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Preparation of thin palladium composite membrane tube by a CVD technique and its hydrogen permselectivity

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Abstract

A thin and firmly deposited palladium membrane applicable to surface catalysis is attempted to be prepared. The technique and equipment developed in this study is based on chemical vapor deposition (CVD) under a forced flow, where due to a pressure difference applied between the outside and the inside of the support tube the chemical vapors enter into the porous layer of the support where they decompose. Palladium diacetate, $(CH_3COO)_2Pd$, was used as a palladium source. The tubular support made from α-alumina powder is porous and has an average pore diameter of 0.15 μm. The forced-flow CVD was carried out by heating according to a temperature program under regulated vacuum pressure. The palladium membrane thus obtained was as thin as 2–4 μm and had a good H_2/N_2 selectivity exceeding 5000.

Keywords: Palladium; Membrane; CVD; Hydrogen separation; Catalysis

1. Introduction

Application of hydrogen separation membranes is now being expanded. In particular, opportunities are there for being introduced in the polymer electrolyte fuel cell (PEFC) system because the PEFC needs very pure hydrogen without containing CO. The membrane performance required for such practical applications is to have a large hydrogen permeability. This means that a thinner membrane without any defects should be prepared. In general, as the membrane thickness becomes small the defect density increases, so that a technique in which the membrane layer grows while repairing defects would be desired. Palladium is considered the most promising material for hydrogen separation and purification. Many efforts have been made to establish preparation techniques for thin and defect-free palladium membranes such as electroless plating [1–6,20], electroplating [8–11], sputtering [3,7,12–13], chemical vapor deposition [14–15], and crystallization-decomposition [16]. Common problems in those techniques concern the difficulty of completing the preparation without any defects (pinholes). An attempt to overcome this problem has been made using, for instance, a combined electroless plating and osmosis [4], where osmosis allows metal ions to penetrate deeper into the porous support during electroless plating, so that thinner and more uniform films can be deposited. Most of the studies employed flat supports [3,5–7,9–13,15–16], where difficult sealing and housing problems, especially for assembling those into a membrane separator or a membrane reactor for high-temperature use, have to be solved before laboratory tests and practical applications. In this sense, as more favorable shapes for practical use are considered to be hollow fibers or tubes, more appropriate techniques for preparing thin and dense films on tubular supports should be developed.

Recently, as another innovative application of palladium membranes, an interesting reaction system has been proposed where benzene is selectively oxidized to phenol on the surface of a palladium membrane by oxygen species formed by reaction of oxygen with hydrogen permeating through the palladium membrane [17,18]. The success of this system depends on how thin and hydrogen-selective a palladium membrane could be prepared because as many oxygen molecules as possible should be activated to become oxygen radicals by utilizing the hydrogen permeating through the

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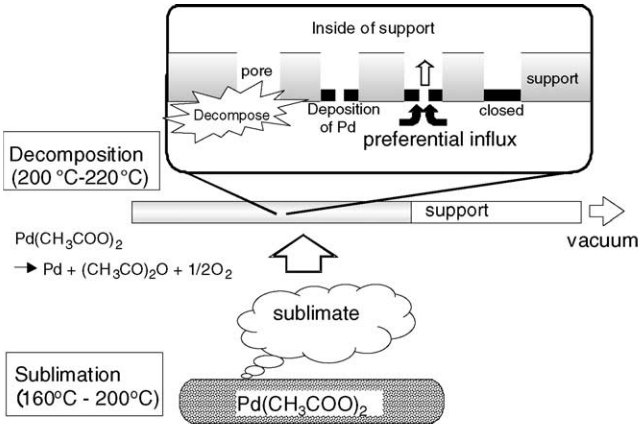

Fig. 1. Schematics of the preparation of thin palladium films using a forced-flow CVD technique.

palladium membrane [19]. For such a purpose, a thin, firm and pinhole-free palladium membrane is required.

