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STATE-OF-THE-ART OF SUPPORTED METAL MEMBRANES FOR GAS SEPARATION

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Summary

An extensive review of current research on supported metal membranes, especially for hydrogen separation is presented. Membrane material, methods for fabrication of thin metal layers on porous substrate and gas transport mechanisms through different types of membranes are summarized followed by a discussion of problems with supported metal membranes. Further developments in this research field are expected to the application for membrane reactor system as one of the environmentally-friendly chemical processes.

1. Introduction

Considerable effort has been exerted on the development of new types of inorganic membranes for gas separation at high temperatures and their application to a membrane reactor[1-5]. Inorganic membranes thus far reported can be classified into two groups from the viewpoint of the raw material: ceramic membranes and metal membranes. Various unique ceramic membranes, for example, not only porous ones with a narrow pore size distribution, such as titania, zirconia, alumina, glass, molecular sieving carbon, silica and zeolite, but also dense ones without any pores or defects such as perovskite, bismuth and solid-electrolyte, have been developed and commercialized. For information on the state-of-the-art of ceramic membranes, published review articles should be consulted[6]. On the other hand, metal membranes, in most cases self-supporting dense palladium-based membranes with a thickness greater than 0.1 mm, for hydrogen separation became unattractive by the 1980s because of their disadvantages of cost, low permeance and low chemical stability. These drawbacks limited their industrial usage only to small-scale hydrogen purification equipment using dense palladium-alloy membranes for electronic, metallurgic, and fine chemical industries and a fusion fuel purification process to separate hydrogen isotopes.

Though reduction in the thickness of metal membranes is effective for improvement of their hydrogen permeance, its reduction has been limited to a certain degree because of insufficient mechanical strength. If a thin metal layer can be supported on a mesoporous ceramic support with sufficient mechanical strength, however, it will be possible to reduce the thickness of the metallic layer. The resulting membranes are called supported metal membranes or metal/porous-ceramic composite membranes. From such a viewpoint, Kikuchi and Uemiya's group(7) first developed a composite membrane consisting of a thin, dense palladium film supported on a glass or alumina ceramic tube with minute, controlled pores of 200-300 nm in diameter by an electroless-plating technique. During the same period, similar attempts were reported by Sakai et al.(8,9) and Konno et al.(10) The distinctive feature of the composite membrane of Kikuchi and Uemiya's group, compared with the other developing composite membranes, was the maintenance of the inherent characteristic of palladium, namely, complete permselectivity for hydrogen permeation, due to lack of any remaining pinholes or cracks. Since the first attempt of preparing palladium composite membrane giving complete permselectivity for hydrogen, much effort has been devoted to the preparation of supported metal membranes, especially for hydrogen separation. Here, the current research concerning them is reviewed.

2. Membrane Materials

2.1 Metal as effective layer for gas separation

Since Graham(11) first discovered that palladium absorbs a substantial amount of hydrogen, much attention has been focused on metal-hydrogen systems such as measurements regarding the phase diagram, solubility, and diffusivity. Recently, many types of metal alloys have been applied to gas separation membranes and hydrogen storage metals.

A practical metal membrane was first invented by Hunter(12), who patented palladium-alloy membranes in 1956. The first commercial application of a metal membrane was hydrogen purification using a palladium-silver alloy membrane by Johnson Matthey in 1964(13). The superiority of palladium and silver alloy, particularly at the silver content of 23 wt%, was attributed to excellent hydrogen permeability as well as the suppression of hydrogen embrittlement by the transformation of palladium hydride from the α- to α'-phases. This transformation is inevitable when pure palladium faces hydrogen below 573 K, as predicted from the palladium-hydrogen phase diagram shown in Fig. 2-1(14). Making the alloy of palladium with silver, however, can lower the critical temperature at which the α- and α'-phases of palladium hydrides co-exist, the so

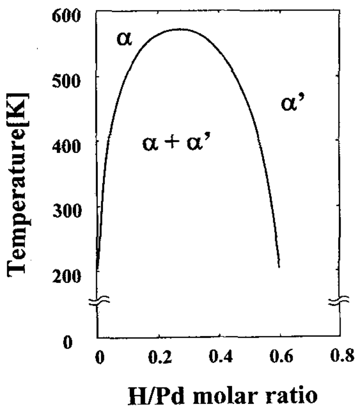

Fig. 2-1 Palladium-hydrogen phase diagram[14] (Reproduced with the permission of Springer-Verlag)

called "spinodal temperature." The operating temperature of a self-supported palladium-silver alloy membrane is suitable for hydrogen permeation at around 700 K, because the growth of the alloy grain becomes remarkable above 673-773 K, resulting in the decomposition of the metal layer along the grains' boundary[15]. It has been reported that an SS-supported palladium membrane can withstand brief operation at temperatures up to 773-823 K, but the suitable temperature is in the range between 573-723 K[16]. Generally group-VIII metals are also added to commercially available palladium-silver alloy membranes in order to avoid grain growth[15]. Though more complicated, multi-component palladium-based alloys are synthesized and currently applied as a separation medium, this purification technology is still standard for ultrahigh pure hydrogen production.

Table 2-1 summarizes the history of the development of supported metal membranes for hydrogen separation. Here, some examples of catalytic membrane reactors as efficient contactors of reactant gas with catalyst may be included. The base metal of most supported metal membranes is palladium or palladium-silver alloy. The others belong to the VIII-group metals or their alloys, including $LaNi_5$ as a hydrogen storage metal[17], except for one example of Ag/Nafion composite membrane for oxygen separation[70].

In most cases where a palladium layer is thicker than micrometers in order, hydrogen permeance is inversely proportional to the thickness. Therefore, it is no exaggeration to say that the history of the development of supported metal membranes has been the challenge to obtain sufficient thinness of a metal layer without compromising its integrity, namely the fabrication of

TABLE 2-1 History of development of supported metal membranes

Metal	Support (porous)	Thickness [μm]	Preparation technique	Inventor	Year	Ref.
$LaNi_5$	Stainless-steel(SS)	10	Flush evaporation	Adachi et al.	1984	17)
Pd	Nafion	Fine particle	Ion exchange	Sakai et al.	1985	8)
Ag	Nafion	Fine particle	Ion exchange	Sakai et al.	1987	9)
Pd	Glass	13	Electroless-plating	Kikuchi & Uemiya	1988	7)
Pd	Anodic alumina	---	Catalytic decomposition of Pd complex	Konno et al.	1988	10)
Pd	α-Alumina	4.5	Electroless-plating	Uemiya & Kikuchi	1990	18)
Pd-Cu	Glass	18.9	Electroless-plating	Uemiya & Kikuchi	1991	19)
Pd-Ag	Glass	21.6	Electroless-plating	Uemiya & Kikuchi	1991	19)
Pd-Ag	α-Alumina	5.0-6.4	Electroless-plating	Uemiya & Kikuchi	1991	20)
Pd	Silver	5.0	Electroless-plating	Govind & Atnoor	1991	21)
Pd, Pt, Ru, Rh	γ-Alumina	Fine particle	Sol-gel (sol including metal-salt)	Chai et al.	1992	22)
Pd	TiH_2/α-alumina	20	Reactive ion plating + electrodeposition	Meunier and Manaud	1992	23)
Ni	TiH_2/α-alumina	15	Reactive ion plating + electrodeposition	Meunier and Manaud	1992	23)
Pd	TiO_2/alumina	2.1	Electroless-plating	Uemiya et al.	1992	24)
Pd-In-Ru	SS	1.5	Magnetron sputtering	Gryaznov et al.	1993	25)

