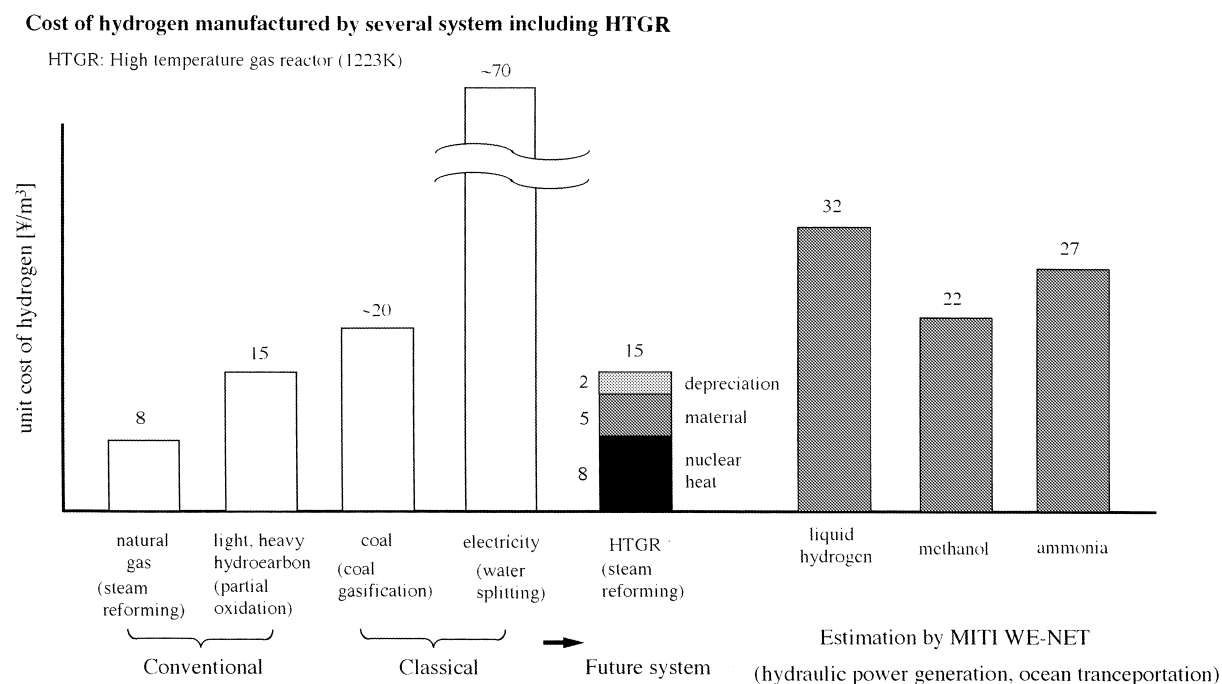


Fig. 1. Cost of hydrogen manufactured by several systems including high temperature gaseous reactor (HTGR) (M. Ogawa, personal communication).

propoxide allows lowering the sintering temperature. With an ordinary electric furnace, it is possible to fabricate composite membranes with separation capability: by the 40 mol% zirconia containing at 823 K [8], 50 mol% at 1073 K [8] and 60 mol% at 1273 K [8]. Moreover, the 70 mol% zirconia containing composite membrane can be fabricated by laser firing method [9].

In this study, 90–100 mol% zirconia containing zirconia–silica composite microporous membrane were prepared in order to investigate the possibility of separating hydrogen from highly corrosive product gas mixture in UT-3 TCWD process.

2. Experimental

2.1. Membrane

Using five types of i-propyl alcohol metal alkoxide coating solutions (solution No, 1–5), $\text{ZrO}_2\text{--SiO}_2\text{--Y}_2\text{O}_3$ membranes (A–G) were prepared via metal-alkoxide

method reported earlier [10], on the surface of three types of porous ceramic support tubings 1, 2, and 3 (Table 1). The compositions of the coating solutions and sintering temperature are also listed in Table 1. More details of the preparing procedure of the composite membranes is reported earlier [10].

2.2. Apparatus, procedures and analysis

Experiments of separation of $\text{CH}_4\text{--CO}_2$ gaseous mixture and pure gas permeation were carried out with the apparatus and experimental procedures almost same as those reported earlier [7,8,10]. In the case of the separation experiment of $\text{H}_2\text{--H}_2\text{O}$ gaseous mixture for membrane A, the transmembrane pressure (TMP), ΔP , was kept at 0.1 and 0.15 MPa and the pressure of permeation side was maintained from 0.005 MPa absolute to 0.1 MPa absolute, using the pressure control valve and the vacuum pump. The compositions of gaseous mixture in the feed and permeation were analyzed with a gas chromatograph (GC-8A and GC-14A, Shimadzu)

