

## PREPARATIONS OF METAL IMPREGNATED POROUS INORGANIC MEMBRANES FOR HYDROGEN SEPARATION BY MULTI-STEP PORE MODIFICATIONS

Jae-Hyun So, Keon-Yeong Yoon, Seung-Man Yang<sup>†</sup> and Seung Bin Park

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,  
373-1, Kusong-dong, Yusong-gu, Taejon 305-701, Korea  
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**Abstract**—In this research, porous inorganic membranes for hydrogen separation were prepared with  $\alpha$ -alumina support by multi-step pore modification method. Porous inorganic membranes were made by three consecutive steps: sol-gel method, *in-situ* hydrolysis of tetraethylorthosilicate (TEOS) and soaking and vapor deposition (SVD) method. In order to enhance the hydrogen selectivity, we used nickel (Ni) and palladium (Pd) particles in the first and final pore modification steps. Although both nickel and palladium induced surface diffusion, palladium was shown more effective for hydrogen selective adsorption than nickel. This multi-step method produced porous membranes with a moderate hydrogen selectivity and excellent hydrogen permeability at high temperature up to 773 K and at transmembrane pressure ( $\Delta P$ ) as high as 310 kPa. The separation factor of hydrogen relative to nitrogen was maintained at about 7 even when the transmembrane pressure was 70 kPa, and the hydrogen permeability was still much higher than that of non-porous polymeric membranes. Furthermore, the distributions of nickel and palladium within the intermediate layer formed at the membrane cross-section were examined by scanning electron microscopy (SEM) and energy dispersive X-ray analysis.

**Key words**: Porous Inorganic Membrane, Hydrogen Separation, Pore Modification, Surface Diffusion, Sol-Gel Method

### INTRODUCTION

As inorganic membranes show excellent chemical and thermal stability, they have been used in water desalination, in ultrafiltration processes in the food industry and in wastewater treatment, and separation of gas mixtures [Leenarrs et al., 1984]. Inorganic membranes can be classified into two types of membranes: non-porous (dense) and porous membranes. Non-porous membranes, which have a dense separation layer, show high selectivity and low permeability, and the separation mechanism is very similar to that of polymeric membrane. On the other hand, porous membranes have much higher permeability than polymer membrane at the expense of the selectivity, which is typical of the membrane separation. This trend is confirmed by the correlation of separation factor versus permeability [Robeson, 1991]. As the polymer membrane is usually non-porous, the fluxes and permeabilities are very low. However, as the separation through polymeric membrane proceeds via solution-diffusion mechanism, the selectivity of polymeric membrane is relatively high. In the mechanism of gas separation by porous alumina membrane or Vycor glass, the pore size of the membrane relative to the mean free path of gas molecules that are to be separated is important [Li and Hwang, 1991; Uhlhorn et al., 1989].

When the mean free path of the gas molecule is much smaller than the pore diameter, the flow of molecules is mainly

due to Poiseuille flow and ordinary diffusion, in which the collisions between permeate gas molecules are important. However, these two contributions are not separative. The important mechanisms of gas separation via porous membrane are Knudsen diffusion and surface diffusion. Knudsen diffusion occurs when the mean free path of the gas molecule is much larger than the pore diameter and, under this condition, the collisions between the permeate gas molecules and the pore wall are important. In Knudsen diffusion, the separation between two permeating gases is mainly governed by the square root of the molecular weight ratio. Thus, when the molecular weight ratio is near unity, the selectivity due to Knudsen diffusion is not high. Another important separation mechanism of surface diffusion is due to the concentration gradient of adsorbed species on the pore wall. Much effort has been made to improve the selectivity of porous inorganic membrane via surface diffusion generated by the poremodification [Chai et al., 1994; Lee et al., 1994, 1995a, b, c; Cho et al., 1995; So et al., 1998]. Metal-dispersed alumina membranes were prepared by 30 times dip-coating of metal impregnated alumina sols [Chai et al., 1994]. These metal-dispersed alumina membranes formed as thin separative layers on the planar substrate showed high hydrogen separation factor at a transmembrane pressure below 80 kPa. Palladium, platinum and rhodium used frequently hydrogen separation membranes are expensive [Chai et al., 1994; Aoki et al., 1996], which restricts their use for practical applications. Moreover, most reported results of gas separation membranes utilized a carrier gas such as helium and argon in the permeation experiments [Lange et al., 1995; Matsuyama et al.,

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: smyang@cais.kaist.ac.kr

1996; Hartel et al., 1996]; and the hydrogen partial pressure in the permeate side was maintained at nearly zero. Thus, these experimental permeation results are not relevant to the practical hydrogen recovery process. This is the primary motivation for the present study.

