

Annual Progress Report

**Palladium/Copper Alloy Composite Membranes for High Temperature Hydrogen  
Separation**

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Submitted by

J. Douglas Way

Paul M. Thoen

Chemical Engineering Department

Colorado School of Mines

Golden, CO 80401-1887

Office: (303) 273-3519

Telefax: (303) 273-3730

EMAIL: [dway@mines.edu](mailto:dway@mines.edu)

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Administrative Contact: Mary Mittag-Miller  
(303) 273-3411

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## Abstract

This report summarizes progress made during the second year of research funding from DOE Grant # DE-FG26-03NT41792 at the Colorado School of Mines. The period of performance was September 1, 2004 through August of 2005. We have reformulated our Pd plating process to minimize the presence of carbon contamination in our membranes. This has improved durability and increased permeability. We have developed techniques for plating the outside diameter of ceramic and metal substrate tubes. This configuration has numerous advantages including a 40% increase in specific surface area, the ability to assay the alloy composition non-destructively, the ability to potentially repair defects in the plated surface, and the ability to visually examine the plated surfaces. These improvements have allowed us to already meet the 2007 DOE Fossil Energy pure H<sub>2</sub> flux target of 100 SCFH/ft<sup>2</sup> for a hydrogen partial pressure difference of 100 psi with several Pd-Cu alloy membranes on ceramic microfilter supports. Our highest pure H<sub>2</sub> flux on inexpensive, porous alumina support tubes at the DOE target conditions is 215 SCFH/ft<sup>2</sup>. Progress toward meeting the other DOE Fossil Energy performance targets is also summarized. Additionally, we have adapted our membrane fabrication procedure to apply Pd and Pd alloy films to commercially available porous stainless steel substrates. Stable performance of Pd-Cu films on stainless steel substrates was demonstrated over a three week period at 400 °C. Finally, we have fabricated and tested Pd-Au alloy membranes. These membranes also exceed both the 2007 and 2010 DOE pure H<sub>2</sub> flux targets and exhibit ideal H<sub>2</sub>/N<sub>2</sub> selectivities of over 1000 at partial pressure difference of 100 psi

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## Executive Summary

This report summarizes progress made during the second year of research funding from DOE Grant # DE-FG26-03NT41792 at the Colorado School of Mines. The period of performance was September 1, 2004 through August of 2005.

Palladium and its alloys, as well as Ni, Pt and the metals in Groups III - V of the Periodic Table are all permeable to hydrogen. Hydrogen-permeable metal membranes made of palladium and its alloys are the most widely studied due to their high hydrogen permeability, their chemical compatibility with many hydrocarbon containing gas streams, and their theoretically infinite hydrogen selectivity. Palladium alloys often possess higher hydrogen permeability than pure palladium. In particular, alloy membranes, such as Pd<sub>95</sub>Au<sub>5</sub> and Pd<sub>60</sub>Cu<sub>40</sub>, have a higher H<sub>2</sub> permeability than pure palladium, are unaffected by thermal cycling, and are resistant to sulfur poisoning. In the case of Pd and Cu, the hydrogen permeability has a sharp maximum at the 40-wt % Cu alloy composition.

A robust, hydrogen permselective palladium membrane has the potential to change the chemical industry by replacing traditional reaction and separation procedures, thereby resulting in sizable savings in energy consumption and capital investment in equipment. This increased functionality and energy saving benefit in combination with high hydrogen permselectivity and flux (throughput) make palladium alloy membranes an attractive hydrogen separation technology. The 2007 U. S. DOE Fossil Energy membrane performance target for the pure hydrogen flux at 400 °C at a differential pressure of 100 psi is 100 ft<sup>3</sup>(STP)/ft<sup>2</sup>•h.

