

Annual Progress Report

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

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Submitted by

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## Abstract

This report summarizes progress made during the first year of research funding from DOE Grant # DE-FG26-03NT41792 at the Colorado School of Mines. The period of performance was September 1, 2003 through August of 2004.

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 zirconia and alumina-based microfilters. The composite membranes thus made were annealed and tested at temperatures ranging from 250 to 500°C, under very high feed pressures (up to 450 psig) using pure gases and gaseous mixtures containing H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>S, with the purpose of determining the effects these variables had on the H<sub>2</sub> permeation rate, selectivity and percent recovery. The inhibition caused by CO/CO<sub>2</sub> gases on a 7 μm thick Pd-Cu composite membrane was less than 17% over a wide range of compositions at 350 °C. H<sub>2</sub>S caused a strong inhibition of the H<sub>2</sub> flux of the same Pd-Cu composite membrane, which is accentuated at levels of 100 ppm or higher. The membrane was exposed to 50 ppm three times without permanent damage. At higher H<sub>2</sub>S levels, above 100 ppm the membrane suffered some physical degradation and its performances was severely affected. The use of sweep gases improved the hydrogen flux and recovery of a Pd-Cu composite membrane.

Recently, we have been able to dramatically reduce the thickness of these Pd alloy membranes to approximately one micron. This is significant because at this thickness, it is the cost of the porous support that controls the materials cost of a composite Pd alloy membrane, not the palladium inventory. Very recent results show that the productivity of our membranes is very high, essentially meeting the DOE pure hydrogen flux target value set by the DOE Hydrogen Program. These results were obtained when a 1.3-micron-thick Pd<sub>95</sub>Cu<sub>5</sub> (composition given in mass %) alloy film was coated on a Pall Corporation Membralox® T1-70 tubular ceramic substrate. The flux of this membrane would be even higher if the alloy composition was 40 wt. % Cu.

## Table of Contents

|                                                          |           |
|----------------------------------------------------------|-----------|
| <b>EXECUTIVE SUMMARY .....</b>                           | <b>5</b>  |
| <b>INTRODUCTION AND OBJECTIVES.....</b>                  | <b>7</b>  |
| <b>TECHNICAL PROGRESS.....</b>                           | <b>7</b>  |
| TASK 1.0 FABRICATION OF PD/CU ALLOY MEMBRANES .....      | 7         |
| TASK 2.0 CHARACTERIZATION OF PD/CU MEMBRANES .....       | 7         |
| TASK 3.0 PURE AND MIXED GAS PERMEATION STUDIES.....      | 8         |
| <i>High temperature permeation tests .....</i>           | 8         |
| <i>Very high permeability Pd-Cu membrane.....</i>        | 8         |
| <i>High pressure tests and pressure cycling.....</i>     | 9         |
| <i>CO/CO<sub>2</sub> effects.....</i>                    | 9         |
| <i>H<sub>2</sub>S effects .....</i>                      | 10        |
| <i>Sweep gas effects .....</i>                           | 10        |
| <i>Conclusions .....</i>                                 | 11        |
| TASK 4.0 EFFECT OF MEMBRANE SURFACE STRUCTURE .....      | 11        |
| <b>TECHNOLOGY TRANSFER ACTIVITY .....</b>                | <b>12</b> |
| JOURNAL ARTICLES PUBLISHED/IN PRESS.....                 | 12        |
| JOURNAL ARTICLES SUBMITTED.....                          | 12        |
| PUBLISHED CONFERENCE PROCEEDINGS.....                    | 12        |
| PRESENTATIONS AT TECHNICAL MEETINGS AND/OR SEMINARS..... | 12        |
| <b>CONCLUSIONS.....</b>                                  | <b>13</b> |
| <b>REFERENCES.....</b>                                   | <b>13</b> |

## Executive Summary

This report summarizes progress made during the first year of research funding from DOE Grant # DE-FG26-03NT41792 at the Colorado School of Mines. The period of performance was September 1, 2003 through August of 2004.