In the present study, a novel method was proposed to prepare a membrane as long as 500 mm, which could be of practical significance for practical applications. In order to obtain permeation data of practical significance, the permeate was not washed out with a carrier gas. The results showed that the membrane prepared here could be used in high transmembrane pressure difference and at high temperature. Furthermore, nickel in addition to palladium was used as a cheap alternative metal for providing hydrogen permselective adsorption sites. By doing this, we prepared a metal-impregnated inorganic membrane through which the transport mechanism was mainly governed by surface diffusion.

### EXPERIMENTAL

Porous  $\alpha$ -alumina support (Noritake Co.) of 500 mm in length with a symmetric structure was used as a support. The inner and outer diameters of this membrane support are 7 mm and 10 mm, respectively. The inner layer of the support is thin and dense with an average pore size of 80 nm and a thick and coarse outer layer. A cross-sectional structure of this  $\alpha$ -alumina support is presented in Fig. 1. To prepare porous inorganic membrane for hydrogen separation, we used multi-step pore modification, which was processed sequentially as follows—dip-coating of metal impregnated alumina sol [Lee et al., 1994, 1995b], *in-situ* hydrolysis of TEOS [Yoon, 1996], and soaking and vapor deposition (SVD) [Lee et al., 1995c; So et al., 1998]. The procedure for the membrane preparation was illustrated in Fig. 2.

First,  $\gamma$ - $\text{Al}_2\text{O}_3$  sol was prepared by following Yolda's optimum condition, and  $\gamma$ - $\text{Al}_2\text{O}_3$  sol was directly mixed with palladium chloride (Sigma) or nickel (II) chloride (Aldrich), respectively. After sonication for 20 min, metal impregnated  $\gamma$ - $\text{Al}_2\text{O}_3$  sol was layered onto the  $\alpha$ - $\text{Al}_2\text{O}_3$  support using dip-coating and maintaining the inner side support under vacuum.

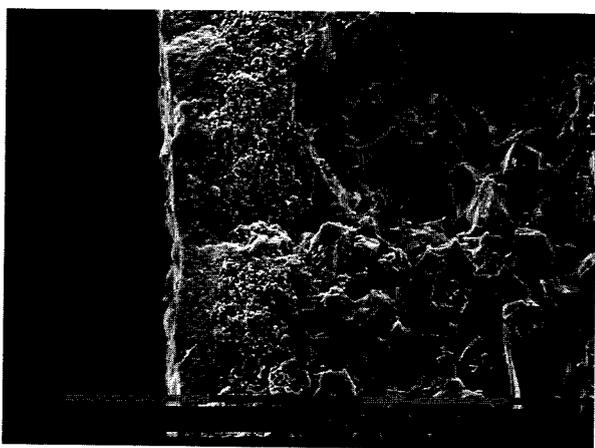


Fig. 1. The structure of the  $\alpha$ -alumina support.

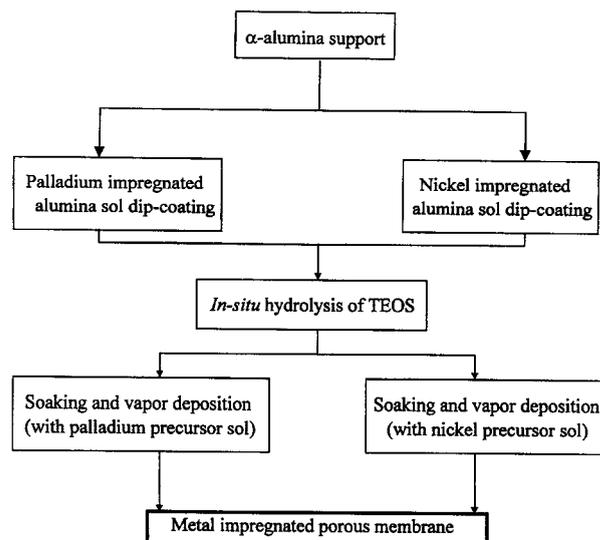


Fig. 2. Procedure of metal impregnated membrane by multi-step pore modifications.

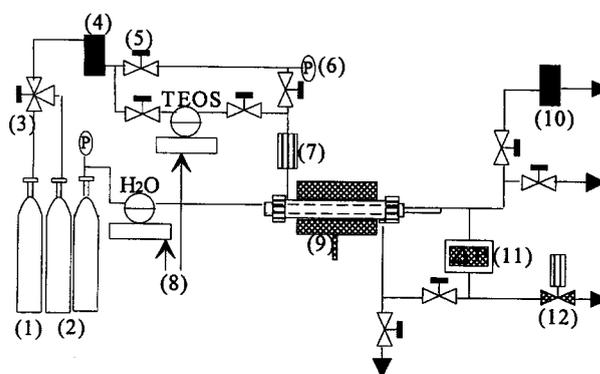


Fig. 3. Schematic of the apparatus used in *in-situ* hydrolysis of TEOS.