Composite membranes, consisting of a thin Pd alloy film supported on a porous substrate have been investigated as a means of reducing the membrane cost and improving H<sub>2</sub> flux. An electroless plating technique was utilized to deposit subsequent layers of palladium and copper over ceramic and stainless steel microfilters. The composite membranes thus made were annealed and tested at temperatures ranging from 250 to 500°C, at feed pressures (up to 100 psig) using pure gases. We have successfully modified our membrane fabrication methods to reduce carbon contamination in the Pd film and to deposit the Pd alloy films on the outside of the porous support tubes. This “outside film” configuration has several important advantages including:

- An increase in specific surface area of approximately 40%
- The deposited films can be easily examined visually
- The ceramic support tubes are much stronger in compression, allowing operation at higher feed or differential pressures
- Simple leak check methods can determine the location of leaks and methods can be devised to repair fabricated membranes
- Non-destructive characterization methods such as ESEM (environmental scanning electron microscopy), x-ray spectroscopy (EDX and XRF), and x-ray diffraction can be utilized to analyze the membranes.

These improvements have allowed us to exceed the 2007 and 2010 DOE Fossil Energy pure H<sub>2</sub> flux targets with several Pd-Cu and Pd-Au alloy membranes on inexpensive, symmetric ceramic microfilter supports.

Pd and Pd alloy films were deposited on commercially available porous stainless steel substrates from the Mott Corporation. A ceramic diffusion barrier was deposited onto the steel substrates prior to electroless plating of Pd and Pd alloy films. Stable performance of a Pd-Cu film on a stainless steel substrate was demonstrated over a three week period at 400 °C suggesting that the ceramic diffusion barrier layer was effective in preventing intermetallic diffusion between the stainless steel substrate and the palladium alloy film.

## Introduction and Objectives

The feasibility of preparing and using pure Pd-membranes for H<sub>2</sub> separation is well known. However, pure Pd membranes suffer from embrittlement, and poisoning by sulfur. Furthermore, the ability of thick Pd-Cu alloy membranes to separate H<sub>2</sub>, and the high temperature stability and resistance to poisoning of these materials has been demonstrated. During our previous UCR Grant, we have demonstrated that very thin, 1 μm thick Pd-Cu composite membranes can be fabricated that exhibit high H<sub>2</sub> flux and are also resistant to H<sub>2</sub>S. However, we observed several very interesting phenomena associated with these membranes including the influence of surface structure on H<sub>2</sub> transport and inhibition of H<sub>2</sub> flux by H<sub>2</sub>S. The proposed research plan is designed to further investigate these phenomena, while also providing a fundamental understanding of:

- Factors important in membrane fabrication, particularly on stainless steel supports,
- Optimization of membrane crystal and surface structure and bulk composition,
- Effect of temperature, pressure, and gas composition on H<sub>2</sub> flux and membrane selectivity,
- Mechanisms that may lead to different separation factors observed during mixture measurements, especially the inhibition of H<sub>2</sub> flux in the presence of H<sub>2</sub>S, and
- The “air purge” phenomenon, where a controlled air oxidation leads to higher flux, but reduced selectivity.

## Technical Progress

### Task 1.0 Fabrication of Pd/Cu Alloy Membranes.

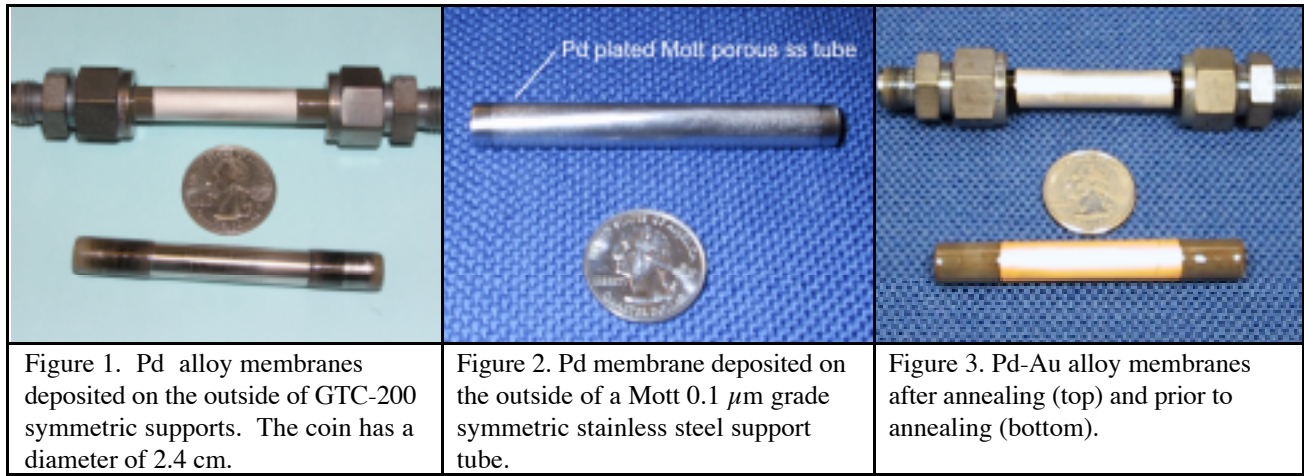
Composite Pd alloy membranes were fabricated by sequential deposition of palladium and copper by electroless plating onto porous ceramic and stainless steel filter supports. Our prior publications describe this procedure in detail[1, 2].