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  $Pd_{77}Ag_{23}$  and  $Pd_{60}Cu_{40}$ , have a higher  $H_2$  permeability than pure palladium, are unaffected by thermal cycling, and are resistant to sulfur poisoning ( $Pd_{60}Cu_{40}$ ). 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 U. S. DOE membrane performance target for the pure hydrogen flux at 400 °C and a differential pressure of 20 psi is 200  $ft^3(STP)/ft^2\cdot h$ .

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  $H_2$  flux. An electroless plating technique was utilized to deposit subsequent layers of palladium and copper over zirconia and alumina-based microfilters. The composite membranes thus made were annealed and tested at temperatures ranging from 250 to 500°C, under very high feed pressures (up to 450 psig) using pure gases and gaseous mixtures containing  $H_2$ , CO,  $CO_2$ ,  $H_2O$  and  $H_2S$ , with the purpose of determining the effects these variables had on the  $H_2$  permeation rate, selectivity and percent recovery. We found that after testing several membranes over several days to weeks at a time under feed pressures varying from 150 to 450 psig, the hydrogen to inert gas selectivity they exhibited remained unchanged, showing their ability to withstand high pressures. Regarding the effects that different gas exposures had on the permeation characteristics of these membranes, we observed that when the membranes were exposed to mixtures containing carbon dioxide and carbon monoxide, their hydrogen fluxes were depressed, probably by competition over surface dissociation sites.

Specifically, the inhibition, or reduction in  $H_2$  flux caused by  $CO/CO_2$  gases on a 7  $\mu m$  thick Pd-Cu composite membrane was less than 17% over a wide range of compositions at 350 °C.  $H_2S$  caused a strong inhibition of the  $H_2$  flux of the same Pd-Cu composite membrane, which is accentuated at levels of 100 ppm or higher. The membrane was exposed to 50 ppm three times without permanent damage. At higher  $H_2S$  levels, above 100 ppm the membrane suffered some physical degradation and its performances was severely affected. The use of sweep gases improved the hydrogen flux and recovery of a Pd-Cu composite membrane.

Recently, we have been able to dramatically reduce the thickness of these Pd alloy membranes to approximately one micron. This is significant because at this thickness, it is the cost of the porous support that controls the materials cost of a composite Pd alloy membrane, not the palladium inventory. Very recent results show that the productivity of our membranes is very high, essentially meeting the DOE pure hydrogen flux target value set by the DOE Hydrogen Program. These results were obtained when a 1.3-micron-thick  $Pd_{95}Cu_5$  (composition given in

mass %) alloy film was coated on a Pall Corporation Membralox® T1-70 tubular ceramic substrate. The flux of this membrane would be even higher if the alloy composition was 40 wt. % Cu.

Unfortunately, this membrane failed after approximately five days of continuous operation due to delamination of the Pd alloy film from the zirconia substrate, presumably due to weak adhesion. In our previous work, electroless plating under an osmotic pressure gradient was used to deposit Pd-Cu alloys on  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  ceramic supports using a sequential plating method. Electroless plating offers advantages because it can deposit uniform films on complex shapes and large substrate areas with sufficient hardness, using simple equipment. The palladium film is first deposited followed by Cu and then the membranes are annealed in hydrogen at temperatures above 350°C for formation of a homogeneous alloy. Pd electroless plating is autocatalytic, and the surface to be plated must be first seeded with Pd nuclei, in order to make the heterogeneous nucleation and growth process fast compared to the formation of Pd particles in solution. Our hypothesis is that the adhesion of the palladium alloy film to the ceramic support is controlled by the activation or seeding process.

## Introduction and Objectives

The feasibility of preparing and using pure Pd-membranes for H<sub>2</sub> separation is well known, although these 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  $\mu\text{m}$  thick Pd-Cu composite membranes can be made and they exhibit high H<sub>2</sub> flux and exhibit resistance 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 the 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,
- Investigate 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
- Investigation of 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 electroless plating baths onto porous ceramic filter supports. Our prior publications describe this procedure in detail[1, 2].

Examples of supports used include: symmetric 0.2  $\mu\text{m}$  cut-off  $\alpha$ -alumina tubes from CoorsTek(GTC-200) and asymmetric 0.02 and 0.05  $\mu\text{m}$  cut-off zirconia-coated  $\alpha$ -alumina tubes (USF-020, USF-050) from Exekia, a subsidiary of the Pall Corporation. Ceramic support tubes are cleaned, cut to approximately 7 cm, and end-sealed using potter’s glaze. 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. The osmotic pressure, generated by circulating concentrated sucrose solutions on the outside of the tubes, insured reduced porosity and promoted surface homogeneity and densification of the plated Pd film[3].