Metal	Support (porous)	Thickness [μm]	Preparation technique	Inventor	Year	Ref.
Pd-Ru	SS	10	Magnetron sputtering	Gryaznov et al.	1993	25)
Pd-Ru	$MgO-Y_2O_3$	10	Magnetron sputtering	Gryaznov et al.	1993	25)
Pd	Alumina	11.4-20.0	Electroless-plating	Collins & Way	1993	26)
Pd-Ag	SS	---	Electroless-plating	Shu et al.	1993	27)
Pd-Ag	α-Alumina	1.5-2.0	Spray pyrolysis	Li et al.	1993	28)
Pd	Vycor glass	5-8	Magnetron sputtering	Gobina & Hughes	1994	29)
Pd-Ag	Vycor glass	6	Magnetron sputtering	Gobina & Hughes	1994	30)
Pd	α-Alumina	3.3	CVD	Uemiya et al.	1994	31)
Pd	α-Alumina	ca. 2.0	CVD	Yan et al.	1994	32)
Pd-Ag	Polymer	0.025-0.1	Magnetron sputtering	Athayde et al.	1994	33)
Pd	Alumina	ca. 20	Electroless-plating	Deng et al.	1994	34)
Ni	γ-Alumina	Fine particle	Sol-gel (sol including metal-salt)	Chai et al.	1994	35)
Pd	Alumina	Fine particle	Sol-gel (sol including metal-salt)	Lee et al.	1994	36)
Pd	SS	14.1-20.3	Electroless-plating	Shu et al.	1994	37)
Pd	Vycor glass	0.8-3.5	Electroless-plating	Yeung et al.	1995	38)
Pd	γ-Alumina	---	Sol-gel (metal-coated sol)	Zhao et al.	1995	39)

(continued)

TABLE 2-1 (Continued)

Metal	Support (porous)	Thickness [μm]	Preparation technique	Inventor	Year	Ref.
Pd	γ-Alumina	0.1	RF-Magnetron sputtering	Basile et al.	1995	40)
Pd	γ-Alumina	0.06-0.5	RF-Magnetron sputtering	Jayaraman et al.	1995	41)
Pd-Ag	γ-Alumina	0.25-0.5	RF-Magnetron sputtering	Jayaraman & Lin	1995	42)
Pd	α-Alumina		Electroless-plating (under osmotic pressure)	Yeung & Varma	1995	43)
Pd-Ag	α-Alumina		Electroless-plating (under osmotic pressure)	Yeung & Varma	1995	43)
Pd	Glass	0.05-5.0	Magnetron sputtering	Bryden & Ying	1995	44)
Pd, Pt, Cu, Ni	γ-Alumina	Fine particles	Sol-gel	Deng et al.	1995	45)
Pd	γ-Alumina	0.5	CVD	Xomeritakis & Lin	1996	46)
Pd-Ag	Ceramic	7.5	---	Booth et al. (Johnson Matthey)	1996	13)
Pd	SS	6	Shot peening + Electroless-plating	Jemaa et al.	1996	47)
Pd-Ag	TiN-SS	ca. 17	Electroless-plating	Shu et al.	1996	48)
Pd	modified alumina	---	Electroless-plating	Li et al.	1996	49)
Pt	α-Alumina	2.2-2.9	Electroless-plating	Uemiya et al.	1997	50)

Metal	Support (porous)	Thickness [μm]	Preparation technique	Inventor	Year	Ref.
Pt	α-Alumina	5.8	CVD	Uemiya et al.	1997	51)
Ru	α-Alumina	3.2	CVD	Uemiya et al.	1997	51)
Pd	Alumina	10	Solvated metal atom deposition	Barbieri et al.	1997	52)
Pd-Ag	Alumina	10	Electroless-plating	Barbien et al.	1997	52)
Pd-Ag	γ-Alumina	0.1-1.5	CVD, Sputtering	Xomeritakis & Lin	1997	53)
Pd-Ag	SS	30	Electroless-plating	Garnier et al.	1997	54)
Ni-P	Ceramic (SiO_2)	14-20	Electroless-plating	Liu et al.	1997	55)
Pd	γ-Alumina	0.72-2.1	Electroless-plating	Shu et al.	1997	56)
Pd, Pd-Ag	γ-Alumina	---	MOCVD	Meng et al.	1997	57)
Pd-Fe	---	---	Pulsed electrodeposition	Bryden & Ying	1997	58)
Pd-Y	Bronze Phosphorus nickel	3	DC magnetron sputtering	M.L. Trudeau et al.	1997	59)
Pd-M*	γ-Alumina	Fine particles	Sol-gel	CaO et al.	1997	60)
Pd	γ-Alumina	0.5-5	MOCVD	Xomeritakis & Lin.	1998	61)
Pd	SS	19-28	Electroless-plating	Mardilivich et al.	1998	16)
Pd	γ-Alumina	1	Electroless-plating	Zhao et al.	1998	62)

* M indicates Ru, Rh, Ni, Ag.

(continued)

TABLE 2-1 (Continued)

Metal	Support (porous)	Thickness [μm]	Preparation technique	Inventor	Year	Ref.
Pd-Ag	Alumina	1.3	Electroless-plating	Yu et al.	1998	63)
Pd-Ag	γ-Alumina	0.163-0.525	Magnetron sputtering	McCool et al.	1998	64)
Pd-Ag	Alumina	15-20	Electroless-plating + electroplating	Yang et al.	1998	65)
Ni-Ru-P	γ-Alumina		Electroless-plating	Wu et al.	1998	66)
Pd-Ag	α-Alumina	ca. 41	Electroless-plating	Kokugan et al.	1998	67)
Pd-Ni	Anodic oxidized alumina	ca. 1	Sputtering + Electroplating	Itoh et al.	1998	68)
Ir	α-Alumina	17	CVD	Kajiwara & Uemiya	1999	69)
Rh	α-Alumina	8	CVD	Kajiwara & Uemiya	1999	69)

defect-free or defect-poor metal layer with a thickness on the micrometers order, preferably submicron order. The hydrogen-permeable metals introduced in Table 2-1 do not have high mechanical strength and ductility by themselves. Thus, much effort has been devoted to the development and establishment of potential routes to form a thin metal layer on a porous substrate.

Except for pure palladium and palladium-silver alloy, group Va metals of tantalum, vanadium, and niobium71-73), various palladium-based alloys (Pd-Cu with bcc phase14), Pd-Ce74,75), Pd-Y74-76), Pd-Y-In(Sn, Pb)77), Pd-Gd78), Pd-Y(Gd)-Ag79), and Pd-Ta80)), and amorphous metals such as Pd-Si81), have been emphasized as new potential metals for hydrogen separation and purification from a gas mixture. The hydrogen permeabilities of various pure metals and palladium alloys are shown in Figs. 2-282) and 2-374), respectively. Though tantalum, vanadium, and niobium give 10-10^5 times greater values than palladium, oxide layers are easily formed on both surfaces of such metals even under ultrahigh vacuum conditions and consequently excellent hydrogen permeance cannot be preserved71,72). In-situ coating of an ultra-thin palladium or platinum layer was reported to be an effective countermeasure for the oxidation; however, no development of supported membranes has been reported probably due to the requirement of a complicated preparation procedure. Besides such metals for hydrogen separation, dense silver is known to be permeable only to oxygen. Nevertheless, utilization of silver membranes will be restricted only to oxygen separation at relatively low temperatures, which will be unsuitable for the application to a catalytic membrane reactor for various oxidations of hydrocarbons and so on, because of its low melting temperature of 1,235 K.

2.2 Porous substrate as supporting material

Materials used as supporting substrates are also summarized in Table 2-1. Porous glass, alumina, and stainless steel have been selected in most cases due to their commercial availability. Both disk and tube shapes were generally used; however, only tubular-type supported metal membranes can be applied to a membrane reactor without any difficulty.

