

Multiple tube preparation characteristics of silica hydrogen permselective membrane

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Abstract—The multiple tube preparation of a silica membrane using a porous α -alumina tube as a support tube was carried out by chemical vapor deposition (CVD) to scale up the membrane reactor. A porous alumina tube with a pore size of 100 nm was modified by chemical vapor deposition using tetraethoxysilane as an Si source. The single-component permeance of H_2 and N_2 in the prepared silica membrane that was achieved by a multiple tube membrane preparation system was measured at 300–600 °C. Hydrogen permeance of the modified membrane at a permeation temperature of 600 °C was $5 \times 10^{-8} \text{ mol} \cdot \text{Pa}^{-1} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. H_2/N_2 selectivity at 600 °C was about 32. It was confirmed that permeance of H_2 and N_2 and the selectivity for H_2 to N_2 in the prepared silica membrane by the multiple tube membrane preparation system had almost the same value compared to those of the silica membrane prepared by the single-tube system.

Key words: Inorganic Membrane, Silica-alumina Membrane, Chemical Vapor Deposition, Multiple Layered Membrane Preparation, Hydrogen Permselectivity

INTRODUCTION

Membrane-based systems are anticipated in the future because they can achieve separation and purification of chemicals in an energy efficient and cost-effective manner to improve the efficiency of industrial chemical processes [1,2]. In particular, inorganic membranes have been developed for use in a variety of industrial applications, such as the hydrogen production, CO_2 separation, and so on due to their thermal, chemical, and structural stability. Therefore, ceramic membranes have been used for high temperature applications, such as catalytic reactions in membrane reactors and gas separation. The membrane materials for these applications are silica, titania, and palladium and its alloys, and silica and palladium and its alloys are being investigated to develop a dense hydrogen permselective membrane at high temperatures [3–13].

The palladium membrane that utilizes the hydrogen dissolution-diffusion mechanism has a good hydrogen permselective property [14,15]; however, it is limited in its applications because the membrane property decreases in the hydrocarbon and steam environment, and also its preparation cost is high [16].

The developed silica membrane has good chemical stability at high temperatures and it has a wide range of applications. Research efforts continue in the focus of improving the separation performance and the hydrogen permeation flux by controlling the pore size and film thickness by altering the sol-gel and CVD (chemical vapor deposition) preparation method [17–23].

In our previous papers [24–27], a silica hydrogen permselective membrane was prepared by CVD to utilize it in an HI decomposition reaction in a IS (iodine-sulfur) process, which is a hydrogen production method using the heat of a VHTR (very high temperature gas-cooled reactor). The silica membranes utilizing γ -alumina

and α -alumina tubes as support tubes were prepared. The CVD treatment was carried out continuously until the membrane exhibited specified selectivity of He/N_2 . From this CVD treatment method, the H_2/N_2 selectivity was controlled. The prepared silica hydrogen permselective membrane had good stability in an $HI-H_2O$ gaseous mixture at 450 °C. The silica membrane that used α -alumina as the support tube was more stable than the membrane that used γ -alumina as the support tube in the $HI-H_2O$ gaseous mixture. The number of membranes needed in the membrane reactor that are used to prepare the silica membrane for the HI decomposition reaction is over 3×10^4 to achieve a hydrogen production rate of $1 \times 10^2 \text{ m}^3/\text{h}$ in the IS process [27]. So, a multiple silica membrane preparation method is needed for the scale up of the membrane reactor.

In this study, we tried to use a multiple tube preparation for the membrane reactor. The multiple tube preparation of the silica membrane using the porous α -alumina tube as the support tube was performed by using the chemical vapor deposition (CVD) method, and its H_2/N_2 selectivity performances and permeance of H_2 and N_2 were evaluated.

EXPERIMENTAL

1. Support Tube

A porous α -alumina tube (o.d., 5.5 mm; i.d., 3.5 mm; length, 350 mm), supplied by Nano-Porous Materials Co. (South Korea), was used as a support. The tube had an average pore size of 100 nm and a porosity of about 35%.