- |                            |                                       |
|----------------------------|---------------------------------------|
| (1) $\text{H}_2$ gas       | (8) Heating mantle                    |
| (2) $\text{N}_2$ gas       | (9) Electric furnace and thermocouple |
| (3) 3 way-valve            | (10) Flow meter                       |
| (4) Mass flow controller   | (11) Differential pressure gauge      |
| (5) On-off valve           | (12) Needle valve                     |
| (6) Digital pressure gauge |                                       |
| (7) Pre-heater             |                                       |

Then, the prepared membrane was calcinated at 553 K with raising the temperature rate 0.12 K/s in the electric furnace to prevent crack formation during the calcination stage. The dip-coating and calcination procedure was repeated 6-7 times. It had been shown that the palladium intermediate layer was successfully formed by dip coating of palladium impregnated  $\gamma$ - $\text{Al}_2\text{O}_3$  sol under vacuum [Lee et al., 1994; 1995b].

After applying dip-coating of metal-impregnated alumina sol and calcination several times, *in-situ* hydrolysis of TEOS was carried out in the cylindrical pores of the membrane. As shown in Fig. 3 for schematic of *in-situ* hydrolysis, TEOS (Aldrich) and distilled water were bubbled by heating mantle to about 442 K and 373 K, respectively, to avoid thermal decomposition of each reactant. TEOS vapor was driven to the outside of the membrane with water vapor driven to the inside of the

membrane.  $N_2$  stream was used as a carrier gas and the amount of each reactive vapor was controlled by the gas flow rate of carrier gas which is  $6.67 \times 10^{-6} \text{ m}^3/\text{s}$  at both side of the membrane. The two vapors reacted within the pores of the support and, as a result, membrane pores were narrowed by  $\text{SiO}_2$  plugging. The temperature of the membrane was maintained at about 453-473 K to avoid thermal decomposition of TEOS. This method was very effective in narrowing the pores of the membrane, and the membranes prepared by this method showed better separation performance when the transmembrane pressure increased.

Finally, to enhance the hydrogen selectivity of the membrane, we applied soaking and vapor deposition (SVD). In SVD, the metal source, palladium (II) acetate (Korea Engel-Hard) or nickel (II) acetylacetonate (Aldrich), each of 0.5 g was dissolved in acetone (Merck) 20 ml, and hydrogen chloride (Junsei) was added to make the metal precursor sol. For 1 hr, metal precursor sol solution was stirred vigorously with a spin bar, and soaked into the membrane pore for 30 min. Before drying, the inside of the membrane was maintained under vacuum (13.3-40.0 kPa) for 20 min to facilitate the penetration of the soaked precursor sol solution fully into the inner layer. To evaporate the acetone used as a solvent, soaked membrane was dried at 373 K for 3 hr in a dry oven. After drying, metal acetate was decomposed, as the temperature was gradually increased from room temperature to 453 K under reduced pressure. And to enhance palladium or nickel deposition, nitrogen stream was passed through membrane from outside to inside at the rate of 50 ml (STP)/min for 1 min with 10 min interval. An intermediate layer of palladium or nickel was formed in the vicinity of the interface between the two layers of the support by this SVD [Lee et al., 1995c; So et al., 1998]. After SVD was conducted several times of SVD, the amount of precursor sol solution soaked into the membrane pore decreased sharply. Therefore, to increase the amount of metal inside of the pore, a soaking step was conducted under vacuum (13.3-40.0 kPa), which is henceforth denoted as ESVD (enhanced soaking and vapor deposition).

The gas permeation experiments were carried out for  $H_2$  and  $N_2$ . The gas permeation experiments were also conducted within the apparatus shown in Fig. 3 by adjusting on-off valves. The gas flow rate was controlled by the mass flow controller (UFC-1500A, Unit) and the transmembrane pressure  $\Delta P$  by the differential pressure gauge (7354 Series, Cole Parmer). The transmembrane pressure was controlled by needle valve in the retentate side. To examine the changes of the microporous structure during the sequential pore modification, Scanning Electron Microscopy (SEM, Philips 535 M) was used; the sol particles were observed by Transmission Electron Microscopy (TEM, Philips CM20).

