Title: **Sulfur-Tolerant Pd/Cu and Pd/Au Alloy Membranes for Hydrogen Separation with High Pressure CO_2 for Sequestration**

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Objectives:

The objectives of this research were:

- to test Pd/Cu membranes with an FCC alloy on the top layer for H_2S tolerance by investigating the reversibility, permeance decline and permeance recovery
- to examine the surface morphology of the Pd/Cu membranes
- to investigate methods of synthesizing Pd/Au alloy membranes
- to characterize the Pd/Au alloy membranes

Accomplishments to date:

Two Pd/Cu membranes (8 % wt and 19 % wt Cu) were deposited on porous Inconel supports by electroless deposition. The intermetallic diffusion barrier between the membrane and the support for the 8 % wt Cu membrane was formed by oxidizing the support at 700 °C for 12 hours while a 0.5 μm Ru film was plated as the barrier for the 19 % wt Cu membrane. Pd plating was carried out until the membranes were impermeable to He. Following this, Cu was plated. Both membranes had a total thickness of approximately 14 μm. To ensure an FCC Pd/Cu phase on the top layer, the 8 % wt and 19 % wt membranes were annealed for 5 and 10 hours respectively in H_2 at 500 °C. After hydrogen permeation characterization, both membranes were tested for H_2S tolerance by exposing the membranes to a H_2 stream containing 42.7 ppm H_2S for two hours at 400, 450 and 500 °C and then switching back to pure H_2 to study the recovery of the permeance. Each exposure was performed twice at each temperature to test for repeatability.

Exposure of the 8 % wt membrane to H_2S at each temperature resulted in a permeance decline of 81 % of the original value at 500 ºC, 82 % at 450 ºC, and 83 %, at 400 ºC, showing that the permeance decline had a weak (if any) dependence on temperature in the range tested. Only part of the permeance was recovered at each temperature which

showed that the poisoning was partly irreversible at these conditions. The recovery time decreased with increasing temperature, which was caused by the increasing rate of desorption with temperature.

The permeance of the 19 % wt membrane completely returned to the original value at 450 °C after H_2S exposure showing that the poisoning was completely reversible at this temperature. However, the permeance did not recover the original value at 400 °C. The partial irreversibility of the H_2S adsorption at 400 °C was further substantiated by the fact that reheating the membrane to 450 °C did not enable the permeance to fully recover to the original value at 450 °C before the H_2S exposure at 400 °C. This membrane was not exposed to H_2S at 500 °C because intermetallic diffusion between the membrane and support metals had occurred in the previous testing, decreasing the permeance.

The He leak in both membranes decreased after every exposure to H_2S except at 500 °C. The reason for the decrease in the He leak could be because the Cu segregated to the surface in between the grain boundaries in the presence of H_2S. The He leak at 500 °C increased in accordance with the leak growth rate previously measured at this temperature.

EDS analysis detected no sulfur on the surface of the 19 % wt membrane showing that sulfide compounds had not been formed. Cross sectional electron micrographs showed that the Cu gradient of the metal remained intact throughout the entire testing period and that intermetallic diffusion had indeed occurred between the membrane and support metals.

A Pd-Au membrane was prepared by electroless plating Pd on a porous metal support until the membrane was gas tight. Au was deposited by displacement in a $NaAu(Cl)_4{\cdot}2H_2O$ solution. The total membrane thickness was 18 μm with approximately 5~20 % wt Au.

The H_2 permeation through the membrane followed Sieverts' law with a permeance of 13.1 $m^3/(m^2*h*atm^{0.5})$ at 250 °C and 30.8 $m^3/(m^2*h*atm^{0.5})$ at 400 °C. The permeances were about 50 % higher than those of pure Pd films. The activation energy for H_2 permeation was 12.9 kJ/mol, which was lower than that of a pure Pd film (15.6 kJ/mol).

The higher H_2 permeance and lower activation energy of the membrane were believed to be a result of the Pd/Au alloy formation. Although the leak rate of the membrane increased slightly with temperature, the large increase in H_2 permeance resulted in an increase of the ideal H_2/He separation factor from 540 at 250 °C to 860 at 400 °C. The membrane was stable for over 1000 hours between the temperatures of 250 °C and 400 °C.

Future work:

- to examine the long term stability of the permeance and selectivity of Pd/Cu membranes in the presence of H_2S and the influence of exposure time on permeance recovery at 350, 400 and 450 °C
- to investigate the H_2S tolerance of the Pd/Au membrane

Presentations/Papers:

Pomerantz, Natalie and Yi Hua Ma, "Surface modification of Pd membranes with Cu for H_2S resistance in H_2 separation", Presentation, AIChE 2006 Annual Meeting, November 12 – 17, San Francisco, CA.

Chen, Chao-Huang and Yi Hua Ma. "Preparation of Pd/Au H_2 separation membrane by galvanic displacement", Presentation, NAMS 2007 Annual Meeting, May 12 – 16, Orlando, FA.

Pomerantz, Natalie and Yi Hua Ma, "Effect of H_2S poisoning of Pd/Cu membranes on H_2 permeance and membrane morphology", Accepted for Presentation, 234th ACS National Meeting, August 19 – 23, 2007, Boston, MA.

Chen, Chao-Huang and Yi Hua Ma. "Characterization of composite Pd/Au hydrogen separation membrane prepared by galvanic displacement", Accepted for Presentation, 234th ACS National Meeting, August 19 – 23, 2007, Boston, MA.

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