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 $\text{H}_2$ separation. These membranes consist of a thin (~1 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 $\text{H}_2$ separation, and resist poisoning by $\text{H}_2\text{S}$ 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 $\text{H}_2$ separation. These following advantages of these membranes for processing of coal-derived gas will be demonstrated:

- High $\text{H}_2$ 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 $\text{H}_2$ 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 both symmetric and asymmetric ceramic filters during the second year of the project. The fabrication method is described by Paglieri [1]. The total thickness of the membranes has been reduced from approximately 10 µm to 1 µm. At the same time, the the $\text{H}_2$ flux and ideal $\text{H}_2$/N$_2$ selectivity have been increased to 0.8 moles/m$^2$•s and 1400, respectively at 345 kPa (50 psi) pressure driving force. This is a four-fold increase in $\text{H}_2$ flux compared to membrane #4, which is typical of the Pd-Cu membranes made using a symmetric, 0.2 µm pore size alumina support.

Task 1: Program Startup Activities-Completed

Task 2: Fabrication of Pd-Cu Membranes-Three new Pd-Cu alloy composite membranes have been prepared and characterized as shown in Tables 1 and 2 (#5, 6, and 20). Our hypothesis was that by using a support material with less surface roughness, the Pd-Cu film thickness could be reduced. Furthermore, asymmetric ceramic filters were used, where the small pore top layer is supported on several layers of larger particles, reducing the hydraulic resistance in the support. Effective pore sizes of these filters ranged from 0.02 to 0.05 µm. This is approximately an order of magnitude reduction in pore size compared to the membranes made during year 1 of this project such as membrane #4 in Table 1. An SEM image of the cross-section of an asymmetric ceramic is shown in Figure 1.

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 $\text{H}_2$/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. The thicknesses of these new membranes ranged from 1 to 10 µm, which satisfies our goal of reducing the Pd-Cu membrane thickness to less than 5 µm stated in our proposal.

A typical electron micrograph of the cross section of membrane #6 is shown in Figure 1. The thickness of this membrane is approximately 1 µm. This reduction in Pd-Cu alloy membrane thickness is particularly important with respect to the economics of membrane fabrication. As an example, our materials cost to produce a 1 µm film containing 60 mass % Pd is about $2, compared to $200 for an 25 cm long, Ti-70 asymmetric ceramic filter from the U. S. Filter Company. Consequently, at a thickness of 1 µm, the Pd cost is approximately 1% of the total materials cost.

The alloy compositions of our Pd-Cu composite membranes ranges from 10 to 30 mass % Cu as determined by EDAX. This is lower than our target of 40 mass % where the highest H₂ permeability has been reported [2]. Increasing the Cu plating time show allow us to increase the Cu alloy composition in our future work.

Task 4: H₂ Separation Performance Measurements-Pure gas transport measurements were performed for all membranes with H₂ and N₂ over a range of temperatures at 345 kPa pressure driving force. These data are summarized in Table 2. Hydrogen fluxes ranged from 0.2 to 0.8 moles/m²•s for the 5 cm long, 1 cm OD membranes, having an approximate surface area of 11 cm². The ideal selectivity, or the ratio of pure gas fluxes measured at the same conditions, ranges from 50 to 1400.

A plot of both the H₂ and N₂ fluxes for membrane #20 is given in Figure 3 at a temperature of 623 K (350 °C) using a driving force of 345 kPa (50 psi). It has been shown in the literature [3] that brief (0.5 to 1 hour) air oxidations or air purges at temperature can significantly increase the H₂ flux. This was also observed for our data as the first air purge more than doubled the H₂ 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 [4] 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 believe that the formation of a Pd oxide causes the surface to rearrange, creating new sites for H₂ dissociation or simply increasing the surface area of the film. We will continue to investigate the mechanism of the air purge during the the final year of the project.