## RESULTS AND DISCUSSIONS

### 1. Gas Permeation and Ideal Separation Factors

As noted earlier, the  $\alpha$ -alumina support used in this study has asymmetric structure and the pore size distribution is very broad (few  $\mu\text{m}$ -80 nm). Thus, it is very difficult to determine the exact

pore size distribution directly. An alternative way to examine the changes in the pore size distribution during the pore modification is a measurement of the gas permeance and the particle size distribution used in the modification step. From these results, the pore size can be estimated indirectly. In this present work, the permeance  $F$  of a membrane is defined as

$$F = \frac{Q}{2\pi rL(\Delta P)}$$

where  $Q$  is the volumetric flow rate at the standard state, and  $r$  and  $L$  denote the outer radius and the length of the support, respectively. The permeances of hydrogen and nitrogen were measured as functions of temperature ( $T$ ) and transmembrane pressure difference ( $\Delta P$ ). And the ideal separation factor was defined as the ratio of hydrogen to nitrogen permeance. The changes in permeance and ideal separation factor during multi-step pore modifications are shown in Fig. 4 to Fig. 7.

Fig. 4 and Fig. 5 showed the changes in  $H_2$  and  $N_2$  permeances and ideal separation factor of palladium-impregnated

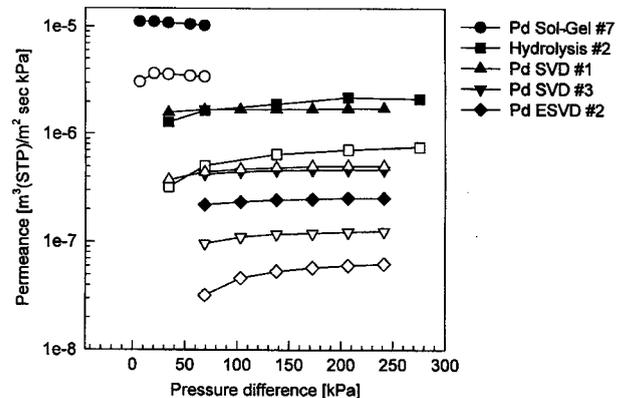


Fig. 4. Permeance changes of Pd impregnated membrane during multi-step pore modifications (at 673 K, filled;  $H_2$ , unfilled;  $N_2$ ).

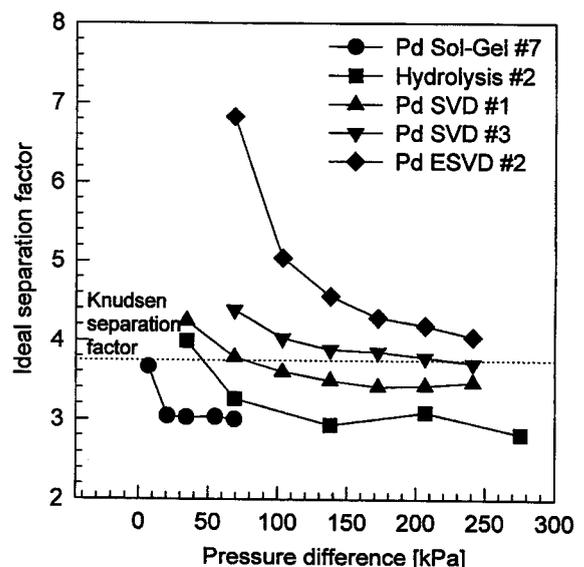


Fig. 5. Ideal  $H_2$  separation factors of Pd impregnated membrane during multi-step pore modifications at 673 K.

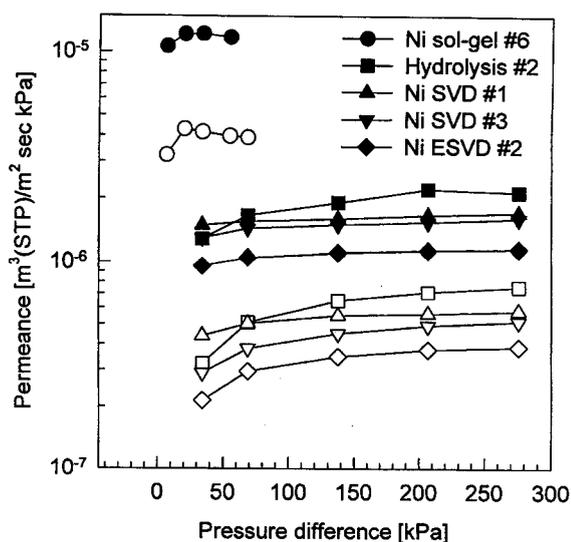


Fig. 6. Permeance changes of Ni impregnated membrane during multi-step pore modifications (at 673 K, filled; H<sub>2</sub>, unfilled; N<sub>2</sub>).

