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Separation of Hydrogen Using Electroless Deposited Thin-Film Palladium-Ceramic Composite Membrane

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INTRODUCTION

The development of high temperature membranes to recover hydrogen is a topic of considerable scientific interest. Since coal gasification and several high-temperature industrial processes generate hydrogen as a byproduct, the recovery of hydrogen is of significant commercial importance. Many heterogeneous catalytic reactions can not achieve high conversion 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 [1]. 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 needed for desired conversion can be lowered. These principles can be applied to several other industrially significant reactions where the efficiency of the process depends on the effectiveness of hydrogen removal. Hence, 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 equilibrium shift in a catalytic reactor [2]. However, the productivity of these membrane reactors is 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 acts as a poor perm-separator. Thus, the major challenge lies in developing a perm-selective thin film, without compromising the integrity of the film.

To develop a new class of perm-selective inorganic membranes, we identified electroless plating to deposit a thin metal film on microporous substrate. Electroless plating is the 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. This method can be used to make thin films of metals, alloys and composites on both conducting and nonconducting surfaces.

OBJECTIVES

The primary objective of this project was to prepare and characterize a hydrogen permselective palladium-ceramic composite membrane for high temperature gas separations and catalytic membrane reactors. Electroless plating method was used to deposit a thin palladium film on microporous ceramic substrate. 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. In this paper, we also present a model to describe the hydrogen transport through the palladium-ceramic composite membrane in a cocurrent flow configuration.

PROJECT DESCRIPTION

Membrane Preparation and Characterization

The major tasks involved in the development of a thin-film palladium-ceramic composite membrane are (a) electroless plating of palladium on ceramic substrate, (b) characterization of palladium-ceramic composite membrane formed, (c) measurement and evaluation of perm-selectivity of the composite membrane for hydrogen separation. 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 three step process involving pretreatment of the substrate, sensitization and activation of the substrate surface, and electroless plating. The details of the plating procedures and formulations of the plating solutions are reported elsewhere [3]. The palladium-ceramic membranes were studied by taking SEM (scanning electron microscope) micrographs, EDX (energy-dispersive X-ray) analysis and measuring the thickness of the coated film by a weight-gain method.

Permeability Measurements

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. 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 gas sources, a diffusion cell, a tubular furnace, rotameters and a gas chromatograph. Experimental details are reported elsewhere [3].

Modeling of Gas Separation Module

The permeation of hydrogen through a palladium film is a complex process. The process begins with sorption of hydrogen molecules on the film surface and ends with hydrogen desorption from the ceramic substrate. It is believed that the hydrogen molecule dissociates into hydrogen atoms on one side of the film. The hydrogen atoms then diffuse through the film and reassociate on the other

side. Since the reaction kinetics of formation of hydrogen atoms from molecules and the reverse reaction are assumed to be very fast, the permeation of the hydrogen atoms through the film is the rate limiting step. The permeability can be considered as product of solubility and diffusivity. The permeation rate of hydrogen can be given by [4]:

$$J_a = \frac{Q_a}{h} [(Px_a)^n - (py_a)^n] \quad (1)$$

If diffusion through the bulk metal is the rate limiting step and hydrogen atoms form an ideal solution in the metal, then Sievert's law hydrogen solubility dependence holds and n is equal to 0.5. The hydrogen flux is inversely proportional to the palladium film thickness (h) when the bulk diffusion is the rate limiting step. In case of polymeric membrane where selective transport of a gas is by a solution-diffusion process, the index n in Eqn. (1) has always been taken as 1. For thin-film palladium-ceramic composite membrane, since n lies between 0.5 to 1.0, the designs of membrane modules require detailed analysis of flow patterns for gas separations using Eqn. (1). In this paper, we present a generalized mathematical model for a cocurrent flow pattern in a membrane separator with n varying from 0.5 to 1.0 which depend on the type of membrane used.

Figure 1 illustrates a single permeation stage of gas separation by permeation with cocurrent plug flow on both sides of the membrane. In this flow pattern, the concentrations and flow rates of the feed and sweep gases are fixed. The design problem is to determine the states of the product and residue gas streams and membrane area requirement for a desired residue or product concentration.

