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S. Ilias[a]; N. Su[a]; U. I. Udo-Aka[a]; F. G. King[a]
[a] Department of Chemical Engineering, North Carolina A&T State University, Greensboro, NC

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APPLICATION OF ELECTROLESS DEPOSITED THIN-FILM PALLADIUM COMPOSITE MEMBRANE IN HYDROGEN SEPARATION

S. Ilias*, N. Su, U.I. Udo-Aka, and F.G. King
North Carolina A&T State University
Department of Chemical Engineering
Greensboro, NC 27411

ABSTRACT

In recent years, there has been increased interest in developing inorganic and composite membranes for in-situ separation of hydrogen to achieve an equilibrium shift in catalytic membrane reactors. The productivity of these membrane reactors, however, is severely limited by the poor permeability and selectivity of available membranes. To develop a new class of permselective inorganic membranes, electroless plating has been used to deposit palladium thin-films on a microporous ceramic substrate. A palladium thin-film coating was deposited on a microporous ceramic disk (α-alumina, $\varnothing$ 39 mm $\times$ 2 mm thickness, nominal pore size 150 nm and open porosity $\approx$ 42%) by electroless deposition. The film was evaluated by SEM and EDX analysis. A steady-state counter-diffusion method, using gas chromatographic analysis, was used to evaluate the permeability and selectivity of the composite palladium membrane for hydrogen separation at temperatures from 373 to 573 K. The pressure on the high pressure side of the membrane ranged from 170 to 240 kPa and the low pressure side was maintained at 136 kPa. The measured hydrogen permeabilities at 573 K were found to be 1.462×10^{-9} $mol\cdot m/m^2\cdot s\cdot Pa^{0.778}$, and 3.87×10^{-8} $mol\cdot m/m^2\cdot s\cdot Pa^{0.501}$ for palladium film thicknesses of 8.5 and 12 μm, respectively. The results indicate that the membrane has both high permeability and selectivity for hydrogen and may find applications in high temperature hydrogen separation and membrane reactors.

* To whom correspondence should be addressed

INTRODUCTION

The potential application of membranes in high temperature gas separation and reactor technology has been recognized by many investigators [1-6]. The development of high temperature resistant membranes to recover hydrogen is a topic of considerable scientific interest. The gasification of coal offers a potentially significant source of hydrogen for use in clean power generation and as a primary chemical feedstock. However, hydrogen recovered from coal continues to be more expensive than hydrogen recovered from petroleum or natural gas. The higher cost is due in large part to the expense of separating hydrogen from the mixture of gases produced during coal gasification. Many heterogeneous catalytic reactions can not achieve high conversions because of the limit imposed by the reaction equilibrium. For example, the dehydrogenation reaction of cyclohexane, catalyzed with platinum/alumina at 215°C in a conventional reactor, is limited to 33% conversion [7]. If, however, hydrogen is continuously removed from the reaction mixture through an inorganic membrane, the equilibrium is displaced towards the product side and the conversion is increased to nearly 80%. Since, this reaction is also favored by an increase in temperature, the temperature can be lowered. There are many other industrially significant reactions where the efficiency of the process depends on the effectiveness of hydrogen removal and the conversion of reactants can be enhanced dramatically if a method can be developed for recovering hydrogen at higher temperatures.

Recently, there has been increased interest in developing inorganic and composite membranes for in-situ separation of hydrogen to achieve an equilibrium shift in catalytic reactors [7-11]. However, the productivity of these membrane reactors has been severely limited by the poor permeability of currently available membranes. Commercially available non-porous membranes are either thick film or thick walled tubes. Since permeability is inversely proportional to film thickness, a thick-film membrane is a poor perm-separator. Thus, a major challenge lies in developing a permselective thin film, without compromising the integrity of the film. The success of membranes in these applications will largely

depend on the availability of membranes with acceptable permselectivity and thermal stability [12]. The availability of such a membrane for high temperature application could open new areas of research in membrane reactor technology and gas separation.