Table 1
List of successful and unsuccessful membranes

Name	Coating			Support tubing		Result
	Solution No. ^a	Coating times	Sintering temperature (K)	Name ^b	Abrasion	
(a) Membranes on alumina support tubings						
A	1	15	1373	1		Successful
B	3	15	1473	2		Successful
(b) Membranes on zirconia support tubings						
C	2	40	1373	3	○	Successful
D	3	15	1473	3	○	Unsuccessful
D'	3	20	1473	3	○	Unsuccessful
D''	3	15	1373	3		Unsuccessful
D'''	3	15	1473	3		Unsuccessful
D ^{IV}	3	15	1573	3		Unsuccessful
D ^V	3	15	1773	3		Unsuccessful
E	4	15	1473	3		Unsuccessful
E'	4	15	1773	3		Unsuccessful
F	5	15	1573	3		Unsuccessful
F'	5	15	2073			Unsuccessful
G	3	20	1473	3	○	Successful
	2	10	1373			
G'	3	20	1473	3	○	Successful
	2	15	1373			
G''	3	20	1473	3	○	Successful
	2	20	1373			

^a See Table 2.

^b See Table 3.

using Gaskuropack 54 column and Porapak Q (GL Sciences).

3. Results and discussion

3.1. Estimation of pore size

Fig. 2 shows the relationship between transmembrane pressure, ΔP and the separation factors for CH_4 over CO_2 , $\alpha_{\text{CH}_4/\text{CO}_2}$ defined as the following equation.

$$\alpha = \frac{y_{\text{CH}_4}/(1 - y_{\text{CH}_4})}{x_{\text{CH}_4}/(1 - x_{\text{CH}_4})} [-] \quad (1)$$

The maximum separation factors for membrane A, and G'' were 1.16, and 1.15 at 0.1 MPa of ΔP , respectively. The maximum separation factor for membrane B was 1.21 at 0.15 MPa of ΔP . As an example of the unsuccessful membrane, the relationship for membrane D''' is shown in the Fig. 2, and found the maximum $\alpha_{\text{CH}_4/\text{CO}_2}$ 1.03. From the data for the separation experiment and the equation of Present and de Bethune [11], the average diameters of the micropores were estimated as about 3.0, 2.0 and 3.0 nm for membrane A, B and G'', respectively. The solid lines in Fig. 2 are the calculated results based on the Present and de Bethune equation.

3.2. Strategy to obtain successful membrane

The highest separation factor is obtained with membrane B fabricated on alumina support tube (No. 1) using solution type 3 and the higher with membrane A using solution type 1. With the increase of ZrO_2 content (from solution 1 to 3), separation factor increases. For the purpose to increase the ZrO_2 content, fabricating temperature should be increased, because of Tammann temperature as ca. 2100 K for ZrO_2 . Membrane B, (using solution 3) was fabricated at 1473 K, slight below Tammann temperature of Al_2O_3 (1500 K). It seems alumina support tube would not be suitable for solution type 3 ($\text{ZrO}_2:\text{SiO}_2=0.925:0.075$), because it might melt and large pores would be plugged (blocked or lost).

Therefore, the material of support tube should be changed from Al_2O_3 to others having higher Tammann temperature. ZrO_2 (2100 K) will be one of the choices. But only one membrane tried was successful at 1373 K, with $\text{ZrO}_2=90\%$. It seems impossible to obtain 100% ZrO_2 membrane (membrane F and F') at 2073 K which is more than upper limit of the furnace used (2023 K by manufactures recommendation) as shown in Table 1 (membranes F and F').

As shown in Table 1, slight addition of SiO_2 to the solution 5 (solution 3 and 4) does not seem to work. The reasons might be due to the roughness of support

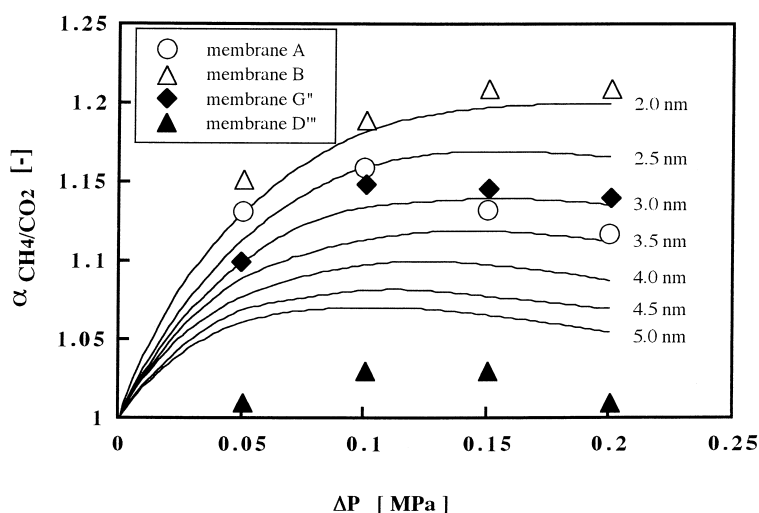


Fig. 2. Relationships between the transmembrane pressure and the separation factors for CH_4 over CO_2 for membrane A, B, D''' and G'' at room temperature.

