Title: **Sulfur-Tolerant Palladium-Copper Alloy Membranes for Hydrogen Separation with High Pressure CO_2 for Sequestration**

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OBJECTIVES

The primary objective of the proposed research is to develop sulfur-tolerant composite Pd/Cu alloy porous stainless steel (PSS) membranes for hydrogen separation with high pressure CO_2 appropriate for recycling or sequestration, or conversion to industrially useful products or creation of natural CO_2 sink. The specific objectives of each phase are: (1) to synthesize sulfur-tolerant composite Pd/Cu alloy PSS membrane electroless plating, (2) to obtain the kinetics of Pd/Cu alloy formation and to investigate the effects of changes in nanostructure properties as a function of temperature and rate of heating and cooling during the alloy formation process, (3) to characterize the membrane permeation performance, which will be related to the changes in nanostructure properties of the alloy and (4) to test the membrane in pilot scale units using simulated coal gases to achieve the ultimate goal of applying the obtained knowledge to develop low-cost, high-flux ultra-thin sulfur-tolerant Pd/Cu membranes for simultaneous hydrogen separation and production of pressurized CO_2, readily for sequestration.

ACCOMPLISHMENTS TO DATE

The grant was awarded on 1 October, 2004. We were unable to start the Grant immediately because it was quite difficult to recruit graduate students in the middle of a semester. Through our continuing recruiting effort, one graduate student started her graduate work in May, 2005 and the second one started in September, 2005. Because of the delay in starting the project, a one-year no-cost extension has been granted. Therefore, the work reported here covers the first 10 months of the Grant.

Coupon studies were first performed to examine the effects of the annealing time and temperature on the copper gradient in the palladium film and the surface concentration of copper. Pd and Cu were plated sequentially on a series of coupons of Grade 0.2 μm 316L porous stainless steel (PSS) of size 1.5 cm^2. SEM micrographs showed that copper covered the PSS uniformly both inside and outside the pores, similar to the palladium plating. The deposition of 1.1 μm of copper on top of the palladium layer showed no cracking on the surface, but as the clusters of copper enlarged and pressed against each other, the relaxation of stress and strain caused cracks to form.

A composite Pd membrane on porous metal support was prepared. The support was oxidized at 700ºC for 12 hours. It has 12.5 microns of Pd and 1.5 microns of Cu (~ 8 wt%). The permeance of the bare support was180 m^3/m^2*h*bar and 130 m^3/m2*h*bar before and after oxidation, respectively.

A system is being built for sulfur resistance testing. The test unit consists of a tube furnace and a stainless steel reactor where the membrane is housed in a shell-and-tube arrangement and sealed with stainless steel and graphite ferrules. An Eurotherm 2116 temperature controller is used to control the temperature at the reactor wall and adjusted to have the desired temperature at the tube side. MKS pressure transducers are used to measure the pressure in the tube and shell side. The H_2 and He flow rates are measured using digital mass flow meters (MKS M10MB model). All the parameters including tube temperatures, pressures and flow rates are logged continuously into a computer using a TBX-68T Terminal block (National Instruments) data acquisition box and NI 4351 high precision voltage meter (National Instruments).

FUTURE WORK

Membrane synthesis will continue to be the main focus of the project. The poisoning resistance of a membrane is determined by whether or not the permeance declines, and how much. These test runs will be short since the poisoning generally happens almost immediately. Permeance sharply declines, and the system will quite possibly reach steady state in a short period of time (e.g., one hour). The membranes will have the permeance and selectivity tested before and after exposure to H_2S in H_2.

The sulfur resistance will be tested in the temperature range of 350 – 500ºC and a H_2S concentration range of 200 – 1000 ppm. The H_2S concentration will be monitored by a GC. Smaller concentrations and higher temperatures will be tested first since higher temperatures cause less poisoning. All membranes will be cut and analyzed with SEM following test runs.

Membranes which are deemed resistant to the presence of H_2S in H_2 will be tested for durability in a simulated syngas atmosphere to see if other components in the feed stream such as water have an effect on the poisoning. The syngas composition will be around 25 – 30 % H_2, 30 – 60 % CO, 5 – 15 % CO_2, 2 – 30 % H_2O and 1000 ppm H_2S. If the membranes are not poisoned, permeance and selectivity will be monitored for 30 days or more in the temperature range of 350 – 500ºC after which the membranes will be cut and analyzed by SEM