Annual Progress Report

Palladium/Copper Alloy Composite Membranes for High Temperature Hydrogen Separation from Coal-Derived Gas Streams

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Submitted by

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Introduction and Objectives
Recent advances have shown that Pd-Cu composite membranes are not susceptible to the mechanical, embrittlement, and poisoning problems that have prevented widespread industrial use of Pd for high temperature H_2 separation. These membranes consist of a thin (~1 μm) film of metal deposited on the inner surface of a porous metal or ceramic tube. Based on preliminary results, thin $Pd_{60}Cu_{40}$ films are expected to exhibit hydrogen flux up to ten times larger than commercial polymer membranes for H_2 separation, and resist poisoning by H_2S and other sulfur compounds typical of coal gas. Similar Pd-membranes have been operated at temperatures as high as 750°C. The overall objective of the proposed project is to demonstrate the feasibility of using sequential electroless plating to fabricate $Pd_{60}Cu_{40}$ alloy membranes on porous supports for H_2 separation. These following advantages of these membranes for processing of coal-derived gas will be demonstrated:

- High H_2 flux.
- Sulfur tolerant, even at very high total sulfur levels (1000 ppm).
- Operation at temperatures well above 500 °C.
- Resistance to embrittlement and degradation by thermal cycling.

The proposed research plan is designed to providing a fundamental understanding of:

- Factors important in membrane fabrication.
- Optimization of membrane structure and composition.
- Effect of temperature, pressure, and gas composition on H_2 flux and membrane selectivity.
- How this membrane technology can be integrated in coal gasification-fuel cell systems.

Technical Progress
As shown in Tables 1 and 2 below, we have made a series of Pd-Cu composite membranes supported on both symmetric and asymmetric ceramic filters during the second year of the project. The fabrication method is described by Paglieri [1]. The total thickness of the membranes has been reduced from approximately 10 μm to 1 μm. At the same time, the the H_2 flux and ideal H_2/N_2 selectivity have been increased to 0.8 moles/m^2•s and 1400, respectively at 345 kPa (50 psi) pressure driving force. This is a **four-fold** increase in H_2 flux compared to membrane #4, which is typical of the Pd-Cu membranes made using a symmetric, 0.2 μm pore size alumina support.

Task 1: Program Startup Activities-Completed

Task 2: Fabrication of Pd-Cu Membranes-Three new Pd-Cu alloy composite membranes have been prepared and characterized as shown in Tables 1 and 2 (#5, 6, and 20). Our hypothesis was that by using a support material with less surface roughness, the Pd-Cu film thickness could be reduced. Furthermore, asymmetric ceramic filters were used, where the small pore top layer is supported on several layers of larger particles, reducing the hydraulic resistance in the support. Effective pore sizes of these filters ranged from 0.02 to 0.05 μm. This is approximately an order of magnitude reduction in pore size compared to the membranes made during year 1 of this project such as membrane #4 in Table 1. An SEM image of the cross-section of an asymmetric ceramic is shown in Figure 1.

Nitrogen leak tests were performed after Pd and Cu plating cycles. The results are given in Table 1. Improvements in surface preparation and plating were responsible for reduction in the N_2 leak rate after the Cu layer was deposited. Reductions in the N_2 leak rate correlated well with improvements in high temperature H_2/N_2 ideal selectivity as will be described below.

Task 3: Characterization of Pd-Cu Membranes-Characterization was performed using x-ray diffraction, electron microscopy, and EDAX/EPMA as well as characterization of transport properties using pure gases. Table 2 summarizes the thickness and alloy composition

measurements. The thicknesses of these new membranes ranged from 1 to 10 μm, which satisfies our goal of reducing the Pd-Cu membrane thickness to less than 5 μm stated in our proposal.

A typical electron micrograph of the cross section of membrane #6 is shown in Figure 1. The thickness of this membrane is approximately 1 μm. This reduction in Pd-Cu alloy membrane thickness is particularly important with respect to the economics of membrane fabrication. As an example, our materials cost to produce a 1 μm film containing 60 mass % Pd is about $2, compared to $200 for an 25 cm long, T1-70 asymmetric ceramic filter from the U. S. Filter Company. Consequently, at a thickness of 1 μm, the Pd cost is approximately 1% of the total materials cost.