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

The composite membranes fabricated in Task 1 will be 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 1. For membranes containing 60 weight % Pd, annealing in hydrogen produces a phase change from an FCC  $\alpha$  phase to the more permeable BCC  $\beta$  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 2 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 until the membrane reached 350°C. Annealing the two metals was achieved during the initial single gas permeability tests. Transmembrane pressure differentials varied from a 10 psig to as high as 435 psig, while typical operating temperatures varied from 250°C to 400°C. Permeate pressure was local atmospheric pressure (12 psia), except for the test using sweep gas.

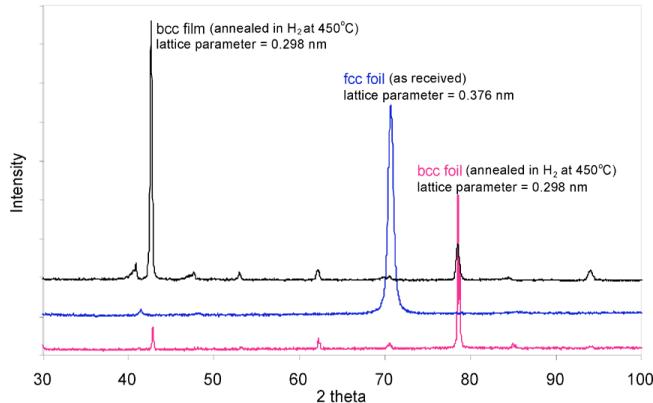


Figure 1. Typical X-ray diffraction patterns for electroless Pd-Cu membrane (film) and cold-rolled, 25  $\mu$ m thick Pd<sub>60</sub>Cu<sub>40</sub> foil membrane. The foil is in the FCC phase prior to annealing in hydrogen at 450 °C where the higher permeability BCC phase is formed.

### Very high permeability Pd-Cu membrane

The DOE Hydrogen Fuels Initiative (HFI) Solicitation target goals for a hydrogen selective membrane operating at a temperature of 400°C and pressures of 20 psi are as follows:

Table 1. Target Performance Goals for Hydrogen Separation Membranes

| Characteristics | Units                | Targets |
|-----------------|----------------------|---------|
| Flux rate       | Scfh/ft <sup>2</sup> | 200     |
| Cost            | \$/ft <sup>2</sup>   | <100    |
| Durability      | Hours                | 100,000 |
| Parasitic Power | Kwh/1000 scfh        | 2.8     |

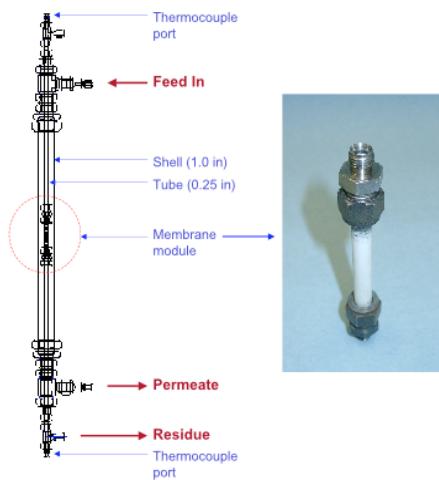


Figure 2. Photograph of a typical membrane and the high temperature module.

As discussed below and shown in Figures 3 and 4, we have recently fabricated very thin Pd-Cu composite membranes that meet 96% of the DOE pure hydrogen flux target, or a flux of 191 SCFH/ft<sup>2</sup> at 400 °C for a feed pressure of 20 psig. Since atmospheric pressure in Golden, CO is 12 psia, the absolute feed pressure is 32 psia. These results were obtained when a 1.3-micron-thick Pd<sub>95</sub>Cu<sub>5</sub> alloy film was coated on a Pall Corporation Membralox® tubular ceramic substrate

with a particle size cut-off of 20 nm or 0.02  $\mu\text{m}$ . The ideal  $\text{H}_2/\text{N}_2$  separation factor of this membrane was 96 at a feed pressure of 50 psig. As Figure 4 also shows, the  $n$ -value, or pressure dependence of the hydrogen flux is 0.553, very close to the theoretical value of 0.5 in Sievert's law. This suggests that hydrogen diffusion through the Pd-Cu film is likely to be rate controlling.