2. Multiple Tube Membrane Preparation and Single-component Gas Permeation Test

Before the chemical vapor deposition (CVD) treatment, the support tube was glazed with a SiO_2 -BaO-CaO sealant (Nippon Electric Glass, GA-13) that was calcined at 1,200 °C, except for the 140 mm permeating portions.

The chemical vapor deposition (CVD) method and experimental

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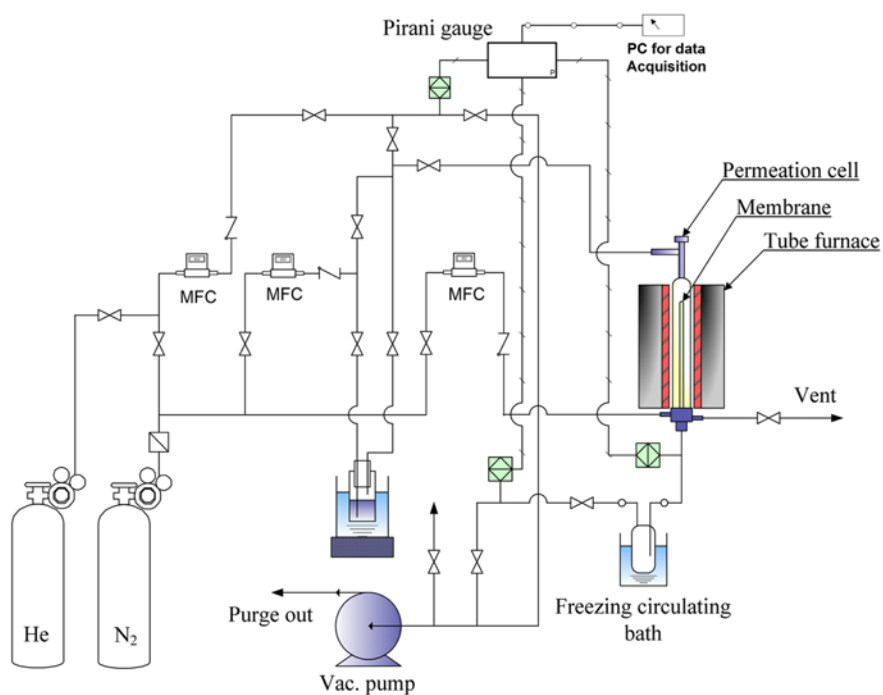


Fig. 1. Schematic diagram of chemical vapor deposition apparatus for the multiple tube preparation of the silica membrane.