The technique and equipment developed in this study is based on a chemical vapor deposition under forced-flow CVD [14], where due to a pressure difference applied between the outside and the inside of the support tube the vapors of a metal organic salt can enter the porous layer of the support and probably decompose anywhere at the support wall. The CVD therefore is expected to be the most appropriate method for preparing a composite palladium membrane tube. A schematic drawing to explain this idea is shown in Fig. 1. It can be said that the main feature of this method is that membrane formation proceeds with mending pinholes preferentially, and therefore a thinner membrane with less defects is likely to be obtained. In the forced-flow CVD, the sublimated vapor of the metal organic salt may flow into all pores of the support according to the fluid dynamics. If the Hagen–Poiseuille law can be applied to the flow through the pores, the volumetric flow rate is proportional to the fourth power of the pore diameter so that more organic vapor can be sucked into larger pores compared to smaller pores and then deposited on the pore wall. As far as this process continues all pores will be finally plugged with metallic deposits. Since the sublimated vapors no longer flow into perfectly plugged pores, it is expected that an efficient deposition becomes possible.

2. Experimental

Palladium diacetate, $(CH_3COO)_2Pd$, was used as a palladium source. In the forced-flow CVD process for palladium composite membrane preparation, it is very important that the sublimation and the successive decomposition of the palladium organic salt can occur efficiently. The two processes therefore must be phenomenologically analyzed and understood to enable a suitable design and operation of the CVD apparatus. However, the thermal behavior, such as sublimation and decomposition temperatures of palladium diacetate under reduced pressures, is not known very well. Therefore a thermal analysis of palladium diacetate was carried out using simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) equipment, which was connected to a vacuum control system as shown in Fig. 2. The pressure inside the TG-DTA equipment was controlled by adjusting the flow rate of argon gas with a needle valve.

The tubular supports made from α-alumina powder have pores of an average pore diameter of 0.15 μm with a porosity of 43%, an outer diameter of 3 mm, an inner diameter of 2.3 mm and a length of 100 mm. The CVD was carried out using a box-like apparatus (Fig. 3) where the palladium salt placed on the lower heating plate was heated by heater 1 according to a temperature program under regulated pressure. Heater 2 was used to regulate the temperature of the support tube. The pressure inside the CVD chamber was regulated by vacuum pump 2, whereas that inside the support tube was regulated by vacuum pump 1. The latter was always controlled to be lower than the former in order to maintain a forced gas flow from the outside to the inside of the support tube. More appropriate conditions for successful preparation

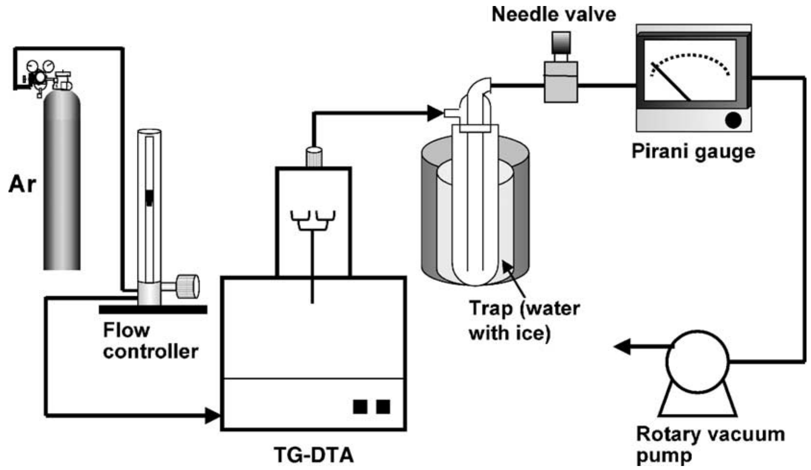

Fig. 2. Experimental set-up for thermal analysis under reduced pressure.

