Separation of Hydrogen from a H_2–H_2O–HI Gaseous Mixture Using a Silica Membrane

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Hydrogen separation characteristics of silica membranes prepared by chemical-vapor deposition (CVD)-in an H_2-H_2O- HI gaseous mixture were evaluated for the application to hydrogen iodide decomposition in the thermochemical iodine−sulfer (IS) process. Porous alumina tubes with a pore size of 10 nm and different gas-permeating-portion lengths [20 mm (S membranes) and 100 mm (L membranes)] were modified by CVD using tetraethoxysilane as the Si source. Pore closure was controlled by CVD to maintain high hydrogen permeance while lowering only HI permeance. At a certain point, CVD was stopped using He/N_2 selectivity as the indicator of pore closure. H_2/N_2 selectivities of the modified membranes, which were measured by a single-component permeation experiment, showed 53, 9.2, 4.1, 135, and 6.6 at 600°C for S1, S2, S3, L1, and L2 membranes, respectively. Separation experiments of the H_2-H_2O-HI gaseous mixture (a molar composition of 0.09:0.78:0.13) in the modified membranes were carried out at 300−600°C. Hydrogen permeance was almost the same as the single-component permeance. The separation factors of H_2-H_2O and H_2-HI were over 3 and 150, respectively. The S3 membrane showed the highest hydrogen permeance (on the order of 10^{-7} $mol \cdot Pa^{-1} \cdot m^{-2} \cdot s^{-1}$) and the highest separation factor of H_2-HI (650 at 450°C).

Introduction

Hydrogen is an attractive fuel for the future because it is renewable as an energy resource and it is also flexible as an energy carrier. One of the promising methods for large-scale hydrogen production is thermochemical water decomposition using heat energy from nuclear, solar sources, among others.

The Japan Atomic Energy Research Institute (JAERI) has been conducting R&D on an iodine−sulfur (IS) process that was first proposed by General Atomic Co. (Norman et al., 1981), and the hydrogen production under closed-cycle operation has been demonstrated on a laboratory scale (Onuki et al., 1997; Nakajima et al., 1998).

The cycle is composed of the following reactions;

$$I_2(l)+SO_2(g)+2H_2O(l) \rightarrow 2HI(aq)+H_2SO_4(aq) \quad (1)$$

$$H_2SO_4(aq) \rightarrow H_2O(g)+SO_2(g)+(1/2)O_2(g) \quad (2)$$

$$2HI(g) \rightarrow H_2(g)+I_2(g). \quad (3)$$

The so-called Busen reaction (Eq. 1) is an exothermic SO_2 gas absorbing reaction, which proceeds spontaneously in the temperature range of 20−100°C. Sulfuric acid (H_2SO_4) decomposition reaction (Eq. 2) is an endothermic reaction, which proceeds in two stages: gaseous H_2SO_4 decomposes spontaneously into H_2O and SO_3 at 400−500°C, and then SO_3 decomposes into SO_2 and O_2 at about 800°C in the presence of a solid catalyst. Hydrogen iodide (HI) decomposition reaction (Eq. 3) can be carried out in the gas phase or in the liquid phase. The process has such attractive characteristics that all chemicals circulate in the process as fluid, H_2SO_4 decomposition proceeds stoichiometrically with a high conversion ratio, and there is a large entropy change, the temperature range of which is suitable for utilizing the nuclear heat supplied by the high-temperature gas-cooled reactor (HTGR).

In JAERI's demonstration experiment, hydrogen was produced by thermal decomposition of gaseous HI. H_2 was separated from the $H_2-H_2O-HI-I_2$ mixture by selective condensation. This scheme suffers from the low-equilibrium de-

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composition ratio of hydrogen iodide (about 20%). This low decomposition ratio leads to an increase in the amounts of recyclable materials (HI, I_2, H_2O), which decreases the thermal efficiency. In order to enhance the decomposition ratio, we focus on the application of a membrane reactor and try to prepare the hydrogen separation membrane based on ceramics that have thermal resistance and corrosion resistance in the process environment.