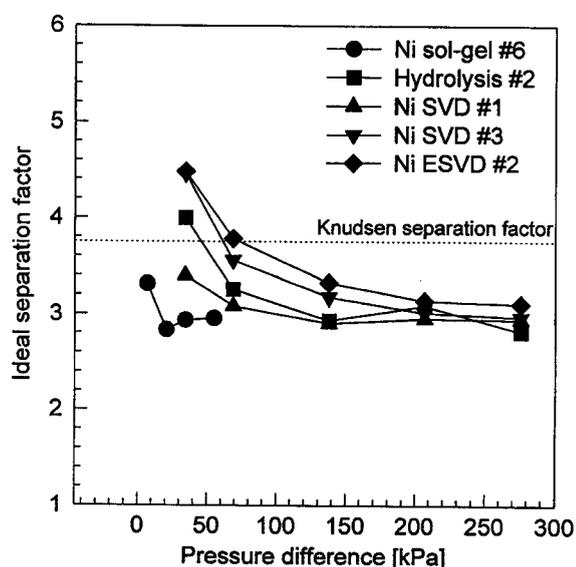


Fig. 7. Ideal H<sub>2</sub> separation factors of Ni impregnated membrane during multi-step pore modifications at 673 K.

membrane prepared by multi-step pore modification at 673 K, and Fig. 6 and Fig. 7 were for nickel impregnated membrane. From these results, it could be confirmed that the permeances of H<sub>2</sub> and N<sub>2</sub> decreased sequentially and the ideal separation factor increased gradually as the pore modification proceeded. As shown in Fig. 5 and Fig. 7, pore modification by sol-gel method was effective only at low transmembrane pressure difference i.e.,  $\Delta P=1-70$  kPa, and the ideal separation factors reached the ideal Knudsen limit only at low pressure difference. These agree well with previous results [Lee et al., 1994, 1995b]. Although palladium- or nickel-impregnated membrane by repeated dip-coating alumina sol could show a high separation factor above the Knudsen limit ( $\approx 3.74$ ) at same  $\Delta P$  [Chai et al., 1994], the membrane pore must be modified for a practical separation process at large  $\Delta P$ .

Therefore, after the sol-gel method had been carried out 6-7 times, *in-situ* hydrolysis of TEOS followed twice. This pore modification step made the separation layer of the alumina support dense enough for a very high transmembrane pressure ( $\Delta P=250$  kPa). However, as SiO<sub>2</sub> was not effective compared with palladium in hydrogen adsorption, the hydrogen selectivity was not satisfactory at high pressure difference as shown in Fig. 6 and Fig. 7. This could be explained as follows: the hydrogen separation of the sol-gel driven membrane was induced by weak surface diffusion due to the hydrogen chemisorption onto palladium or nickel, but that of the hydrolysis-adopted membrane was due to Knudsen diffusion through the narrowed membrane pores. From the permeance measurement, *in-situ* hydrolysis of TEOS provided a very dense membrane layer.

After effective pore densification by the *in-situ* hydrolysis of TEOS, Soaking and Vapor Deposition (SVD) was carried out to improve high hydrogen selectivity. Since the sizes of palladium (II) acetate and nickel (II) acetylacetonate precursor sols were nanometer scale, it could be easily deposited onto the pore wall of the hydrolysis-modified membrane. After SVD was performed 5 times and ESVD 2 times were performed, the ideal hydrogen separation factor was increased up to 7, and the permeance of each gas was much decreased as shown in Fig. 4 and Fig. 5. This reflects that by the SVD, the surface diffusion of hydrogen adsorbed on palladium becomes pronounced. The nickel-impregnated membrane, which was prepared by three times SVD and two times ESVD with nickel precursor sol solution after sol-gel and *in-situ* hydrolysis, showed similar trends as seen in Fig. 6 and Fig. 7. Relatively low hydrogen selectivity and higher permeance compared with palladium-impregnated membrane can be explained by two reasons. First, nickel has a relatively lower hydrogen adsorption ability than palladium [Chai et al., 1994]. And, secondly, the nickel precursor sol used in the SVD step is larger than the palladium precursor sol, which will be discussed in next section.