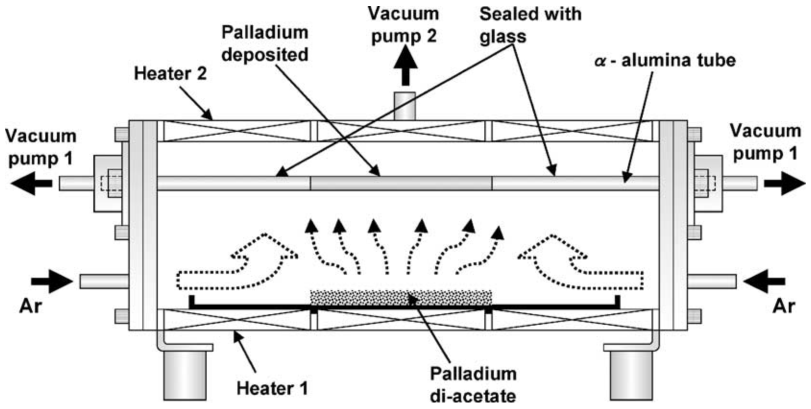

Fig. 3. Apparatus for preparing tubular palladium composite membranes by means of forced-flow CVD.

of thin and defect-free palladium layer onto the porous alumina support were examined.

The one-end closed membrane tube was set up in a shell-and-tube permeation cell made of stainless steel using a Swagelock fitting with a carbon ferrule. The test gas (H_2, N_2) was fed from the shell side while the flow rate of the permeate from the tube side was measured with a soap-film flowmeter.

3. Results and discussion

3.1. Thermal analysis of palladium salt

First, the TG-DTA results carried out at 2 K/min under a regulated pressure of 10 Pa are shown in Fig. 4. Although from the TG chart (weight loss) it seems difficult to distinguish between the sublimation and the decomposition processes, those are clearly seen to take place consecutively from the two peaks attributable to the endothermic phenomena in the DTA chart. A smaller peak is observed for the decomposition process; this is because most of the palladium diacetate has already sublimated. Such a result suggests that a more strict control of the temperatures of sublimation and decomposition in the CVD apparatus is required.

It can be assumed that the most sensitive factor for the sublimation is the ambient pressure that should affect the sublimated fraction of the precursor very much. Fig. 5 shows the sublimated fraction when the pressure varies from 1 to 0.01 bar. The sublimated fraction can be estimated from the initial weight of the palladium diacetate sample and the total weight loss using Eq. (2) in Fig. 6. It was found that only a few percent of the palladium diacetate sublimate at atmospheric pressure (10^5 Pa). The sublimated fraction, however, can be increased by decreasing the pressure inside the thermal analysis equipment (Fig. 2). If the temperature dependence of the sublimation pressure can be described by the Clausius–Clapeyron equation, the sublimation temperature will drop with decreasing pressure, and therefore sublimation will start to occur at lower temperature. In fact, an empirical relation was obtained that the sublimated fraction is inversely proportional to the logarithm of the sublimation pressure as shown in Fig. 5. Thus, it becomes clear that regulating the

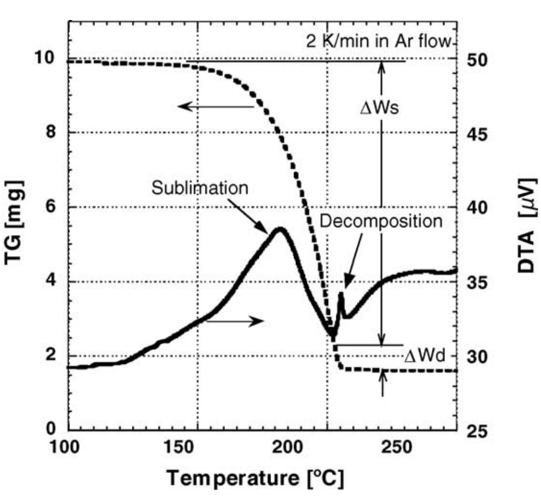

Fig. 4. TG and DTA chart for examining the thermal characteristics of palladium diacetate under reduced pressure of 10 Pa.

