TITLE: PALLADIUM/COPPER ALLOY COMPOSITE MEMBRANES FOR HIGH TEMPERATURE HYDROGEN SEPARATION FROM COAL-DERIVED GAS STREAMS

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Background. For hydrogen from coal gasification to be used economically, processing approaches that produce a high purity gas must be developed. Palladium and its alloys, nickel, platinum and the metals in Groups 3 to 5 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, chemical compatibility with many hydrocarbon containing gas streams, and infinite hydrogen selectivity. Our Pd composite membranes have demonstrated stable operation at high temperatures for over 50 days. Coal derived synthesis gas will contain up to 15,000 ppm H2S as well as CO, C02, N2 and other gases. Highly selectivity membranes are necessary to reduce the H2S concentration to acceptable levels for solid oxide and other fuel cell systems. Pure Pd-membranes are poisoned by sulfur, and suffer from mechanical problems caused by thermal cycling and hydrogen embrittlement. 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 I'd for high temperature H2 separation. These membranes consist of a thin (-10 gm) film of metal deposited on the inner surface of a porous metal or ceramic tube. Based on preliminary results, thin Pd60Cu40 films are expected to exhibit a hydrogen flux up to ten times larger than commercial polymer membranes for H2 separation, and resist poisoning by H2S and other sulfur compounds typical of coal gas. Similar Pd-membranes have been operated at temperatures as high as 750'C. CSM has developed practical electroless plating procedures for fabrication of thin Pd-Cu composite membranes at any scale.

Objective. The feasibility of preparing and using pure Pd-membranes for H2 separation is well known, although these suffer from embrittlement, and poisoning by sulfur. Furthermore, the ability of thick Pd-Cu alloy membranes to separate H2, and the high temperature stability and resistance to poisoning of these materials has been demonstrated. What remains to be shown is that thin (-10 gm) Pd-Cu alloy films that have both high H2 flux and high selectivity can be fabricated. The stability of these films with respect to embrittlement (thermal cycling), sulftir, and other components of coal-derived gas must also be demonstrated. The proposed research plan is designed to answer these questions, while also 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.

These thin Pd-Cu. films are being characterized in detail using x-ray diffraction, SEM/EDAX, chemical analysis, x-ray photoelectron spectroscopy, and other methods. Their performance for hydrogen separation at high temperatures and in the presence of high concentrations of sulfur containing gases will be evaluated in a laboratory test system. Binary separations as well as separation of hydrogen from a simulated coal gas will be examined. Models useful for design and prediction of membrane performance will be developed.

Results to Date. Prior to the start of this project, one Pd-Cu film on an alumina supports was made using sequential electroless plating. In this fabrication procedure, a leak free electroless plated Pd-film is first prepared by electroless plating under an osmotic pressure gradient. Then the appropriate mass of Cu is deposited via a second electroless plating step to produce a target composition of 60 wtO/o Pd and 40 wtO/o Cu. The membrane was annealed at temperatures above 350 'C causing interdiff-usion of the two metals, ideally to form an alloy of uniform composition. The Pd-Cu phase diagram shows that the two metals are completely miscible over all compositions. XRD data for the Pd-Cu alloy membrane after annealing showed the presence of the Pd-Cu intermetallic but with a composition of 80% Pd and 20% Cu. The membrane thickness was 28 @tm as determined by SEM. The H_2 flux increased to a steady- state value of 0.05 moles/m^2-s over a four day period at 450'C as interdiff-usion occurred and the Pd-Cu alloy was formed. The steady-state H_2 flux was quite low due to the large thickness of this membrane. The final H_2/N_2 selectivity (permeability ratio) of this membrane was only about 15. It was anticipated that optimization of fabrication procedures will result in much thinner Pd-Cu alloy membranes with higher flux and selectivity.

Very recently, our process to prepare the "base" Pd films has been improved resulting in higher selectivity membranes. During preparation, the final H_2/N_2 selectivity is estimated by performing a nitrogen leak test at ambient conditions. The lower the nitrogen permeability, the higher the expected selectivity during high temperature permeation tests. Our latest batch of pure Pd membranes have N_2 permeabilities one to two orders of magnitude less than those membranes described in a recent publication'. Consequently, the H_2/N_2 selectivities we expect during high temperature permeation testing should exceed 1000. Our ability to improve the base Pd layer selectivity should dramatically improve the selectivity of the Pd/Cu alloy membranes being prepared.

Paglieri, S. N., Foo, K. Y., Way, J. D., Collins, J. P., Harper-Nixon, D. L. " A New Preparation Technique for Pd/Alumina Membranes with Enhanced Stability at High Temperatures," *Ind. Eng. Chem. Res.*, 38,1925-1936(1999).

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Journal Articles

Paglieri, S. N., Roa, F. Way, J. D. and R. M. McCormick, "Preparation of Pd-Cu/Alumina Composite Membranes for H2Separations," submitted to *Separation and Purification Technology*, June, 2000.

Presentations

King Mongkutt's University of Technology, Thonburi, Thailand, November 15, 1999, "Metal Membranes for H2Separation."

Sixth International Conference on Inorganic Membranes, June 26-30, 2000, Montpellier, France, "Preparation of Pd-Cu/Alumina Composite Membranes for H2Separations"

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