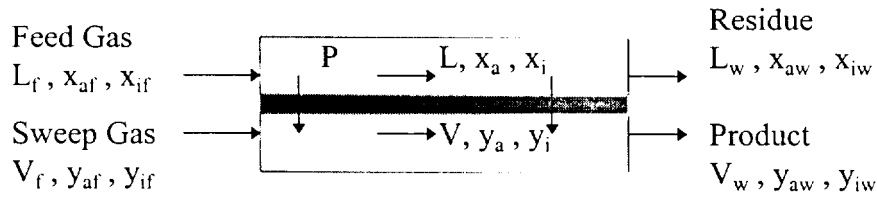


Figure 1. Schematic of Co-Current Flow Patterns of Gas Separation Module

The material and component balances between the inlet and at any point along the membrane, under certain simplifying assumptions, may be given as:

$$\begin{aligned} L + V &= L_f + V_f ; & Lx_a + Vy_a &= L_f x_{af} + V_f y_{af} \\ Lx_i &= L_f x_{if} = \text{constant} ; & Vy_i &= V_f y_{if} = \text{constant} \\ x_a + x_b + x_i &= 1 ; & y_a + y_b + y_i &= 1 \end{aligned} \quad (2a,b,c)$$

The rates of permeation of the permeable components per unit membrane area are given by:

$$\begin{aligned} \frac{d(Vy_a)}{dS} &= \left(\frac{Q_a}{h} \right) [(Px_a)^n - (py_a)^n] \\ \frac{d(Vy_b)}{dS} &= \left(\frac{Q_b}{h} \right) [(Px_b)^n - (py_b)^n] \end{aligned} \quad (3a,b)$$

Equations (3a,b) along with the material balance Eqns. (2a,b,c) are solved subject to initial conditions:

$$\text{At } S = 0, \quad L = L_f; \quad x_a = x_{af}; \quad x_i = x_{if} \quad \text{and} \quad V = V_f; \quad y_a = y_{af}; \quad y_I = y_{if}$$

The equations were solved numerically to evaluate the performance of the membrane module. The details of the model developments and solution methodology is given elsewhere [5].

RESULTS AND DISCUSSIONS

Thin-film, Pd-ceramic composite membrane was developed by electroless deposition of palladium on planar ceramic substrate. Two sample 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 showed that the palladium film was essentially pure. SEM micrographs of the composite membrane specimen showed that the substrate pores were fully covered by solid palladium film. No pin holes were detected. The membrane specimens were fabricated by electroless deposition method as discussed. The palladium film thicknesses were estimated to be 8.5 μm and 12 μm by a weight-gain method. The permeability experiments were conducted in a diffusion cell at temperatures of 373K, 473K and 573K. The pressures on the high-pressure side ranged from 170 kPa to 240 kPa and the low pressure side was maintained at about 136 kPa. 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. For the 8.5 μm and 12 μm films, the average values of n were estimated as 0.778 and 0.501, respectively. From this analysis, it appears that a palladium film of 12 μm thickness approaches the limiting definition of dense Pd-film according to Sievert's law.

Table 1 shows measured hydrogen permeability data at specific temperatures along with that reported by Collins and Way [6]. In their work, Collins & Way used ceramic substrate with 200 nm pore and hydrogen permeability measurements were performed at temperatures in the range of 773K to 873K. In our work, we used ceramic substrate with 150 nm pore and hydrogen permeabilities were measured at temperatures in the range of 373K to 573K. Although the palladium thicknesses were not same, one can use Arrhenius type equation to extrapolate the

TABLE 1. Summary of Hydrogen Permeability Data at Specific Temperatures for Palladium-Ceramic Composite Membranes

Membrane Description	Temperature (K)	Permeability (P_H) [#]
8.5 μm Pd-film on ceramic membrane with 150 nm pore (n=0.778) [*]	373	7.62×10^{-10}
	473	1.16×10^{-9}
	573	1.46×10^{-9}
12 μm Pd-film on ceramic membrane with 150 nm pore (n=0.501) [*]	373	8.84×10^{-9}
	473	2.47×10^{-8}
	573	3.87×10^{-8}
17 μm Pd-film on ceramic membrane with 200 nm pore (n=0.573) ^{**}	723	2.34×10^{-9}
	773	4.04×10^{-9}
	823	6.82×10^{-9}
11.4 μm Pd-film on ceramic membrane with 200 nm pore (n=0.580) ^{**}	823	3.23×10^{-9}
	873	5.84×10^{-9}