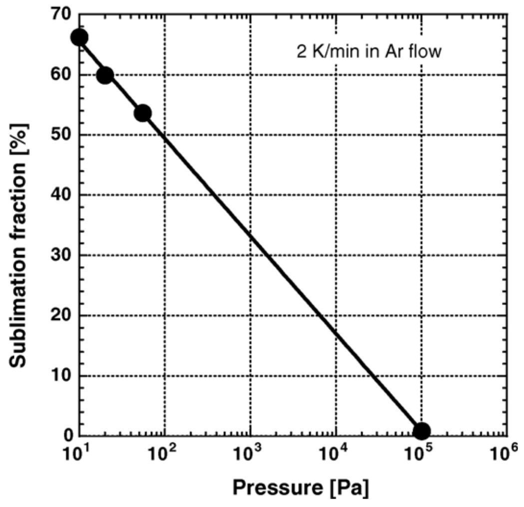

Fig. 5. Sublimated fraction as a function of the inside pressure of the TG-DTA apparatus.

The total weight loss can be given by the following expression.

$$\Delta W = \Delta W_d + \Delta W_s = \underbrace{W(1-x)\delta}_{\textbf{Decomp.}} + \underbrace{Wx}_{\textbf{Sublim.}} \qquad (1)$$

W : Initial weight of $(CH_3COO)_2Pd$ [g]
ΔW: change in weight [g]
x : sublimation fraction [-]
δ : theoretical weight loss only by decomposition, which is given by,

$$\delta = \frac{(CH_3COO)_2}{(CH_3COO)_2Pd} = \frac{118.11 g/mol}{224.51 g/mol} = 0.526$$

By arrangingEq. (1), the sublimation fraction can be estimated as follows.

$$\textbf{Sublimation fraction} \quad x = \frac{\frac{\Delta W}{W} - \delta}{(1-\delta)} \qquad (2)$$

Fig. 6. Estimation of the sublimated fraction from the total weight loss by thermogravimetry.

pressure to be lower is favorable for an efficient sublimation, which could occur before decomposition.

Next, the effect of the heating rate on the sublimated fraction was examined in the range of 2–5 K/min. Fig. 7 shows the results at a fixed pressure of 10 Pa, indicating that there is an optimum of the heating rate, that is, 4 K/min. This valuable information can be used to define the optimum operation conditions of the CVD apparatus.

3.2. Preparation of composite palladium membrane tubes by CVD

As a result of exploring the conditions to obtain palladium composite membranes with a good H_2/N_2 selectivity, it was found that the temperature and pressure inside the CVD chamber should be controlled as shown in Fig. 8. The temperature of the sublimation part ($(CH_3COO)_2Pd$ powder) was increased by two steps. For 30 min between the steps, as plotted in Fig. 8, the temperature of the sublimation part was kept constant to prevent the decomposition of the metal source before sublimation. The decomposition part (support tube) was heated up by one step at a constant rate, and then kept at constant temperature. The pressure inside the CVD chamber changed as indicated by the line in Fig. 8, where a large peak due to the sublimation followed by the decomposition is seen. On the other hand, the support-side pressure, which was produced by an increase of pressure due to the sublimation, is found to decrease with increasing chamber-side pressure, and finally becomes almost zero. This is because the pores of the support tube were sufficiently blocked by deposited palladium. One side of the two parts of the composite membrane sealed with a glass tube as illustrated in Fig. 3 was cut, plugged with glass, and photographed for Fig. 9. A SEM photo showing the cross-section of the composite palladium membrane is presented in Fig. 10. It can be seen that the palladium layer grows from the inside of the porous support, thereby increasing the adhesion between the metal film and the support. The one-side closed membrane tube thus obtained was 10 cm long and 3 mm in diameter (external surface area = 9.42 cm^2) and was used for gas permeation tests.

