TITLE: PALLADIUM/COPPER ALLOY COMPOSITE MEMBRANES FOR HIGH TEMPERATURE HYDROGEN SEPARATION

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1. ABSTRACT

INTRODUCTION AND OBJECTIVES

In the January 2003 State of the Union Address, President Bush reaffirmed the Nation's commitment to energy independence and an improved environment by research funding for hydrogen technologies over the next five years. Subsequently, the President proposed a Hydrogen Fuel Initiative to develop both a hydrogen infrastructure for the low-cost production of hydrogen and advanced hydrogen fuel cell vehicles. New separation technology, such as hydrogen selective membranes, will contribute to this goal of reducing the cost of producing H_2 for distributed power generation (fuel cells) as well as transportation applications.

Pd and its alloys as membranes are capable of producing hydrogen with low levels of impurities for use in the electric power, petrochemical, semiconductor, and aerospace industries. Important aspects to consider in the development of Pd membranes include the membrane cost and high temperature stability. 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. With support from the DOE University Coal Research Program, my group has developed methods to make Pd and Pd alloy composite membranes that are highly selective for H_2 over a wide range of temperatures and high pressures. Recently, we have been able to dramatically reduce the thickness of these Pd alloy membranes to approximately one micron (See Figure 1 below). 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.

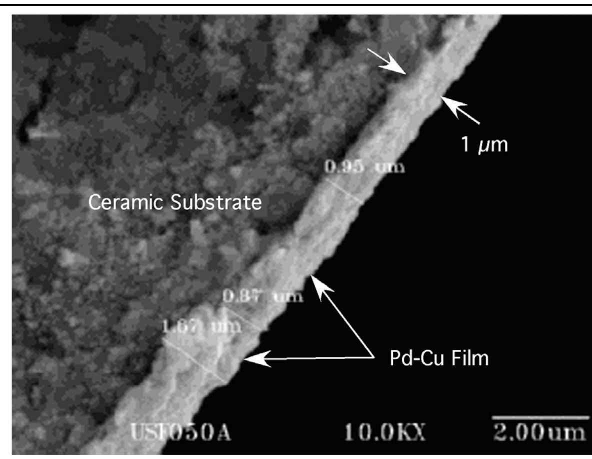

Figure 1. SEM image of the cross section of a Pd-Cu alloy composite membrane

The overall objective of this project is to further optimize our $Pd_{60}Cu_{40}$ (weight %) alloy membranes on porous supports for H_2 separation with respect to minimizing the membrane thickness while maximizing hydrogen flux and selectivity. Additional basic science objectives are to investigate the relationships

between membrane surface structure and alloy composition on separation performance, particularly with mixtures representative of coal-derived synthesis gas.

The specific objectives that we have pursued during the last year are:

- To identify the structural changes that electrolessly deposited palladium-copper metal films on porous supports undergo when exposed to gas mixtures at a range of temperature and pressure conditions with the purpose of determining the effect of non-metallic impurities such as carbon,

- To determine the permeation properties and physical and mechanical resistances of these membranes when exposed to gaseous mixtures containing such gases as CO, CO_2, H_2O and H_2S at different compositions,

- To determine the membranes' resistance to very high pressures and pressure and temperature cycling.

Sequential layers of palladium and copper metals were electrolessly deposited on ceramic substrates as well as modified stainless steel 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 30 bars) using pure gases and gaseous mixtures while recording their H_2 permeation rate, H_2 to non-hydrogen selectivity and percent recovery.

ACCOMPLISHMENTS TO DATE

It was found that when electrolessly deposited thin Pd and Pd-Cu membranes were exposed to air at temperatures ranging from 350 to 500°C, their H_2 flux increased substantially right after the air exposure but eventually dropped back to a new steady state. While this was a quasi-reversible change, the flux of insoluble species increased irreversibly with every air purge but by a much smaller extent. The extent of these changes was found to be dependent on the time and the temperature of the air exposure.

Further study revealed that when a membrane was exposed to air, its surface morphology changed with the appearance of new features such holes and large peaks. Additionally it was found that the air exposure produced some oxidation of the film and that the carbon content of the film was reduced significantly. This led us to believe that the combination of these changes might explain the previously described change in the permeation behavior for these membranes.

This air treatment was also found to be particularly effective in recovering membrane activity in membranes that had been poisoned after being exposed to mixtures containing H_2S and CO.

In another set of experiments to determine the mechanical resistance of the membranes, it was found that after testing several membranes over several days to weeks at a time under feed pressures varying from 10 to 30 bars, they not only survived intact these conditions but also their hydrogen to other gases selectivity remained unchanged. Under these conditions, a number of these membranes experienced sudden cooling and reheating cycles caused by power outages which, nevertheless, caused minimal effects on their permeation properties. These results significantly illustrate the excellent mechanical stability and thermal cycling resistance of these membranes.

In a different series of tests, several membranes were exposed to mixtures resembling a water gas shift product stream. The purpose of that was to simulate expected industrial applications and to try to anticipate what challenges might be still ahead in the development process for these membranes. When the membranes were exposed to mixtures containing carbon dioxide, their hydrogen fluxes were depressed, probably by competition over surface sites for hydrogen dissociation. In some cases this inhibition caused the H_2 fluxes to drop over 35% when the H_2 recovery was pushed to 80%. Yet this inhibition was completely abated when the membrane was purged with pure H_2 for 1 hr. Most interestingly perhaps was the fact that the CO_2 exposure was found to remove bulk carbonaceous contaminants; residue left presumably from electroless plating path constituents.

Similarly, when gas mixtures containing carbon monoxide or hydrogen sulfide were fed to the Pd-Cu membranes, these gases caused inhibition of the H_2 flux. In the case of CO, the membrane lost some of its H_2 flux but the loss was not as significant as with CO_2. However, the strongest inhibition was occasioned by mixtures containing H_2S and steam, causing up to a 50% drop in the H_2 flux. Yet, this inhibition was reversible if the H_2S concentration was kept below 50 ppm. This reversibility might be due to the addition of copper to palladium, which might have promoted the formation of less stable H_2S chemisorbed species on the metal film.

FUTURE WORK

- Continue working with pure SS and modified SS supports in order to duplicate the performance of Pd alloy membranes supported on porous ceramic filters,

- Improve the quality and reproducibility of our deposition techniques to minimize impurities and produce Pd alloy membranes containing the highest performance 40 weight % copper concentration.

2. LIST OF PAPERS PUBLISHED, CONFERENCE PRESENTATIONS, STUDENTS SUPPORTED

REFEREED JOURNAL ARTICLES

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.*, accepted, 3/2004.

Roa, F. and J. D. Way, The Effect of Air Exposure on Palladium-Copper Composite Membranes,"submitted to *Journal of Membrane Science*, 4/2003.

Kulprathipanja, A., Alptekin, G. O., Falconer, J. L., and J. D, Way, "Pd and Pd-Cu Membranes: Inhibition of H_2 Permeation by H_2S, "submitted to *Journal of Membrane Science*, 4/2003.

CONFERENCE PRESENTATIONS

"The Effect of Air Exposure on Palladium-Copper Composite Membranes," paper #POLY 20 to be presented at The 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004.

"Effect of CO_2, H_2O, CO on a Electrolessly Eeposited Palladium ceramic Composite Membrane," paper to be presented at the 8th International Conference on Inorganic Membranes, Cincinnati, OH, July 19-21, 2004.

STUDENTS SUPPORTED

Omar Ishteiwy, M. S. student (U. S. citizen)