The development of a process for producing ultra thin-film, defect-free composite membranes is important. If such a process is to be developed in a generally applicable form for use with most advanced materials, a high-productivity, high-selectivity coating must be applied on an inexpensive support. To develop a novel permselective inorganic membranes, we have used electroless plating to deposit a palladium thin-film on a microporous ceramic substrate [13]. Electroless plating is a controlled autocatalytic deposition of a continuous film on the surface of a substrate by the interaction of a metal salt and a chemical reducing agent. The electroless plating method can deposit thin films of metals, alloys and composites on both conducting and nonconducting surfaces. The objective of this paper is to discuss the preparation and characterization of a thin-film palladium-ceramic composite membrane for selective separation of hydrogen at elevated temperatures and pressures.

EXPERIMENTAL METHODS

Three types of experiments were performed: electroless plating of palladium on a ceramic substrate, characterization of palladium thin-film composite membranes, and evaluation of the perm-selectivity of the composite membrane for hydrogen separation.

Electroless Plating of Ceramic Substrate

Microporous ceramic alumina membranes (α-alumina, $\varnothing$ 39 mm $\times$ 2 mm thickness, nominal pore size 150 nm and open porosity $\approx$ 42% obtained from Velterop Ceramic Membrane Company of the Netherlands) were coated with a thin palladium film by electroless plating. Electroless plating is a combination of the cathodic deposition of metal and the anodic oxidation of reductant at the immersion

potential [14]. Palladium deposition occurs as the result of the following simultaneous reactions:

Anodic Reaction:

$$N_2H_4 + 4OH^{-1} \rightarrow N_2 + 4H_2O + 4e^-$$

Cathodic Reaction:

$$2Pd[NH_3]_4^{2+} + 4e^- \rightarrow 2Pd^0 + 8NH_3$$

Autocatalytic Reaction:

$$2Pd[NH_3]_4^{2+} + N_2H_4 + 4OH^{-1} \rightarrow 2Pd^0 + N_2 + 4H_2O + 8NH_3$$

Electroless plating is a three step process involving pretreatment of the substrate, sensitization and activation of the substrate surface, and electroless plating. The electroless plating bath compositions used are given in Table 1. The plating bath compositions are similar to ones used by others [15, 16].

In electroless plating, pretreatment of the substrate is essential in order to deposit metals effectively. One of the common procedures is the two-step immersion sequence using an acidic stannous chloride solution followed by an acidic palladium salt solution. The first bath is referred to as the sensitizer (stannous chloride solution), while the second bath is referred as the activator (palladium salt solution). The net result of the pretreatment sequence is the formation of finely-divided palladium nuclei which initiate the autocatalytic plating process. The formation of the palladium metal nuclei is believed to be due to a redox reaction taking place between the adsorbed or absorbed stannous ions on the surface and the palladium ions in the activation solution. The sensitization and activation step can be described by the following reaction:

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0$$

The sensitization process controls whether the final metallic film is uniform. The composition of the sensitization and activation solutions is given in Table 2. The procedure used for electroless plating of palladium on ceramic substrate may be summarized as follows:

Pretreatment of the Substrate: The ceramic disks were cleaned by boiling in 0.1N NaOH solution for 10 to 30 minutes and then boiling in 0.1N HCl

TABLE 1. Typical Electroless Plating Bath Composition

Component/Variables	Concentration
Palladium chloride	5.4 g/l
Ammonium hydroxide (5N)	290 ml/l
Hydrazine (1 molar solution)	10 ml/l
EDTA	40 g/l
pH	11
Temperature	25 °C

TABLE 2. Composition of Sensitization and Activation Solutions

Sensitization Solution		Activation Solution	
Component	Concentration	Component	Concentration
$SnCl_2$	1 g/l	$PdCl_2$	0.09 g/l
HCl	0.2N	HCl	0.2N

solution for 10 minutes. The cleaning was done to remove any organisms, residual metals and dust. The disks were then washed in boiled distilled water for 10 minutes, dried at 120 °C and weighed. The cleaning was essential for activation and plating to take place across the diameter and into the porous substrate.

Sensitization and Activation: One face, and the edges, of the pretreated ceramic disk was wrapped with Teflon tape to prevent sensitization and activation. The ceramic substrate was seeded with palladium by being dipped successively in acidic $SnCl_2$ solution followed by acidic $PdCl_2$ solution at room temperature. Each dip lasted for about 4 to 5 minutes and was followed by washing with distilled water for about one minute between each dip. The sensitization and activation step

took about 0.5 to 1 hour. After sensitization and activation, the disks appeared grayish brown. The discs were dried at 120 °C for 1 hour and then weighed.