Modification of porous ceramics by thin silica film using chemical-vapor deposition (CVD) was investigated to achieve selective gas separation, targeting the large diffusivity difference of H_2 and other gases in amorphous silica (Ha et al., 1993; Wu et al., 1994; Yan et al., 1994; Tsapatis and Gavalas, 1994; Kim and Gavalas, 1995; Xomeritakis and Lin, 1996; Morooka et al., 1996; Sea et al., 1997). In a previous paper (Hwang et al., 1999), the authors also reported that the silica membrane prepared by the CVD method had hydrogen permeance of about 4×10^{-9} mol $Pa^{-1}m^{-2}s^{-1}$ in the H_2-H_2O-HI gaseous mixture at a permeation temperature of 600°C.

For the application to the IS process, however, the hydrogen permeance of those modified membranes were too low. In this study, we tried to control the extent of pore closure by CVD in order to remain high hydrogen permeance while lowering only HI permeance. The CVD was stopped at a certain point using He/N_2 selectivity (permeance ratio of He to N_2 measured by a single-component permeation experiment). The modified membranes were evaluated by hydrogen permselectivity in the H_2-H_2O-HI gaseous mixture. The stability of the modified membranes in the H_2-H_2O-HI gaseous mixture also had preliminary examination.

Experimental

Membrane modification and single-component gas permeation

The porous alumina tube (OD, 5.5 mm; ID, 3.5 mm; length, 250 mm), supplied by Noritake Co., was used as a support. The tube had a three-layer structure, that is, an α-alumina support layer, an α-alumina second layer about 50 μm thick, and a γ-alumina third layer a few μm thick, whose average pore sizes were 1 μm, 80 nm, and 10 nm, respectively.

Before CVD treatment, the support was glazed with an $SiO_2-BaO-CaO$ sealant (Nippon Electric Glass, GA-13) calcined at 1,200°C, except for the permeating portions. Two types of membrane with different permeating portion lengths were prepared, that is, 20 and 100 mm. Hereafter, the membranes with the 20-mm permeating portion length are called S membranes, and those with the 100-mm permeating portion length are called L membranes.

The CVD experimental apparatus was described elsewhere (Hwang et al., 1998). The support tube was fixed in a quartz reactor (OD, 20 mm; ID, 18 mm; length, 500 mm) and placed in an electric furnace. The CVD was carried out at 600°C with a nitrogen carrier gas flow rate of $1.5 \sim 2.0$ l/min and a bubbler temperature of TEOS was kept at 35°C. Throughout the CVD treatment, the inside of the tube was continuously evacuated by a rotary vacuum pump (Yan et al., 1994). The pressure in the evacuation side decreased continuously as the CVD progressed. In the course of the CVD treatment, the permeance of nitrogen and helium were intermittently measured by a pressure-rise technique. The CVD was stopped at a certain point using He/N_2 selectivity as the indicator of the pore closure. After the CVD treatment, the temperature was decreased slowly with a cooling rate of 60°C/h. The modified membrane was then kept in an atmospheric environment.

Single-component gas permeation experiments of hydrogen and nitrogen were performed at 300–600°C. Permeance was measured by a pressure-rise technique (Kim and Gavalas, 1995; Tsapatis and Gavalas, 1994; Hwang et al., 1998, 1999).

Separation of a mixture of H_2-H_2O-HI and the stability test

The separation experiment of the H_2-H_2O-HI gaseous mixture was performed at 300–600°C. The experimental apparatus was described elsewhere (Hwang et al., 1998, 1999). The modified membrane was fixed in a quartz reactor (OD, 20 mm; ID, 18 mm; Length, 500 mm) that was placed in an electric furnace. Test gas was produced by vaporizing hydriodic acid and mixed it with hydrogen. The hydrogen flow rate was kept at 10 mL/min and a molar composition of H_2-H_2O-HI was maintained at 0.09:0.78:0.13.

The nitrogen gas was introduced into the inside of the membrane to make a pressure difference and to carry the permeating gas. The total pressure on both sides of the membrane was maintained at atmospheric pressure. The permeating HI gas was caught in a cold trap and analyzed by titration. The permeating H_2 and H_2O were analyzed by a gas chromatograph without using the cold trap.

The stability of the membrane was examined by exposing it in an H_2-H_2O-HI gaseous mixture at 450°C and monitoring the H_2 and H_2O permeance. The experimental apparatus and the flow system were the same as for the H_2-H_2O-HI gaseous mixture separation experiment.