Until the early years of the 1990s, two types of porous membranes were mainly used as supports in basic studies of supported metal membranes: one was a porous glass such as porous Vycor glass (silica glass) with symmetric structure and a mean average pore size of 4 nm, supplied by Corning Glass Works, and the other was a microfiltration (MF) porous ceramic such as porous α-alumina with asymmetric multilayer structure, for example Membralox, supplied by SCT/U.S. Filter. Porous Vycor glass, however, has a thickness of ca. 1 mm with a symmetric structure, thereby giving large resistance to gas permeation through its micropores, compared with that through a metallic layer. Furthermore, the surface was so smooth that a fabricated metal film

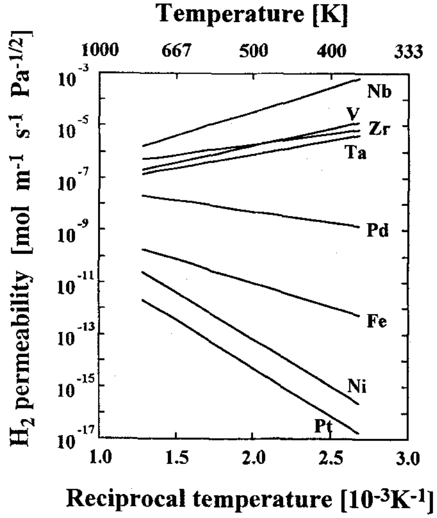

Fig. 2-2 Hydrogen permeabilities of various pure metals[82]

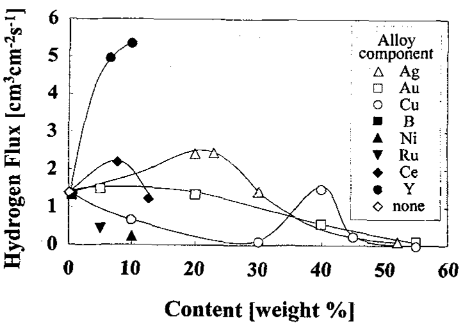

Fig. 2-3 Hydrogen permeabilities of various palladium-based alloys[74]

with a few micrometers in thickness was easily stripped off due to the loss of an anchor effect, which supplies a mechanically assisting bond between the metal film and porous support just like the fluke of an anchor. Appropriate roughness is necessary for utilization as the support of a metal layer.

Another type of porous glass material made of SiO_2, Al_2O_3, and B_2O_3 was also used for supported palladium membranes. Uemiya et al.[7,19] formed a palladium layer on the porous glass with 200-300 nm in mean pore size, composed of 75-80% SiO_2, 4-6% Al_2O_3, and 10-12% B_2O_3 supplied from Ise Chemical Industries Co. Ltd. This support gave an excellent anchor effect and adherence. Nevertheless, sufficient thermal and mechanical durability was scarcely obtained as a metal support usable at high temperatures for catalytic reactions, namely, the maximum operating temperature is 823 K, and in some cases the glass was broken at the sites sealed by a gas-tight O-ring.

On the other hand, porous ceramic supports give good adherence as well as sufficient mechanical strength. Their pore sizes, however, were large compared with that of the porous glass, typically in the microfiltration range of 0.1-5.0 μm in average pore size. A dense palladium film of 4.5-μm thickness was critical to cover the entire surface of this support without any defect such as a crack or pinhole and to gave almost 100% permselectivity for hydrogen, when prepared by an electroless-plating technique[20)]. Furthermore, their structure is complicated; typical porous alumina with the effective layer of 200 nm in mean pore size consists of three layers, thereby some pinhole or intolerable roughness can be observed at the top layer, resulting in the fatal defect of a metal layer.

In order to decrease the critical thickness of a metal layer, surface modification or coating of a supporting substrate is required. In general cases using ceramic supports prepared by a sol-gel derived dip-coating technique, a decrease in the grain size of sintered particles for the top layer leads to a decrease in the effective mean pore size and surface roughness. In fact, as shown in Table 2-1, mesoporous γ-alumina (mean pore size, ca. 5 nm) supported on microporous α-alumina has been realized by the remarkable recent progress of a sol-gel modification technology. However, it is difficult from present collected findings to declare that this support is most suitable as a support for metal membranes. Further information will be necessary on kinetics, especially about the rate-determining step for hydrogen permeance, as well as adhesion between the metal layer and support surface, relating to surface roughness, homogeneity and chemistry.

Recently, porous stainless steel (PSS) has been the focus because of its mechanical durability, its thermal expansion coefficient close to that of palladium, and the ease of gas sealing. The fatal shortage of PSS supports is the alloy formation with a metal layer at relatively high temperatures, leading to degradation of hydrogen permeability. To prevent the alloy formation, a diffusion barrier of TiN with a thickness of about 0.1 μm was formed on the surface of a 316L PSS support by a sputtering technique[48)]. Other materials, for example, porous silica, tungsten, tantalum oxide, magnesia, zirconia, and alumina were used as a diffusion barrier[83, 84)].

Modification of a PSS support was investigated to reduce the thickness of a palladium film. Jemma et al.[47)] performed a shot peening treatment on the surface of a PSS to modify its surface pore size. From the SEM observation of the morphology of the original and treated PSSs, it was observed that the surface pore diameter was decreased from 5-6 μm to about 1 μm. The thickness of the resulting membrane was 6 μm. Furthermore pretreatment of PSS is important to prepare a defect-free supported palladium membrane. Mardilovich et al.[16)] emphasized mechanical treatment, cleaning in an ultrasonic bath with alkaline solution below 333 K, and complete rinsing before an electroless-plating procedure.

Itoh et al.[85)] prepared tubular anodic aluminum oxide membranes with straight pores. These membranes had a thickness of 35-45 mm, a pore diameter of 20-50 nm and $6\mathrm{x}10^{13}$-$11\mathrm{x}10^{13}$ straight pores per square meter and are applicable as a support for metal membranes.

Table 2-2 summarizes the thermal stability of the reported membrane materials[6)]. The upper temperature limits of the porous membranes depend on the material, atmosphere and pore characteristics such as porosity and pore diameter. Macroporous α-alumina membranes have the superior upper temperature limit of 1,573 K because α-alumina is the most thermodynamically-stable form. On the other hand, in the case of a mesoporous γ-alumina membrane with a pore size of 4 nm, its permeability was scarcely affected below 673 K, but was drastically changed at 773-873 K. The suitable operating temperature of developed supported pure palladium membrane may be around 673 K from the previous considerations of the grain growth of palladium, hydrogen embrittlement, and heat resistance of supporting material, especially with micropores.

3. Fabrication of thin metal layer

3.1 Membrane structure

According to the structure of the metal layer effective for gas separation, supported metal membranes so far reported can be divided into four types, as shown in Fig. 3-1, based on modified grouping proposed by Kikuchi[86)] and Zhao et al.[39)]. Type 1 membranes have the structure of a thin metal layer supported on the surface of a porous substrate. Exactly speaking, these membranes have two different modes of metal layer formed: porous structure in Type 1-a and dense structure in Type 1-b. In Type 2, the metal layer is formed on the pore walls of a porous support. Type 3 means that a microporous ceramic layer is formed on the surface of a support. Type 3 is divided into two modes based on the difference in the structure of the supporting layer: metal particles are finely dispersed inside the pores of a supporting layer in Type 3-a, and metal-coated particles are sintered on the surface of a support to form a supporting layer in Type 3-b. Most of the supported metal membranes belong to Type 1. Recently, some research groups attempted to prepare Type 2 composite membranes. The merit of this type exists in the decrease in the essential amount of metal for plugging the pores, resulting in the promotion of gas permeation and improvement in the mechanical strength of the metal layer.

TABLE 2-2 Thermostability of supporting materials[4)]

Material	Upper temperature limit [K]	
	Oxidizing atmosphere	Reducing atmosphere
Stainless steel	673	813
Inconel	863	1,083
Hastelloy X	1,053	1,203
γ-alumina	673	673
Zirconia/titania	623	623
Alumina/titania	673	673
Alumina	973	973
Carbon	---	438

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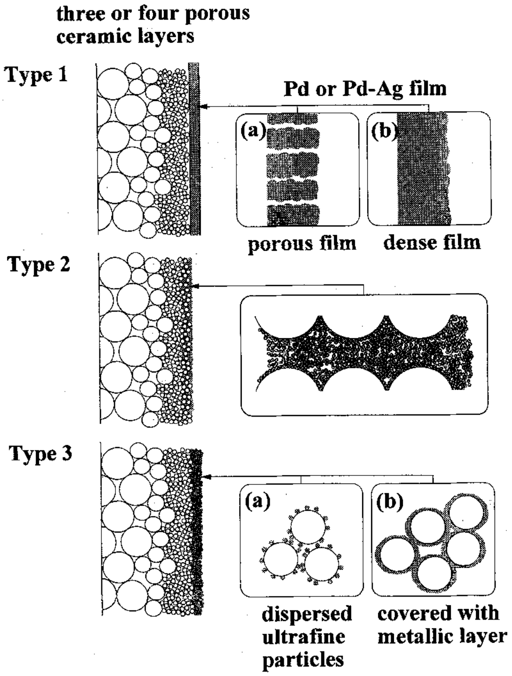


Fig. 3-1 Classification of supported metal membranes based on structure of metal layer effective for gas separation

3.2 Preparation and fabrication method

Several techniques are available to reduce the thickness of palladium film; for example, chemical vapor deposition (CVD), physical vapor deposition (PVD) such as evaporation and sputtering, electroplating, electroless-plating, spray pyrolysis, and so on. Refer to the general description of fabrication methods in review articles and books[4, 6,87,88).