The alloy compositions of our Pd-Cu composite membranes ranges from 10 to 30 mass % Cu as determined by EDAX. This is lower than our target of 40 mass % where the highest H_2 permeability has been reported [2]. Increasing the Cu plating time show allow us to increase the Cu alloy composition in our future work.

Task 4: H_2 Separation Performance Measurements-Pure gas transport measurements were performed for all membranes with H_2 and N_2 over a range of temperatures at 345 kPa pressure driving force. These data are summarized in Table 2. Hydrogen fluxes ranged from 0.2 to 0.8 moles/m^2•s for the 5 cm long, 1 cm OD membranes, having an approximate surface area of 11 cm^2. The ideal selectivity, or the ratio of pure gas fluxes measured at the same conditions, ranges from 50 to 1400.

A plot of both the H_2 and N_2 fluxes for membrane #20 is given in Figure 3 at a temperature of 623 K (350 °C) using a driving force of 345 kPa (50 psi). It has been shown in the literature [3] that brief (0.5 to 1 hour) air oxidations or air purges at temperature can significantly increase the H_2 flux. This was also observed for our data as the first air purge more than doubled the H_2 flux. Air purges are shown as vertical dotted lines in Figure 3. The mechanism of the flux increase has been attributed to removal of carbon and other impurities from the surface [4] but our hypothesis is that the formation a surface oxide and subsequent reduction of the oxide layer rearranges the surface to increase the surface area , and presumably the number of sites for hydrogen dissociation. We believe that the formation of a Pd oxide causes the surface to rearrange, creating new sites for H_2 dissociation or simply increasing the surface area of the film. We will continue to investigate the mechanism of the air purge during the the final year of the project.

Technology Transfer Activity

The following presentations were made at technical meetings related to this project:

- Roa, F. Way, J. D., McCormick, R. L. and S. N. Paglieri, "Preparation and Characterization of Pd-Cu Composite Membranes for Hydrogen Separation," submitted to *The Chemical Engineering Journal*, 6/2001.
- Los Alamos National Laboratory, Los Alamos, NM, 12/00, New Materials for Gas and Liquid Separations
- ACS National Meeting, San Diego, CA, 4/01, Micron Scale Pd-Cu Alloy Composite Membranes for Hydrogen Separations
- The North American Catalysis Society annual meeting, Toronto, Canada, 6/01, Scale Pd-Cu Alloy Composite Membranes for Hydrogen Separations and Membrane Reactors
- Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID, 7/01, New Materials for Gas and Liquid Separations

Conclusions

Excellent progress is being made in all aspects of this project. Research activity in the next year will focus on continuing to reduce the membrane thickness, increasing hydrogen flux, optimization of the Pd-Cu alloy composition, and understanding how the air purge increases the hydrogen flux.

References

1. Paglieri, S.N., *Palladium and palladium-copper composite membranes for hydrogen separation,* in *Dept. of Chemical Engineering*. 1999, Colorado School of Mines: Golden, CO. p. 197.
2. McKinley, D.L., Method for hydrogen separation and purification, U.S. Patent 3,439,474, Apr. 22, 1969.
3. Paglieri, S.N., K.Y. Foo, J.D. Way, J.P. Collins and D.L. Harper-Nixon, *A new preparation technique for Pd/alumina membranes with enhanced high temperature stability*. Ind. Eng. Chem. Res., 1999. **38**(5): p. 1925-36.
4. Yang, L., O. Sakai, S. Kosaka, T. Kawae and T. Takahashi. *Experimental Study on Hydrogen Permeation and Surface Property of Pd-Ag/Ceramic Composite Membranes*. in *Proc. 5th Intl. Conf. Inorganic Membr.* 1998. Nagoya, Japan.

Table 1. Room Temperature Leak Testing of Pd–Cu Membranes.