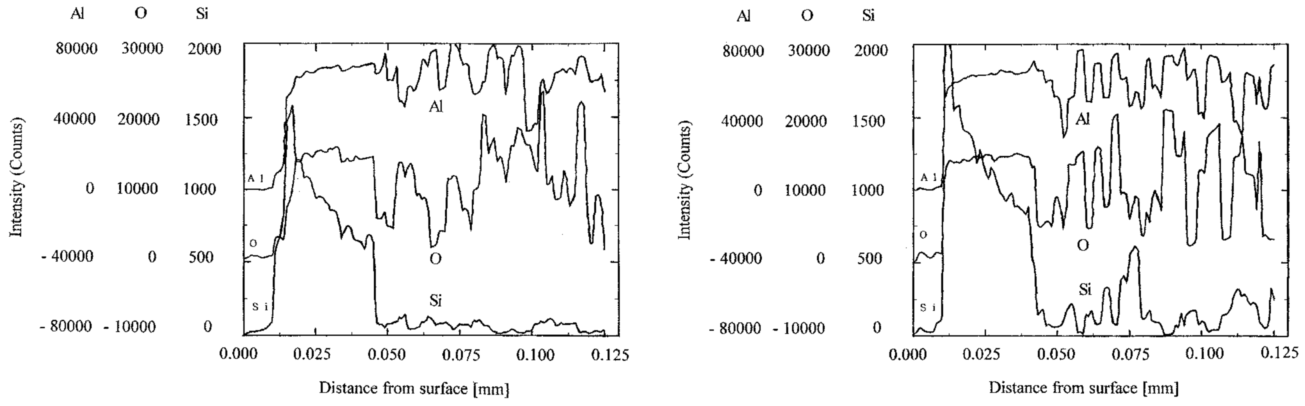
Results and Discussion

Morphology and structure of the membranes

Table 1 shows the properties of the modified membranes. S membranes had a gas permeating portion length of 20 mm. CVD treatment was stopped when He/N_2 selectivity indicated 110.4, 11.4, and 2.8, and the prepared membranes were named S1, S2, and S3, respectively. L membranes had a gas permeating portion length of 100 mm. CVD treatment was stopped when He/N_2 selectivity indicated 228 and 6.4, and the prepared membranes were named L1 and L2, respectively. In the CVD treatment of the L membranes, it took about 4–5 times longer than it did with the S membranes to have the same He/N_2 selectivity.

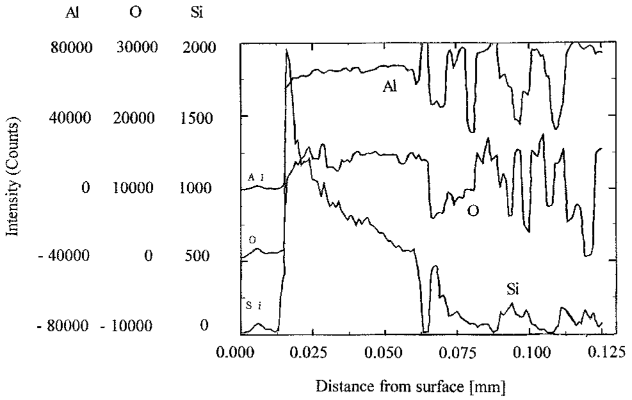
Table 1. Properties of the Modified Membranes

Membrane	Gas Permeating Portion (mm)	Selectivity of He/N_2 (= 2.64) after CVD
S1	20	110.4
S2	20	11.4
S3	20	2.8
L1	100	228
L2	100	6.4



(a) S1 membrane

(b) S3 membrane



(c) L1 membrane

Figure 1. Si depth profile in S1, S3, and L1 membrane obtained with electron probe X-ray microanalyzer.

An electron probe X-ray microanalyzer (EPMA) was used to analyze the Si depth profile. From this analysis it was confirmed that the SiO_2 was deposited inside the support tube as shown in Figure 1, and it reached to the α-alumina second layer. The dense SiO_2 layer, believed to be responsible for the appearance of the gas separation factor, was formed near the surface.

Figure 2 shows the morphologies of the surface and the cross section of the S and L membranes obtained with a scanning electron microscope (SEM).