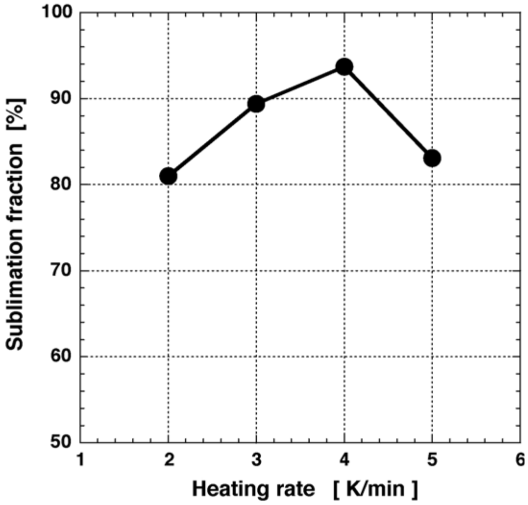

Fig. 7. Effect of the heating rate on the sublimated fraction.

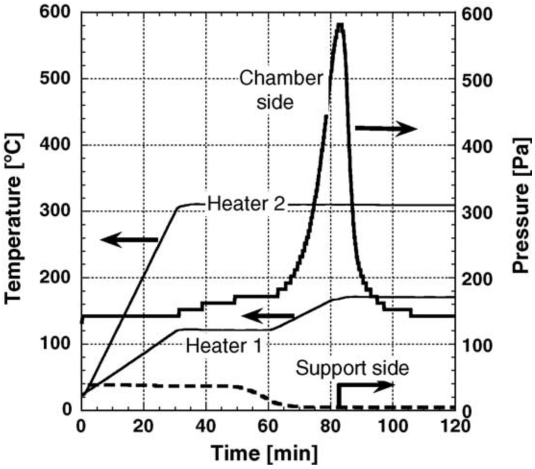

Fig. 8. Changes of temperature and pressure inside the CVD chamber during palladium film fabrication.

3.3. Gas permeation test

First, the hydrogen flow rate (273 K, 1 atm) across the membrane measured at 573 K is plotted against the difference of the square root of the up-stream pressure, P_h, and the down-stream pressure, P_l, in Fig. 11. A good linearity suggests that the atomic hydrogen produced on the membrane surface from the hydrogen molecule participates in the diffusion process as the rate-determining step. An extrapolation of the hydrogen flux at $P_h = 2$ bar and $P_l = 1$ bar gives a value of roughly 70 cm^3/cm^2/min, being one of

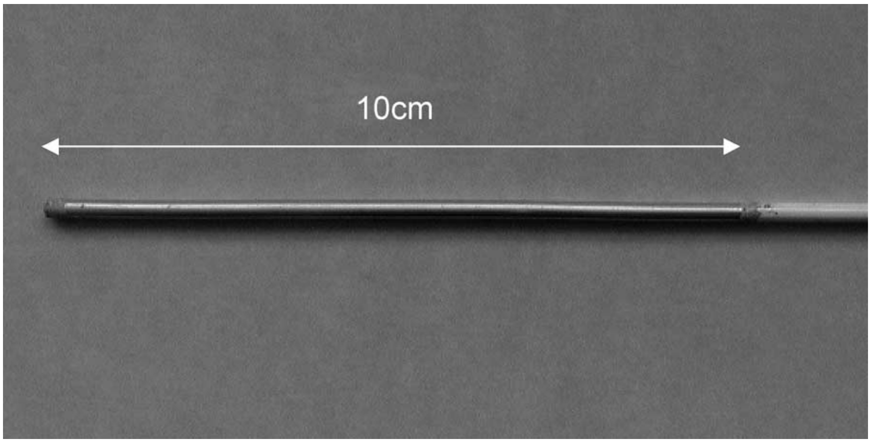

Fig. 9. Appearance of the palladium film deposited on a porous alumina tube by the forced-flow CVD technique.