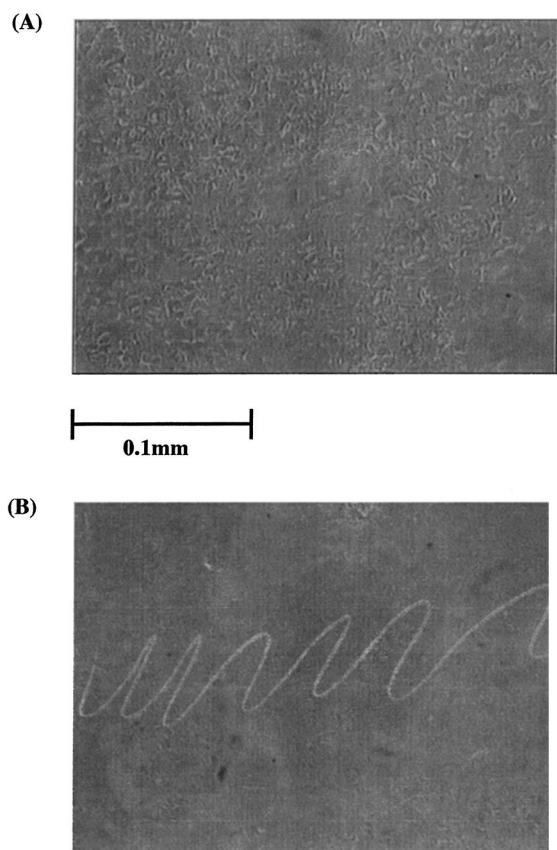


Fig. 3. Surface of the zirconia support tubing (Video microscope, Olympus, OVM1000NM) (A) without abrasion (B) after abrasion.

tubing 3, which is shown in Fig. 3(A). After smoothing the surface roughness mechanically by abrasive paper #1200 (shown also in Fig. 3(B)), membrane was fabricated applying solution 3 with 15 coating times (membranes D, D'–D^V and 20 (membrane D') at 1373 K, but unsuccessful (Tables 2 and 3).

The unsuccessful membrane coated with 20 times with solution 3 and sintered at 1473 K was coated sev-

Table 3

Support No.	Material	o.d. [mm] o.d. [mm]	i.d. [mm] i.d. [mm]	Average pore diameter [μm]
1	Al ₂ O ₃	5.5	3.5	0.1
2	Al ₂ O ₃	10	7	0.1
3	ZrO ₂	15	9	0.05

eral times with solution 2 and sintered at 1373 K. The resulted conjugated membranes were subjected to test the separation characteristics ($\alpha_{\text{CH}_4/\text{CO}_2}$) results of which are shown in Fig. 4. With the increase of coating times of solution 2, the conjugated membrane shows better separation characteristics. Comparing the results obtained with membrane C (40 time coating of only solution 2), the conjugated membrane G'' (20 times of solution 3 conjugated with 20 times of solution 2), shows better separation characteristics, $\alpha_{\text{CH}_4/\text{CO}_2}$ increased from 1.08 to 1.15 without sacrificing flux.

3.3. Pure gas permeance

Fig. 5 shows typical relationship between ΔP and the pure gas permeation fluxes of H₂ and H₂O through the membrane A at 573 K. Permeation fluxes for each gas increase linearly with the increase of ΔP .

Permeance, P_{Ti} , for each gas is calculated using Eq. (2) and plotted against the reciprocal of square root of the quantity of the absolute temperature times molecular weight as shown in Fig. 6.

$$P_{\text{Ti}} = \frac{J_{\text{Ti}}}{\Delta P_i} \quad (2)$$

All gases except H₂O can be correlated with one linear line. This fact means that the main permeation mechanism for all the gas tested except H₂O is estimated as Knudsen diffusion. Main H₂O permeation mecha-

Table 2
Compositions (molar ratio)

Solution No.	Zr(OC ₃ H ₇) ₄	Si(OC ₂ H ₅) ₄	Y(CH ₃ COO) ₄ H ₂ O	i-C ₃ H ₇ OH
Compositions (molar ratio)				
1	0.9	0.1	0.054	20
2	0.9	0.1	0.054	25
3	0.925	0.075	0.056	25
4	0.95	0.05	0.057	25
5	1.0	0.0	0.06	25