Examples of supports used include: symmetric 0.2 μm cut-off α-alumina tubes from CoorsTek(GTC-200), asymmetric 0.02 and 0.05 μm cut-off zirconia-coated α-alumina tubes (USF-020, USF-050) from Exekia (Pall Corporation), and 0.1 and 0.5 grade porous stainless steel supports from the Mott Corporation. Ceramic supports are prepared by cutting to length, cleaning and sealing the ends with a silica glaze. Stainless steel supports are prepared by cutting to length, cleaning, and then applying a porous diffusion barrier. A seeding procedure is used prior to the palladium plating. That step involves impregnation of the ceramic support with an organic Pd salt solution, followed by calcination and reduction in flowing hydrogen.

Pd and Cu electroless plating baths were then used in sequence with osmotic pressure gradients to deposit films ranging from 1 to 10 microns in thickness on either the inside or outside of the support tubes. Plating on the outside of a nominal 1 cm OD support tube with a 1.5 mm wall thickness increases the specific surface area by 43% compared to plating the same tube on the inside. The osmotic pressure, generated by circulating concentrated sucrose solutions on the opposite side of the support from the plated film, insured reduced porosity and promoted surface homogeneity and densification of the plated Pd film[3]. We have reformulated our Pd plating bath recipe in an effort to minimize or eliminate the presence of carbon contamination in our membranes. All carbon containing chemicals, such as EDTA have been removed. This has improved durability and increased permeability.

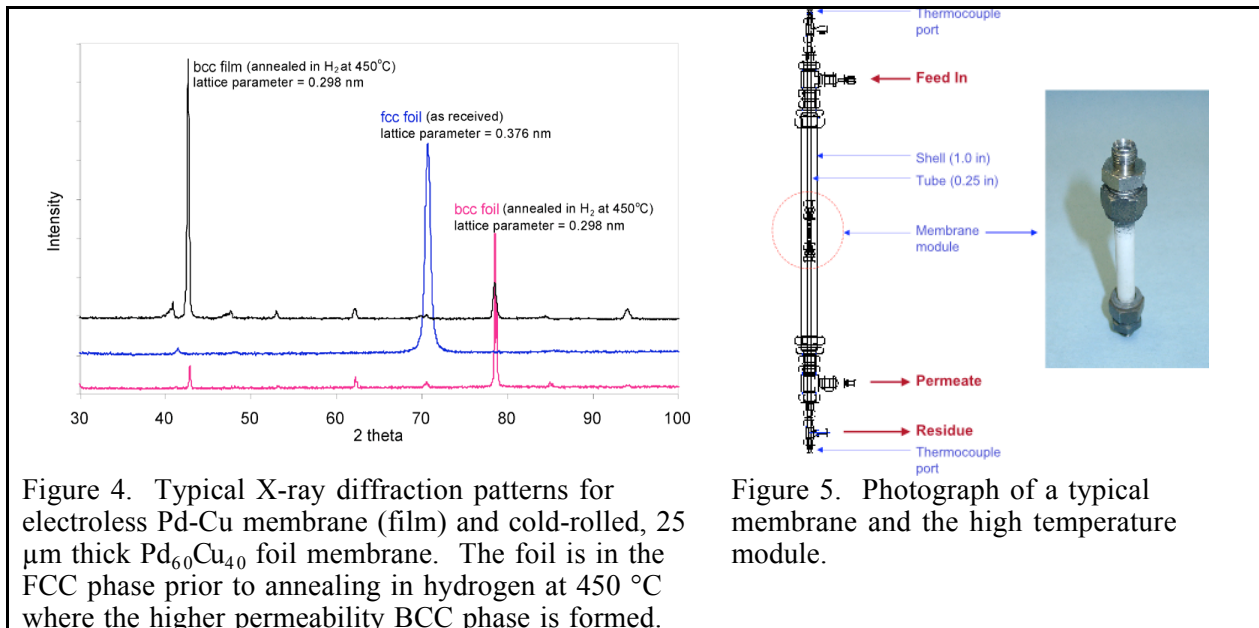
Symmetric, 0.2 μm pore size Al<sub>2</sub>O<sub>3</sub> tubes from CoorsTek (GTC-200) plated on the outside with PdCu alloys are shown in Figure 1. Figure 2 shows a symmetric, porous stainless steel substrate (Mott Corporation) plated with pure Pd. Pd-Au membranes were also fabricated during this