^{*} This work [3] ^{**} Collins & Way [6]
[#] Permeability, P_H ($\text{mol} \cdot \text{m} / \text{m}^2 \cdot \text{s} \cdot \text{Pa}^n$)

TABLE 2. Computed Hydrogen Permeability Using $P_H = P_{HO} \exp(-E_H / RT)$ at Indicated Temperatures for New Palladium-Ceramic Composite Membranes:
 $P_{HO} = 4.99 \times 10^{-9} \text{ mol} \cdot \text{m} / \text{m}^2 \cdot \text{s} \cdot \text{Pa}^n$; $E_H = 5,684 \text{ J/mol}$ for 8.5 μm Pd-film
 $P_{HO} = 6.63 \times 10^{-7} \text{ mol} \cdot \text{m} / \text{m}^2 \cdot \text{s} \cdot \text{Pa}^n$; $E_H = 12,995 \text{ J/mol}$ for 12 μm Pd-film

Membrane Description	Temperature (K)	Permeability (P_H)
8.5 μm Pd-film on ceramic membrane with 150 nm pore (n=0.778)	773	2.02×10^{-9}
	823	2.14×10^{-9}
	873	2.24×10^{-9}
12 μm Pd-film on ceramic membrane with 150 nm pore (n=0.501)	773	8.39×10^{-8}
	823	9.52×10^{-8}
	873	1.06×10^{-7}

hydrogen permeabilities at different temperatures. Table 2 presents computed hydrogen permeabilities of our membranes at temperatures similar to that of Collins & Way [6]. The results clearly shows that the electroless plated palladium-ceramic composite membranes developed in this work provides significantly higher hydrogen permeability.

For a cocurrent permeation cell, we conducted a parametric study of the effects of various operating parameters on the separation process. The factors considered were stage-cut, selectivity, pressure ratio, membrane area and membrane specific characteristic index, n . Figure 2 shows the variation of enrichment factor as a function of membrane selectivity with pressure ratio as a parameter. The example shown here is for cocurrent permeation with $n=0.501$, and the feed composition (more permeable component, hydrogen) changing from 0.71 at the inlet to 0.40 mole fraction as residue. The results show that with decreasing pressure ratio (increasing pressure on the feed side), nearly pure permeate may be obtained at relatively high membrane selectivity. However, at high pressure ratio the membrane selectivity has marginal effect on permeate purity.

The effect membrane surface area on residue concentration is shown in Figure 3 for various pressure ratio. In this example, membrane selectivity is taken as 650 with $n=0.501$, feed flow rate 1 mol/s and the low pressure side pressure as 1 bar. The results indicate that with increasing pressure, a larger membrane area would be required for the same residue concentration. In other words, for a given membrane module area higher separation (low residue concentration) is achieved if the module is operated at low pressure ratios.

CONCLUSIONS

A thin-film palladium-ceramic composite membrane was developed by depositing palladium on ceramic substrate by electroless plating. 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 dictate the hydrogen flux through the composite membrane. As the film thickness increases, one may approach the case of thick dense metallic film. Based on this work, it appears that a film thickness of 12 μm approaches the limit of dense film (with index n estimated as 0.501). A mathematical model is presented to describe the performance of a cocurrent permeation cell. The model includes the effect of membrane specific characteristic index n which varies from 0.5 to 1.0. We believe that the new Pd-ceramic composite membrane has great potential in high temperature hydrogen separations and membrane reactors if the fabrication process can be perfected.

CONTRACT INFORMATION

Research sponsored by the U.S. DOE - METC, under contract DE-FG22-93MT93008 with North Carolina A&T State University, Greensboro, NC 27411; (910) 334-7995. Drs. S. Ilias and F.G. King are the PIs of the project and Dr. V.K. Venkataraman is the METC Project Manager.