Electroless Plating: The activated discs were wrapped with fresh tape and then suspended in temperature controlled electroless plating. The bath was preheated to the plating temperature. The total plating time was 0.5 hour for each run. The plated disc was then dried at 120 °C for 1 hour and then weighed. For thicker film, it was necessary to use fresh electroless plating solution. For recoating the same surface, the Teflon tape needed to be replaced with new tape.

Membrane Characterization

The membranes were evaluated by taking SEM (Scanning Electron Microscope) micrographs, performing EDX (Energy-Dispersive X-ray) analysis and measuring the thickness of the coated film. EDX analysis was used to determine the composition of the plated membrane. The thickness of the palladium film was determined by a weight gain method. Membrane surface structure was evaluated from the SEM micrographs.

Permeability Studies

A steady-state counter-diffusion method, using gas chromatographic analysis, was used to measure the permeability and selectivity of the composite palladium membrane for hydrogen separation. The method consists of a diffusion cell designed to allow permeation of two different gases through a membrane or porous sample. Details of the method and calculation of permeability have been presented elsewhere [13]. The membranes were evaluated for hydrogen separation by conducting permeability measurements with hydrogen and argon at various temperatures and transmembrane pressure differentials. The permeability testing assembly consisted of two pure gas sources, a diffusion cell, a tubular furnace, rotameters and massflow meters. The composite membrane was mounted in the center of cell. The diffusion cell was assembled and placed in a tubular furnace (Lindberg Type 55347). Each side of the cell was connected to a gas supply line. All inlet and outlet gas supply lines were constructed of stainless steel tubing. The

temperature was controlled by a temperature controller. The pressure of the gas streams were measured by pressure gauges and regulated using valves as well as a pressure transducer. Calibrated rotameters and massflow meters were used to measure the flow rates of each of the inlet and exit gas streams. A differential pressure gauge was connected to each side of the cell to measure the differential pressure across the membrane. The composition of each exit gas was determined by manual sampling, using a syringe, and injected the sample in the Gas Chromatograph. A schematic of the experimental setup is shown in Figure 1.

During the early phase of this work, a stainless-steel diffusion cell was used to measure the permeability and diffusivity of hydrogen through the ceramic substrate and Pd-composite membrane. At elevated temperature, the leakage of hydrogen through the seals was a serious problem. To overcome the hydrogen leakage problem, we obtained and tested a new cell (designed by Velterop Ceramic Membrane Company of the Netherlands, Model LTC Type K-500). The new cell was selected because it is self-sealing at high temperature. The cell consisted of outer parts, inner parts, graphite seals, Cu-seals and the membrane is mounted on nonporous endseals, as shown in Figure 2.

The outer parts of the cell are made of stainless steel, AISI 310 and the inner parts are made of titanium. The outer diameter of the cell housing is 86 mm and the thickness of the housing is 37 mm. The cell accepts ceramic disks, ⌀ 39 mm × 2 mm, with ceramic sealing edge ⌀ 60 mm ×35 mm. The effective surface area for diffusion is 12 cm^2. The cell assembly can be used up to 500°C. The thermal expansions of the two metals are such that the cell is selfsealing at elevated temperature. Graphite seals were used for sealing the ceramic edge and the copper-seals were used for connecting tubes. The result was very satisfactory. No external leakage of hydrogen was detected at operating pressures by the bubble test method. The ease of assembly of the cell also makes it convenient to use the membrane in repetitive applications without damaging the cell or membrane assembly.

A Perkin-Elmer Sigma 2000 Gas Chromatograph (GC), which was connected with a Perkin-Elmer 7700 computer and Perkin-Elmer LCI-100 Computing Integrator, was used to analyze the composition of the exit gas streams.