No.	Type of support material	Support pore size (nm)	Estimated Thickness of Pd film (μm)	N_2 Flux $(mol/m^2s)^1$ x 10^4	Estimated Thickness of Cu film (μm)	N_2 Flux $(mol/m^2s)^2$ x 10^4
4	Symmetric α-alumina	200	8	0.985	8	0.061
5	Asymmetric zirconia	50	8	0.438	6	0.021
6	Asymmetric zirconia	50	1.5	0.248	1	0.042
20	Asymmetric zirconia	20	1	-	1	-

[1] The membrane, coated with Pd, is pressurized with N_2 at 896.3 kPa. The time for the pressure to drop at 827.4 kPa is measured and the flux is calculated.

[2] As above but now the membrane is coated with both Pd and Cu.

Table 2. Pd–Cu Membrane Performance and Characterization.

No.	ΔP (kPa)	Heated to (K)	H_2 flux @ 773 K (mol/m^2s)	Highest Ideal Selectivity[4]	Thickness from SEM (μm)	Pd/Cu from EDAX (wt%)
4	345	723	0.18[†]	270	12.5±1.5	78/22
5	345	723	0.80	1400	12±1.0	91/9
6	345	723	0.66[#]	47	1.5 ±0.2	70/30
20	345	723	0.51	1217	0.5-1.0	80/20

[3] Temperature = 723 K

[4] Ideal Selectivity = pure hydrogen flux/ pure nitrogen flux

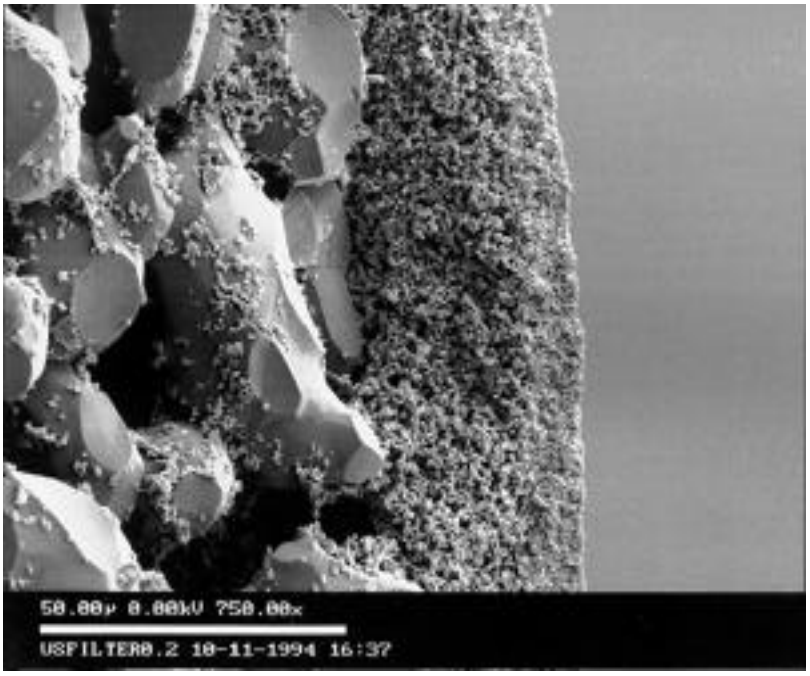

Figure 1. Cross-section of an asymmetric, alumina ultrafilter. Scalebar is 50 μm.

