

Final Technical Progress Report

Palladium/Copper Alloy Composite Membranes for High Temperature Hydrogen Separation

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Submitted by

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Abstract

This report summarizes progress made during the a three year University Coal Research grant (DE-FG26-03NT41792) at the Colorado School of Mines. The period of performance was September 1, 2003 through August of 2006. We made excellent progress toward our goal of contributing to the development of high productivity, sulfur tolerant composite metal membranes for hydrogen production and membrane reactors. Composite Pd and Pd alloy metal membranes with thin metal films (1-7 μm) were prepared on porous stainless steel and ceramic supports that meet or exceed the DOE 2010 and 2015 pure hydrogen flux targets at differential pressure of only 20 psi. For example, a 2 μm pure Pd membrane on a Pall AccuSep® substrate achieved an ideal H_2/N_2 separation factor of over 6000, with a pure hydrogen flux of 210 SCFH/ft² at only 20 psig feed pressure. Similar performance was achieved with a $\text{Pd}_{80}\text{Au}_{20}$ composite membrane on a similar stainless steel substrate. Extrapolating the pure hydrogen flux of this PdAu membrane to the DOE Fossil Energy target conditions of 150 psia feed pressure and 50 psia permeate pressure gives a value of 508 SCFH/ft², exceeding the 2015 target. At these thicknesses, it is the support cost that will dominate the cost of a large scale module. In a direct comparison of FCC phase PdCu and PdAu alloys on identical supports, we showed that a $\text{Pd}_{85}\text{Au}_{15}$ (mass %) alloy membrane is not inhibited by CO, CO₂, or steam present in a water-gas shift feed mixture at 400 °C, has better resistance to sulfur than a $\text{Pd}_{94}\text{Cu}_6$ membrane, and has over twice the hydrogen permeance.

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Executive Summary

This report summarizes progress made during the a three year University Coal Research grant (DE-FG26-03NT41792) at the Colorado School of Mines. The period of performance was September 1, 2003 through August of 2006.

Palladium and its alloys, as well as Ni, Pt and the metals in Groups III - V 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, their chemical compatibility with many hydrocarbon containing gas streams, and their theoretically infinite hydrogen selectivity. Palladium alloys often possess higher hydrogen permeability than pure palladium. In particular, alloy membranes, such as PdAu and Pd₆₀Cu₄₀, have a higher H₂ permeability than pure palladium, are unaffected by thermal cycling, and are have some resistance to sulfur poisoning.

A robust, hydrogen permselective palladium membrane has the potential to change the chemical industry by replacing traditional reaction and separation procedures, thereby resulting in sizable savings in energy consumption and capital investment in equipment. This increased functionality and energy saving benefit in combination with high hydrogen permselectivity and flux (throughput) make palladium alloy membranes an attractive hydrogen separation technology. The 2015 U. S. DOE Fossil Energy membrane performance target for the pure hydrogen flux at 400 °C at a differential pressure of 100 psi is 300 ft³(STP)/ft²•h.

In this grant from the DOE University Coal Research program, we made excellent progress toward our goal of contributing to the development of high productivity, sulfur tolerant composite metal membranes for hydrogen production and membrane reactors. Composite Pd and Pd alloy metal membranes with thin metal films (1-7 µm) were prepared on porous stainless steel and ceramic supports that meet or exceed the DOE 2010 and 2015 pure hydrogen flux targets at differential pressure of only 20 psi. A 2 µm pure Pd membrane on a Pall AccuSep® substrate achieved an ideal H₂/N₂ separation factor of over 6000, with a pure hydrogen flux of 210 SCFH/ft² at only 20 psig feed pressure. Similar performance was achieved with a Pd₈₀Au₂₀ composite membrane on a similar stainless steel substrate. Extrapolating the pure hydrogen flux of this membrane to the DOE Fossil Energy target conditions of 150 psia feed pressure and 50 psia permeate pressure gives a value 508 SCFH/ft², exceeding the 2015 target. At these thicknesses, it is the support cost that will dominate the cost of a large scale module. In a direct comparison of FCC phase PdCu and PdAu alloys on identical supports, we showed that a Pd₈₅Au₁₅ (mass %) alloy membrane is not inhibited by CO, CO₂, or steam present in a water-gas shift feed mixture at 400 °C, has better resistance to sulfur than a Pd₉₄Cu₆ membrane, and has over twice the hydrogen permeance.