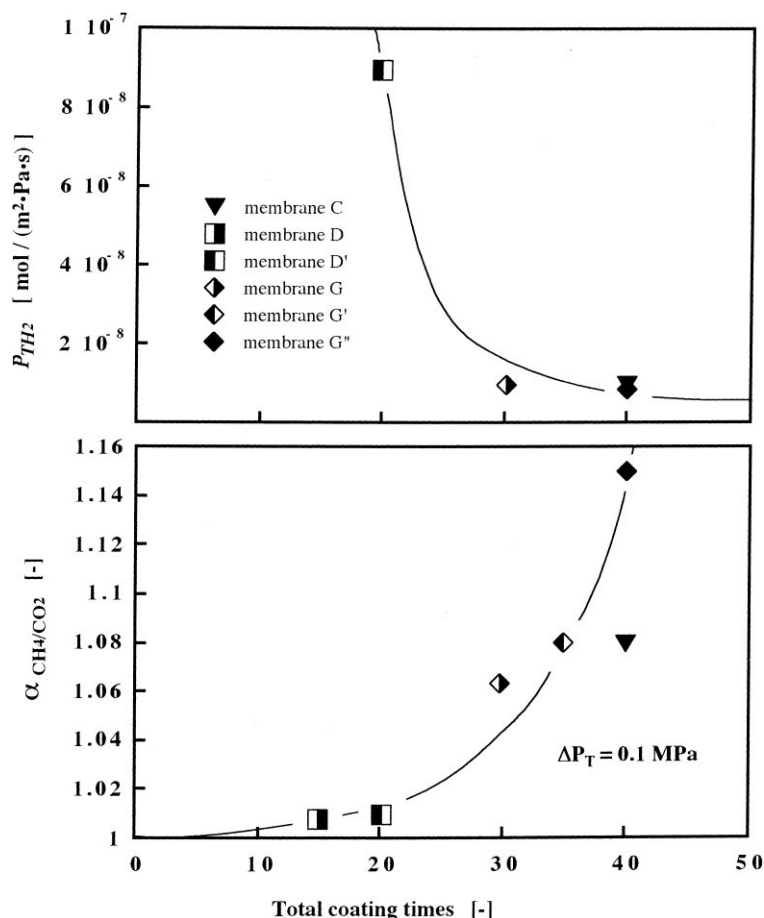


Fig. 4. Relationships between total coating times and the separation factor for CH₄ over CO₂, the pure gas permeance of H₂ for membrane C, D, D', G, G' and G'' at room temperature.

nism might be surface diffusion. It is interesting to note that the discrepancies of H₂O permeance from the lines of Knudsen diffusion become larger for the membrane having smaller gradient.

Fig. 7 shows the temperature dependency of permeance for all the gases. With the increase of temperature, permeance for all gases except H₂O decreases and takes minimum value and increases, but permeance for H₂O stays almost constant and starts to decrease at about 573 K. The decrease of permeance for H₂O might be due to the transition of permeation mechanism from surface diffusion to Knudsen diffusion because the effect of the potential energy between H₂O molecule at solid surface becomes weak at high temperature. The

increase of permeance for the gases except H₂O might be due to the activated diffusion proposed by Asaeda [12]. Therefore, the total flux, J_{Ti} for i th component, through the membrane might be defined as sum of the flux due to Knudsen diffusion [13] J_{Ki} , surface diffusion [13], J_{Si} and activated diffusion [12] J_{Ai} .

$$J_{Ti} = J_{Ki} + J_{Si} + J_{Ai} \quad (3)$$

$$J_{Ti} = \frac{K \Delta P (M_i T)^{-1/2}}{(1 + c/T)} + a \Delta P (M_i T)^{-1/2} \times \left[\exp\left(\frac{b}{T}\right) - 1 \right] + P_0 \Delta P \exp\left(\frac{-E_A}{RT}\right) \quad (4)$$

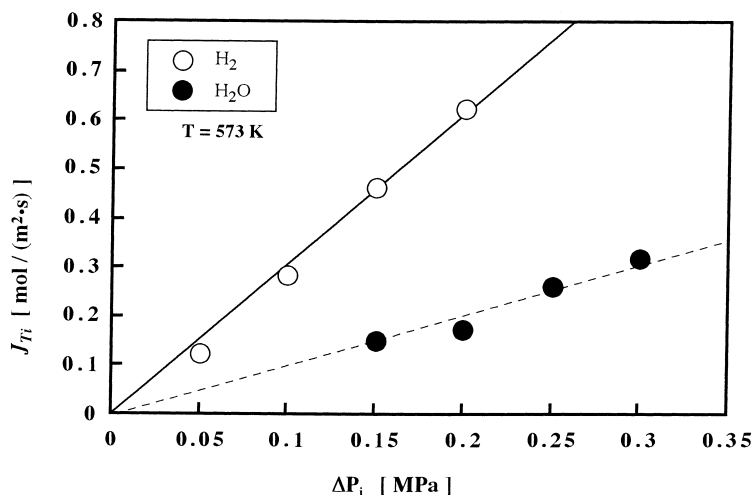


Fig. 5. Relationships between the transmembrane pressure and the pure gas permeation fluxes of H_2 and H_2O for membrane A at 573 K.