The flux of the membrane shown in Figure 4 would be even higher if the alloy composition was 40 wt. % Cu. Unfortunately, this membrane failed after approximately five days of continuous operation due to delamination of the Pd alloy film from the zirconia substrate, presumably due to weak adhesion.

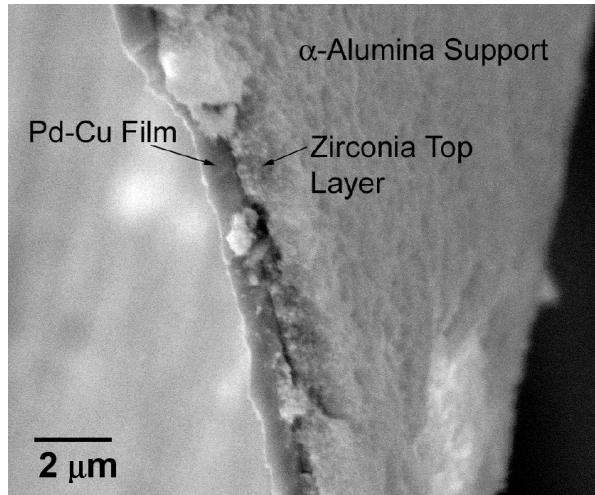


Figure 3. SEM image of a Pd-Cu composite membrane, 95 mass % Pd, on a 20 nm cut-off asymmetric ceramic filter. Flux data for this membrane in Figure 4.

#### High pressure tests and pressure cycling

A membrane supported on a GTC-200 tube (#6 shown below in Figure 5) was tested at high pressures repeatedly for 1 month to determine the effects on the permeation properties under large loads as well as the mechanical resistance of these materials. It was observed that the membrane was able to mechanically endure pressures as high as 30 bars with no apparent failure. More importantly, its permeation properties were maintained during the entire duration of the test. In other words, we were unable to detect any non- $\text{H}_2$  gas permeating through the membrane for the duration of this first pressure test.

#### $\text{CO}/\text{CO}_2$ effects

Pd-Cu membrane #6, shown in Figure 5, supported on a GTC-200 was fed a gaseous mixture containing 51%  $\text{H}_2$ , 21% water and varying concentrations of CO and  $\text{CO}_2$  making up the balance to demonstrate the impact of these gases on the performance of membrane. Figure 6 shows the effect of varying the  $\text{CO}/\text{CO}_2$  concentrations on its  $\text{H}_2$  flux at 350°C and 250 psig of total pressure. Shown also are the exiting concentrations of the gases on the permeate side.  $\text{H}_2$  recovery was about 40%. We can see that the flux of the membrane was relatively unaffected by the changing conditions as was the purity of the product. The copper alloy concentration was 10% which may have increased the resistance of the membrane to inhibition or coking by CO.

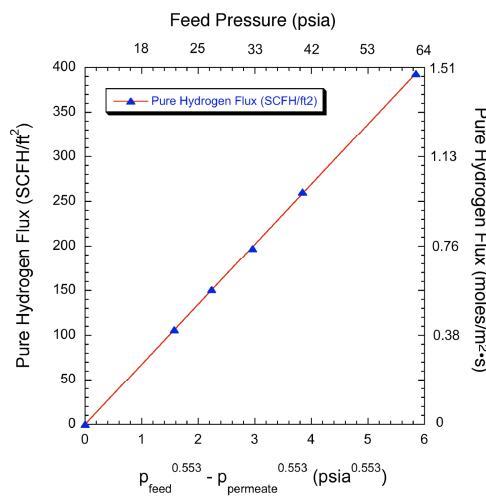


Figure 4. Influence of pressure driving force on the pure gas  $\text{H}_2$  flux for a 1.3  $\mu\text{m}$  Pd-Cu membrane having 95 mass % Pd at 400°C.