reporting period. These membranes were prepared by displacement plating of gold onto a Pd membrane. Figure 3 shows two Pd-Au alloy membranes. The top membrane in Figure 3 is has been tested and annealed, while the bottom membrane has not been tested or annealed.



### Task 2.0 Characterization of Pd/Cu Membranes.

The composite membranes fabricated in Task 1 were extensively characterized using a nitrogen leak test, ESEM, EDAX, AFM, and XRD. Since these instrumental methods are destructive, these were performed as needed after the permeation studies in Task 3. XRD patterns for our electroless films and reference Pd<sub>60</sub>Cu<sub>40</sub> foil membranes are shown in Figure 4. For membranes containing 60 weight % Pd with the balance being Cu, annealing in hydrogen produces a phase change from an FCC phase to the more permeable BCC phase[4].



### Task 3.0 Pure and Mixed Gas Permeation Studies.

#### *High temperature permeation tests*

The membrane to be tested was loaded into a stainless steel module, which in turn was mounted in a tube furnace. Figure 5 shows a sketch of the module and a photograph of a typical membrane. To avoid embrittlement, the membranes were heated under helium and no H<sub>2</sub> was introduced into the module until the membrane reached 350°C. Annealing the two metals was achieved during the initial single gas permeability tests. Trans-membrane pressure differentials varied from a 10 psig to as high as 435 psig, while typical operating temperatures varied from 250°C to 500°C. Permeate pressure was local atmospheric pressure (12 psia), except for tests using a permeate side sweep gas.

The DOE Fossil Energy target goals for a hydrogen selective membranes are summarized in Table 1 below. We have added a column to show how our composite membranes on low cost supports compare to the DOE target values.

Table 1. DOE Hydrogen Membrane Performance Goals and Current Status of CSM Pd/Cu Alloy Membrane Technology

Performance Criteria	2007 Target	2010 Target	2015 Target	CSM Status
Flux <sup>a</sup>	100	200	300	215
Operating Temperature (°C)	400 – 700	300 – 600	250 – 500	350 - 450
Sulfur Tolerance	Yes	Yes	Yes	Yes
Membrane Cost (\$/ft <sup>2</sup> )	150	100	<100	110 <sup>b</sup>
WGS Activity	Yes	Yes	Yes	Yes
Operating Pressure Capability (psi)	100	400	800 – 1000	300
CO Tolerance	Yes	Yes	Yes	Yes <sup>c</sup>
Hydrogen Purity	95%	99.5%	99.99%	99.94% <sup>d</sup>
Stability/Durability (years)	3	7	>10	Stable over 3 month test

a) SCFH/ft<sup>2</sup> @ 100 psi ΔP H<sub>2</sub>@ 50 psia perm side pressure. This value is calculated from data in Figure 7.

b) Calculations based on \$30/ft<sup>2</sup> for alumina support, \$25/ft<sup>2</sup> for 5 μm thick Pd/Cu membrane and \$55/ft<sup>2</sup> to incorporate membrane elements into a module.

c) Tested up to 8 mol% CO with small, reversible reduction in H<sub>2</sub> flux rate.