In Fig. 8, the N<sub>2</sub> and H<sub>2</sub> permeances of the Pd and Ni impregnated membranes prepared by multi-step pore modification (i.e., sol-gel method, *in-situ* hydrolysis and SVD) were plotted as a function of the transmembrane pressure  $\Delta P$  at two different temperatures,  $T=298$  and 673 K. It could be seen that the gas permeances of those membranes were nearly independent of the transmembrane pressure up to 250 kPa and decreased as temperature was increased. It is obvious that the permeances should be independent of  $\Delta P$  and inversely proportional to  $\sqrt{T}$  when the Knudsen flow is predominant. As noted from Fig. 8, the rate of increase in the nitrogen permeance with the transmembrane pressure  $\Delta P$  was slightly larger than that of the hydrogen permeance. Indeed, Fig. 5 shows that the ideal separation factor of Pd impregnated membrane modified by SVD increased as  $\Delta P$  decreased. Furthermore, the ideal separation factor was larger than that which would be obtained by Knudsen flow alone up to  $\Delta P=250$  kPa. The latter is 3.74 for the binary system of hydrogen and nitrogen. It is noteworthy from Fig. 5 that the ideal separation factor be-

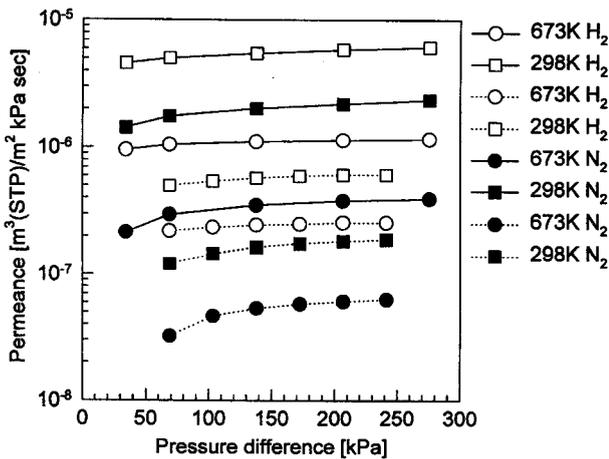


Fig. 8. Comparison of gas permeance between Pd and Ni impregnated membrane prepared by multi-step pore modification.

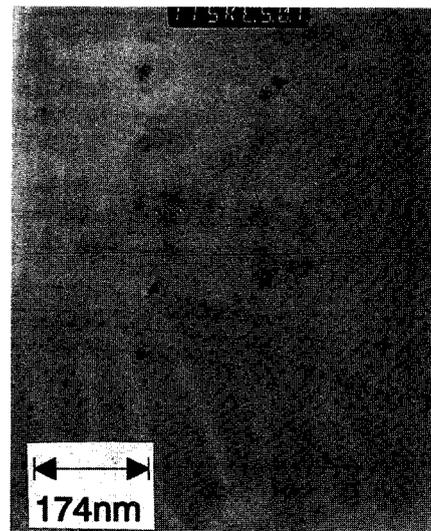
solid line ; Ni-impregnated membrane by multi-step pore modification, dotted line ; Pd impregnated membrane by multi-step pore modification

came much larger than the Knudsen limit, especially in the low transmembrane pressure limit. However, in Fig. 7, the Ni impregnated membrane modified by SVD exhibited relatively low separation factor. This is due to the fact that nickel is not so effective as palladium that provides the selective adsorption sites for hydrogen molecules within the pores. And, moreover, since the nickel precursor sol has much larger than palladium, SVD of nickel does not occur efficiently. Considering these effects, SVD and ESVD of nickel were carried out 3 and 2 times, respectively.

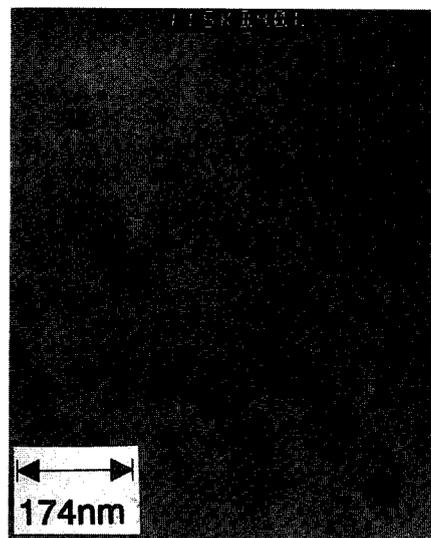
In this permeation test, the permeate side was maintained at atmospheric pressure which was almost equal to the hydrogen partial pressure at steady state. Therefore, considering that the present separation data were collected without using a carrier gas and in view of the largest scale in the membrane size (500 mm long), the membrane prepared in this study is of practical significance for practical application. For example, the present membrane can be utilized for hydrogen recovery from a waste gas stream, especially at high temperature (up to 673 K) and at large pressure difference (about 300 kPa).