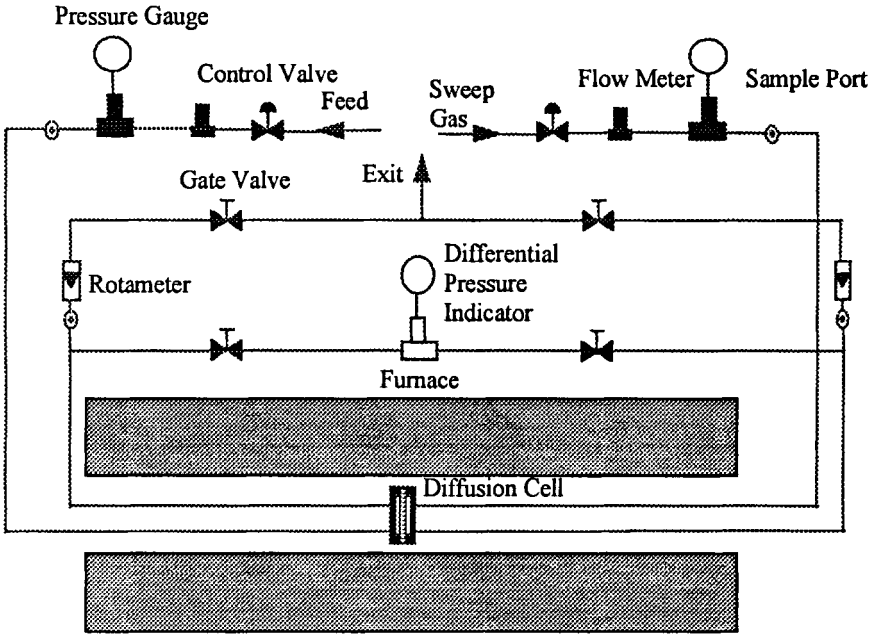

FIGURE 1. Schematic of Permeability Measurement Setup.

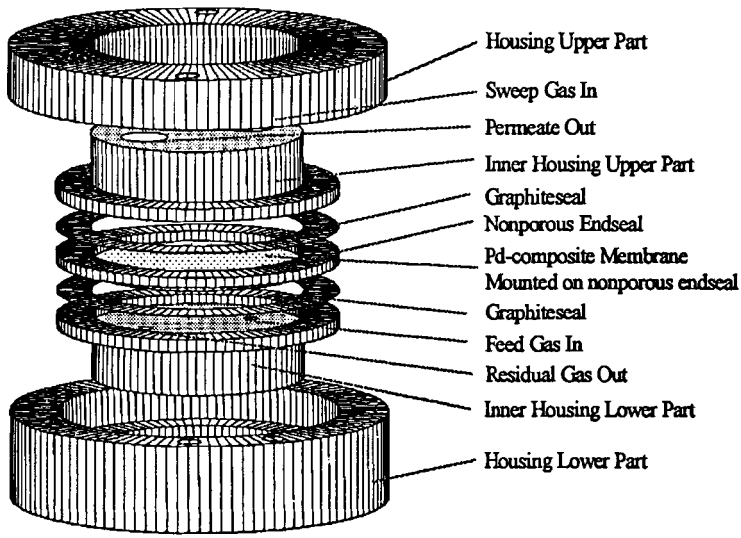

FIGURE 2. Details of Diffusion Cell.

A 15 ft long, 1/8" OD Carboxon™ 1000 column (Supleco, Inc.) connected to thermal conductivity detector (TCD), was used for gas separation in the GC. Helium was used as the carrier gas in all GC analyses.

RESULTS AND DISCUSSIONS

Thin-film palladium-ceramic composite membrane was developed by electroless deposition of palladium onto a planar ceramic substrate. Two Pd-ceramic composite membranes were fabricated and tested for hydrogen separation at high temperatures. The membranes were characterized by SEM and EDX analysis. The EDX analysis of the membrane specimen is shown in Figure 3. The analysis showed that the palladium film deposited on the ceramic substrate is essentially pure but contains a small amount of carbon in the plating. We are not sure about the source of carbon contamination in the palladium film.

Figure 4a shows a schematic of the composite membrane showing the location of palladium film and palladium activated seed on one side of the cleaned microporous ceramic substrate. Figures 4b, 4c and 4d show the SEM micrographs of the ceramic substrate, sensitized and activated substrate (palladium seed) and the electroless deposited palladium film. Based on SEM micrographs, no significant surface modifications were observed after the substrate was activated and sensitized. The pore size remained more or less the same. However, the surface structure changed dramatically after the thin film was plated. All pores were fully covered by the solid palladium film and no pin holes were detected.