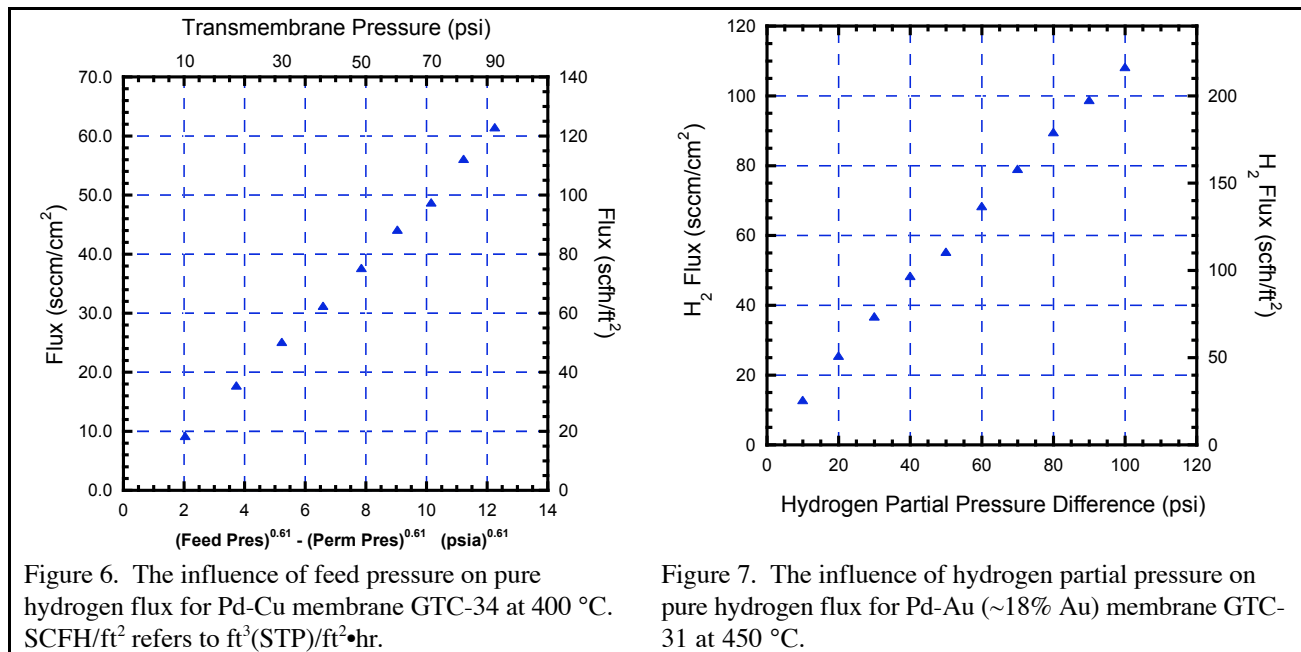
d) Calculated based on ideal H<sub>2</sub>/N<sub>2</sub> selectivities.

The pure H<sub>2</sub> flux of a Pd-Cu alloy film plated onto a GTC 0.2 μm, symmetric support (membrane GTC-34) is shown in Figure 6 below as a function of feed pressure over the range of 10 to 90 psig. Please note that the flux of membrane GTC-34 is about 125 scfh/ft<sup>2</sup> at 400 °C for a 90 psig feed pressure. As shown in Table 1, the calculated H<sub>2</sub> flux for membrane GTC-24 at 400 °C is 140 scfh/ft<sup>2</sup> at the DOE test conditions of 150 psia feed pressure and 50 psia permeate pressure. Therefore, this composite membrane, fabricated on an inexpensive, symmetric support easily exceeds the 2007 DOE Fossil Energy hydrogen flux target. The H<sub>2</sub>/N<sub>2</sub> pure gas selectivity of membrane GTC-34 is about 3000 at a partial pressure difference of 100 psi. The calculated “n-value” for GTC-34 is 0.61, which is slightly higher than the theoretical value of 0.5, which is observed when diffusion of hydrogen atoms through the bulk Pd film is limiting hydrogen permeation. The n-value of 0.61 may indicate some hydrogen mass transfer resistance of the symmetric ceramic support.