Introduction and Objectives

The feasibility of preparing and using pure Pd-membranes for H_2 separation is well known. However, pure Pd membranes suffer from embrittlement, and poisoning by sulfur. Furthermore, the ability of thick Pd-Cu alloy membranes to separate H_2 , and the high temperature stability and resistance to poisoning of these materials has been demonstrated. During our previous UCR Grant, we have demonstrated that very thin, 1 μm thick Pd-Cu composite membranes can be fabricated that exhibit high H_2 flux and are also resistant to H_2S . However, we observed several very interesting phenomena associated with these membranes including the influence of surface structure on H_2 transport and inhibition of H_2 flux by H_2S . Our objectives for this research grant were the investigate the following:

- Identify factors important in membrane fabrication, particularly on metal supports and to fabricate composite membranes on tubular, porous stainless steel substrates,
- Optimize the membrane crystal and surface structure and bulk composition,
- Investigate the effect of temperature, pressure, and gas composition on H_2 flux and membrane selectivity,
- Seek to understand mechanisms that may lead to different separation factors observed during mixture measurements, especially the inhibition of H_2 flux in the presence of H_2S and CO, and
- Fabricate composite Pd alloy membranes that meet the DOE Fossil Energy pure hydrogen flux targets

Technical Progress

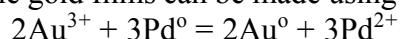
Task 1.0 Fabrication of Pd and Pd Alloy Membranes.

Composite Pd alloy membranes were fabricated by sequential deposition of palladium and copper or gold by electroless plating onto porous ceramic and stainless steel filter supports. Our prior publications describe this procedure in detail[1, 2]. We have reformulated our Pd plating bath recipe in an effort to minimize or eliminate the presence of carbon contamination in our membranes [3]. All carbon containing chemicals, such as EDTA, have been removed. This has improved durability and increased permeability.

Examples of supports used include: symmetric 0.2 μm cut-off α -alumina tubes from CoorsTek(GTC-200), asymmetric 0.02 and 0.05 μm cut-off zirconia-coated α -alumina tubes (USF-020, USF-050) from Exekia (Pall Corporation), 0.1 and 0.5 grade porous stainless steel supports from the Mott Corporation, and, most recently, 0.08 μm zirconia coated stainless steel AccuSep substrates from the Pall Corporation. Ceramic supports are prepared by cutting to length, cleaning and sealing the ends with a silica glaze. Stainless steel supports are prepared by cutting to length, cleaning, and then applying a porous ceramic diffusion barrier, if needed. A seeding procedure is used prior to the palladium plating. That step involves impregnation of the ceramic support with an organic Pd salt solution, followed by calcination and reduction in flowing hydrogen.

Pd electroless plating baths were then used with osmotic pressure gradients to deposit films ranging from 1 to 10 microns in thickness on either the inside or outside of the support tubes. Plating on the outside of a nominal 1 cm OD support tube with a 1.5 mm wall thickness increases the specific surface area by 43% compared to plating the same tube on the inside. The osmotic pressure, generated by circulating concentrated sucrose solutions on the opposite side of the support from the plated film, insured reduced porosity and promoted surface homogeneity and densification of the plated Pd film[4]. Pd alloy membranes with Au or Cu can easily be fabricated from these pure Pd

membranes by simply depositing the additional alloying metal layer. A copper layer is deposited using electroless plating[1] while gold films can be made using displacement plating [5]:



Once the alloying metal is deposited, the membrane is heated to above 300 °C in an inert gas, the feed gas is switched to hydrogen, and the composite membrane is annealing in-situ. Symmetric, 0.2 μm pore size Al_2O_3 tubes from CoorsTek (GTC-200) plated on the outside with PdCu alloys are shown in Figure 1. Figure 2 shows two Pd-Au alloy membranes on GTC-200 supports. The top membrane in Figure 2 is has been tested and annealed, while the bottom membrane has not been tested or annealed.