3.2.1 Rolling

Commercially available metallic foils are often fabricated by the cold rolling method[2). A metal ingot is made at a high temperature, for example using an electric-arc furnace. It is then forged and pressed, followed by repeated cold rolling and annealing to reach a desired or critical thickness. The merits of this technique may be simplified procedure, high productivity, and reliability as one of the current manufacturing processes of metal plates, sheets, and foils on a commercially large scale. Thus, membrane manufacturers maybe prefer this reliable technique for commercial-scale production of supported metal membranes, compared with thin-film fabrication techniques introduced below.

Yamauchi et al.[15) reported in the 1970's that the critical thickness of palladium film without any defect or pinhole was 60 μm for the tubular type or 30 μm for the sheet type. According to the review article of Shu et al.[2), however, palladium or palladium alloy with a thickness under 1 μm can be prepared using a special rolling technique developed in the 1980's. A Japanese company is now investigating the application of this technique to develop various supported membranes of palladium binary, ternary, or muliticomponent alloy systems, which will be applicable to a membrane reactor for hydrocarbon dehydrogenation.

3.2.2 Electroless-plating

Electroless-plating is a method of metal plating by autocatalytic chemical reduction of the corresponding metal ions with simultaneous oxidation of a reducing agent[89). Thus, this technique can also be applied to the formation of metal coating even on a non-conductive support such as porous ceramic and glass. The application of this technique, however, is limited to metals exhibiting the high-reduction activity of corresponding metal ions such as Ni, Co and precious metals, compared with that of proton, based on the theory of ionization tendency. Furthermore, autocatalytic reaction, namely continuous reduction of metal ions on deposited metal, should proceed for the purpose of forming a metal layer with a desired thickness. Palladium has sufficient autocatalytic activity; thereby, electroless-plating becomes the most popular technique for the preparation of supported palladium-based membranes.

In practical use, the control of the reaction between metal ions and reducing agent is required not only to form a metal layer on the desired part of a support, but also to avoid spontaneous decomposition of electroless-plating solutions and to prolong their life. Therefore, electroless-plating solutions so far reported include all or parts of a complexing agent, a pH-buffer or control agent, an additive such as a brightener for the resulting metal surface or a stabilizer, except for a metal salt and a reducing agent. A typical electroless-plating bath of palladium is shown in Table 3-1[7]. The rate of palladium deposition was about 1 μm/h. Palladium electroless-plating bathes for the preparation of supported palladium membranes have been improved and optimized by some researchers.

Because nonconductive supporting materials, e.g. ceramics, do not have sufficient catalytic activity to proceed with the reaction between metal ions and reducing agent on its surface, it is necessary to form finely-dispersed metallic palladium nuclei by the widely-accepted two-step immersion procedure with stannous chloride and palladium chloride solution. The nucleation can be described by the following reaction: $Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd$ (metal).

Kikuchi and Uemiya's group first proposed to fabricate a supported palladium membrane using this electroless-plating technique[7]. The dense and crack-free, pure palladium layer was deposited on the outer surface of a supporting, shown as Type 1-a in Fig. 3-1. Both ends of the support were sealed to deposit palladium only on the outer surface of a cylindrical porous support. The thickness of a dense palladium film without any remaining pinholes could be decreased with a decrease in the mean pore size of the effective layer of a support; 13 μm for the mean pore sizes of 0.3 μm, 4.5 μm for 0.2 μm and 2.2 μm for 0.1 μm[90]. The minimum thickness of about 2 μm, however, was unchanged for the mean pore sizes of 100 and 5 nm. The resulting membranes were only permeable to hydrogen; reliable results of hydrogen separation tests conducted by a Japanese gas-producing and purifying company proved the permeated gas purity of 99.9999%.

Since the development by Kikuchi and Uemiya's group in 1988, new supported palladium-based membranes with Type 1-a or 1-b structure have been proposed by several researchers using a conventional electroless-plating technique. Govind and Atnoor[21] prepared a palladium film supported on a porous silver disk with an average pore size of 200 nm. It is known in electroless-plating that some impure elements included in a reducing agent invade a metal film. In fact, their palladium film included 6 wt% phosphorus impurity because a reducing agent was sodium hypophosphite. Selection of bath composition is important, because the impurity elements sometimes cause a decrease in hydrogen permeance and selectivity.

Collins and Way[26] also prepared a composite membrane of a palladium film supported on the inside surface of asymmetric porous alumina (pore diameter of top layer, 10-200 nm).

TABLE 3-1 Typical electroless-plating bath of palladium[7)]

$[Pd(NH_3)_4]Cl_2\ H_2O$	5.4	[g dm^{-3}]
EDTA 2Na	67.2	[g dm^{-3}]
NH_3 (28% aq. soln.)	651.3	[mm^3 dm^{-3}]
$H_2NNH_2\ H_2O$	0.35	[mm^3 dm^{-3}]
pH	12.2	
temperature	323	[K]

According to their results, the hydrogen selectivity drastically decreased in the case of a palladium film below *about 10 μm in thickness. They proved experimentally that their membrane with a* palladium thickness of 11.4 μm could be used under the severe conditions of temperature up to 913 K and transmembrane pressure difference up to 2,330 kPa. Yeung et al.[38)] used porous Vycor glass with smaller pores of 5 nm. The minimum thickness could be reduced to 0.8 μm. These results demonstrate that the minimum thickness of supported metal film showing hydrogen permselectivity depends on the pore size of the support used.

Attractive, modified electroless-plating procedures were proposed by some researchers. Yeung and Varma[43)] modified a conventional electroless-plating technology with the use of osmosis phenomena to systematically manipulate the microstructure of the deposited metal. In the case of palladium plating, the film had loose aggregates with a grain size of about 200 nm for the conventional procedure, while that under osmotic pressure using sucrose solution had smaller grains *of about 60 nm in size and a dense structure.* Especially, this technique was also useful to form a dense silver film.

Shu et al.[56)] attempted to deposit palladium on the inner side surface of a mesoporous ceramic tube by circulating the electroless-plating solution through the supporting tube and two-step deposition procedure using two electroless-plating solutions with a 10 fold difference in concentration. This method gives Type 2 membrane structure. The resulting membrane had a palladium thickness of about 2 μm.

Zhao and co-workers[62)] claimed that activation procedure before electroless-plating should be conducted by the sol-gel process of a Pd(II)-modified boehmite sol and the concentration of hydrazine as a reducing agent in the electroless-plating bath should be increased. Though the thickness of the palladium film was decreased to 1 μm, the selectivity of hydrogen over nitrogen had moderate values of 20-130.

As previously mentioned, the use of a pure palladium membrane is restricted as the distortion caused by α–α' hydride transformation occurs in contact with hydrogen below 573 K. In order not only to prevent the membrane from rupturing but also to enhance hydrogen permeability, Kikuchi and Uemiya's group[20)] attempted to fabricate a supported, miscible palladium-silver alloy membrane (Type 1-a in Fig. 3-1). The alloy film was prepared by a conventional method called a "coating and diffusion treatment"[91)]. Namely, a thin film consisting of double layers of silver/palladium was formed on the outer surface of a thermally durable, porous alumina support and then treated at a relatively high temperature. The formation of the miscible alloy was accomplished above 1,073 K. The suitable content was 23 wt% from the viewpoint of hydrogen permeability. Detailed investigation on the effect of the silver content on hydrogen diffusivity and solubility led us to the conclusion that the enhanced hydrogen permeability resulted from the increased hydrogen solubility.