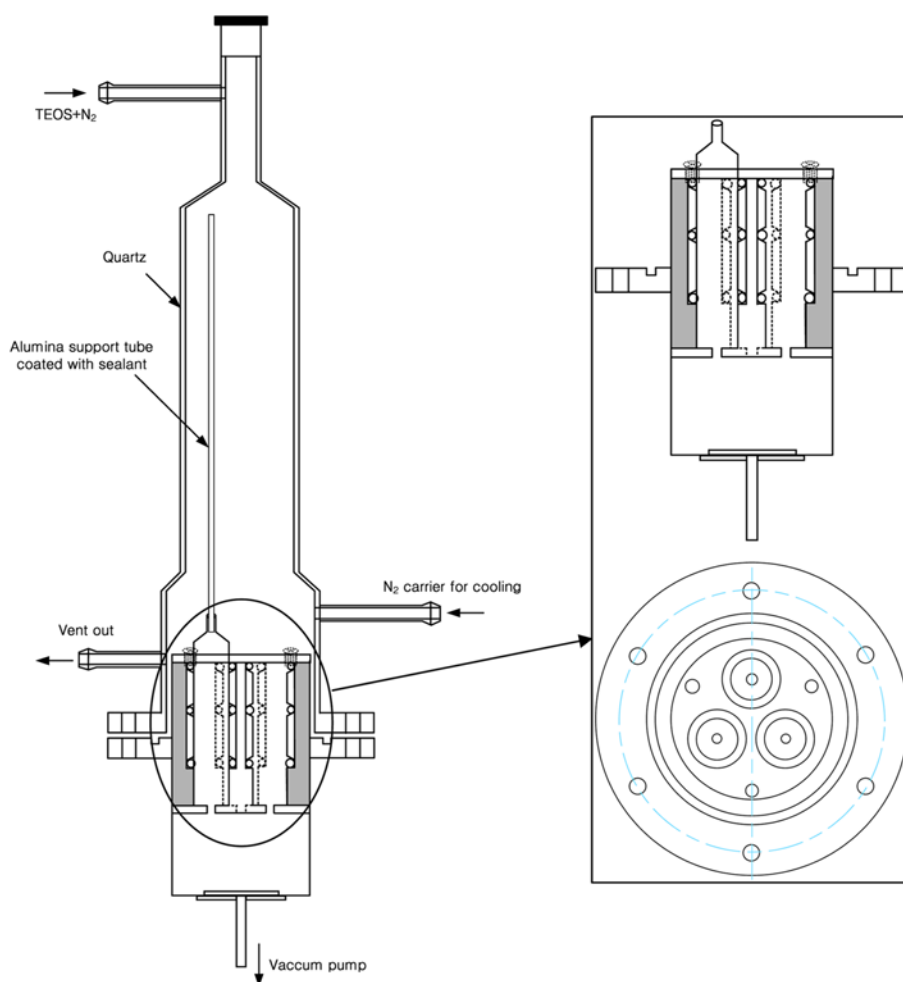


Fig. 2. Schematic drawing of multiple tube membrane preparation system.

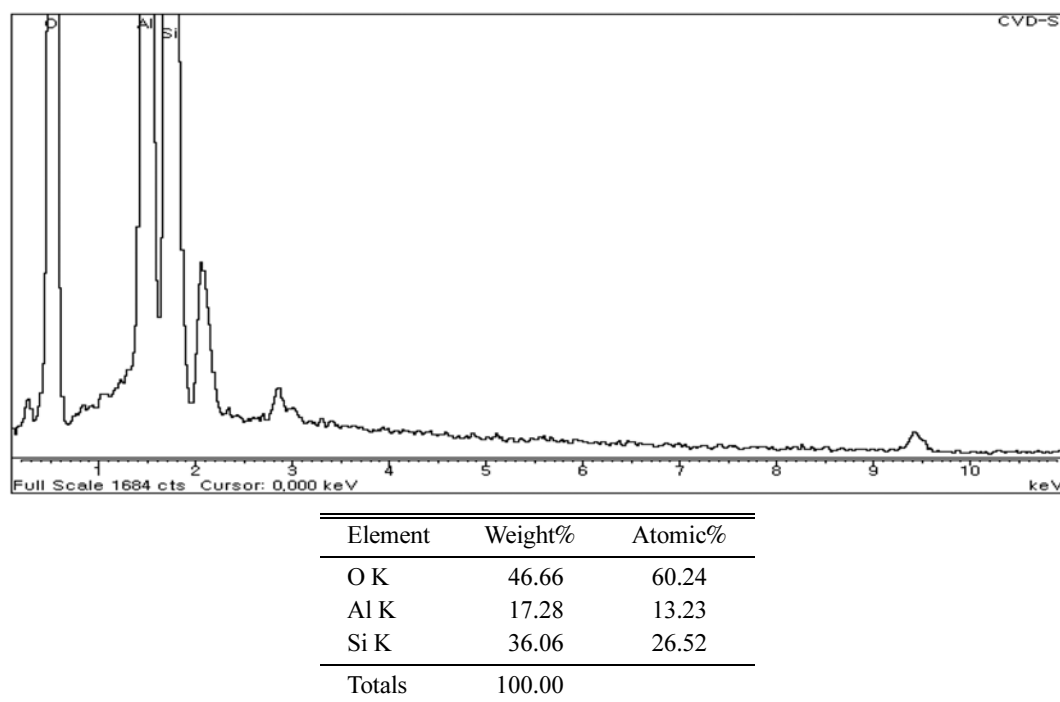


Fig. 3. EDX (energy dispersive X-ray spectroscopy) analysis of the prepared silica membrane by the multiple tube membrane preparation system.

apparatus for the single-tube membrane preparation are described elsewhere [24-26,28].