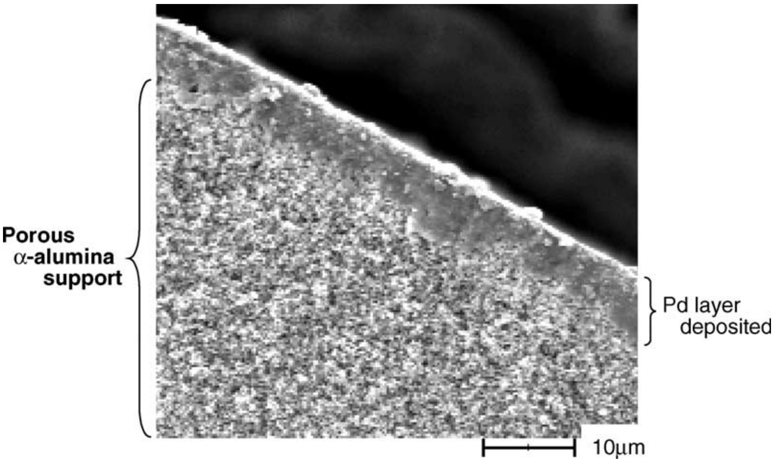

Fig. 10. Cross-sectional SEM view of the composite palladium membrane.

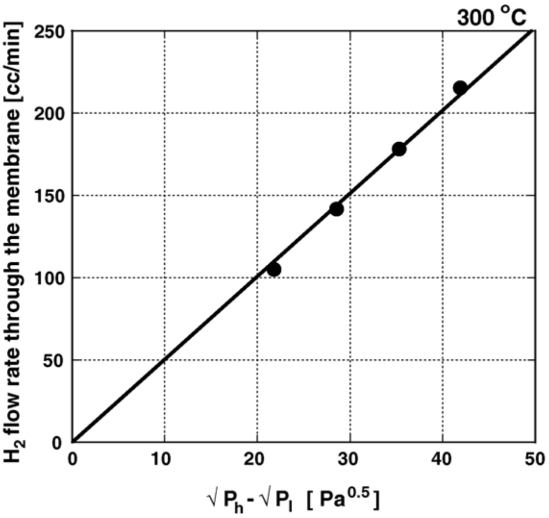

Fig. 11. Hydrogen flow rate correlated against the difference between the square root of up-stream pressure, P_h, and that of down-stream pressure, P_l (300 °C).

the highest fluxes reported for composite palladium membranes developed so far.

Fig. 12 shows the single gas fluxes of N_2 and H_2 measured at $P_h = 1.3$ bar and $P_l = 1$ bar in the range of 250–300 °C. At these conditions, the palladium membrane should be stable against hydrogen exposure because of being within the α-phase region according to the pressure–composition isotherm for the palladium–hydrogen system [21]. The N_2 flux was very small and was found to decrease with increasing temperature. This is because a small number of pinholes remain, through which gas molecules can pass according to a Knudsen flow mechanism, that is, the permeation rate, Q, through these pinholes becomes as follows:

$$Q = \frac{K}{\sqrt{MT}}(P_h - P_l) \quad (1)$$

where M is the molecular weight, T is the absolute temperature, and K is the proportionality constant, respectively. Eq. (1) means that the N_2 leak decreases as temperature goes up: this is supported by the experimental results. On the

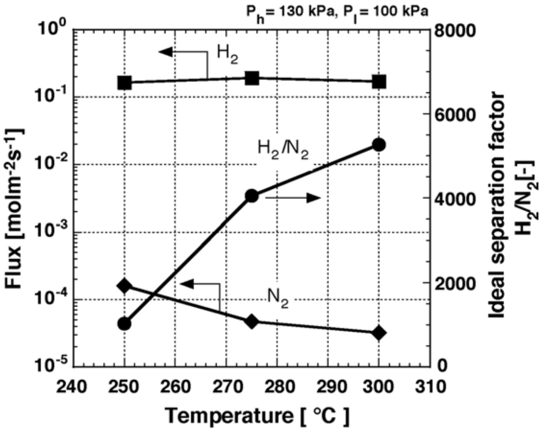

Fig. 12. Temperature dependence of the H_2 and N_2 flux and the ideal H_2/N_2 separation factor.