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

- Los Alamos National Laboratory, Los Alamos, NM, 12/00, New Materials for Gas and Liquid Separations
- ACS National Meeting, San Diego, CA, 4/01, Micron Scale Pd-Cu Alloy Composite Membranes for Hydrogen Separations
- The North American Catalysis Society annual meeting, Toronto, Canada, 6/01, Scale Pd-Cu Alloy Composite Membranes for Hydrogen Separations and Membrane Reactors
- Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID, 7/01, New Materials for Gas and Liquid Separations
**Conclusions**
Excellent progress is being made in all aspects of this project. Research activity in the next year will focus on continuing to reduce the membrane thickness, increasing hydrogen flux, optimization of the Pd-Cu alloy composition, and understanding how the air purge increases the hydrogen flux.

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

<table>
<thead>
<tr>
<th>No.</th>
<th>Type of support material</th>
<th>Support pore size (nm)</th>
<th>Estimated Thickness of Pd film (µm)</th>
<th>N\textsubscript{2} Flux (mol/m\textsuperscript{2}s)\textsuperscript{1} x 10\textsuperscript{4}</th>
<th>Estimated Thickness of Cu film (µm)</th>
<th>N\textsubscript{2} Flux (mol/m\textsuperscript{2}s)\textsuperscript{2} x 10\textsuperscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Symmetric α-alumina</td>
<td>200</td>
<td>8</td>
<td>0.985</td>
<td>8</td>
<td>0.061</td>
</tr>
<tr>
<td>5</td>
<td>Asymmetric zirconia</td>
<td>50</td>
<td>8</td>
<td>0.438</td>
<td>6</td>
<td>0.021</td>
</tr>
<tr>
<td>6</td>
<td>Asymmetric zirconia</td>
<td>50</td>
<td>1.5</td>
<td>0.248</td>
<td>1</td>
<td>0.042</td>
</tr>
<tr>
<td>20</td>
<td>Asymmetric zirconia</td>
<td>20</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{1} The membrane, coated with Pd, is pressurized with N\textsubscript{2} at 896.3 kPa. The time for the pressure to drop at 827.4 kPa is measured and the flux is calculated.

\textsuperscript{2} As above but now the membrane is coated with both Pd and Cu.

Table 2. Pd–Cu Membrane Performance and Characterization.

<table>
<thead>
<tr>
<th>No.</th>
<th>ΔP (kPa)</th>
<th>Heated to (K)</th>
<th>H\textsubscript{2} flux @ 773 K (mol/m\textsuperscript{2}s)</th>
<th>Highest Ideal Selectivity\textsuperscript{4}</th>
<th>Thickness from SEM (µm)</th>
<th>Pd/Cu from EDAX (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>345</td>
<td>723</td>
<td>0.18\textsuperscript{†}</td>
<td>270</td>
<td>12.5±1.5</td>
<td>78/22</td>
</tr>
<tr>
<td>5</td>
<td>345</td>
<td>723</td>
<td>0.80</td>
<td>1400</td>
<td>12±1.0</td>
<td>91/9</td>
</tr>
<tr>
<td>6</td>
<td>345</td>
<td>723</td>
<td>0.66\textsuperscript{‡}</td>
<td>47</td>
<td>1.5 ±0.2</td>
<td>70/30</td>
</tr>
<tr>
<td>20</td>
<td>345</td>
<td>723</td>
<td>0.51</td>
<td>1217</td>
<td>0.5-1.0</td>
<td>80/20</td>
</tr>
</tbody>
</table>

\textsuperscript{3} Temperature = 723 K

\textsuperscript{4} Ideal Selectivity = pure hydrogen flux/ pure nitrogen flux

Figure 1. Cross-section of an asymmetric, alumina ultrafilter. Scalebar is 50 µm.
Figure 2. Electron micrograph of the cross section of membrane #6.

Figure 3. Pure gas transport data for membrane #20. Fluxes were measured with a pressure driving force of 345 kPa (50 psi). Air purges are shown as vertical dotted lines on the graph.