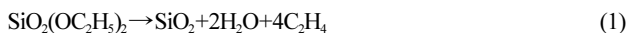
Fig. 1 shows a schematic diagram of the chemical vapor deposition apparatus for the multiple tube preparation of the silica membrane.

Fig. 2 shows a schematic drawing of the multiple tube membrane preparation system.

The three support tubes were fixed in a quartz reactor (o.d., 44 mm; i.d., 42 mm; length, 620 mm), as shown in Fig. 2, and placed in an electrical tube furnace, as shown in Fig. 1. The CVD was performed at 600 °C and 700 °C with a nitrogen carrier gas flow rate in the range of 0.0637-0.1 m/s and the bubbler temperature of tetraethoxysilane (TEOS) was kept at 30 °C.

The reason for the two fixed nitrogen carrier gas flow rates was that the He/N₂ selectivity over the Knudsen diffusion was not obtained over 0.1 m/s and below 0.06 m/s with increases in the CVD treatment time [22].

The pyrolysis reaction of TEOS is as follows:



Throughout the CVD treatment, the inside of the tube was continuously evacuated by a rotary vacuum pump. The pressure in the evacuation side decreased continuously as the CVD progressed. In the course of the CVD treatment, the permeability of nitrogen and helium was intermittently measured by a pressure-rise technique. The CVD was stopped at a certain value using He/N₂ selectivity as the indicator of pore closure. After the CVD treatment, the temperature was reduced slowly with a cooling rate of 60 °C/hr.

Single-component gas permeation experiments for hydrogen and nitrogen were performed at 300-600 °C. The permeability was measured by a pressure-rise technique.

ured by a pressure-rise technique.

RESULTS AND DISCUSSION

1. Morphology of the Prepared Membrane by the Multiple Tube Membrane Preparation System

Fig. 3 shows an EDX (energy dispersive X-ray spectroscopy) analysis of the silica membrane prepared by the multiple tube membrane preparation system.

From this result, it was confirmed that silica was uniformly formed on the porous alumina support tube. SiO₂ was deposited on the top and inside the support tube and a dense SiO₂ layer was formed near the surface and it was responsible for the appearance of the gas separation factor [26].

Fig. 4 shows the morphologies of the surface of the support tube and the silica membrane prepared by the multiple tube membrane preparation system obtained with a scanning electron microscope (SEM).

The deposited silica layer exhibits good uniformity on the support Al₂O₃ layer. Most of the deposited silica particles did not exceed 11 nm.

Fig. 5 shows the morphologies of the cross section of the prepared silica membrane prepared by the multiple tube membrane preparation system at 600 °C and 700 °C obtained with a scanning electron microscope (SEM).

The SiO₂ layer thickness of the prepared silica membrane by the multiple tube membrane preparation system was 400-500 nm and 2-3 μm at 600 °C and 700 °C, respectively. The CVD treatment time to reach a pressure drop of 1 torr in the permeate side of the membrane by evacuation with a rotary vacuum pump was 10 h at a CVD temperature of 600 °C and it was 4 h at a CVD temperature of 700 °C.