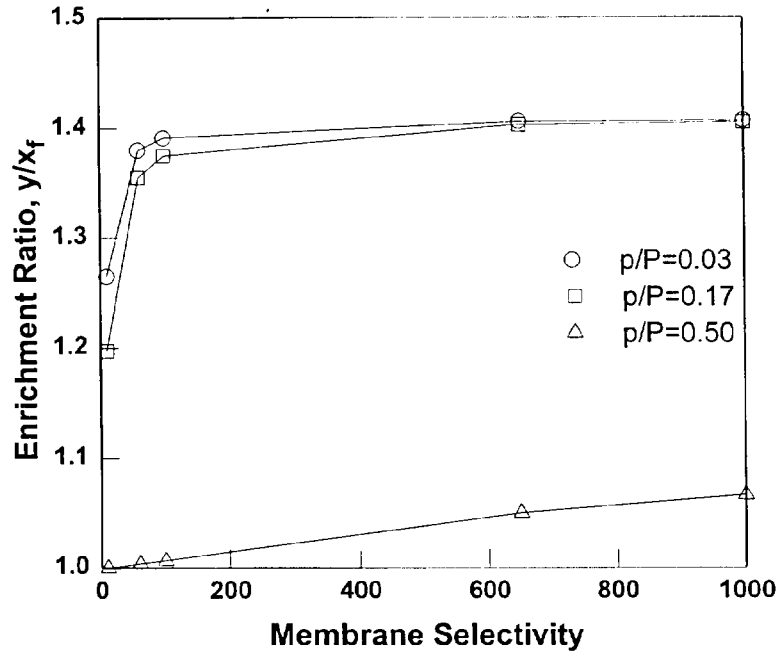


Figure 2. Effect of pressure ratio on enrichment factor as a function of membrane selectivity in a cocurrent permeation cell ($n=0.501$, mole fraction of hydrogen in feed, $x_f=0.71$ and residue $x_w=0.4$)

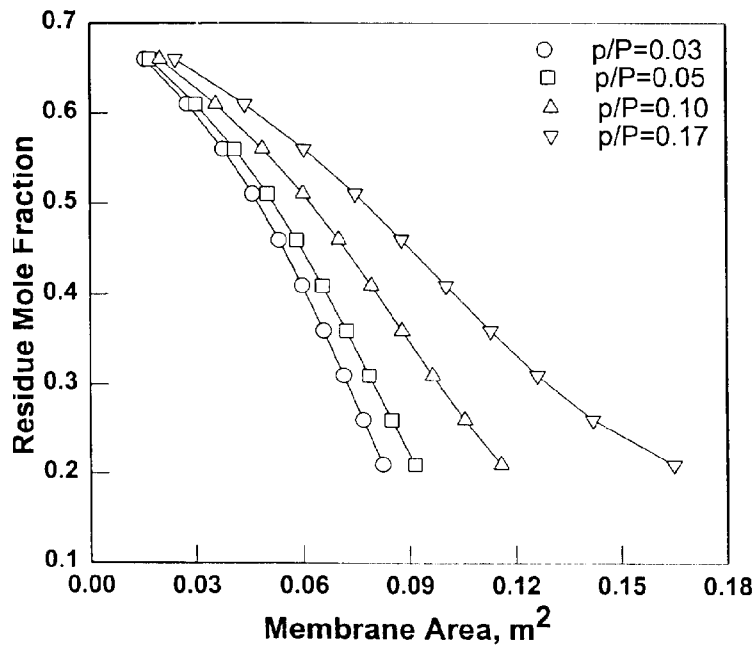


Figure 3. Effect of pressure ratio on residue concentration as a function of membrane area ($n=0.501$, $x_f=0.71$, $\alpha=650$, $p=1$ bar, $L_f=1$ mol/s).

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NOMENCLATURE

h	Membrane thickness, m
L	Feed-side flow rate, mol/hr
L_f	Inlet feed flow rate, mol/hr
P	Feed-side pressure, Pa
p	Permeate-side pressure, Pa
Q_a	Membrane permeability of more permeable component A, mol-m/m ² -hr-Pa ⁿ
Q_b	Membrane permeability of less permeable component B, mol-m/m ² -hr-Pa ⁿ
S	Membrane area, m ²
V	Permeate-side flow rate, mol/hr
V_f	Sweep gas flow rate, mol/hr
x_s	mole fractions in feed side (a=more permeable, b=less permeable, af=feed gas, aw=residue, I=inert, if=inert in feed gas, iw=inert in residue)
y_s	mole fractions in permeate side (a=more permeable, b=less permeable, af=feed inlet end, aw=residue end, I=inert, if=inert in feed inlet end, iw=inert at residue end)
α	Membrane selectivity, Q_a/Q_b
γ	p/P, permeate to feed pressure ratio

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