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 (~10 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 0.2 µm alumina microfilters during the first year of the project. The total thickness of the membranes has been reduced from approximately 30 µm to 10 µm. At the same time, the the H_2 flux and ideal H_2/N_2 selectivity have been increased to greater than 0.2 moles/m^2•s and 270, respectively at 345 kPa (50 psi) pressure driving force.

Task 1: Program Startup Activities-Completed

Task 2: Fabrication of Pd-Cu Membranes-Three new Pd-Cu alloy composite membranes have been prepared as shown in Tables 1 and 2 (#2, 3, and 4) . Slightly different metal deposition and annealing methods have been employed. In all cases Pd was deposited first and Cu was then deposited onto the Pd film formed after heating. It was found that Pd is not a particularly good catalyst for electroless plating of Cu. Consequently several approaches to activation of the surface to enhance the Cu deposition rate were attempted. It was found that cleaning and activating the surface with 50% nitric acid passivated the surface via formation of a practically permanent Pd-oxide layer. Cu could not be plated onto this surface. Brief immersion in aqua regia did remove some of the oxide layer and alloy deposition of a highly non-uniform layer of Cu. Cleaning and activating of the Pd film surface with a much more dilute, 5% hot nitric acid solution appeared to clean and activate the surface well for plating of Cu.

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. Membranes 2, 3 and 4 were all approximately 80 mass % Pd and 20 mass % Cu, lower than the target composition of 40 mass % Cu. The thicknesses of these membranes ranged from 11 to 12.5 µm, a significant reduction from our first alloy membrane, shown as membrane #1 in Table 2.

A typical electron micrograph of the cross section of membrane #2 is shown in Figure 1. The thickness of this membrane is approximately 11 µm. The SEM image also shows the excellent "lock and key" adhesion of the metal film to the porous ceramic substrate.

The alloy composition profile of membrane #2 is shown in Figure 2 as determined by electron microprobe analysis (EPMA). This measurement was made for us by Mary Anne Alvin and coworkers at the Siemens Westinghouse Research Center in Pittsburgh. The composition profiles are reasonably uniform throughout the membrane cross section. On average, the composition of membrane #2 is 80 mass % Pd and 20 mass % Cu. This is lower than our target of 40 mass %. 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 membranes 2, 3, and 4 with H_2 and N_2 over a range of temperatures at either 690 or 345 kPa pressure driving force. These data are summarized in Table 2. Hydrogen fluxes ranged from 0.2 to 0.5 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, range from 70 to 270.

A plot of both the H_2 and N_2 fluxes for membrane #2 is given in Figure 3 over the temperature range of 723 K (450 °C) to 823 K (550 °C) at a driving force of 345 kPa (50 psi). It has been shown in the literature (Paglieri, 1999) 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 essentially 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 (Yang et al., 1998), 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 will continue to investigate the mechanism of the air purge during the next years work.

Technology Transfer Activity

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

- J. Douglas Way and Robert L. McCormick "Palladium/Copper Alloy Composite Membranes For High Temperature Hydrogen Separation From Coal-Derived Gas Streams" poster presented at University Coal Research Contractors Review Meeting, Pittsburgh, June, 2000.

- Robert L. McCormick and J. Douglas Way "Palladium/Copper Alloy Composite Membranes For High Temperature Hydrogen Separation From Coal-Derived Gas Streams" poster presented at ARO Workshop on Fuel Processors for Proton Exchange Membrane Fuel Cells, Detroit, June 19-21, 2000.

- J. Douglas Way, Robert L. McCormick, Fernando Roa, and Stephen Paglieri "Palladium-Copper Alloy Composite Membranes for H_2 Separation" invited presentation at the IUPAC Workshop on the Standardization of Methods for the Characterization of Inorganic Membranes, Montpellier, France, June 26, 2000.

· J. Douglas Way, Robert L. McCormick, Fernando Roa, “Palladium-Copper Alloy Composite Membranes for H_2 Separation” presented at the Sixth International Conference on Inorganic Membranes, Montpellier, France, June 27-30, 2000.