The SEM images showed nearly the same structure in the S1, S3, and L1 membranes. The thickness of the dense SiO_2 layer formed near the surface of the membrane was less than 1 μm. However, the He/N_2 selectivities of the S1, S3, and L1 membranes decreased in the order L1 > S1 > S3, as shown in Table 1. This indicates that the pores inside the tube of the L1 membrane were more closed than were those of the S3 membrane.

Single-component gas permeation

Figure 3 shows single-component permeance of H_2 and N_2 through the modified membranes.

Permeances of H_2 through the S1, S2, L1, and L2 membranes increased with an increase in temperature, and those through the S3 membrane was independent of temperature. With an increase in temperature, the permeance of N_2 through the modified membranes did not change or decreased a little.

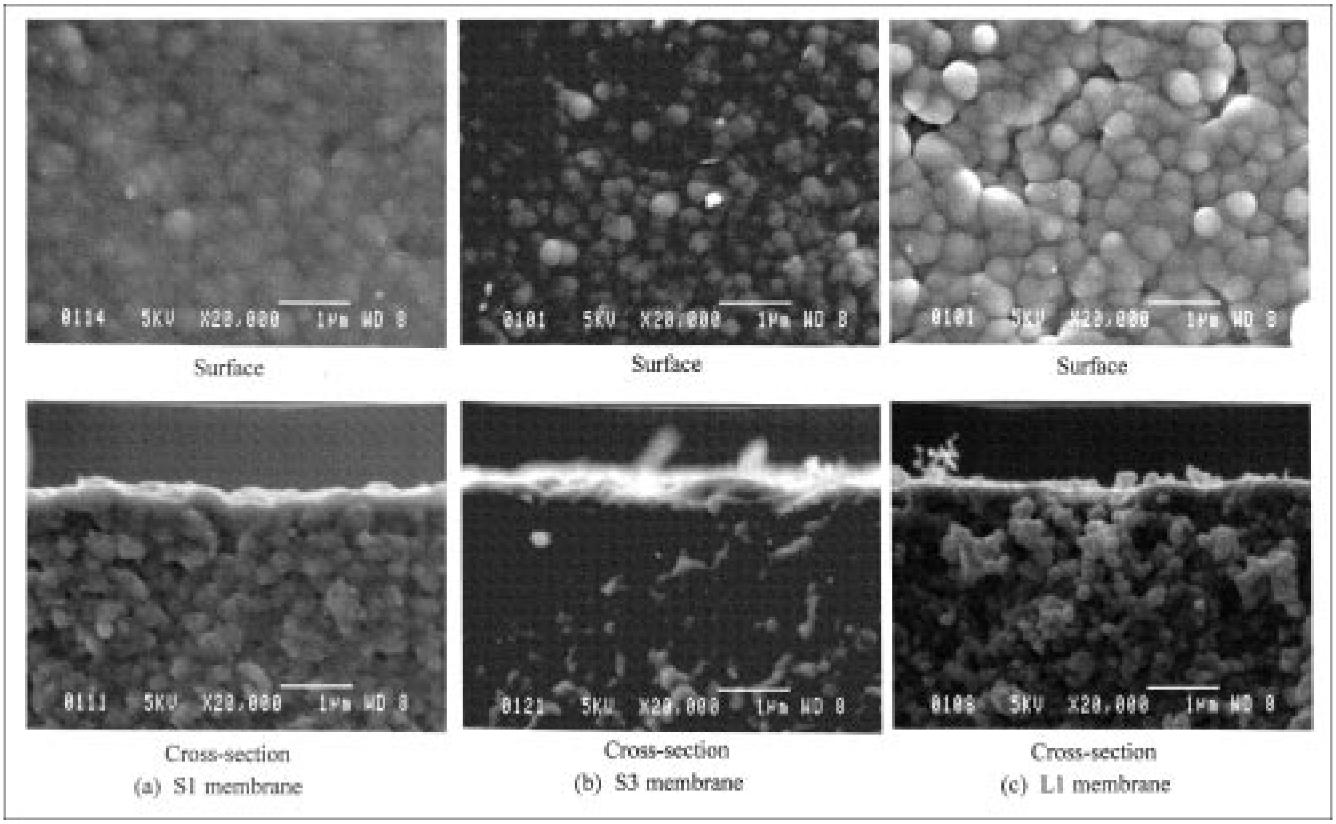
In the S1, S2, L1, and L2 membranes H_2 permeation was dominated by the activated diffusion. The activation energies of H_2 in the 300 ~ 600°C range were 19, 9, 17, and 9 kJ/mol in the S1, S2, L1, and L2 membranes, respectively. The higher activation energies in the S1 and L1 membranes compared with those in the S2 and L2 membranes indicate the presence of a dense SiO_2 layer in the former membranes. In the S3 membrane, H_2 permeation was dominated by the Knudsen diffusion.