Shu et al.[27)] carried out simultaneous deposition of palladium and silver on a PSS support. Their bath contained palladium and silver salts, EDTA, hydrazine and ammonia as major components. Unfortunately, silver was preferentially deposited, though the alloy could be obtained via heat treatment of the deposited layer at 673 K. Later the same group[48)] adopted a similar technique as that of Kikuchi and Uemiya's group; namely, after successive electroless-platings of palladium and silver on a TiN/PSS substrate, the as-deposited film was annealed at a temperature ranging from 773 K to 1,073 K to make the miscible alloy. Yu et al.[63)] also tried to prepare a supported palladium-silver alloy membrane using a similar technique.

Kikuchi and Uemiya's group also studied the co-deposition of palladium and silver before the publication of the vigorous study of Shu et al. The palladium and silver co-deposited film was successively formed, but it was so porous that it could not to be used as a separation membrane selective for hydrogen. Recent results of Uemiya's group[92)] indicate that although the standard redox potential of Ag^+/Ag (0.80 V) is comparable to that of Pd^{2+}/Pd (0.93 V), palladium(II) ions were strongly stabilized in the plating bath with the coordinate bond of the N site of ammonium ions or complexing agents such as EDTA. They concluded that electroless-plating should be carried out under the conditions of acid or neutral pH, or using a bath including a complexing agent without the amino group instead of ammonia and EDTA.

Most of the supported metal membranes so far reported were dominated by palladium and palladium-based alloy. Similarly, thin metal films of nickel-phosphorous amorphous alloy (Ni-P)[55)] and platinum[50)] were also prepared by the electroless-plating technique. The former membrane, however, gave a relatively low ideal selectivity of hydrogen over nitrogen similar to the value predicted by the Knudsen diffusion mechanism. Their performance for hydrogen separation should be improved for practical use.

3.2.3 Electroplating

In conventional electroplating, metal ions are reduced to the corresponding metal at the cathode by electricity. If a supporting material should be conductive such as PSS, supported palladium membranes can be easily fabricated. However, an electrodeposited film often has a considerable number of pinholes left, because metal deposits preferentially at the part of high current density and the crystals grow perpendicularly to the substrate surface. Furthermore, produced hydrogen is also generated to the solute inside the deposited metal, resulting in hydrogen embrittlement. Little has been published about the preparation of dense metallic films, probably for these reasons.

NGK Insulators' group(65) prepared thin palladium-silver alloy membranes supported on a porous alumina alloy film by successive electroless-plating and electroplating. The membrane structure belongs to Type 1-a. Details were not published, but the author obtained some information by personal communication. This membrane was prepared by a procedure in which an ultrathin palladium film was formed on the porous alumina support and then palladium and silver were co-deposited on the thin palladium film, followed by annealing. They investigated the relationship between the surface conditions of the film and hydrogen permeance.

Bryden and Ying(58) synthesized nanostructured palladium-iron membranes by pulse electrodeposition effective for decreasing crystalline sizes and forming a crack-free film. In fact, their obtained film was crack-free and had grain sizes of 10-40 nm. The small grain sizes would result in superior hydrogen permeance due to the large volume fraction of grain boundaries if protons diffuse along the grain boundaries. Furthermore, the nanostructured film was reported to suppress transformation of $\alpha-\alpha'$ hydrides and to exhibit chemical resistance to hydrogen sulfide poisoning.

Recently, Itoh et al.(68) proposed a supported palladium-nickel alloy membrane supported on a tubular anodic oxidized alumina with a relatively sharp pore distribution. A sputtered metallic film used as a cathode was deposited on the surface of the alumina tube, followed by electroplating of palladium-nickel alloy, when a anode was placed inside the alumina tube. As a result, the alloy film was deposited only inside the pores.

3.2.4 Evaporation

Evaporation is one of the physical vapor deposition (PVD) techniques. The evaporated film is formed by heating a membrane-constituent material under vacuum to the temperature where a large number of atoms or molecules leave the surface of the material and deposit on a substrate. Adachi et al.17) prepared a thin $LaNi_5$ membrane with a thickness of 10 μm supported on a PSS disc by a flash evaporation method. The tendency of the decreasing hydrogen flux with increasing temperature is the opposite of what was observed for a palladium membrane; hydrogen scarcely permeated through the resulting membrane at temperatures of 333 K or above. It is reported that palladium can be easily evaporated at about 1,830 K and yields a good deposit; however, this method has rarely been applied to the preparation of supported palladium-based membranes due to the high temperature required.

3.2.5 Sputtering

In the sputtering method, a target is bombarded with high-energy particles that eject atoms from the surface of a desired material to deposit onto the surface of a substrate. The high-energy particles are produced by glow discharge, in most cases using an RF magnetron-type equipment. The film or coating with desired composition and minimal impurity can be easily obtained because the deposited film has almost the same composition as that of the target alloy or compound except for cases of completely different sputtering yields. The films deposited by this method have a thickness from 0.025 to 10 μm, especially on the submicron order in many cases, and furthermore provide the possibility of nano-scale structure design.

Gryazonov and co-workers25) investigated the possibility of various supported palladium alloy membranes used as membrane catalysts. They deposited binary and ternary palladium alloys with manganese, cobalt, ruthenium, tin, and lead onto PSS supports covered with an 0.8-μm-thick interlayer of tungsten, tantalum oxide, magnesia or zirconia, or porous plate made of magnesia and 15% yttria. The sputtering was performed at an argon pressure of 0.1-1.0 Pa, and the deposition was about 1 μm/min. All of their supported membranes were permeable only to hydrogen and gave about a hundred times higher hydrogen permeance than those of dense membranes and good stability during 1,000-h test at 1,073 K. During the same period, Govina and Hughes30) also prepared a composite membrane of a thin continuous palladium-silver film (6 μm) supported on porous Vycor glass with a mean pore size of 4 nm, and Athayde et al.33) prepared a composite membrane of an ultrathin palladium-silver film (25-100 nm) supported on a conventional polymeric gas separation membrane. They studied the hydrogen permeation mechanism through their membranes, which is summarized in the following chapter.

A nanostructure palladium film has a higher hydrogen diffusivity than conventional palladium membranes due to its large volume fraction of grain boundaries. From this viewpoint, Bryden and Ying44) synthesized nanostructured palladium membrane supported on a porous Vycor glass disk. The deposited films were defect-free on the submicron scale and were also free from the phase transformation of α–α' hydrides. In the case of pure palladium, grain growth occurred above 473 K. Therefore, they expanded their studies to some nanocrystalline palladium-alloys such as palladium-yttrium and palladium-silver alloys. We can expect that these studies will lead to the development of highly hydrogen permeable alloy materials in the near future.

Jayaraman and Lin[42)] also investigated the synthesis and gas permeation properties of supported ultrathin palladium-silver alloy membranes with a thickness of 250-500 nm. They used a sol-gel derived γ–alumina support with a pore size of 3 nm. The separation factors of hydrogen over nitrogen were not very high, for example 5.69 at 523 K. The formation of pinholes and cracks will be closely related to the smoothness and cracks of the γ–alumina support. They also studied the hydrogen permeation mechanism and emphasized the surface reaction at low temperatures in the case of an ultrathin metallic membrane. Recently, they have been interested in investigating the relationship between the average grain size and hydrogen permeance[61)]. It was experimentally demonstrated that average grain size could be controlled by substrate temperature, but the relationship is under investigation.