Conclusions

Excellent progress is being made in all aspects of this project. Research activity in the next year will focus on the reduction of membrane thickness, increasing hydrogen flux, and optimization of the Pd-Cu alloy composition.

References

S. N. Paglieri, K. Foo, J. D. Way, J. P. Collins, D. Harper-Nixon, I&EC Res., 38 (1999) 1925.
Yang et al., *Proceedings of ICIM 5*, Nagoya, Japan page 482, 1998.

Acknowledgements

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

No.	Type of support material	Support pore size (nm)	Estimated Thickness of Pd film	N_2 Flux $(mol/m^2s)^1$ x 10^4	Estimated Thickness of Cu film	N_2 Flux $(mol/m^2s)^2$ x 10^4
1	Symmetric α-alumina	200	47	-	10	-
2	Symmetric α-alumina	200	10	5.332	4	0.337
3	Symmetric α-alumina	200	6.5	1.073	4	0.105
4	Symmetric α-alumina	200	8	0.985	8	0.061

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%)
1	689.5	723	0.048[3]	13.7	27.6 ±8.5	72/28
2	689.5	973	0.35	70.0	11.0±1.0	80/20
3	344.7	773	0.52	170	11.6±1.0	81/19
4	344.7	723	0.18	266	12.5±1.5	78/22

3 Temperature = 723 K

4 Ideal Selectivity = pure hydrogen flux/ pure nitrogen flux

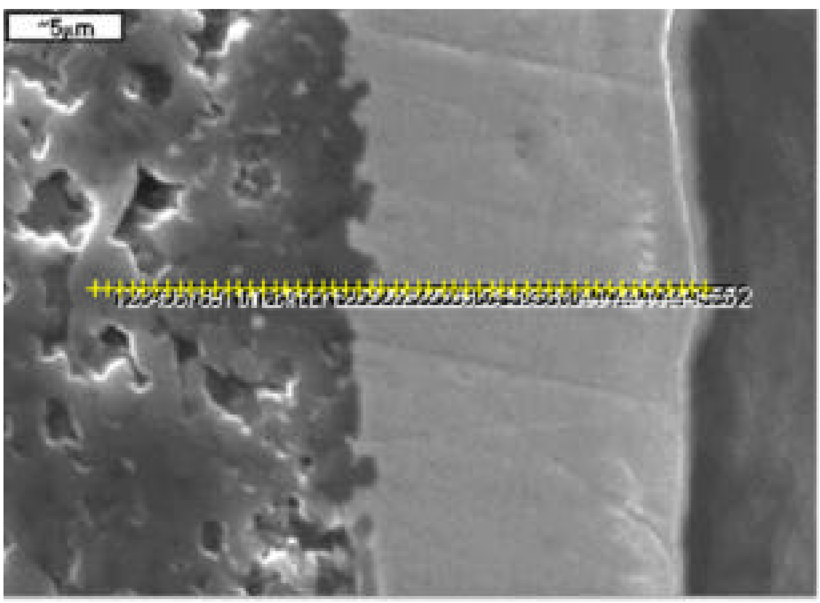

Figure 1. Electron micrograph of the cross section of membrane #2. Note the excellent adhesion of the metal film to the alumina subtrate. The numbers shown horizontally across the SEM show the locations of the EPMA analysis, shown in Figure 2 below.