## *H<sub>2</sub>S effects*

Figure 7 presents permeation and exit gas concentration data corresponding to a permeation experiment for Pd-Cu membrane #6 fed a mixture containing 51% H<sub>2</sub>, 21% water, 26% CO<sub>2</sub>, 2% CO at 250 psig and 350 °C in which H<sub>2</sub>S was added at different concentrations from 0 to 250 ppm to study its effect on the permeation behavior of the membrane. H<sub>2</sub>S causes a strong inhibition on the H<sub>2</sub> flux at all concentrations with the effects of this inhibition being greatest at higher H<sub>2</sub>S levels. For example, in the presence of 10 ppm H<sub>2</sub>S, the H<sub>2</sub> flux was reduced by approximately 50% of its level without H<sub>2</sub>S being present. The H<sub>2</sub> flux is not shown in Figure 7 from 100 to 400 minutes due to an equipment malfunction, but the experiment continued. The solid grey bars at about 500 minutes and 950 minutes indicate a period when the membrane was exposed to pure H<sub>2</sub>. Note that the flux was recovered each time to the levels prior to H<sub>2</sub>S exposure. At approximately 1600 minutes, the membrane was exposed to 250 ppm H<sub>2</sub>S and the H<sub>2</sub> flux increased continuously until the H<sub>2</sub>S concentration was reduced again to 0 ppm when the H<sub>2</sub> flux was 0.18 mole/m<sup>2</sup>•s. We interpreted this H<sub>2</sub> flux increase as membrane failure due to pore formation.

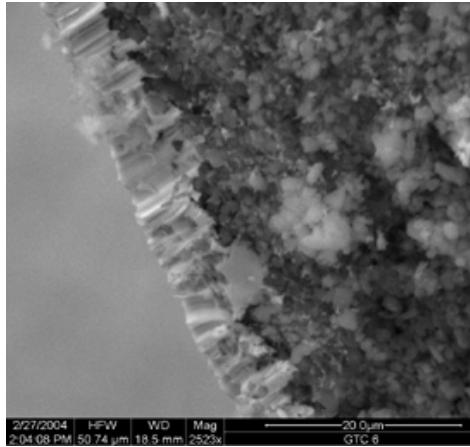


Figure 5. SEM image of membrane #6 used for CO/CO<sub>2</sub>/H<sub>2</sub>S tests. Transport data are shown in Figures 6 and 7. Scale bar represents 20  $\mu$ m.

## *Sweep gas effects*

A membrane was fed a gas mixture consisting of 51% H<sub>2</sub>, 26% CO<sub>2</sub>, 21% H<sub>2</sub>O, 2% CO and 1 ppm H<sub>2</sub>S, at 350°C and 250 psig. Two conditions were run, a helium sweep and a helium and steam sweep. We observed that the composition of the permeate was affected little by the introduction of the sweep gases with the H<sub>2</sub> fraction remaining fairly constant over the period of the testing at ~91%. The effect of the different sweep gases on the total flux of the membrane was a bit more pronounced. The use of helium and helium/steam sweep gases improved, although marginally, the performance of the membrane with the first condition producing an H<sub>2</sub> flux increase of about 5% and the latter of 9%. This result was unexpected due to the inhibition effects previously reported for steam[5].

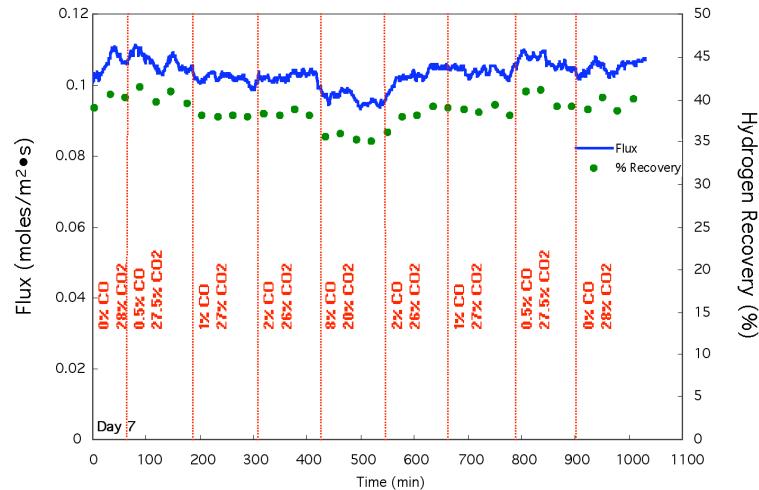


Figure 6. The impact of the CO/CO<sub>2</sub> inlet concentrations on the H<sub>2</sub> flux for a Pd-Cu composite membrane #6. Feed balance was 51% H<sub>2</sub> and 21% water, at 250 psig and 350°C.