other hand, hydrogen shows a large flux of 0.1–0.2 mol/m^2/s with high ideal separation factors for H_2/N_2 over 5000 at 300 °C. With the usual value of 3.74 for ideal Knudsen selectivity for permeation of H_2 and N_2, it can be estimated that only 0.075% of the total hydrogen flux at 300 °C is through these pinholes.

Finally, the hydrogen permeance and the H_2/N_2 selectivity of the composite palladium membranes prepared by electroless-plating (ELP), sputtering (SPUTT), chemical vapor deposition (CVD) and electroplating (EP) in literature [2–15] are compared in Fig. 13. When the reported H_2/N_2 selectivity was infinite, a value of 10^5 was used for simplicity to represent these data points in Fig. 13. The data from literature were measured in the range of 473–723 K with different transmembrane pressures. Regarding the pressure, the permeance was converted to that per 1 bar of transmembrane pressure, but no correction was made for the temperature due to the difficulty and uncertainty of such a correction. Therefore, the correlation in Fig. 13 should be regarded as a rough comparison. Nevertheless, since one can know the present status concerning the performance of composite palladium membranes prepared by different methods, it is thought to be useful and provides some information for setting a target. Roughly speaking, it seems that a composite palladium membrane with better performance (both larger permeance and higher H_2/N_2 selectivity) can be obtained in the following order: electroless-plating = electroplating > chemical vapor deposition. On the other hand, regarding the sputtering, not enough data are available for an impartial evaluation. Because the CVD method developed in this study has been employed by fewer investigators compared to the electroless-plating and electroplating methods, further improvement in the CVD technique will be expected in the future.

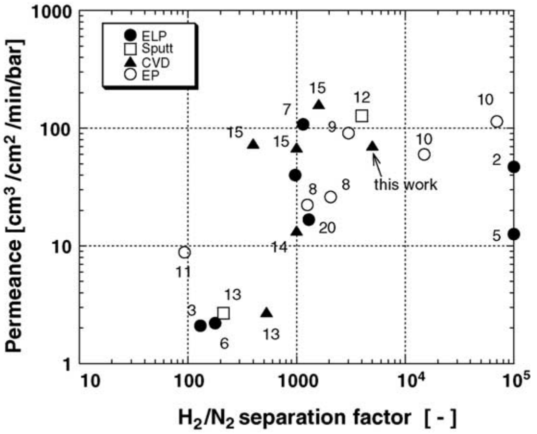

Fig. 13. A comparison among H_2 permeances and H_2/N_2 ideal separation factors from literature (ELP: electroless-plating; SPUTT: sputtering; CVD: chemical vapor deposition; EP: electroplating).

4. Conclusions

A chemical vapor deposition technique (CVD) using forced flow through the porous support was applied to prepare thin palladium composite membrane tubes with a high hydrogen permselectivity for application in various catalytic reactions as well as for hydrogen purification. First, it was shown from the results of a thermal analysis that regulating the consecutive sublimation and decomposition processes of palladium diacetate as a palladium source is very important because the sublimation should take place before decomposition and both are strongly affected by temperature and pressure. By controlling both temperature and pressure inside the CVD apparatus properly, a membrane tube covered with a thin palladium layer of a few micrometers on a porous alumina support could be successfully prepared. As a result of gas permeation tests, it was found that the palladium membrane tube has a large flux of 0.1–0.2 mol/m^2/s with a large ideal separation factor for H_2/N_2 over 5000 at 300 °C.

Acknowledgments

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