Figure 1. Pd alloy membranes deposited on the outside of GTC-200 symmetric supports. The coin has a diameter of 2.4 cm.

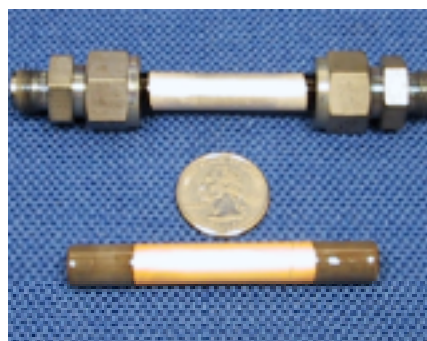


Figure 2. Pd-Au alloy membranes after annealing (top) and prior to annealing (bottom). Substrates are GTC-200 alumina tubes.

The primary challenges in preparing Pd alloy composite membranes on stainless steel supports are twofold. First, the mean pore size of the porous metal material is typically about 2 μm requiring thicker Pd alloy films to bridge these larger pores. Second, a diffusion barrier layer is usually required to prevent intermetallic diffusion between the Pd alloy film and the stainless steel support. A strategy used by the Pall Corporation to mitigate both of these issues is to deposit an oxide coating on the stainless steel filter as shown in Figure 3. This creates a diffusion barrier and reduces the surface roughness of the substrate. However, the oxide coating does reduce the flow through the support, and the Pall Corporation is working to optimize the oxide coating thickness to minimize the pressure drop through the stainless steel support in a separate DOE sponsored program (DE-FG36-05G015093). High temperature sealing is much easier with metal supports as the ends can be easily densified and sealed to a tubing system by welding, brazing, or metal compression fittings. Figure 4 shows a symmetric, porous stainless steel substrate (Mott Corporation) plated with pure Pd. A porous alumina diffusion barrier was applied by CSM prior to Pd plating.



Figure 3. Two Pall AccuSep ZrO_2 coated porous stainless steel filters at top. Pd coated AccuSep filter at bottom. These substrates have approximately 30 cm^2 of active area.



Figure 4. Pd membrane deposited on the outside of a Mott 0.1 μm grade symmetric stainless steel support tube.

Task 2.0 Characterization of Pd and Pd Alloy Membranes.

The composite membranes fabricated in Task 1 were extensively characterized using a nitrogen leak test, ESEM, EDAX, AFM, and XRD. Since these instrumental methods are destructive, these were performed as needed after the permeation studies in Task 3. XRD patterns for our electroless films and reference Pd₆₀Cu₄₀ foil membranes are shown in Figure 5. For membranes containing 60 weight % Pd with the balance being Cu, annealing in hydrogen produces a phase change from an FCC phase to the more permeable BCC phase[6].

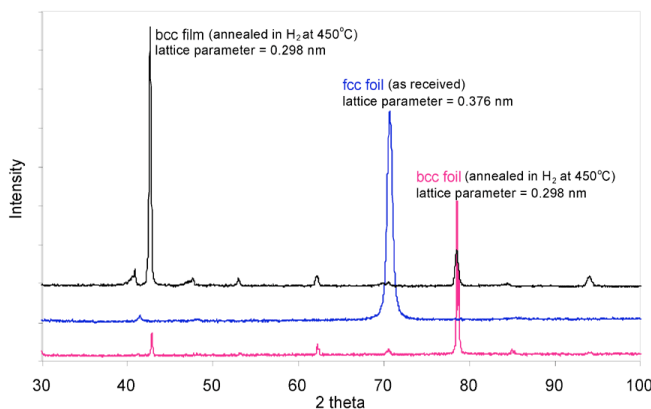


Figure 5. Typical X-ray diffraction patterns for electroless Pd-Cu membrane (film) and cold-rolled, 25 μm thick Pd₆₀Cu₄₀ foil membrane. The foil is in the FCC phase prior to annealing in hydrogen at 450 °C where the higher permeability BCC phase is formed.