## 2. Microstructure Changes during Pore Modification

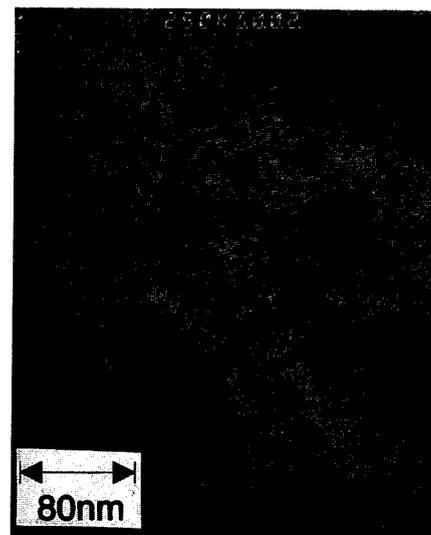
In the pore modification steps, the sols or precursors, which are to be used in pore modification step, must be smaller than the pore size or at least comparable in size to reduce the pore size of the membrane. In this modification step, there are two kinds of alumina sols (i.e., palladium impregnated  $\gamma$ -alumina sol and nickel impregnated  $\gamma$ -alumina sol) for the first step of the sol-gel process and precursor sol solutions (i.e., palladium (II) acetate or nickel (II) acetylacetonate dissolved in acetone) for the final step of the SVD or ESVD process. Each sample was analyzed by TEM, and the microphotographs were reproduced in Figs. 9 and 10. In Fig. 9, TEM micrographs of  $\gamma$ -alumina sol, Pd impregnated  $\gamma$ -alumina sol and Ni impregnated  $\gamma$ -alumina sol were shown. Although the average diameter of  $\gamma$ -alumina sol was 30-40 nm, Pd impregnated  $\gamma$ -alumina sol and Ni impregnated  $\gamma$ -alumina sol were



(a)

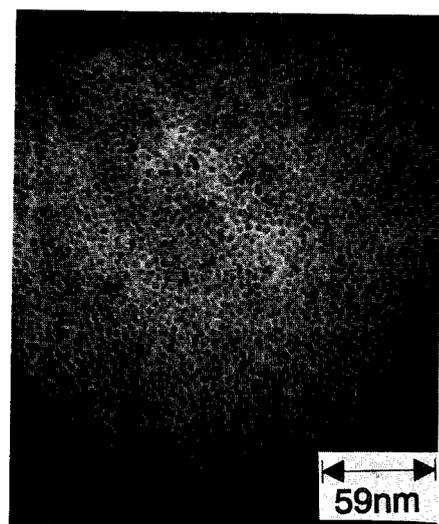


(b)

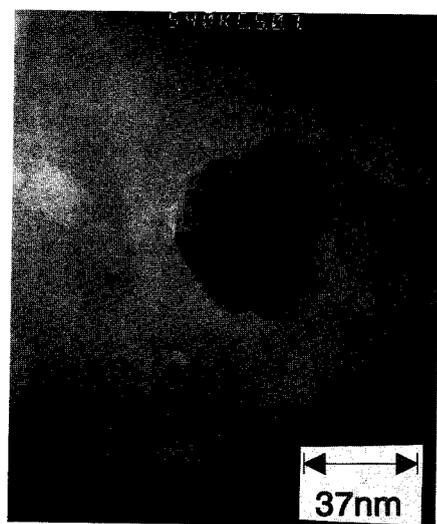


(c)

Fig. 9. TEM micrographs of (a)  $\gamma$ -alumina sol (b) Pd impregnated  $\gamma$ -alumina sol (c) Ni impregnated  $\gamma$ -alumina sol.



(a)

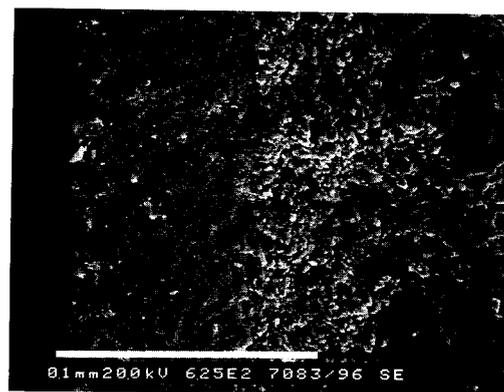


(b)

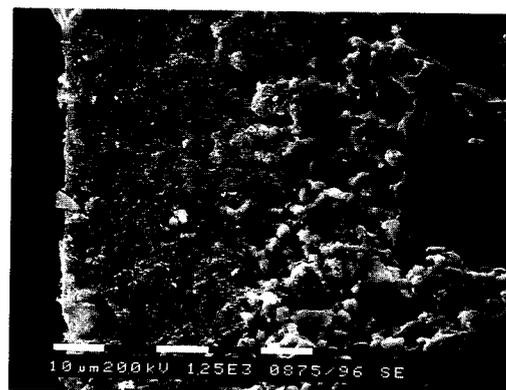
Fig. 10. TEM micrographs of (a) Pd precursor sol (b) Ni precursor sol used in SVD method.