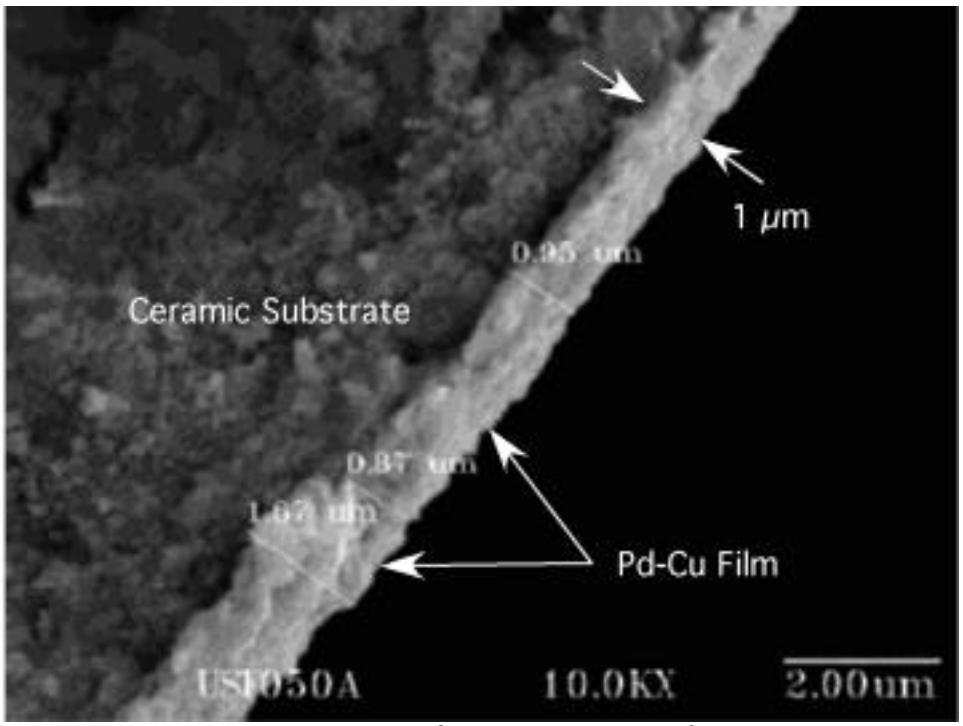

Figure 2. Electron micrograph of the cross section of membrane #6.

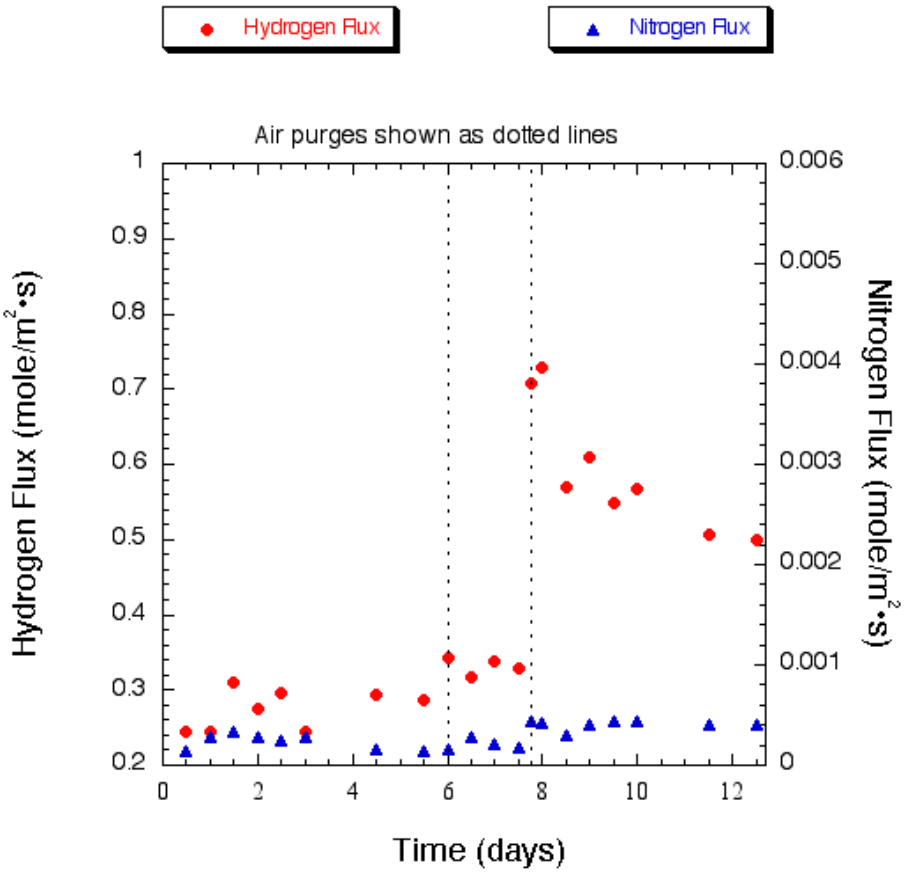

Figure 3. Pure gas transport data for membrane #20. Fluxes were measured with a pressure driving force of 345 kPa (50 psi). Air purges are shown as vertical dotted lines on the graph.