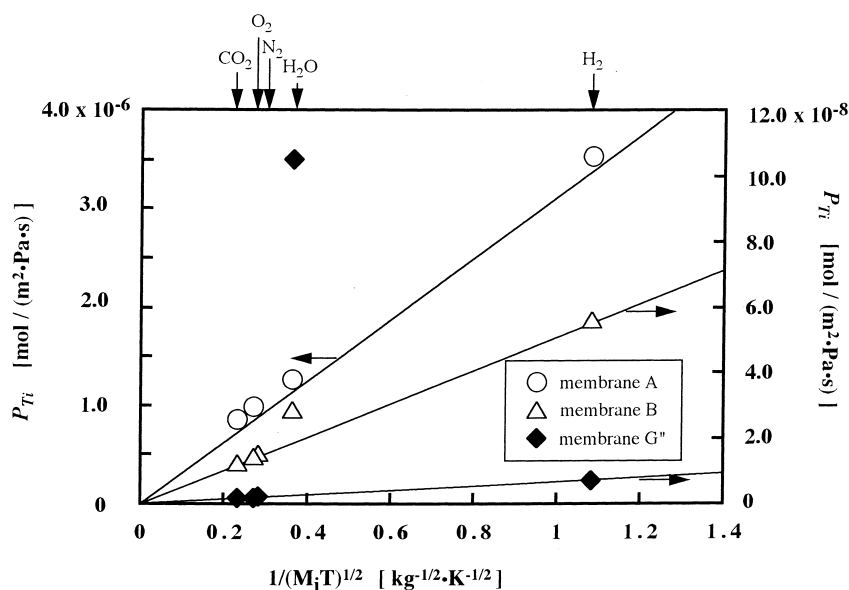


Fig. 6. Relationships between the reciprocal of square root of the quantity of the absolute temperature times molecular weight and the pure gas permeances for membrane A, B and G'' at 423 K.

The measured fluxes were analyzed according to Eq. (4) and the best fit parameters are listed in Table 4 together with the values reported for membranes containing different amounts of Zr [8]. With the increase

of Zr content, the values of K for Knudsen diffusion, and a for surface diffusion increase takes the maximum value at $Zr=0.9$, and then decrease. The value of b for surface diffusion stays almost constant except

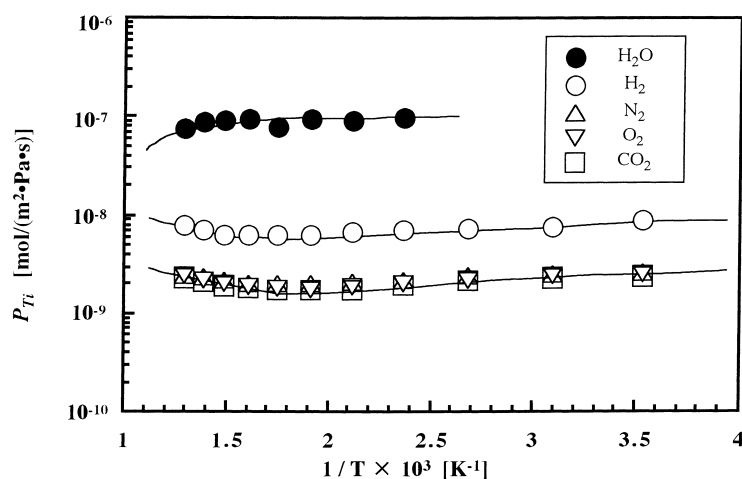


Fig. 7. Relationships between reciprocal of the absolute temperature and the pure gas permeances for membrane G''.

at $Zr=0.9$. The values of P_0 and E_A for activated diffusion stay almost constant until Zr content 0.6 and increase at $Zr=0.9+0.925$. But for membrane A, the values of K and a are peculiarly large by 40 times and 1000 times, respectively, and the values of b is small by one hundredth.

3.4. Separation of H_2 – H_2O gaseous mixture

Fig. 8 shows the results of separation experiment for the gaseous mixture of H_2 and H_2O (feed composition of H_2 : 0.443–0.549 molar ratio). The separation factors α_{H_2/H_2O} are plotted against temperature.

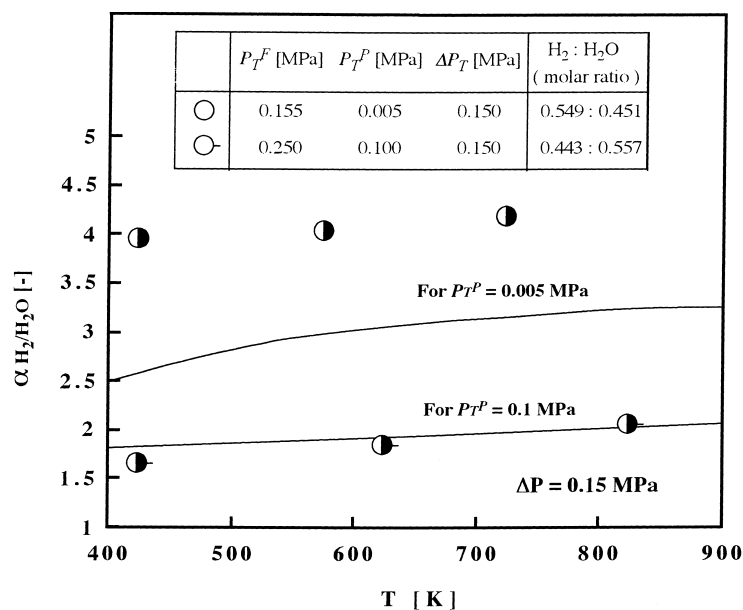


Fig. 8. Relationships between the absolute temperature and the separation factor for H_2 over H_2O for membrane A at transmembrane pressure of 0.15 MPa.