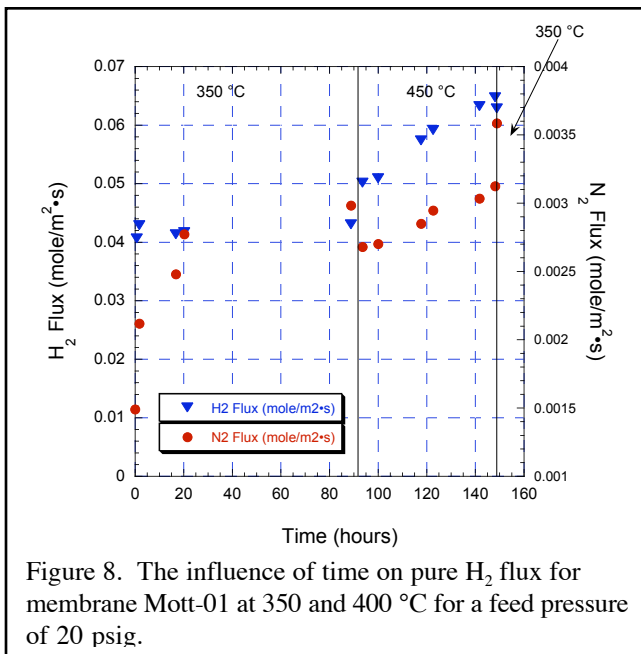
Pd-Au alloy membranes have also been deposited on symmetric, 0.2 μm, alumina GTC supports. As demonstrated by Figure 7, the hydrogen flux, at 450 °C and a partial pressure difference of 100



psi, is 215 scfh/ft<sup>2</sup>, which is over twice the DOE 2007 target and higher than the 2010 target. The ideal H<sub>2</sub>/N<sub>2</sub> selectivity for the membrane ranged from 1020 at 100 psi to 1320 at 10 psi. The data discussed above demonstrate that by reducing the membrane thickness and reducing carbon contamination in the Pd film, we've improved the H<sub>2</sub> flux by about a factor of five compared to similar membranes made using the same symmetric, ceramic support from GTC (CoorsTek) [5].



Using the same improvements developed for the ceramic support tubes, we have begun fabricating Pd and Pd-Cu alloy plated stainless steel tubes. A porous ceramic diffusion barrier was deposited onto the O.D. of the steel support tubes prior to plating. The first tube we plated with approximately 15 μm of Pd that had a low enough N<sub>2</sub> leak rate to test is shown in Figure 8. The support tube was a Mott 0.5 μm grade porous stainless steel tube. The average pore size of this support is about 2 μm. The selectivity of this membrane is modest, approximately 20, as shown by the permeation data in Figure 8. The N<sub>2</sub> leak rate was not constant during this test which we attribute to an inadequate thickness of our diffusion barrier layer. This hypothesis is supported by SEM/EDX analysis, where we detected the presence of Cr and Mo in the Pd film on one end of the tube. We believe that some of the components of the stainless steel were diffusing into the Pd layer and the Pd was being lost by diffusion into the stainless steel support tube (see Figure 10). However, the SEM analysis of the middle of the Pd/ss membrane after permeation



testing, shown in Figure 9, looks very similar to the Pd and Pd alloy/ceramic membranes prepared on ceramic supports.

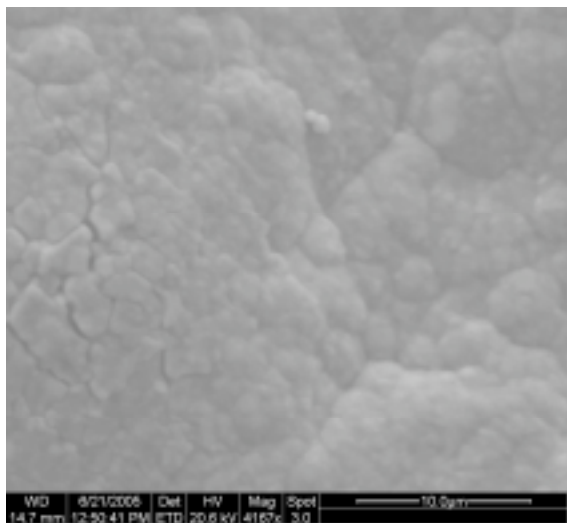


Figure 9. SEM image of the middle of membrane Mott-01 after permeation testing.