3.2.6 Spray pyrolysis

In spray pyrolysis, a thin coating is deposited by spraying slurry on a heated substrate, where the constituents thermally decompose into a coating material. Li et al.[28)] formed a palladium-silver film of 1.5-2.0-μm thickness on the surface of a porous γ–alumina support by the spray pyrolysis of $Pd(NO_3)_2$ and $AgNO_3$ mixed solution in a H_2-O_2 flame. The resulting membrane gave the H_2/N_2 separation factor of about 24 and hydrogen permeation coefficient of about 8×10^{-7} mol m^{-2} s^{-1} Pa^{-1} at 773 K. Unfortunately, the resulting membrane easily slipped off.

3.2.7 Chemical vapor deposition (CVD)

In CVD, a volatile component of coating materials thermally decomposed on the surface of the heated substrate to form a solid deposit like a thin film or coating. Although CVD is an established technique to form a ceramic or metallic film with good quality[87)], there are only a few research papers on the formation of thin films of group VIII metals, especially palladium and its alloy, probably because of lack of a proper precursor. Organometallic complexes, which are usually easy to sublime under mild conditions, are often used as CVD precursors, but are expensive and commercially unavailable. One of the most important features to form a good metallic film is the selection of the CVD precursor.

A composite membrane consisting of palladium, platinum or ruthenium deposited inside the macropores of an α-alumina tubular support was successfully prepared using the corresponding acetyl-acetonato-complexes as CVD sources[31,51]. The object structure of the composite membranes was Type 2. A considerable amount of the vaporized complex, however, had to be deposited and thermally decomposed on the surface of the porous support as well as inside the pores to attain high hydrogen selectivity above 100. The selectivity values of hydrogen over nitrogen were 240, 120, and 210 at 773 K for palladium, ruthenium, and platinum membranes, respectively. Furthermore, the supported platinum membrane prepared by the CVD method showed hydrogen permeance equivalent to that of a supported palladium membrane, though the hydrogen diffusion coefficients between dense palladium and platinum are a thousand-fold different. Details of the hydrogen permeation mechanism will be discussed hereafter. The CVD apparatus used is home-made, as illustrated in Fig. 3-2. The target metal of CVD is now extended not only to iridium and rhodium, but also to various alloys of the group-VIII metals.

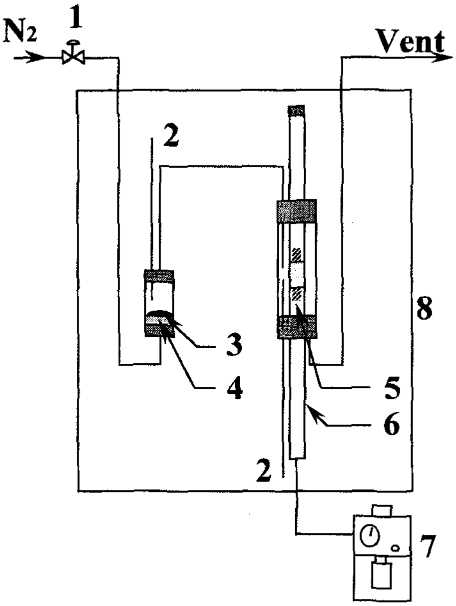
A similar type membrane was developed at the same time by Morooka's group[32]. Their CVD source was palladium acetate. The fabrication of their membrane required preparation conditions at a reduced pressure, leading to denser deposited film (palladium grain size, 80 nm) than that of Uemiya and co-workers. The membrane exhibited higher hydrogen selectivity of 1,000 at 573 K. Their membrane exhibited no hydrogen embrittlement, because expansion and contraction of the lattice accompanied with phase transformation was prevented by small cavities among palladium grains and between grains and pore walls.

Xomeritakis and Lin[53] reported the successful deposition of palladium inside the pores of a mesoporous alumina by counter-diffusion CVD with palladium dichloride vapor as a precursor and hydrogen as a reductant. The resulting membrane had a fairly dense palladium film with the thickness on the submicron order. The size of the palladium grains was in the range of 15-20 nm. They have been eagerly investigating the hydrogen permeation mechanism through supported ultrathin palladium membranes. They claim that surface phenomena become rate-determining in ultrathin membranes.

Recently, co-deposition of palladium and nickel on porous substrates was attempted by Meng et al.[57] using the MOCVD technique with mixed β-diketone precursors of $Pd(acac)_2$ and $Ni(acac)_2$. The resulting membrane was gas-tight and free from pinholes and cracks, but the hydrogen permeance test has not yet been performed. Further study will be necessary on the preparation and characterization of alloy membranes prepared by MOCVD with mixed precursors.

3.2.8 Other techniques

Konno et al.[10] prepared a palladium-impregnated porous alumina membrane from an aqueous solution of $[Pd(NH_3)_4]Cl_2$. First, an ultrathin palladium film of about 10-nm thickness was



1, mass-flow controller; 2, thermocouple; 3, metal source; 4, silicawool; 5, heater; 6, porous alumina tube; 7, aspirator; 8, temperature-controlled oven

Fig. 3-2 Schematic diagram of CVD apparatus[51] (Reproduced with permission of the American Institute of Chemical Engineers. Copyright ©1997 AIChE. All rights reserved.)

deposited on the anodic alumina support by a sputtering method, and then the support was immersed in the aqueous solution of $[Pd(NH_3)_4]Cl_2$. An ultrathin palladium film promoted the deposition of palladium-like electroless-plating.

Arai's group[35] employed a sol-gel technique to prepare a metal-dispersed alumina membrane, whose structure belongs to Type 3-a. A porous alumina substrate was coated with alkoxide-derived boehmite-sol containing a metal salt, such as $RuCl_3$, $Pd(NH_3)_4Cl_2$, $RhCl_3$, H_2PtCl_6, $Ni(NO_3)_2$, $Co(NO_3)_3$, $Fe(NO_3)_3$ or $Cu(NO_3)_2$ using the dip-coating sol-gel method, and then calcined at 773 K. This procedure was repeated 25-30 times, and consequently, a microporous γ-alumina layer with the thickness of 10-15 μm, the pore diameter of 3-5 nm, and the dispersed metal size of 3-5 nm was formed on a porous support. The order of hydrogen selectivity of the metal-dispersed membranes tested selectivity was as follows: Rh~Ru > Pd~Ni > Fe > Cu >Co. Even in the case of the Ru-dispersed membrane, the hydrogen/nitrogen permselectivity experimentally obtained was slightly higher (about 5.9) than the value of 3.7 predicted from the traditional Knudsen diffusion mechanism.

Another unique technique for the preparation of a supported metallic membrane was proposed by Zhao et al.[39)] Their membrane, a Type 3-b structure, was prepared by partial sintering of metal-coated particles on the surface of a support. The membrane integrity was examined by gas permeation measurements using nitrogen and helium, but the hydrogen permeability has not yet been published.

4. Gas transport mechanism

Gas transport mechanisms through most metal membranes can be divided into two types: traditional solution-diffusion mechanism for dense metal membranes such as palladium-based membranes, and Knudsen diffusion mechanism or combined mechanism of Knudsen diffusion and surface diffusion for porous metal membranes, such as porous stainless steel and microporous noble metals.

With the progress of fabrication techniques of thin metal films, the thickness of a metallic film or layer of supported metal membranes decreased from the micron order to submicron order and finally to nanometer order. According to Kirchheim's group report[93)], nanocrystalline palladium has superior hydrogen diffusivity, compared to the single-crystalline case. Based on this result, Bryden and Ying[44)] developed a supported, nanostructured palladium membrane, leading to further improvement in hydrogen permeance by synergistic effects, that is, the thinness of the metal layer as well as enhanced diffusivity. From these viewpoints, an ultrathin metal membrane is thought to be attractive, if the rate-determining step of hydrogen permeation involves the diffusion of proton through the metal layer. Here, the reported hydrogen transport mechanisms are described for dense metals (ultrathin and thin) and porous metal membranes.

In the case of dense palladium-based membranes, hydrogen can dissolve and rapidly diffuse according to the following activated mechanism[94)]:

1) Hydrogen molecule chemisorbs on the membrane surface (high-pressure side).
2) The chemisorbed molecule dissociates into atomic form, proton and electron.
3) The dissociated hydrogen atoms dissolve into the lattice of the metal.
4) The proton and electron diffuse through the lattice.
5) The proton and electron reassociate and recombine into hydrogen molecules.
6) The hydrogen molecule desorbs from the opposite membrane surface.