Table 4
Fitting parameters in Eq. (4)

Membrane ZrO ₂ contents	a [8]		b [8]		c [8]		A		B		D'		G''	
	H ₂	H ₂ O	H ₂	H ₂ O	H ₂	H ₂ O	H ₂	H ₂ O	H ₂	H ₂ O	H ₂	H ₂ O	H ₂	H ₂ O
$a \times 10^7$ [mol ^{1/2} kg ^{1/2} K ^{1/2} /m ² Pa s]	–	0.195	–	0.516	–	0.606	–	609	–	0.46	–	–	–	–
$b \times 10^{-3}$ [K]	–	1	–	1	–	1	–	0.01	–	0.8	–	–	–	–
$K \times 10^8$ [mol ^{1/2} kg ^{1/2} K ^{1/2} /m ² Pa s]	0.307	–	6.13	–	7.96	–	315	213	5.2	5.2	6.96	0.649	–	–
$P_0 \times 10^7$ [mol/m ² Pa s]	1.13	–	1.13	–	1.13	–	–	–	–	–	–	–	2.3	–
E_A [kJ/mol]	6.68	–	6.68	–	6.68	–	–	–	–	–	–	–	28.3	–

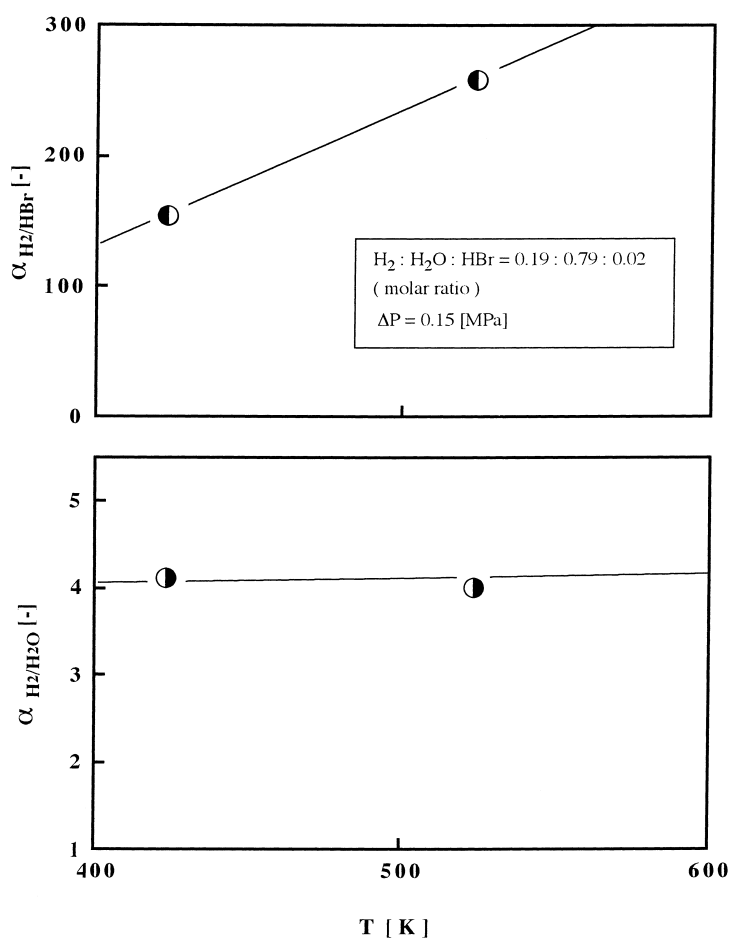


Fig. 9. Relationships between the absolute temperature and the separation factor for H₂ over H₂O and H₂ over HBr for membrane A at transmembrane pressure of 0.15 Mpa.