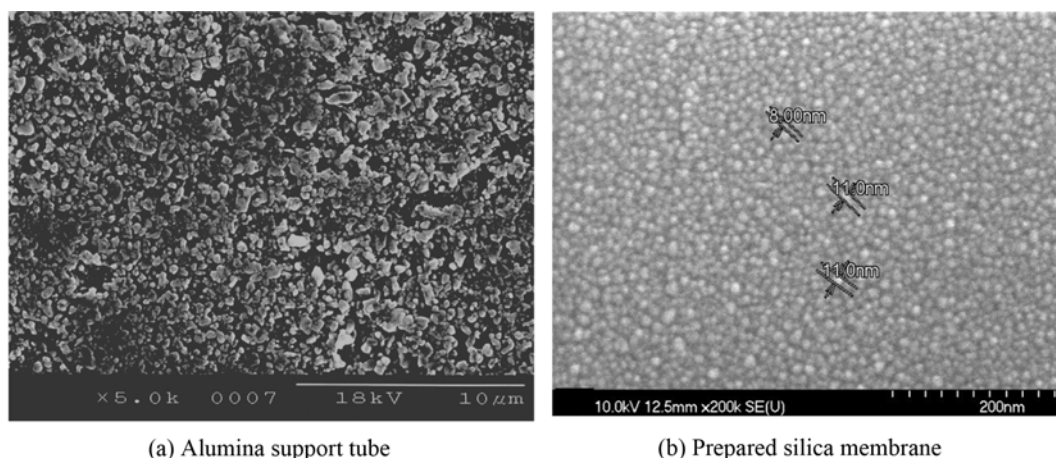


Fig. 4. Morphologies of the surface of the support tube and silica membrane prepared by the multiple tube membrane preparation system obtained with a scanning electron microscope (SEM).

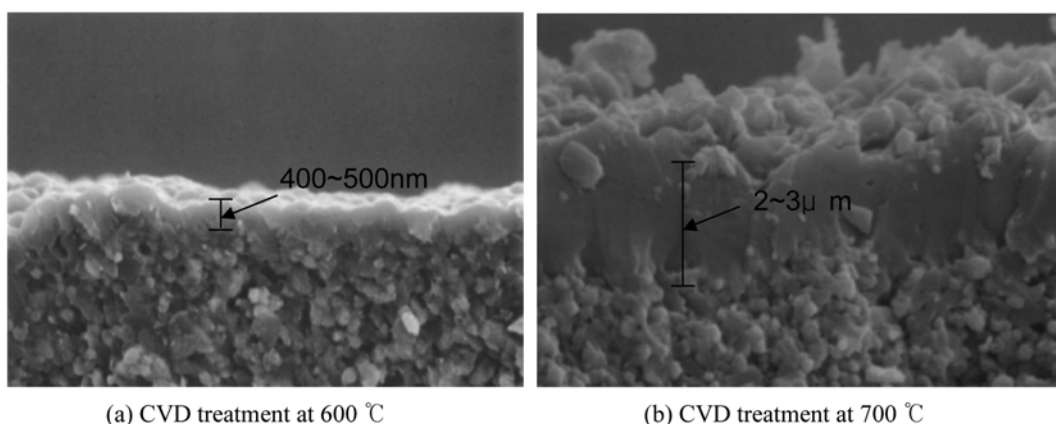


Fig. 5. Morphologies of cross section of the silica membrane prepared by the multiple tube membrane preparation system at 600 °C and 700 °C obtained with a scanning electron microscope (SEM).

The SiO_2 layer thickness of the silica membrane prepared at a CVD temperature of 700 °C was thicker than that prepared at a CVD temperature of 600 °C, while the CVD treatment time was shorter. It seems that SiO_2 was deposited more on top the support tube than inside the support tube with the increased TEOS pyrolysis rate. This also indicates that the pores inside the support tube that was treated at a 600 °C CVD temperature were closed more than those treated at a 700 °C CVD temperature. From these results, it was expected that the CVD treatment temperature in the multiple tube membrane preparation system was suitably carried out at 600 °C.

2. Preparation Characteristics of the Prepared Membrane by the Multiple Tube Membrane Preparation System

Fig. 6 shows the pressure drop in the permeate side of the membrane during CVD treatment in the multiple tube and single-tube system at 600 °C and at a nitrogen carrier gas flow rate of 0.08 m/s. The pressure drop in the permeate side of the membrane during CVD treatment indicates pore closure inside the support tube, and this determines the permeation rate of the gas and selectivity.