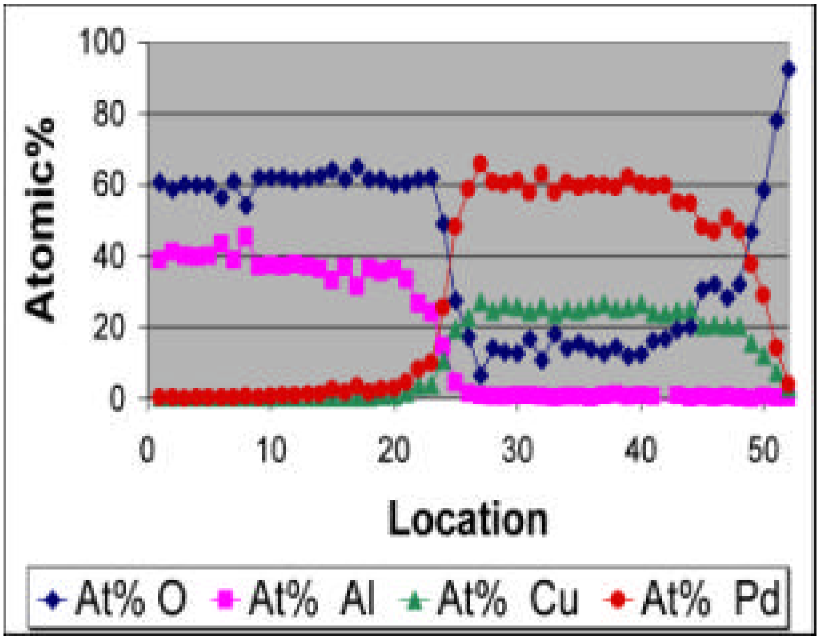

Figure 2. Electron microprobe (EPMA) analysis of the composition of membrane #2. Note the uniformity of the Pd and Cu profiles.

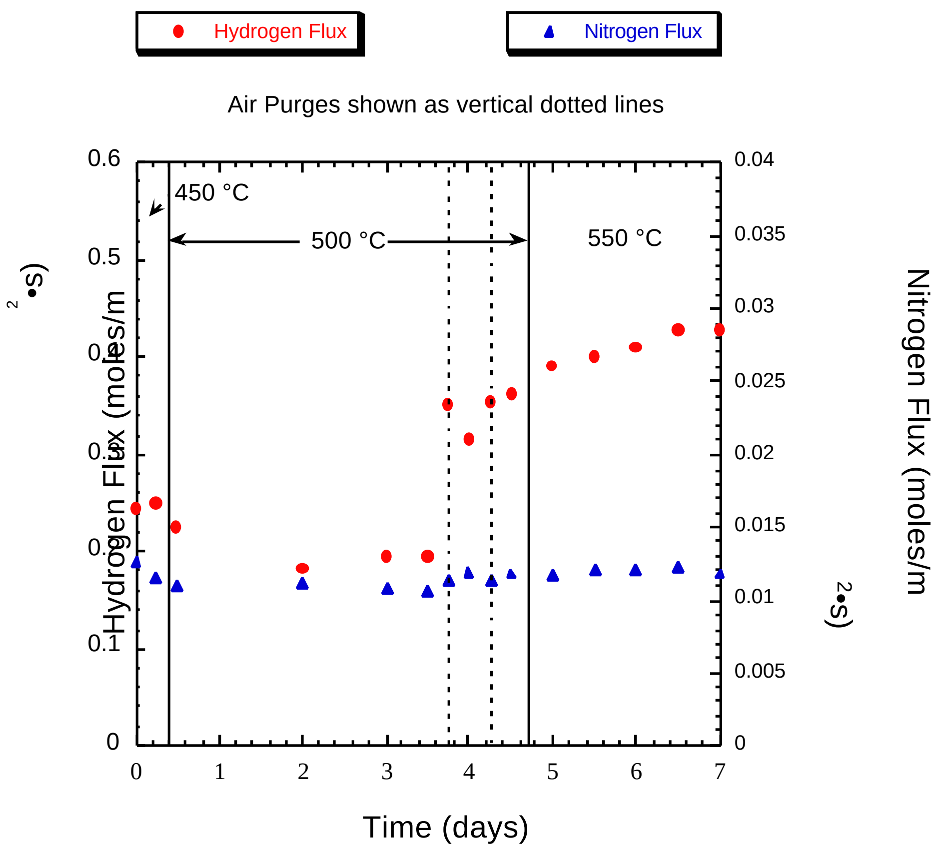

Figure 3. Pure gas transport data for membrane #2. Fluxes were measured with a pressure driving force of 345 kPa (50 psi).