If it is possible to assume that, in the case of separation process for binary gaseous mixture, components i and j permeate without interacting each other, mole fraction of component i in the permeate, y_i , is expressed using permeance ratio, PR, and pressure ratio, p_r , as follows

$$y_i = \frac{-A + \sqrt{A^2 + 4(PR - 1)p_r x_i}}{2(PR - 1)} \quad (5)$$

where

$$A = p_r x_i + PR(1 - x_i) - PR + 1 \quad (6)$$

$$PR = \frac{P_{Tj}}{P_{Ti}} \quad (7)$$

$$p_r = \frac{p_T^F}{p_T} \quad (8)$$

The solid lines in Fig. 8 show the theoretical separation factors which are estimated using Eq. (1) and y_i obtained from Eq. (5) together with Eqs. (7) and (8), and the best fit parameters. The agreement between the

experimentally obtained α_{H_2/H_2O} and the theoretical is relatively good for the membrane A at the condition of the permeated side higher pressure $p_1^P=0.1$ MPa, but not so good at lower pressure, 0.005. H_2 stream might prevent condensation of H_2O of which permeation mechanism through the membrane A mainly depends on the surface diffusion. With the decrease of permeation side pressure, H_2 flux increases and permeation flux of H_2O decreases and then α_{H_2/H_2O} shows the higher value than the theoretical one calculated based on the assumption of no interaction between each component.

3.5. Separation of H_2 – H_2O – HBr gaseous mixture

In Fig. 9, the separation factor for H_2 over H_2O , α_{H_2/H_2O} , and that for H_2 over HBr , $\alpha_{H_2/HBr}$, are plotted against temperature. With the increase of temperature from 423 to 523 K, α_{H_2/H_2O} for the membrane A, shows almost constant values 4.0–4.1, but $\alpha_{H_2/HBr}$ for the membrane A increase from 155 to 259. The dipole moment of H_2O and HBr are 6.1×10^{-30} and

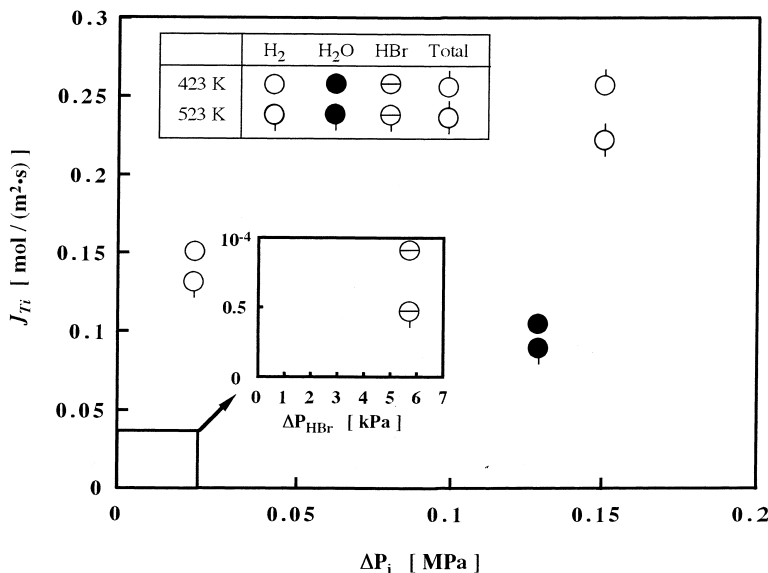


Fig. 10. Relationships between the partial transmembrane pressure and the permeation flux for H_2 , H_2O and HBr with membrane A at 423 and 523 K.

2.6×10^{-30} cm, respectively. The permeation mechanism of HBr might be governed by surface diffusion as well as that of H_2O . In the separation of H_2 – H_2O –HBr gaseous mixture, H_2O and HBr might be adsorbed on the pore wall of the ZrO_2 composite membrane. With the increase of temperature, both the amount of adsorption of H_2O and HBr decreases, however, that of HBr which has smaller dipole moment than H_2O decreases drastically than that of H_2O , because H_2O prevents adsorption of HBr. Therefore, the permeation flux of HBr decreases more rapidly than H_2O and H_2 , resulted into the decrease of $\alpha_{\text{H}_2/\text{HBr}}$. However, further investigation for the permeation mechanism of HBr might be needed. Fig. 10 shows the relationship between the permeation flux of each gas, J_{Ti} , and ΔP_i for the membrane A and found that with the increase of the temperature from 423 to 523 K, J_{HBr} decreased by 50% and J_{H_2} decreased by 12%.

The results of the separation experiments for H_2 – H_2O –HBr gaseous mixture using zirconia composite membranes have been reported earlier [6,8,9]. Morooka et al. [14] conducted the same experiments using a silica (ZrO_2 content 0.0%) membrane formed in micropores of support tube at 473–673 K. Their results of the permeation flux of H_2 and H_2O at 673 K were 2.0×10^{-8} [mol/m² Pa s] and 4.0×10^{-9} , respectively, and $\alpha_{\text{H}_2/\text{H}_2\text{O}}=5.0$. In Fig. 11, the separation factor for H_2 over H_2O $\alpha_{\text{H}_2/\text{H}_2\text{O}}$ and the hydrogen permeance are plotted against zirconia contents in the membrane, together with those reported earlier [8,9]. The previous papers [8] reported that the hydrogen was not detected in the permeated gases, but it will be possible that the permeated hydrogen was saturated with the permeated H_2O , which was freezed by liquid nitrogen. Based on the above assumption, for membranes reported earlier, the hydrogen permeance was estimated and $\alpha_{\text{H}_2/\text{H}_2\text{O}}$ calculated. For the silica/ α -alumina membrane, $\alpha_{\text{H}_2/\text{H}_2\text{O}}$ were calculated from the data of permeance in the literature [14] and shown together in Fig. 11.