There is no universal means for measuring the thickness of metallic coatings [17]. Of the various available methods, weight-gain, differential thickness and SEM methods are considered most common. In this work, the film thickness was measured by the weight-gain method. In this method the weight difference between the unplated and plated disc is divided by product of the disc surface area and the palladium density to obtain the approximate film thickness. We also measured the film thickness from differential thickness measurements using an Alpha-step 200 Scanning Profilometer. To apply this method, we masked part of the disk surface to create layers similar to the schematic shown in Figure 4a. Profilometer scanning

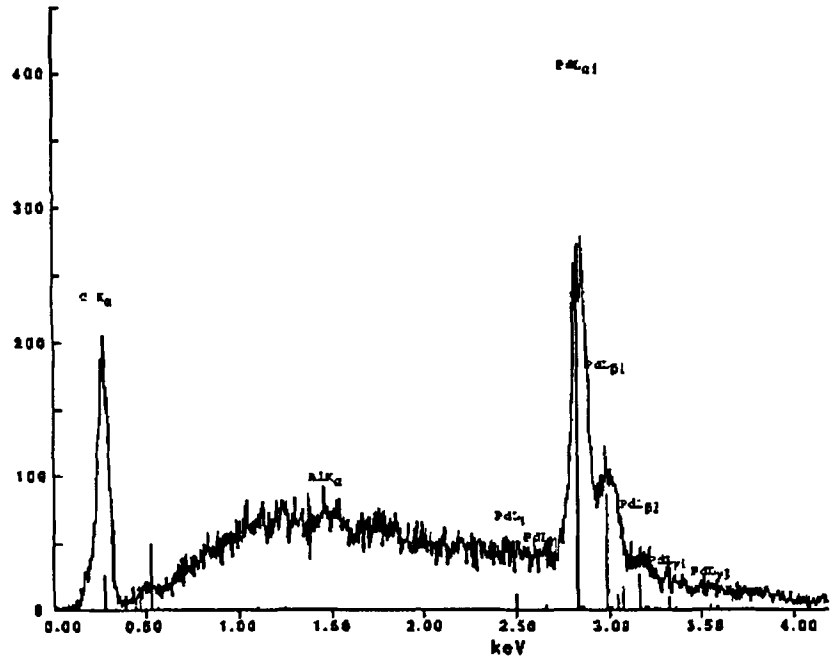

FIGURE 3. Energy Dispersive X-ray (EDX) analysis of Electroless Deposited Palladium Film on Ceramic Substrate.

of a sample membrane from the Pd-film surface to the seed surface and from the seed surface to the substrate were used to measure the differential thickness of palladium film deposit. The Pd-film thickness was found to be 0.83 μm by this method. By the weight-gain method, the film thickness was estimated to be 8.5 μm. One explanation for the difference may be attributed to the so-called "plug-layer" phenomena. In the scanning method, one assumption was that no palladium was seeded in the pores of the substrate and the interface between the Pd-film and the substrate was flat. In reality, however, Pd could fill the pores of the substrate and the profilometer scans only the upper face of the film, while the actual film thickness could be much higher.