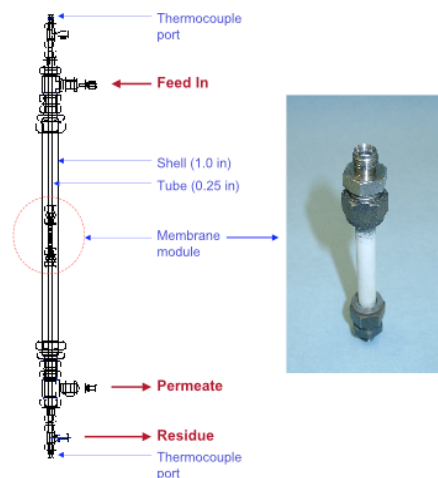


Figure 6. Photograph of a typical membrane and the high temperature module.

Task 3.0 Pure and Mixed Gas Permeation Studies.

High temperature permeation tests

The membrane to be tested was loaded into a stainless steel module, which in turn was mounted in a tube furnace. Figure 6 shows a sketch of the module and a photograph of a typical membrane. To avoid embrittlement, the membranes were heated under helium and no H₂ was introduced into the module until the membrane reached 350°C. Annealing the two metals was achieved during the initial single gas permeability tests. Trans-membrane pressure differentials varied from a 10 psig to as high as 435 psig, while typical operating temperatures varied from 250°C to 500°C. Permeate pressure was local atmospheric pressure (12 psia), except for tests using a permeate side sweep gas.

Figure 7 summarizes the relationship between hydrogen flux and membrane thickness under the test conditions of 400 °C and 20 psi hydrogen partial pressure difference for a series of pure Pd membranes supported on Pall AccuSep© stainless steel supports. A pure Pd composite membrane with a thickness of approximately 1 micron **exceeds** the 2015 DOE Fossil Energy pure hydrogen flux targets shown in Table 1 below **at a differential pressure of only 20 psi**. The ideal H₂/N₂ selectivity of the 2 μm membrane from Figure 7 was greater than 6000. The relationship between hydrogen flux and the inverse of membrane thickness is nearly linear. As described above, Pd alloy membranes with Au or Cu can easily be fabricated from these pure Pd membranes by simply depositing the additional alloying metal layer.

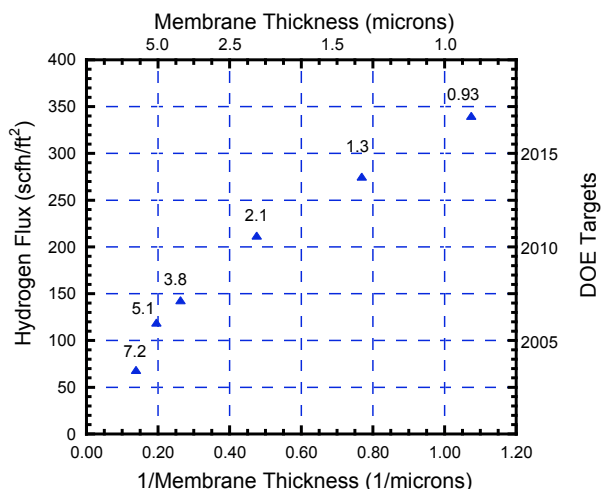


Figure 7. Influence of Pd membrane thickness on pure H₂ flux at 20 psig feed pressure and 400 °C. All membranes prepared on Pall AccuSep ZrO₂/stainless steel substrates.

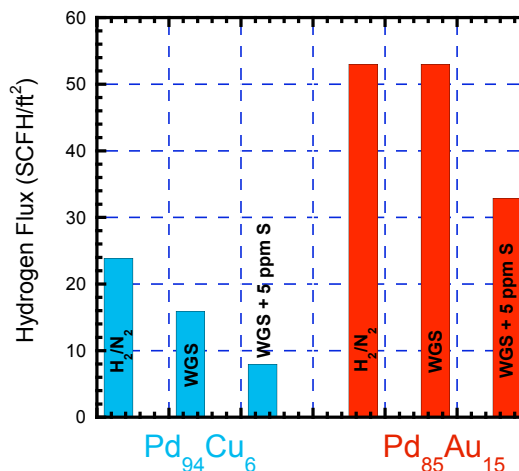


Figure 8. Comparison of PdCu and PdAu alloy membranes for a variety of feed gas streams at 400 °C and 60 psig feed pressure. The same support was used for both membranes. The H₂ partial pressure is the same for all experiments. Alloy composition are in mass %. The WGS mix contains 51% H₂, 26% CO₂, 21% H₂O, 2% CO.