The N_2 permeance was much smaller than the H_2 permeance in any membranes, because the kinetic diameter of N_2 is larger (3.64 Å) than that of H_2 (2.89 Å) and N_2 cannot penetrate through the nonporous layer of the membrane. N_2 gas would permeate only through much larger pores than the molecular dimension. The higher N_2 permeance of the S3 membrane compared to those of the other membranes suggests that the number of pores whose sizes was larger than the molecular dimension was higher than that of the other membranes.

Selectivities of H_2 to N_2 at 600°C were 53, 9.2, 4.1, 135, and 6.6 for the S1, S2, S3, L1, and L2 membranes, respectively.

Separation of H_2-H_2O-HI gaseous mixture

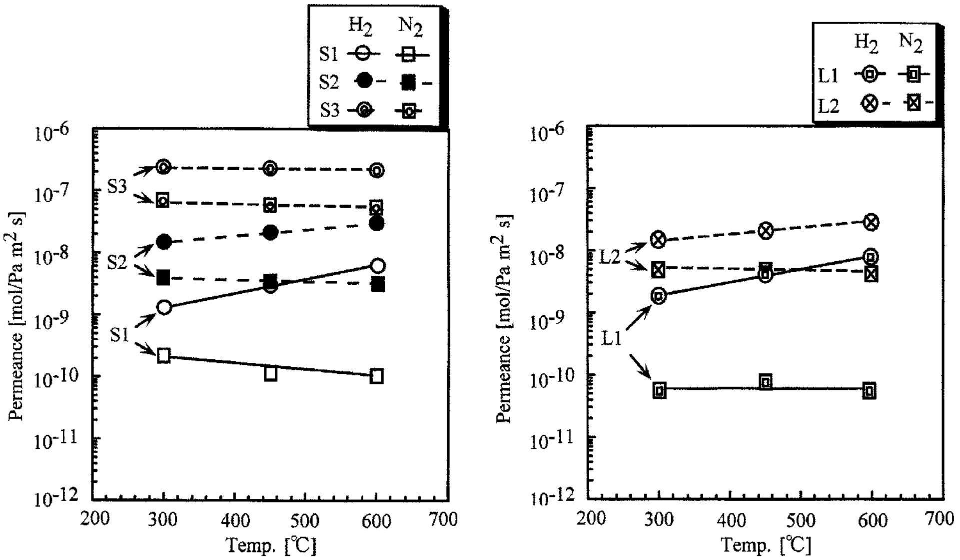
Figure 4 shows permeance of H_2, H_2O, and HI through the modified membranes in the H_2-H_2O-HI (molar composition: 0.09:0.78:0.13) gaseous mixture.