60-80 nm in diameter as an aggregated form. However, since these sols had still smaller pores than the  $\alpha$ -alumina support, metal impregnated  $\gamma$ -alumina sol could penetrate into the pores of  $\alpha$ -alumina support and induce selective surface diffusion. The penetration of sols was also facilitated by maintaining the inner side of the support under vacuum. Fig. 10 showed the palladium precursor sol and nickel precursor sol used in the SVD method. Since Pd precursor sol had a diameter below 10 nm and Ni precursor sol was about 30-40 nm, premodified membrane pores (by sol-gel method and *in-situ* hydrolysis) could be effectively narrowed by SVD and ESVD method and induce surface diffusion. This could be confirmed by the permeation results reproduced in Figs. 4-7. Since Ni precursor sol was larger than Pd precursor sol, Ni-SVD was carried out only 3 times and Ni-ESVD was conducted 2 times while Pd-SVD was performed 5 times.

Cross-sections of Pd-impregnated and Ni-impregnated membranes prepared by multi-step pore modification were repro-



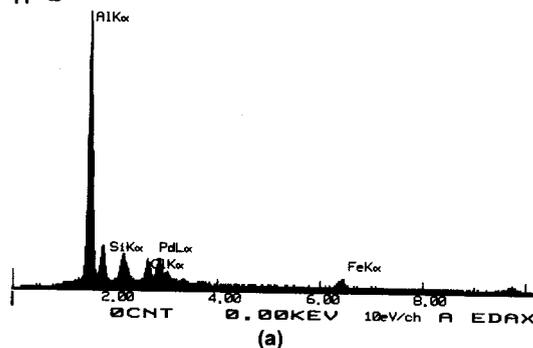
(a)



(b)

Fig. 11. SEM micrographs of cross-section of (a) Pd impregnated membrane (b) Ni-impregnated membrane by multi-step pore modifications.

12-DEC-95 08:37:31 EDAX READY  
RATE= 735CPS TIME= 150LSEC  
FS= 3427CNT PRST= 150LSEC  
A =



(a)

12-DEC-95 09:14:22 EDAX READY  
RATE= 271CPS TIME= 150LSEC  
FS= 1063CNT PRST= 150LSEC  
A =



(b)

Fig. 12. Distributions of (a) Si and Pd, (b) Si and Ni within membrane obtained by EDX.

duced in Fig. 11. Compared with the cross-section of the  $\alpha$ -alumina support in Fig. 1, it could be clearly seen that a selective separation layer was formed within the inner dense and intermediate layers. To observe the metal distribution within the membrane pores, energy dispersive X-ray analysis (EDX) was conducted and the results are shown in Fig. 12. It could be noted that the palladium and nickel were deposited within the membrane pore from Pd and Ni peaks. Around 2.0 KeV, Si peak was observed due to SiO<sub>2</sub> formed during the *in-situ* hydrolysis step.

### CONCLUSIONS

Metal-impregnated porous inorganic membranes for hydrogen separation were prepared by multi-step pore modification; namely, sol-gel method, *in situ* hydrolysis of TEOS and soaking and vapor deposition. Conclusions are as follows:

1. The membranes prepared by the three consecutive pore densification steps showed a moderate hydrogen selectivity at high temperature and at high transmembrane pressure ( $\Delta P$ ). The ideal hydrogen separation factor of Pd-impregnated membrane was above the Knudsen limit (3.74) up to  $\Delta P=250$  kPa.

2. The *in-situ* hydrolysis of TEOS and H<sub>2</sub>O induced effective pore densification. However, because of the relatively low hydrogen affinity of silica, the membranes driven by this method exhibited low hydrogen selectivity.

3. Additional modification of membrane surface by SVD contributed to improvement in surface diffusion at high transmembrane pressure ( $\Delta P$ ). That is due to the fact that particle size of palladium (II) acetate is very small and easily deposited onto the asymmetric porous membrane structure, which is formed at the palladium intermediate layer.

4. Ni impregnated membrane also showed high H<sub>2</sub> permeance, although its hydrogen selectivity was relatively low compared with the Pd-impregnated membrane. This is due to the fact that nickel is not so effective as palladium in providing selective adsorption sites for hydrogen molecules within the pores. And, moreover, the nickel precursor sol is larger than the palladium precursor sol.

### ACKNOWLEDGMENT

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