For commercially available palladium-based membranes, the rates of proton and electron diffusion through the palladium lattice are slow, compared with those of surface reactions including hydrogen adsorption, dissociation, reassociation, and desorption at relatively high temperatures. Under these conditions, the thermodynamic equilibrium between the hydrogen molecules in the gas phase and hydrogen atoms dissolved at the interface would be established. The hydrogen concentration at the interface is proportional to the square root of the hydrogen pressure (Sievert's law). Because the rate of hydrogen diffusion obeys Fick's law, the hydrogen flux can be expressed as the following equations:

$$J = (Q/t) \cdot (P_H^{0.5} - P_L^{0.5}) \tag{4-1}$$

$$Q = D \cdot S \tag{4-2}$$

where Q, D, and S are the hydrogen permeation coefficient, diffusion coefficient, and solubility constant at a given temperature, respectively. P_H, P_L and t are the partial pressure of hydrogen on the high- and low-pressure sides, and the thickness of the metal. The dependence factor of the hydrogen flux on the partial pressure of hydrogen (n), however, sometimes deviates from the ideal value of 0.5. The hydrogen permeation coefficient can be expressed by an Arrhenius-type equation.

$$Q = A \cdot \exp(-E_{ap}/RT) \tag{4-3}$$

where A, E_{ap}, R and T are the pre-exponential factor, apparent activation energy, gas constant, and absolute temperature, respectively.

On the other hand, hydrogen adsorption, dissociation, reassociation, and desorption are rate-determining at relatively low temperatures. The hydrogen flux deviates from the Sievert and Fick's laws under these conditions.

The hydrogen transport mechanism of a supported palladium membrane is affected by the thickness of the palladium film. The first introduced examples are the case of palladium thickness above several micrometers. The supported palladium membrane with a palladium thickness of 13 μm, prepared by the electroless-plating technique, gave the same order of hydrogen permeation coefficient (1.06 x 10^{-8} mol/(m s $Pa^{0.5}$) at 773 K)[7)] and the same apparent activation energy (10.7 kJ/mol)[7)] as the values (1.92 x 10^{-8} mol/(m s $Pa^{0.5}$)[82)], 11.9 kJ/mol[95)]) reported for commercially available thick palladium membranes. The hydrogen fluxes of various electroless-

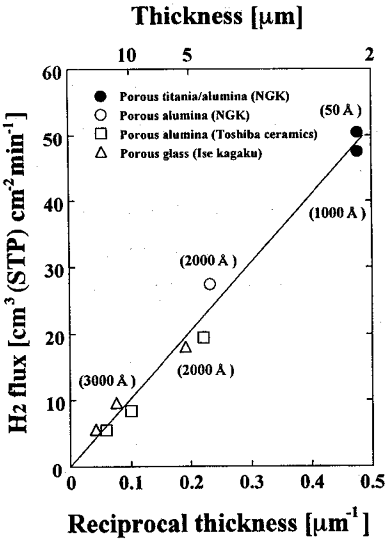


Fig. 4-1 Hydrogen fluxes of various electroless-plated palladium membranes[24)]

plated palladium membranes supported on porous substrates with different pore sizes are plotted in Fig. 4-1 as a function of reciprocal thickness[24)]. Apparently the hydrogen fluxes were inversely proportional to the film thickness. Furthermore, though detailed results are not shown here, the hydrogen fluxes were proportional to the difference of the square roots of transmembrane hydrogen partial pressures. These results indicate that porous substrates had large pore sizes sufficient to be scarcely resistant to hydrogen permeation and the diffusion of the proton through the palladium lattice was rate-determining for hydrogen permeation. A similar tendency was observed by Govind and Atnoor[21)], whose supported membrane had a palladium thickness of 5.0 μm. Furthermore, in the cases of the supported palladium-silver membranes with thickness range of 5-8 μm, the diffusion of the proton through the bulk of the alloy was rate-determining for hydrogen permeation, irrespective of the preparation procedures of electroless-plating and consecutive heat treatment[20)], and magnetron sputtering[33,42)]. Nevertheless, the dependence factor of the hydrogen flux on the partial pressure of hydrogen, n, sometimes deviated from 0.5 even at relatively high temperature; for example, 0.526-0.622 for 11.4-20 μm palladium membranes prepared by Collins and Way[26)]. Many explanations have been proposed for the deviation: contamination of membrane surface, dependence of the hydrogen diffusion coefficient on the dissolved hydrogen,

hydrogen leakage through cracks or defects and so on. However, definite evidence has not been presented for each opinion. According to a recent report of Mardilovich et al.[16)], there is a very small difference in the regression factor between two cases of different hydrogen-pressure dependence factors, n=0.5 and n>0.5, for example, 0.9991 for n=0.5 and 0.9998 for n=0.6. In other words, their membrane with a palladium thickness of 19-28 μm showed a similar tendency for hydrogen permeation. The author also had a similar experience to decide the factor n.

On the contrary, Type 2 membranes prepared using CVD techniques showed a more complicated behavior for hydrogen permeation. The supported palladium membranes prepared by Uemiya et al.[51)] and Yan et al.[32)], although giving almost the same hydrogen permeance, exhibited a different dependence of the hydrogen flux on the partial pressure of hydrogen: n=0.5 for Uemiya et al. and 1.0 for Yan et al. Uemiya et al. concluded that hydrogen permeated through the CVD palladium membrane via the same mechanism as that observed for the membrane prepared using the electroless-plating technique. On the other hand, Yan et al. considered that a combination of the diffusion through palladium lattice and adsorption of hydrogen onto the surface of palladium was responsible for the transport resistance of hydrogen through the membrane.

It has been reported that the hydrogen diffusion coefficient through single-crystalline palladium can be improved by making nanostructured palladium or its alloys because the grain boundary has such a large volume that hydrogen can rapidly diffuse, compared to bulk palladium. Namely, a polycrystalline palladium membrane with small grains gathered will show superior hydrogen permeability. Furthermore, hydrogen embrittlement and chemical resistance for sulfur compounds can also be improved. Based on this strategy, Bryden and Ying[44)] successfully fabricated a nanostructured palladium membrane supported on porous Vycor glass by d.c. magnetron sputtering. Recently, they prepared nanocrystalline palladium-silver and palladium-yttrium films by the magnetron sputtering[59)] and a palladium-iron alloy film by the pulse electrodeposition[58)]. Characterization studies of these nanostructured membranes have been conducted; however, there is insufficient information on their hydrogen permeability. The hydrogen permeance of the latter membrane was reported at AIChE 1997 annual meeting.

As mentioned elsewhere in this manuscript, platinum and ruthenium membranes prepared using the CVD technique showed hydrogen permeance equivalent to that of supported palladium membranes (refer to Fig. 4-2), though the hydrogen diffusion coefficient of platinum is a thousand times lower than that of palladium[51)]. This excellent hydrogen permeability of the CVD platinum membrane resulted not from the traditional solution-diffusion mechanism, but from the surface diffusion mechanism, which has been used to describe CO_2 separation in carbon and ceramic membranes. The schematic mechanism of hydrogen permeation through CVD membranes is shown in Fig. 4-3. The hydrogen permeation mechanism through the CVD palladium membrane

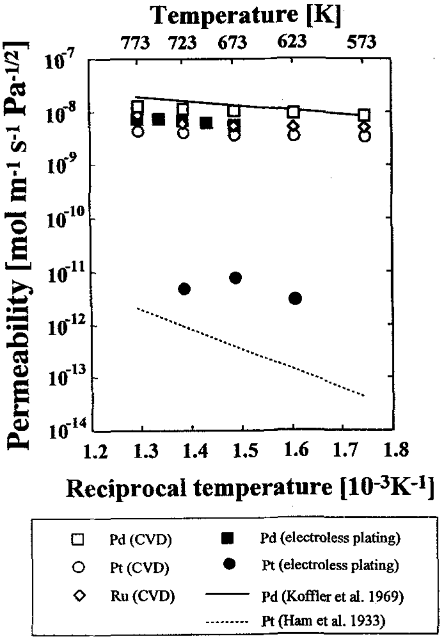


Fig. 4-2 Comparison in hydrogen permeability of various platinum-group metal membranes

is not so obvious, and the author wonders whether hydrogen diffuses on the palladium layer via surface diffusion mechanism, solution-diffusion mechanism (in the bulk of the palladium grain or between the boundary between the grains), or a combined mechanism.