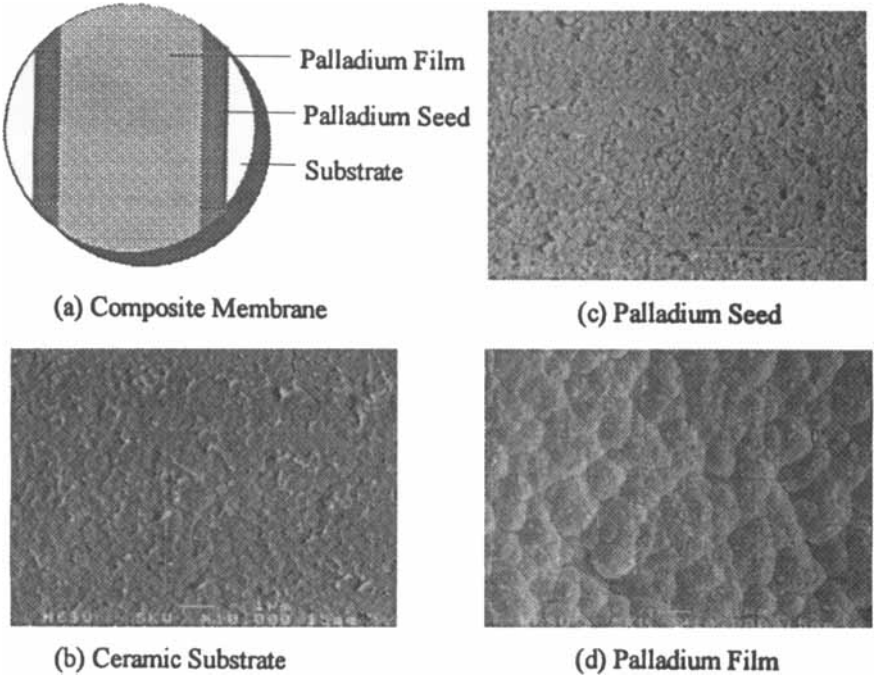

FIGURE 4. SEM Micrographs of Pd-Ceramic Composite Membrane: (a) Sample Specimen, (b) SEM of Substrate, (c) SEM of Sensitized and Activated Substrate Surface, and (d) SEM of Electroless Deposited Pd-Film on Ceramic Substrate.

Two Pd-ceramic composite membrane specimens were fabricated by the electroless deposition method as discussed earlier. The palladium film thicknesses were estimated by the weight-gain method to be 8.5 and 12 μm. The permeability experiments were conducted at temperatures of 373, 473 and 573 K. The pressure on the high pressure side (hydrogen) ranged from 170 to 240 kPa and the low pressure side was maintained at 136 kPa in all permeability measurement experiments.

Hydrogen flux through a dense metallic film may be described by [18]:

$$N_{H_2} = \frac{P_H}{h}\left[(p_H)^n_{H_2} - (p_H)^n_{Ar}\right] \quad (1)$$

where P_H is the permeability coefficient, h is the palladium-film thickness and p_H with subscripts H_2 and Ar represent the partial pressures of hydrogen on the hydrogen and argon sides of the membrane in the diffusion/permeation cell. When diffusion through the bulk metal is the rate limiting step and hydrogen atoms form an ideal solution in the metal, Sievert's law predicts that n equals to 0.5. However, a value of n greater than 0.5 may result when surface processes influence the permeation rate or when Sievert's law is not followed.

Based on Eqn. (1), the hydrogen flux data were analyzed to estimate the value of n by using the Marquardt-Levenberg non-linear least squares method [19]. For the 8.5 and 12 μm films, the values of n were estimated as 0.778 and 0.501, respectively. From this analysis, it appears that a 12 μm palladium film approaches the limiting definition of a dense Pd-film. With values of n equal to 0.778 and 0.501 for the 8.5 and 12 μm Pd-film composite membranes, the hydrogen fluxes are plotted against driving force, $[(p_H)_{H_2}^n - (p_H)_{Ar}^n]$ in Figures 5 and 6, respectively. At a given temperature, the slope of the line provides the value of P_H/h. Since the membrane film thickness is known, one may calculate the membrane permeability from the known slopes of the lines at various temperatures as shown in Figures 5 and 6. From these Figures, it can be seen that the hydrogen fluxes increase with increasing temperature at a given driving force, $[(p_H)_{H_2}^n - (p_H)_{Ar}^n]$.

As stated in the previous section, a steady-state counter-diffusion method was used to measure the hydrogen permeability across the composite membrane in which pure hydrogen was used as feed gas on the high pressure side and pure argon was used as sweep gas on the low pressure side. Feed side gas sample analysis using the Gas Chromatographic System (Perkin Elmer Sigma 200) did not show any presence of argon (within the detection limit). This suggests that the composite membrane has very high selectivity for hydrogen. This was also confirmed by reversing pressures on the argon and hydrogen sides of the permeation cell.

The permeability coefficient is a strong function of temperature and can be described by an Arrhenius type equation as [20]:

$$P_H = P_{HO} \exp\left(- \frac{E_H}{RT} \right) \qquad (2)$$

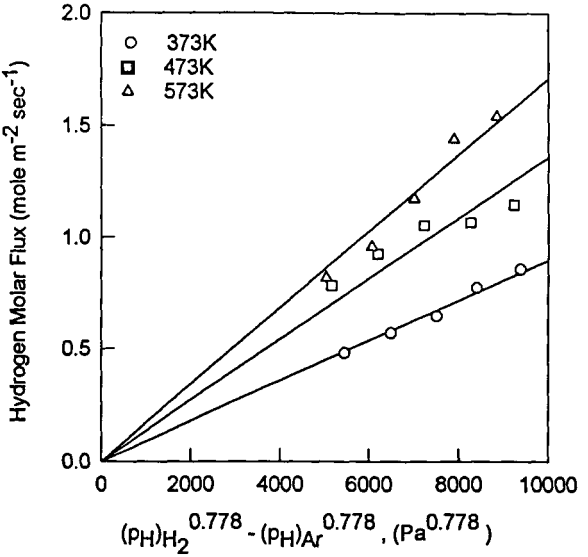

FIGURE 5. Effect of Driving Force, $[(p_H)_{H2}^n - (p_H)_{Ar}^n]$ on Fluxes at Various Temperatures Through Palladium-Ceramic Composite Membrane with a Film Thickness of 8.5 μm and n = 0.778.