The pressure decreased with increases of deposition time in each case, as shown in Fig. 6. The initial pressure in the multiple tube membrane preparation system was higher than that in the single-tube membrane preparation system. It seems that the permeate side

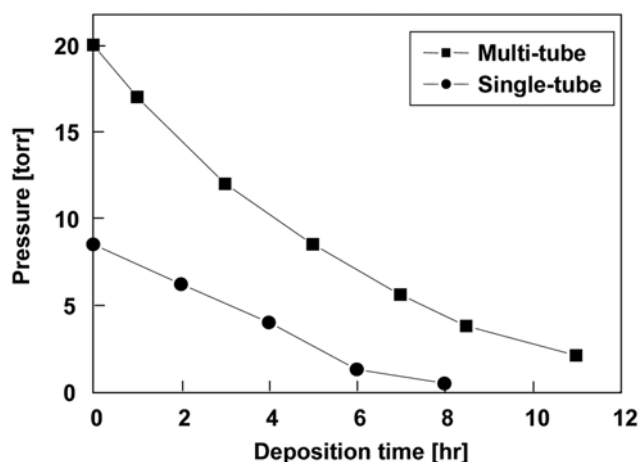


Fig. 6. Pressure drop in the permeate side of the membrane during CVD treatment in the multiple tube and single-tube system at 600 °C and with nitrogen carrier gas flow rate of 0.08 m/s.

area in the multiple tube membrane preparation system was larger than that in single-tube membrane preparation system. From this

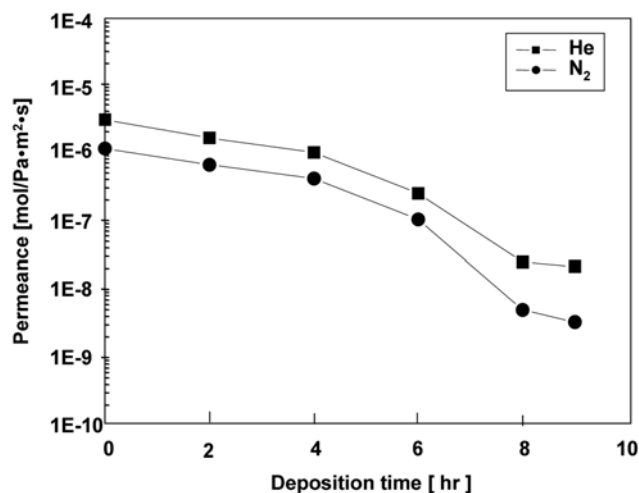


Fig. 7. Relationship between permeances of He and N₂ and deposition time in the silica membrane preparation at 600 °C and with nitrogen carrier gas flow rate of 0.08 m/s by the multiple tube system.

result, it is expected that the deposition time in multiple tube membrane preparation system needs to be longer to have the same performance compared to the membrane prepared by single-tube system, and the deposition time did not change the membrane characteristics, such as morphology and the permeation property of the gas that had the same preparation conditions.

Fig. 7 shows the relationship between permeances of He and N₂ and deposition time in the silica membrane preparation at 600 °C and at a nitrogen carrier gas flow rate of 0.08 m/s by the multiple tube system. With an increase of the deposition time, the permeance of He and N₂ through the membrane decreased slowly as the selectivity ratio of helium to nitrogen increased. The selectivity of He to N₂ at the initial deposition time was 2.4; it increased with increases of deposition time, and the selectivity reached 6.5 after 9 h of deposition time.

The change tendency of the permeance and deposition time in the multiple tube system was the same as those of the prepared silica membrane in the single-tube system that was already reported previ-

ously [25].

3. Single-component Gas Permeation

Fig. 8 shows the single-component permeance of H₂ and N₂ through the modified membranes in the multiple tube and single-tube membrane preparation systems under the same preparation conditions (at 600 °C and at a nitrogen carrier gas flow rate of 0.08 m/s).

In each membrane preparation system, with increases of the temperature, the H₂ permeance through the modified membrane increased a little, and the N₂ permeance decreased a little. The selectivity of H₂ to N₂ in the modified membrane by the multiple tube membrane preparation system was 25, 27, and 32 at 300 °C, 450 °C, and 600 °C, respectively. The selectivity of H₂ to N₂ in the modified membrane by the single-tube membrane preparation system was 25, 27, and 36 at 300 °C, 450 °C, and 600 °C, respectively. The selectivity of H₂ to N₂ in the modified membrane by each membrane preparation system had almost the same value at each temperature, which was higher than that of Knudsen diffusion, and the value was 3.74. In both modified membranes, H₂ permeation was dominated by activated diffusion. The H₂ permeance at 600 °C was about 6×10⁻⁸ mol·Pa⁻¹·m⁻²·s⁻¹ and 5×10⁻⁸ mol·Pa⁻¹·m⁻²·s⁻¹ in the modified membranes that were prepared by single-tube and multiple tube membrane preparation systems, respectively.