We recently fabricated and tested several Pd alloy composite membranes with H₂/N₂ mixtures (51% H₂), a water gas shift (WGS) mixture, and the WGS mixture (51% H₂, 26% CO₂, 21% H₂O, 2% CO) containing 5 ppmv H₂S at 400 °C. The performance of a Pd₈₅Au₁₅ membrane is compared with a similar, FCC phase, Pd₉₄Cu₆ membrane in Figure 8. Both membranes were fabricated using the same 0.2 μm symmetric alumina support from CoorsTek and both are approximately 5 microns thick. During the testing, the partial pressure difference of H₂ was kept constant at 25 psi. **No flux reduction** was observed for the PdAu membrane with the WGS mixture compared to a pure H₂ feed gas. However, we observed about a 33% drop in the H₂ flux for the WGS feed gas for the PdCu membrane. When 5 ppm H₂S was added to the WGS feed mixture, the flux for the PdAu membrane dropped 38% compared to the H₂/N₂ feed mixture. This compares to a 70% drop for the PdCu membrane comparing the H₂/N₂ feed with the WGS mixture containing 5 ppm H₂S. Moreover, the flux of the PdAu membrane was consistently over twice that of the PdCu membrane for the H₂/N₂ feed gas. This is roughly consistent with the ratio expected from the patent literature [7]. With H₂S present, the H₂ flux for the PdAu membrane was four times that of the FCC phase PdCu membrane. An FCC phase Cu membrane was chosen for this comparison because prior research at NETL [8] suggests that the FCC phase PdCu alloy materials have better resistance to inhibition by H₂S.

Two additional PdAu alloy membranes were fabricated and tested with the WGS gas mixture at 400 °C. No inhibition of the H₂ flux was observed in these experiments either. For example, as shown in Figure 9, a ~9 micron thick PdAu membrane on a Pall AccuSep® stainless steel support was fed a WGS mixture and produced an H₂ permeate stream containing only 5 ppm CO and a H₂ permeate purity of 99.9% using graphite seals. The flux of this membrane is modest, only 60 SCFH/ft² for a hydrogen partial pressure difference of only 24 psi. However, reducing the thickness of a PdAu membrane allowed us to substantially increase the hydrogen flux.

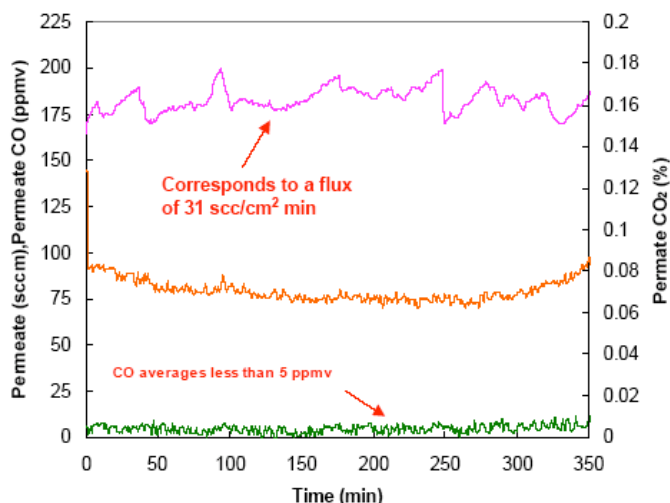


Figure 9. Flux/selectivity data for Pd₈₅Au₁₅ (mass %) P= 60 psig, T= 400 °C, Feed composition= 51% H₂, 26% CO₂, 2% CO and 21% H₂O on volume basis).

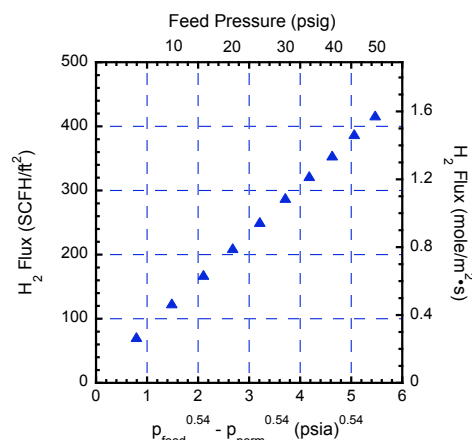


Figure 10. The influence of feed gas pressure on the pure H₂ flux of a Pd₈₀Au₂₀ membrane on a Pall AccuSep support at 400 °C.