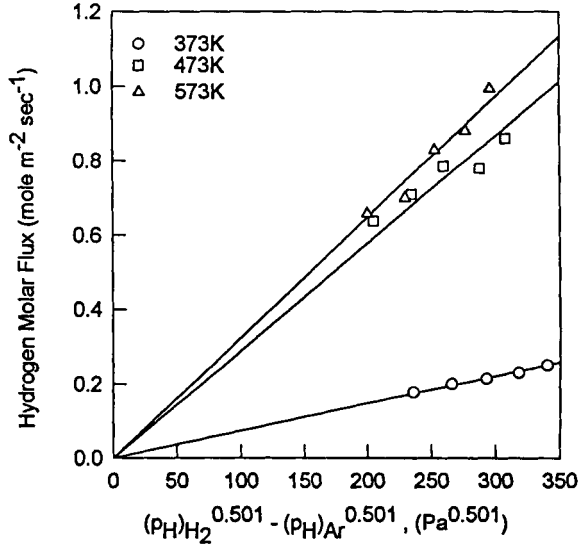

FIGURE 6. Effect of Driving Force, $[(p_H)_{H2}^n - (p_H)_{Ar}^n]$ on Fluxes at Various Temperatures Through Palladium-Ceramic Composite Membrane with Film Thickness of 12 μm and n = 0.501.

where P_{H0} is the pre-exponential factor in the Arrhenius relationship for hydrogen permeability, E_H is the apparent activation energy of hydrogen permeability, T is the absolute temperature and R is the universal gas constant. To correlate the permeability coefficients of the two membranes, permeabilities were plotted against 1/T as shown in Figure 7.The data points correlate very well according to Eqn. (2) since the lines are straight and there is little scatter in the data. From Figure 7, we found that the thicker Pd-film composite membrane has a higher activation energy. The apparent activation energies for the 8.5 and 12 μm membranes were estimated to be 5,684 and 12,995 J/mol, respectively. The pre-exponential factors in the Arrhenius relationship for hydrogen permeability of the 8.5 and 12 μm membranes were found to be 4.99×10^{-9} mol·m/m^2·s·Pa$^{0.778}$ and 6.63×10^{-7} mol·m/m^2·s·Pa$^{0.501}$, respectively.

Our new membrane demonstrated significantly higher hydrogen flux compared to other results on hydrogen flux through composite metal membranes consisting of relatively thin palladium or platinum coating (30 μm) on hydrogen permeable base metals [21,22] and composite metal microporous membranes [8,16]. Table 3 compares measured hydrogen permeability data at specific temperatures with data reported by Collins and Way [16]. They used ceramic substrates with 200 nm pore and hydrogen permeability measurements were performed at temperatures in the range of 773 to 873 K. In our work, we used ceramic substrate with 150 nm pore and hydrogen permeabilities were measured at temperatures in the range of 373 to 573 K. Although the palladium thicknesses were not same, Eqn. (2) can be used to extrapolate hydrogen permeabilities to other temperatures.

Table 4 presents computed hydrogen permeabilities of our membranes at the temperatures used by Collins and Way [16]. The results show that the electroless plated palladium-ceramic composite membranes developed in this work provide significantly higher hydrogen permeability. For example, Collins and Way [16] reported measured hydrogen permeabilities as 6.82×10^{-9} mol·m/m^2·s·Pa$^{0.573}$, and 3.23×10^{-9} mol·m/m^2·s·Pa$^{0.580}$ at 823 K for palladium film thicknesses of 17 and 11.4 μm, respectively on microporus ceramic substrates. At the same temperature, our membranes with palladium film thicknesses of 12 and 8.5 μm