The situation observed for thin palladium membranes with a palladium film thickness on the micrometer order will be changed when the thickness is decreased to the sub-micrometer order or less. Further study will be necessary for the hydrogen permeation mechanism of supported metal membranes with nanostrcutred ultrathin metal film.

Two- and three-dimensional diffusive flow behavior in a coated dense layer of a composite membrane was analyzed by Itoh et al. using a simplified model[96,97]. They focused on the effect of non-porous parts on gas permeation behavior. According to their results, the effective membrane area is A for $t_m/d_p>10$, while it is εA for $t_m/d_p<0.1$. Here, the thickness of the effective layer is t_m, porosity ε, average pore size d_p, effective membrane area A. These results mean that the effective area for gas permeation will be restricted within a formed film on pores (area, εA) in the case of ultrathin films.

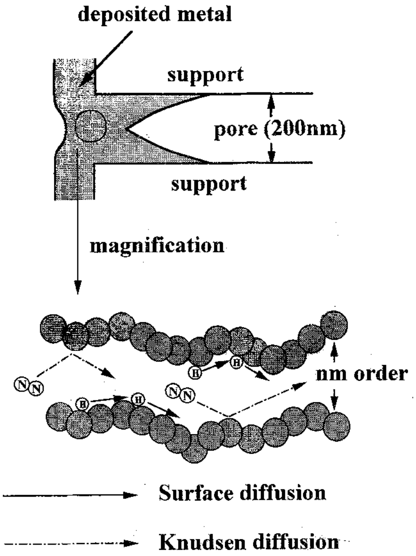


Fig. 4-3 Schematic mechanism of hydrogen permeation through CVD membranes[51)]
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5. Issues and requirements

Supported metal membranes require specific measures to deal with the following issues:

- Excellent permeance while maintaining high separation factor
- Reliability
- Hydrogen embrittlement
- Long-term stability (thermostability)
- Chemical stability (sulfur compound poisoning, carbon deposition, etc.)
- Cost
- Design (module, spiral, etc.)

Here, only long-term stability and chemical stability will be treated and described.

5.1 Long-term stability

The life-time of supported palladium membranes is one of the important factors for their commercialization. It was reported by Paglieri et al.[98)] that a complete selectivity of palladium for hydrogen separation was lost at temperatures above 823 K. They stated that the amount of tin present at the interface of palladium and support was quantitatively related to the reduced hydrogen selectivity at high temperatures. The nuclei were not pure palladium, that is, tin originated from conventional nucleation procedure with stannous chloride and palladium chloride solution for electroless-plating still remained to form a palladium-tin complex. Tin-free nucleation procedure should be necessary to alleviate this problem.

Improved nucleation procedures without tin were proposed. The first example of a tin-free activation procedure applied to the preparation of a supported metal membrane was reported by Li et al.49) They used a sol-gel technique: palladium salt-modified boehmite sol was deposited on the surface of the porous alumina, followed by calcination at 823 K and hydrogen reduction at 673 K. Recently, Way's group proposed a new tin-free procedure98). Prior to electroless-plating, substrates were dip-coated in a chloroform solution of Pd acetate, dried, calcined, and then reduced in flowing hydrogen. The resulting supported palladium membrane prepared using this new procedure gave sufficient thermal stability at 873 K.

The other two explanations for the cause of rupturing of supported palladium membranes at a high temperature are reported: one is the rapid aggregation of palladium grains99), and the other is carbon deposition on the palladium surface99-103) and subsequent interstitial dissolution of carbon in the palladium lattice104). Though all of these phenomena will affect membrane stability, it is not clear which is the main cause for membrane rupturing at high temperatures.

Recently, Mardilovich et al.16) reported that their supported palladium membrane prepared by an electroless-plating technique was stable at 623 K over a period of 1,100 h. This success predicts that a supported palladium membrane will be commercialized in the near future.

5.2 Chemical stability

Several studies have been reported on the effect of impurities on hydrogen permeance for dense palladium membranes, but very few for supported palladium membranes. Impurities such as sulfur compounds, unsaturated hydrocarbons, halogen compounds, and mercury affect hydrogen permeance.

5.2.1 Sulfur compounds

Palladium reacts with sulfur compounds at high temperature to form palladium sulfide99). The lattice constant of palladium sulfide is twice as large as that of pure palladium, and therefore, structural stress leads to the formation of cracks and rupturing. The concentration of hydrogen sulfide should be decreased below 500 ppm, preferably 5 ppm. Ali et al.105) studied the poisoning effect of the sulfur compound on the hydrogen permeance of a commercially available palladium-silver alloy membrane.

Kajiwara et al.[106] experimentally confirmed the formation of cracks for a supported palladium membrane. As a countermeasure, they proposed to use platinum instead of palladium because the lattice constants of pure platinum and platinum sulfide are almost the same, and furthermore, as previously mentioned, a supported platinum membrane prepared by a CVD technique showed excellent hydrogen permeance comparable to supported palladium membranes prepared using an electroless plating technique. The hydrogen permeability of the CVD membrane was dramatically decreased by contact with hydrogen sulfide. The opposite phenomenon was reported by Edlund and Pledger[83,84], namely, the hydrogen permeability of platinum-coated metal membranes was hardly changed by hydrogen sulfide mixed with natural gas.

5.2.2 Unsaturated hydrocarbons

Metallic membranes are usually deactivated due to coke or carbonaceous material deposition on the metal surface[99]. Especially, the contact with unsaturated hydrocarbons causes serious deactivation. When a metal membrane is used as the wall of a membrane reactor, this problem will become most serious. The deactivated palladium membranes, however, can be regenerated by contact with air or oxygen. In fact, a supported palladium membrane deactivated during usage for the dehydrogenation of propane or isobutane was experimentally confirmed to be regenerated by oxygen diluted with nitrogen. Synthetic reformate gas consisting of hydrogen, carbon monoxide and carbon dioxide as well as lower saturated hydrocarbons such as methane scarcely affect the hydrogen permeance of thin palladium and palladium-silver alloy membranes[13].

5.2.3 Other impurities

Other impurities such as halogens and mercury also poison a palladium membrane. For example, chloride compounds react with iron as one of the constituent materials of a separation unit to produce ferric chloride, which deposits on the membrane surface to deactivate hydrogen permeance.

Ali et al.[107] studied the effect of dehydrogenation catalyst components, such as germanium and chlorine, on hydrogen permeance. However, information on the effects of impurities is insufficient at present.

6. Conclusions

Since Graham first discovered that palladium absorbs a substantial amount of hydrogen, much attention has been focused on the metal-hydrogen system and on the development of metallic membranes consisting of palladium-based alloys. Even at present, however, only self-supporting metallic membranes are commercialized, and their application is restricted only to ultrapure hydrogen production for semiconductor manufacturing and metallurgical industries due to economics. In order to expand the application of metallic membranes to chemical processes, breakthroughs are needed to overcome the following challenges and problems of supported metal membranes: excellent permeance while maintaining high separation factor, reliability, hydrogen embrittlement, long-term stability (thermostability), chemical stability especially for sulfur compounds and carbon deposition, cost, and design.

The membrane reactor system is a promising technology as one of the environmentally-friendly chemical processes. At present, large projects on membrane reactors proceed in both the USA and Japan. In the USA, the ceramic membrane reactor is selected for the conversion of natural gas to synthesized gas. On the other hand, both ceramic and metallic membrane reactors are now investigated for the conversion of hydrocarbons. Selection of these two types of membrane reactors should be investigated from all sides. I hope that this review article is helpful for researchers and engineers in the field of developing supported metallic membranes and designing membrane reactor systems.

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