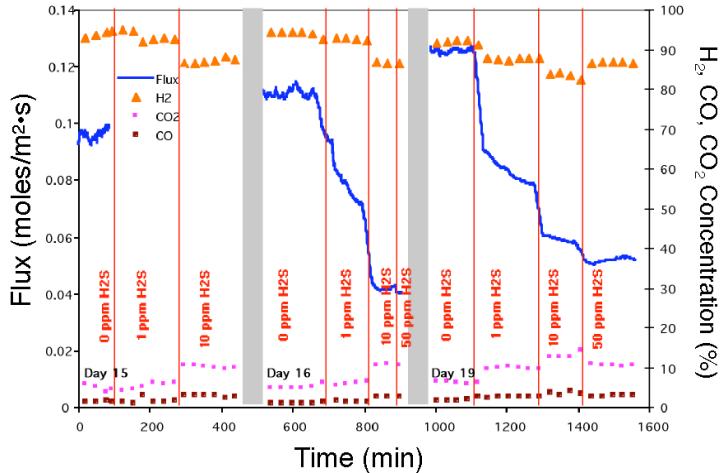


Figure 7. The effect of  $\text{H}_2\text{S}$  inlet concentration on the permeate stream gas concentration and flux for Pd-Cu membrane #6. Feed consisting of 51%  $\text{H}_2$ , 21%  $\text{H}_2\text{O}$ , 26%  $\text{CO}_2$  and 2%  $\text{CO}$ , at 250 psig and 350°C.

### Conclusions

The inhibition caused by  $\text{CO}/\text{CO}_2$  gases on a 7  $\mu\text{m}$  thick Pd-Cu composite membrane was negligible over a wide range of compositions at 350 °C.  $\text{H}_2\text{S}$  caused a strong inhibition of the  $\text{H}_2$  flux of the same Pd-Cu composite membrane, which is accentuated at levels of 100 ppm or higher. The membrane was exposed to 50 ppm three times without permanent damage. At higher  $\text{H}_2\text{S}$  levels, above 100 ppm the membrane suffered some physical degradation and its performances was severely affected. The use of sweep gases improved the hydrogen flux and recovery of a Pd-Cu composite membrane.

### Task 4.0 Effect of Membrane Surface Structure.

We recently published a article in the *Journal Applied Surface Science* describing our investigations of the effects of oxidizing conditions on Pd and Pd alloy membranes, cited below. The abstract for this paper is given below.

It was found that when electrolessly deposited thin Pd and Pd–Cu membranes were exposed to air at temperatures above 350 °C, their  $\text{H}_2$  flux increased substantially immediately after the air exposure, then decreased to a new steady-state value. While this was a quasi-reversible change for the  $\text{H}_2$  flux, the flux of insoluble species, such as  $\text{N}_2$ , irreversibly increased with every air exposure but by a much smaller extent. The extent of these changes was found to be dependent on the exposure time and the temperature of the tests. Thus, we decided to investigate the effect of gas exposures on the properties of these materials. Palladium and palladium–copper films, prepared by electroless deposition on ceramic supports, and commercial foils were exposed to air, hydrogen and helium at 500 and 900 °C for times varying from 1 h to 1 week with the objective of determining the effect of the different exposure conditions on the surface morphology, the flux of different penetrants and the crystalline structure of the materials. Atomic force microscopy (AFM) and X-ray diffraction (XRD) were used to study the changes occurring in the films under those conditions. It was observed that the exposure of both the electroless films and the foils to hydrogen and air markedly modified their surface morphology. The hydrogen exposure tended to smooth the surface features whereas the oxygen exposure created new surface features such holes and large peaks. Additionally it was found that the air exposure produced some oxidation of the film to create  $\text{PdO}$ . These results suggested that a common hypothesis stating that air oxidation just cleans the surface of the membrane might not be

sufficient to explain all of those changes. A contributing effect of air exposure may be the increase in surface area due to the formation of palladium oxide. However, the extent of the surface area increase was insufficient to explain the increase in steady-state H<sub>2</sub> flux.