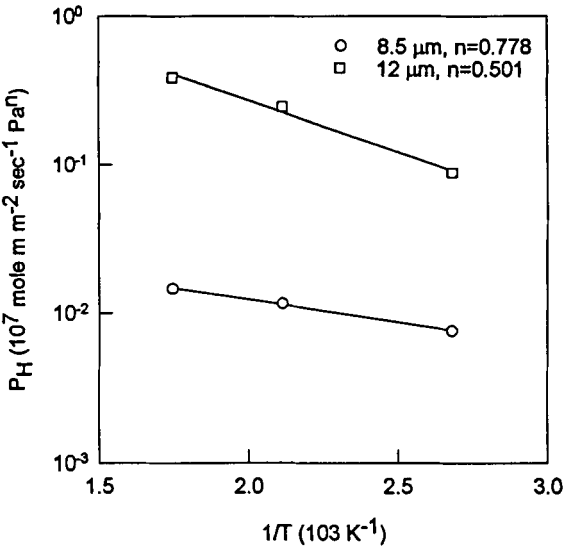

FIGURE 7. Effect of Temperature on Hydrogen Permeability Through Palladium-Ceramic Composite Membranes.

TABLE 3. Summary of Hydrogen Permeability Data at Specific Temperatures for Palladium-Ceramic Composite Membranes.

Membrane Description	Temperature (K)	Permeability, P_H (mol·m/m^2·s·Pa^n)	n	Reference
8.5 μm palladium film on ceramic membrane with 150 nm pore	373 473 573	7.62×10^{-10} 1.16×10^{-9} 1.46×10^{-9}	0.778 0.778 0.778	This work
12 μm palladium film on ceramic membrane with 150 nm pore	373 473 573	8.84×10^{-9} 2.47×10^{-8} 3.87×10^{-8}	0.501 0.501 0.501	This work
17 μm palladium film on ceramic membrane with 200 nm pore	723 773 823 873	2.34×10^{-9} 4.04×10^{-9} 6.82×10^{-9} 9.96×10^{-9}	0.573 0.573 0.573 0.573	[16]
11.4 μm palladium film on ceramic membrane with 200 nm pore	823 873	3.23×10^{-9} 5.84×10^{-9}	0.580 0.580	[16]

TABLE 4. Computed Hydrogen Permeability Using $P_H = P_{HO} \exp(-E_H/RT)$ at Indicated Temperatures for New Palladium-Ceramic Composite Membranes.

Membrane Description	Temperature (K)	Permeability, P_H ($mol \cdot m/m^2 \cdot s \cdot Pa^n$)	P_{HO} ($mol \cdot m/m^2 \cdot s \cdot Pa^n$) E_H (J/mol)
8.5 μm palladium film on ceramic membrane with 150 nm pore	773	2.02×10^{-9}	$P_{HO} = 4.99 \times 10^{-9}$
	823	2.14×10^{-9}	$E_H = 5{,}684$
	873	2.24×10^{-9}	n=0.778
12 μm palladium film on ceramic membrane with 150 nm pore	773	8.39×10^{-8}	$P_{HO} = 6.63 \times 10^{-7}$
	823	9.52×10^{-8}	$E_H = 12{,}995$
	873	1.06×10^{-7}	n=0.501

showed hydrogen permeability of 9.52×10^{-8} $mol \cdot m/m^2 \cdot s \cdot Pa^{0.501}$, and 2.14×10^{-9} $mol \cdot m/m^2 \cdot s \cdot Pa^{0.778}$, respectively. Because of the higher permeability and thinner Pd-films, the new membranes developed here are capable of giving higher hydrogen flux at comparable operating pressures. The thickness of Pd-film dictates the hydrogen flux through the composite membrane.

CONCLUSIONS

In this study, electroless plating of palladium was used to fabricate thin-film Pd-ceramic composite membranes. Permeability measurements at elevated temperatures and pressures showed that the composite membrane has a very high permeability and selectivity for hydrogen. The thickness of Pd-film dictates the hydrogen flux through the composite membrane. As the film thickness increases, one may approach the case of thick dense metallic film. Using the electroless plating method developed in this work, it appears that a film thickness of 12 μm approaches the limit of dense film (with index n estimated as 0.501). We believe that the new Pd-ceramic composite membrane has great potential for high temperature hydrogen separations and membrane reactors if a fabrication process can be perfected.

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