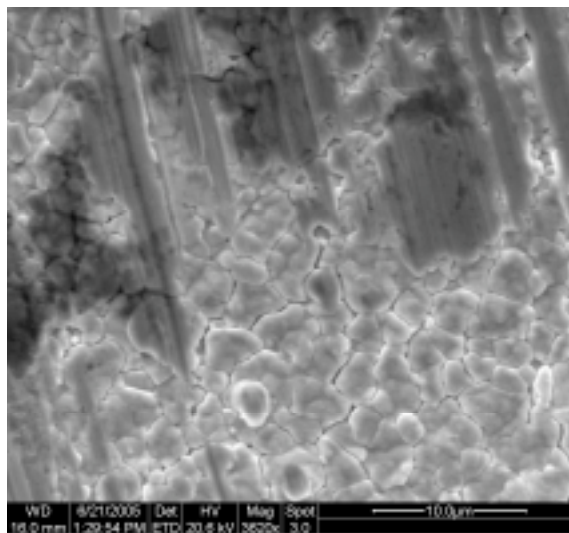


Figure 10. SEM image of one end of membrane Mott-01 after permeation testing. Note the apparently reduced thickness of the Pd layer in some areas.

Data for our second membrane (Mott-28) with a stainless steel support are shown in Figures 11 and 12. In this case, we doubled the thickness of our ceramic diffusion barrier and the uniformity of the diffusion barrier coating on the stainless support was greatly improved based on zero electrical conductivity and an informal visual analysis. Both Pd and Cu layers were sequentially plated to form a film approximately 15 microns thick, with an estimated alloy composition of 33 mass % Cu. Analysis by EDX will confirm the average alloy composition at the conclusion of the permeation test. At this thickness, a significant number of defects remained after plating due to a few large,  $\geq 4 \mu\text{m}$  pores in the Mott grade 0.5 stainless steel substrate. However, the purpose of this test was to evaluate the effectiveness of the diffusion barrier. Therefore, making a membrane with stable performance was more important than demonstrating high selectivity. As shown in Figure 10, the membrane annealed slowly over a period of about 2 weeks at a constant temperature of 400 °C. The  $\text{H}_2$  flux increased steadily during this time due to the annealing of the Pd and Cu layers while the  $\text{N}_2$  “leak” flux was essentially constant. The maximum ideal separation factor is about 40. The performance stability of membrane Mott-28 was greatly improved over our first stainless steel support membrane shown in Figures 8-10. The difference in pure hydrogen flux between the Mott-01 membrane and Mott-28 are due to the greater thickness of Mott-28 and that the permeability of the 33 mass % Cu alloy is a factor of 3 smaller than pure palladium.

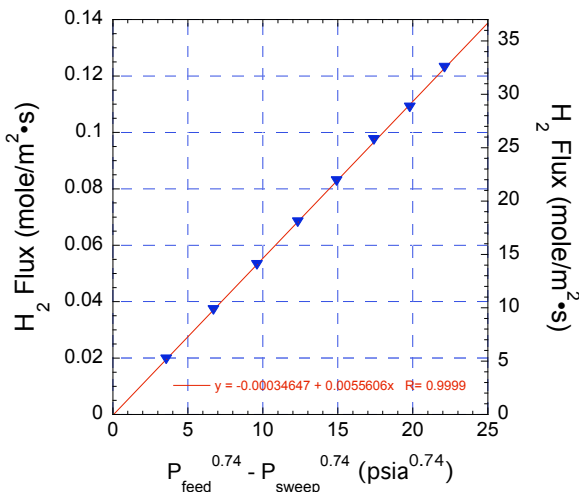


Figure 11. The influence of driving force on the pure H<sub>2</sub> flux of Mott-ss-28 membrane at 400 °C. Data were collected over the feed pressure range 10 – 80 psig.