## Technology Transfer Activity

### Journal Articles Published/In Press

- Roa, F. and J. D. Way, "The influence of alloy composition and membrane fabrication on the pressure dependence of the hydrogen flux of palladium-copper membranes," *Ind. Eng. Chem. Res.*, **42**(23), 5827-5835(2003).
- Kulprathipanja, A., Alptekin, G. O., Falconer, J. L. and J. D. Way, "The Effects of Water Gas Shift Gases on Pd-Cu Alloy Membrane Surface Morphology and Separation Properties," *Ind. Eng. Chem. Res.*, **43**(15), 4188-4198(2004).
- Roa, F. and J. D. Way, "The Effect of Air Exposure on Palladium-Copper Composite Membranes," *Applied Surface Science*, in press, 8/04.

### Journal Articles Submitted

- 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," submitted to the *Journal of Membrane Science*, 4/04.

### Published Conference Proceedings

- Roa, F., DeVoss, S., Alptekin, G. and J. D. Way, "Effect of CO<sub>2</sub>, CO, H<sub>2</sub>S on a Pd-Cu Ceramic Composite Membrane Made by Electroless Plating," Proceedings of the Eighth International Conference on Inorganic Membranes," Cincinnati, OH, July 2004.
- Roa, F., DeVoss, S., Alptekin, G. and J. D. Way, "Palladium-Copper Composite Membranes for Hydrogen Separation," Paper #HFC.33 presented at the World Renewable Energy Conference, Denver, CO, September 2004.

### Presentations at Technical Meetings and/or Seminars

- Pd-Cu Composite Membranes for Hydrogen Separations Idatech, LLC, Bend, OR, 10/03
- Palladium Ceramic Composite Membranes for H<sub>2</sub> Separation, Talk by Fernando Roa, 204th Meeting of The Electrochemical Society, Orlando, Fl, Oct 12-16, 2003
- Effect of Air Exposure on Hydrogen Selective Pd-Cu Membranes, ACS Spring National Meeting, Paper Poly20, Anaheim, CA, March 28, 2004.
- Effect of CO<sub>2</sub>, H<sub>2</sub>O, and CO on a Electrolessly Deposited Palladium Ceramic Composite Membrane, 8<sup>th</sup> International Conference on Inorganic Membranes (ICIM8), Cincinnati, OH, July 18-22, 2004.
- Palladium-Copper Composite Membranes for Hydrogen Separation, Paper #HFC.33 presented at the World Renewable Energy Conference (WREC), Denver, CO, September 2004.

## Conclusions

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, work to deposit Pd-Cu films on Pall AccuSep ZrO<sub>2</sub>/stainless steel substrates, and an investigation of the membrane synthesis parameters that influence adhesion of the Pd alloy films on the porous supports.

## References

1. Roa, F., J.D. Way, R.L. McCormick, and S.N. Paglieri, Preparation and Characterization of Pd-Cu Composite Membranes for H<sub>2</sub> Separation. *The Chemical Engineering Journal*, 2003. **93**(1): p. 11-22.
2. Roa, F. and J.D. Way, The influence of alloy composition and membrane fabrication on the pressure dependence of the hydrogen flux of palladium-copper membranes. *Ind. Eng. Chem. Res.*, 2003. **42**(23): p. 5827-5835.
3. Yeung, K.L., J.M. Sebastian, and A. Varma, Novel preparation of Pd/Vycor composite membranes. *Catal. Today*, 1995. **25**: p. 231-236.
4. Piper, J., Diffusion of Hydrogen in Copper–Palladium Alloys. *J. Appl. Phys.*, 1966. **37**(2): p. 715-21.
5. Li, A. and R. Hughes, The effect of carbon monoxide and steam on the hydrogen permeability of a Pd/stainless steel membrane. *J. Membr. Sci.*, 2000. **165**: p. 135-141.