(a) S1 membrane (b) S3 membrane (c) L1 membrane

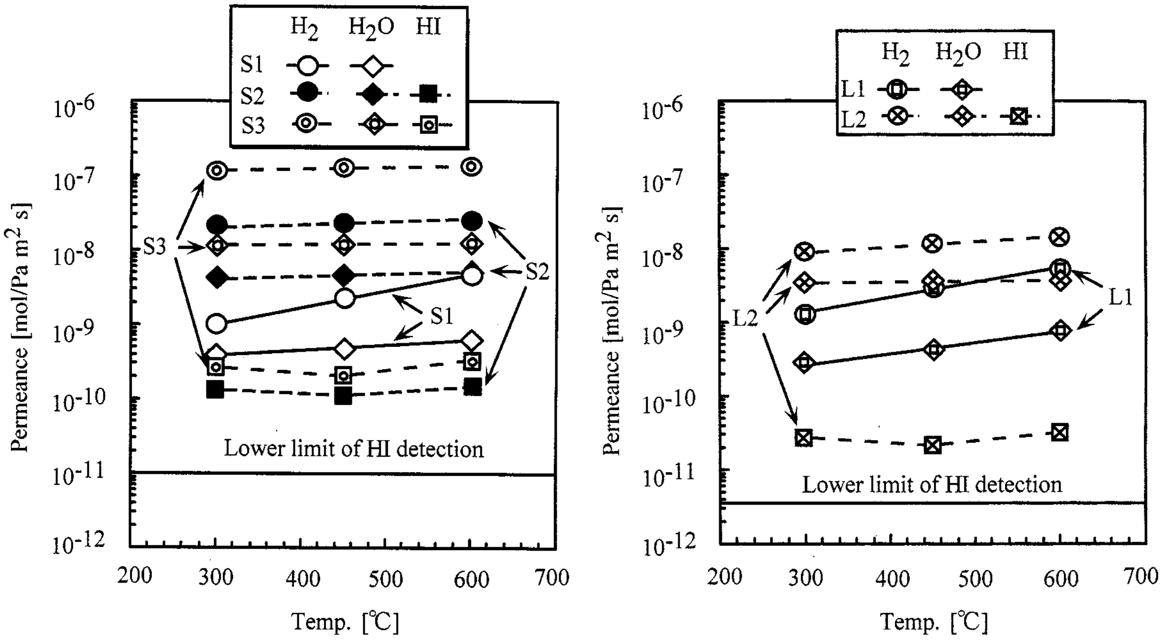
Figure 2. Scanning electron micrograph of the surface and a cross section of the S1, S3 and L1 membranes.

The permeances of H_2 through the modified membranes were nearly the same as for the single-component permeance. Permeation of hydrogen iodide in the S1 and L1 membranes was not detected, indicating that their permeances were below 1×10^{-11} $mol\cdot Pa^{-1}\cdot m^{-2}\cdot s^{-1}$. Permeances of H_2O through the S1, S2, and L1 membranes increased with an increase in temperature, and those through the S3 and L2 membranes were independent of temperature. It seems that the permeances of H_2O through the S3 and L2 membranes were dominated by the Knudsen diffusion.



(a) S membranes (b) L membranes

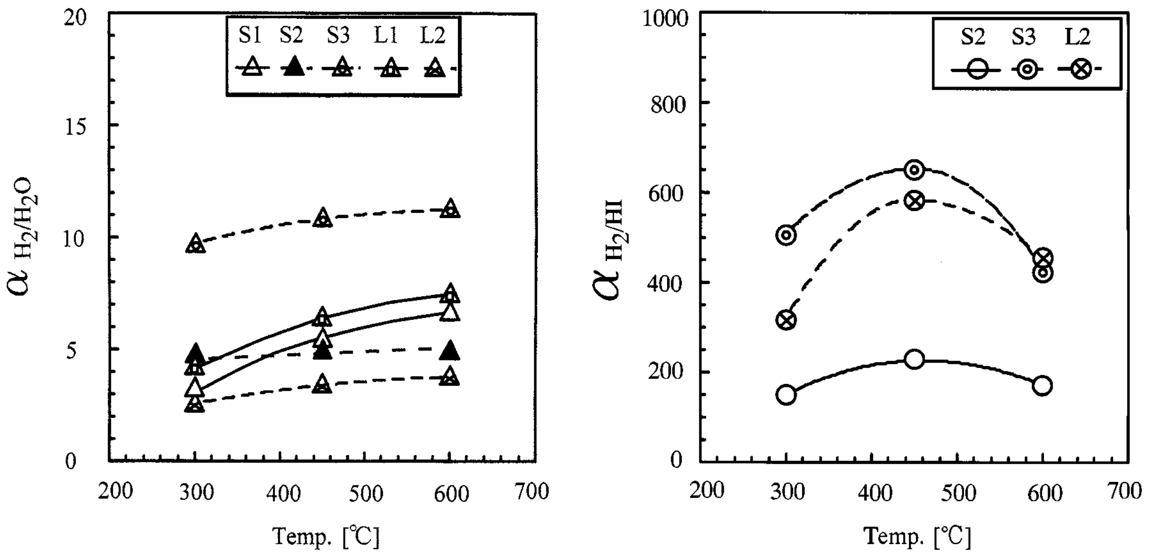
Figure 3. Single-component permeances of H_2 and N_2 through modified membranes at 300–600°C.