From this result, it was confirmed that the permeance of H₂ and N₂ and the selectivity of H₂ to N₂ in the silica membrane prepared by multiple tube membrane preparation system had almost the same value compared to those of the prepared silica membrane in single-tube system. Based on the above results, it was confirmed that the multiple silica hydrogen permselective membrane prepared by CVD treatment can be prepared by controlling the reaction conditions, such as CVD temperature and nitrogen carrier gas flow rate in a quartz reactor.

CONCLUSIONS

(1) The multiple tube preparation of silica membranes by a CVD treatment was carried out to develop a scaled up membrane reactor. A porous α -alumina tube with a pore size of 100 nm was used as the support tube. The silica hydrogen permselective membrane was prepared by the multiple tube membrane preparation system.

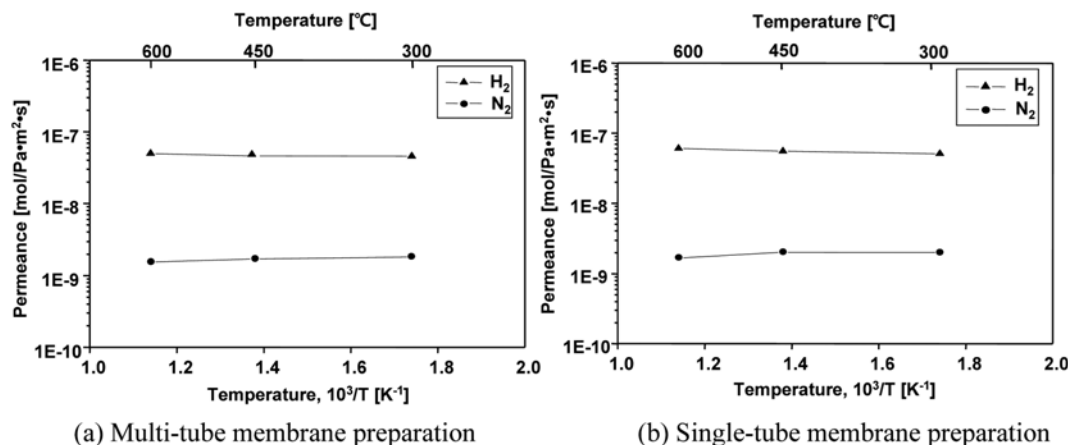


Fig. 8. Single-component permeance of H₂ and N₂ through the modified membranes in the multiple tube and single-tube membrane preparation systems at the same preparation conditions (at 600 °C and 0.08 m/s of nitrogen carrier gas flow rate).

(2) The CVD treatment was carried out at 600 °C and with a nitrogen carrier gas flow rate of 0.08 m/s in the multiple tube system. The change tendency of the permeance and deposition time in the multiple tube system was almost the same compared to those of the prepared silica membrane in the single-tube system.

(3) Single-component permeance to H₂ and N₂ in the silica membrane prepared by the multiple tube and single-tube membrane preparation systems was measured at 300-600 °C. The selectivity of H₂ to N₂ in the modified membrane by each membrane preparation system had almost the same value at each temperature, which was higher than that of Knudsen diffusion, and it was 3.74. This confirmed that the permeance of H₂ and N₂ and the selectivity of H₂ to N₂ in the prepared silica membrane by the multiple tube membrane preparation system had almost the same value compared to those of the prepared silica membrane in the single-tube system.

(4) The results confirm that the multiple silica hydrogen permselective membrane prepared by the CVD treatment can be prepared by controlling the reaction conditions, such as CVD temperature and nitrogen carrier gas flow rate in a quartz reactor.

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