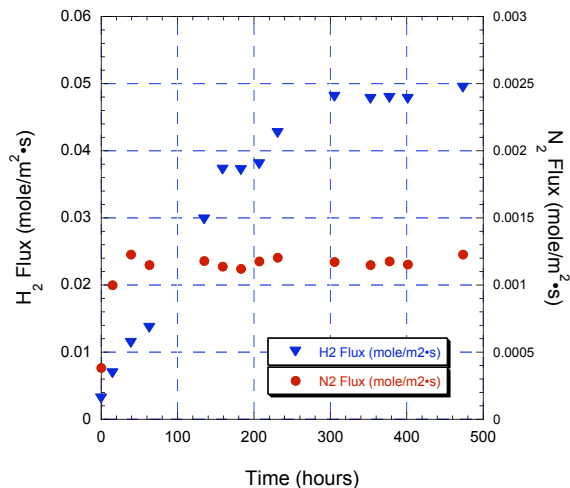


Figure 12. The influence of time on pure hydrogen and nitrogen fluxes for membrane Mott-ss-28 at 400 °C for a feed pressure of 20 psig. The estimated thickness = 15 μm with an alloy composition of ~33 mass % Cu.

## Conclusions

Composite membranes, consisting of a thin Pd alloy film supported on a porous substrate have been investigated as a means of reducing the membrane cost and improving H<sub>2</sub> flux. An electroless plating technique was utilized to deposit subsequent layers of palladium and copper over ceramic and stainless steel microfilters. The composite membranes thus made were annealed and tested at temperatures ranging from 250 to 500°C, at feed pressures (up to 100 psig) using pure gases. We have successfully modified our membrane fabrication methods to reduce carbon contamination in the Pd film and to deposit the Pd alloy films on the outside of the porous support tubes. This “outside film” configuration has several important advantages including:

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These improvements have allowed us to already exceed both the 2007 and 2010 DOE Fossil Energy pure H<sub>2</sub> flux targets with several Pd-Cu and Pd-Au alloy membranes on inexpensive, symmetric ceramic microfilter supports.

## Technology Transfer Activity

### Journal Articles Published/In Press

- Roa, F. and J. D. Way, “The Effect of Air Exposure on Palladium-Copper Composite Membranes,” *Applied Surface Science*, **240**(1-4), 85-104(2005).

- Kulprathipanja, A., Alptekin, G. O., Falconer, J. L. and J. D. Way, "Pd and Pd-Cu Membranes: Inhibition of H<sub>2</sub> Permeation by H<sub>2</sub>S," *Journal of Membrane Science*, **254**, 49-62(2005).

### Journal Articles Submitted

- Thoen, P. M., Roa, F., and J. D. Way, "High Flux Palladium-Copper Composite Membranes for Hydrogen Separations," *Desalination*, in press, 9/2005.
- Roa, F., Thoen, P. M., Way, J. D., DeVoss, S. and G. Alptekin, Effect of CO<sub>2</sub>, CO, H<sub>2</sub>S and Sweep Gas on the Hydrogen Flux of a Pd-Cu Alloy Membrane," ACS Symposium Series: Membranes for Fuels and Energy, accepted, 7/05.

### Presentations at Technical Meetings and/or Seminars

- Palladium-Copper Composite Membranes for Hydrogen Separation, Paper #HFC.33 presented at the World Renewable Energy Conference (WREC), Denver, CO, 8/04.
- Palladium-Copper Composite Membranes for Hydrogen Separation, Paper presented at the DOE University Coal Research Contractor's Meeting, Pittsburgh, PA, 6/05.
- Palladium-Copper Composite Membranes for Hydrogen Separation, paper presented at the International Conference on Membranes (ICOM), Seoul, Korea, 8/05.
- Palladium-Copper Composite Membranes for Hydrogen Separation, Paper presented at the Joint China-Japan-USA Chemical Engineering Conference, Beijing, China, 10/05.

### Future Work

Excellent progress is being made in all aspects of this project. Research activity in the next year will focus on work to improve the reproducibility of the Pd-Cu alloy composition, continued work to deposit thinner Pd-Cu films on Mott or Pall stainless steel substrates, and to improve the inexpensive symmetric ceramic support to reduce resistance to permeate gas flow.

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