(a) S membranes (b) L membranes

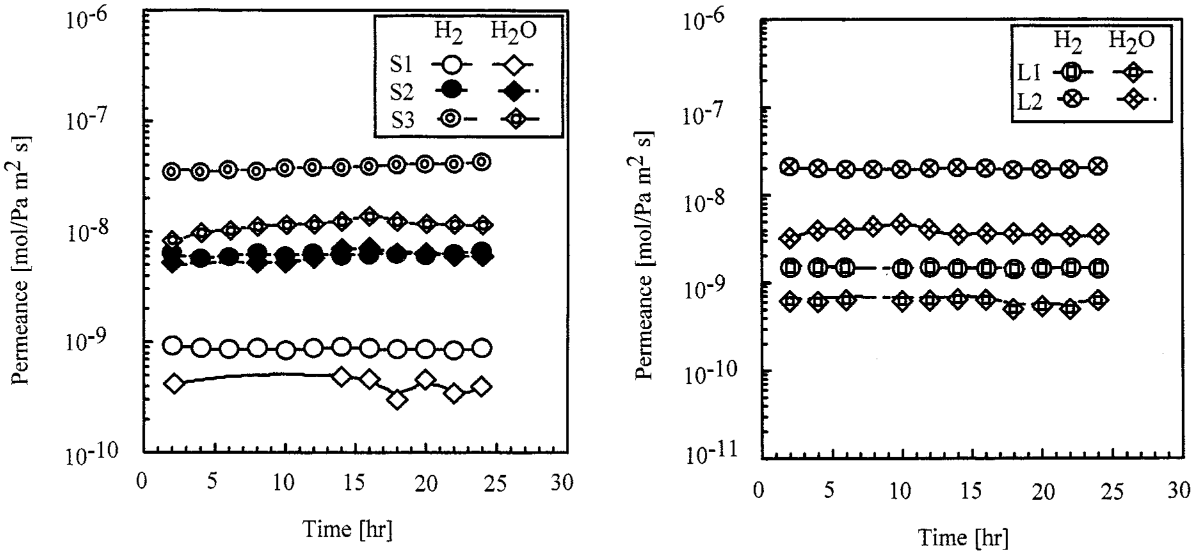
Figure 4. Permeances of H_2, H_2O, and HI through the modified membranes in a mixture of H_2–H_2O–HI (molar composition: 0.09:0.78:0.13) at 300–600°C.

As for the non-CVD membrane (a bare support), single-component hydrogen permeance was on the order of $3-5\times 10^{-6}$ $mol\cdot Pa^{-1}\cdot m^{-2}\cdot s^{-1}$ at 300 ~ 600°C. In the separation experiments of the H_2–H_2O–HI gaseous mixture under the same conditions described earlier, the permeances of H_2, H_2O, and HI through the non-CVD membrane were $3-4\times 10^{-8}$ $mol\cdot Pa^{-1}\cdot m^{-2}\cdot s^{-1}$, $2-4\times 10^{-8}$ $mol\cdot Pa^{-1}\cdot m^{-1}\cdot s^{-1}$, and $3-4\times 10^{-9}$ $mol\cdot Pa^{-1}\cdot m^{-2}\cdot s^{-1}$, respectively. The results can be explained by follows. When H_2O was introduced in the feed side, the H_2O was strongly concentrated in pores of the non-CVD membrane, which restrained the permeation of hydrogen gas (Ohya et al., 1994). It is interesting to note that in any modified membranes, a reduction in the H_2 permeance was not observed in the separation experiment.



(a) Separation factor of H_2/H_2O (b) Separation factor of H_2/HI

Figure 5. Relationship between the separation factor and temperature in the modified membranes at 300–600°C.



(a) S membranes

(b) L membranes

Figure 6. Stabilities of the modified membranes in a mixture of H_2–H_2O–HI (molar composition: 0.09:0.78:0.13) at 450°C.

It is also interesting that in the S3 membrane, hydrogen permeance remained a relatively high value, while HI permeance was far lower than that of the non-CVD membrane. As the pore size was reduced by the CVD treatment, pores that allow H_2, but not a gas with a larger kinetic diameter, such as hydrogen iodide (4.21 Å), to pass through probably appeared in the membrane.