For the zirconia composite membranes containing 40–60 mol% zirconia, the permeance of HBr, H_2O and H_2 in the gaseous mixture decrease in this order. On the contrary, for the 90% containing zirconia composite membrane, the permeance of H_2 , H_2O and HBr in the gaseous mixture decrease in this order. The separation factor, $\alpha_{\text{H}_2/\text{H}_2\text{O}}$, of this work was as same order as that of the silica/ α -alumina membrane reported by

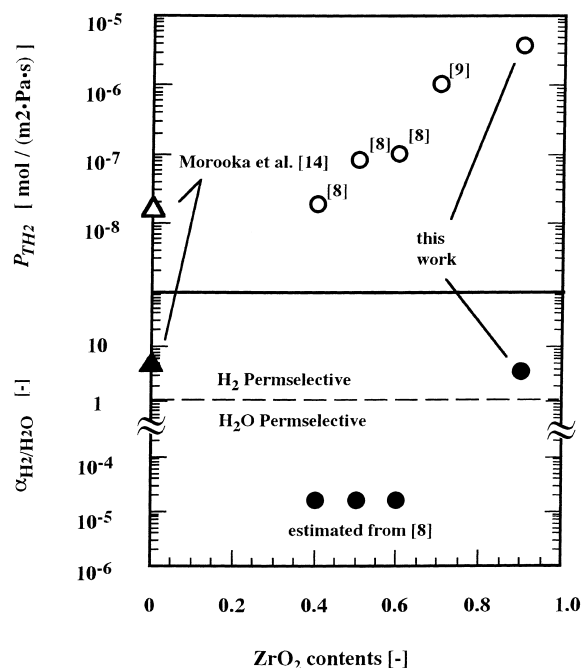


Fig. 11. Relationships between zirconia contents and the separation factor for H_2 over H_2O , and the pure gas permeance of H_2 .

Morooka et al. [14], but the 90% containing zirconia composite membranes showed higher hydrogen permeance of two order more than that of the silica only membranes, 10^{-6} [mol/(m² Pa s)].

4. Conclusions

- Several ZrO_2 – Y_2O_3 – SiO_2 membranes of which, (ZrO_2 – Y_2O_3) content were in the range of 90–100%, were prepared via metal alkoxide method. The sintering temperature was increased with the increase of ZrO_2 contents from 1373 for 90% to 2073 K for 100%. On alumina (Tammamm temperature ~ 1500 K) support tubing, two membranes having ZrO_2 contents 90 and 92.5% show separation for 50–50% CH_4 – CO_2 gas mixture.
- As for zirconia support tubings, successful membranes were obtained on the smoothed surface with 40 coating times. Membranes coated with 20 times of $\text{ZrO}_2=92.5\%$ solution followed by 20 times

of 90% (membrane G'') shows better separation factor $\alpha_{\text{CH}_4/\text{CO}_2}$ than that with 40 times of 90% (membrane C).

3. With our technology at this stage, it seems impossible to obtain successful membranes of ZrO_2 contents more than 95%.
4. The pore diameter of the successful membranes were estimated as 2–3 nm by Present and de Bethune equation [11].
5. From the correlation of the pure gas permeances against the reciprocal of square root of the quantity of the absolute temperature times molecular weight, the main permeation mechanism for all gases except H_2O are estimated as Knudsen diffusion and main H_2O permeation mechanism surface diffusion. At higher temperature, permeation mechanism for all gases except H_2O shifts to the activated diffusion but for H_2O to Knudsen diffusion.
6. In the separation experiments of H_2 – H_2O – HBr gaseous mixture, it was found that the maximum separation factors $\alpha_{\text{H}_2/\text{H}_2\text{O}}$ and $\alpha_{\text{H}_2/\text{HBr}}$ were 4.1 and 259.

5. Nomenclature

J_i	permeation flux [$\text{mol}/(\text{m}^2 \text{ s})$]
M	molecular weight [kg/mol]
p	pressure [Pa]
p_r	pressure ratio [–]
ΔP	transmembrane pressure [Pa]
P_{Ki}	permeance [$\text{mol}/(\text{m}^2 \text{ Pa s})$]
PR	permeance ratio [–]
T	absolute temperature [K]
x	mole fraction in the feed [–]
y	mole fraction in the permeate [–]
α	separation factor [–]

Superscripts

F	feed side
P	permeate side

Subscripts

k : T	total
S	surface diffusion
K	Knudsen diffusion

A	Activated diffusion
i, j	component

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