The separation factors of H_2 to H_2O and HI are determined by Eq. 4:

$$\alpha_{H_2/i} = \left[J_{H_2}/J_i \right] / \left[y_{H_2}/y_i \right]. \tag{4}$$

Figure 5 shows the relationship between the separation factor and the temperature.

The separation factors of H_2 to H_2O in the modified membranes, α_{H_2/H_2O}, were over 3 under the present experimental conditions. α_{H_2/H_2O} increased with an increase in temperature, because the temperature dependency of the H_2 permeance was higher than that of the H_2O permeance, as shown in Figure 4. The separation factors of H_2 to HI in the S2, S3, and L2 membranes ($\alpha_{H_2/HI}$) were over 150 under the present experimental conditions. This result indicates that the modified membranes could be effectively employed in the separation of hydrogen and hydrogen iodide. $\alpha_{H_2/HI}$ showed maximum value at 450°C, because HI permeance showed minimum value at 450°C, while H_2 permeance monotonically increased with temperature.

Stability of the modified membrane in H_2–H_2O–HI gaseous mixture

Figure 6 shows that the stabilities of the modified membranes were carried out in the H_2–H_2O–HI gaseous mixture (molar composition: 0.09:0.78:0.13) for one day.

The data of the S and L membranes in Figure 6 were measured after being in the atmospheric environment for 5 and 3 months, respectively, after the separation experiments of the H_2–H_2O–HI gaseous mixture.

As for the L membranes, the H_2 and H_2O permeances were almost the same as those in Figure 4, and the H_2 and H_2O permeances did not change after a one-day exposure in the H_2–H_2O–HI gaseous mixture at 450°C. As for the S membranes, the H_2 permeances decreased and the H_2O permeances did not change compared with those in Figure 4. From these results, it was suggested that the L membranes would be more stable than the S membranes. In the S membranes, the H_2 and H_2O permeances remained nearly constant during a one-day exposure in the H_2–H_2O–HI gaseous mixture at 450°C, indicating that the SiO_2 structure was not altered. It is assumed that the structure of the deposited SiO_2 finished changing during the exposure to the atmospheric environment for 5 months.

The reason for the difference between the stability of the S and L membranes is not clear at present. However, the only difference in the experimental conditions of CVD for preparing the S and L membranes was the CVD treatment time. The CVD treatment time for the L membranes was about 4–5 times longer than that for the S membranes, which was 5–7 hours. Therefore, the longer CVD time might influence the increasing stability of the L membranes, by, for example, facilitating the relaxation of the stress in the deposited SiO_2. It may be that the long CVD time causes the formation of a thick deposition layer on the surface of the support, which may then reduce the stability of the membrane, as discussed by Ha et al. (1993). In this study, however, this phenomenon was not observed in the L membranes, as shown in Figure 2. This may be due to the forced cross-flow condition adopted in the present CVD treatment (Morooka et al., 1996).

Further study is necessary to clarify the stability of the modified membranes.

Conclusions

1. Several kinds of membranes were prepared by controlling the CVD treatment using $He-N_2$ selectivity as the indicator of the pore closure. The H_2-N_2 selectivities of the modified membranes at 600°C were 53, 9.2, 4.1, 135, and 6.6 for the S1, S2, S3, L1, and L2 membrane, respectively.

2. From the separation experiments in the H_2-H_2O-HI gaseous mixture, it was confirmed that the hydrogen permeances of the modified membranes were almost the same as the single-component permeance. The separation factors were over 3 for H_2-H_2O, and over 150 for H_2-HI.

3. The S3 membrane showed the highest hydrogen permeance (on the order of 10^{-7} mol·Pa^{-1}·m^{-2}·s^{-1}), and also the highest separation factor of the H_2-HI (650, at 450°C).

4. Preliminary study of the stability suggested that the L membranes were more stable than the S membranes.

Notation

J_{H_2} = permeation rate of H_2, mol/m^2·s
J_i = permeation rate of i, mol/m^2·s
y_{H_2} = mole fraction of H_2
y_i = mole fraction of i
$\alpha_{H_2/i}$ = separation factor of H_2 to i

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