Most recently, a thinner 2.5 μm thick PdAu alloy membrane was prepared on a Pall AccuSep substrate and a series of pure gas permeation tests were performed over a range of feed pressures. These data are shown in Figure 10. The pure H₂ flux of this membrane exceeds the 2010 flux target at a feed pressure of 20 psig and exceeds the 2015 target at 35 psig. The n-value, or pressure dependence of the flux is 0.54, very close to the theoretical value of 0.5 in Sievert's law. Using a least-squares fit, we can estimate that the pure hydrogen flux at DOE Fossil Energy target conditions of 150 psia feed pressure and 50 psia permeate pressure would be 508 SCFH/ft².

A longer term mixture test was done with Pd₈₅Au₁₅ membrane GTC-75, supported on a porous alumina support. In between binary and water gas shift mixture tests, the pure hydrogen permeate flow was measured at 400 °C and 20 psig feed pressure. The hydrogen partial pressure was approximately the same as during the mixture permeation tests. As shown in Figure 11, the permeate flow was essentially constant over a two week period.

We have also developed a technique for using electroless plating to prepare free-standing Pd foil membranes $\geq 3 \mu\text{m}$ thick on polished stainless steel substrates where the plated foil can be peeled from the steel substrate after plating. The pure H₂ permeation data are shown in Figure 12 for this membrane and are compared with the patent literature [7]. Our transport and activation energy data agree very well with the literature values.

The DOE Fossil Energy target goals for a hydrogen selective membranes are summarized in Table 1 below. We have added a column to show how our composite membranes compare to the DOE target values with respect to pure hydrogen flux. The extrapolated pure H₂ flux for a Pd₈₀Au₂₀ membrane supported on a Pall AccuSep® stainless steel support is 508 SCFH/ft² at the DOE Fossil Energy conditions of 150 psia feed pressure and 50 psia permeate pressure. PdAu membranes are resistant to poisoning by 5 ppm H₂S in a water gas shift feed mixture as shown in Figure 8. Perhaps more importantly, the hydrogen flux for PdAu membranes is not inhibited (reduced) by components of a water gas shift feed mixture (51% H₂, 26% CO₂, 21% H₂O, 2% CO) at 60 psig feed pressure and 400 °C. In a permeation test with a PdAu membrane on a stainless steel support using graphite seals, the permeate hydrogen purity was 99.93% with a CO composition of only 5 ppmv (Figure 9).

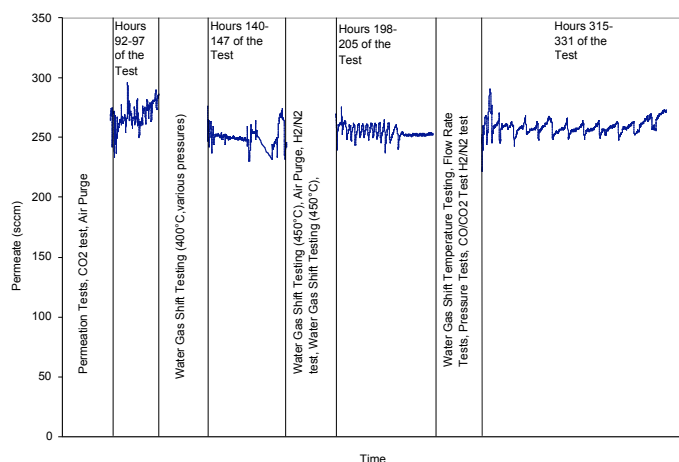


Figure 11. Influence of time on the hydrogen permeate flow from PdAu membrane GTC-75. Test temperature = 400 °C, pure H₂ feed pressure = 20 psig. Water gas shift mixture contains 51% H₂, 26% CO₂, 21% H₂O, 2% CO.

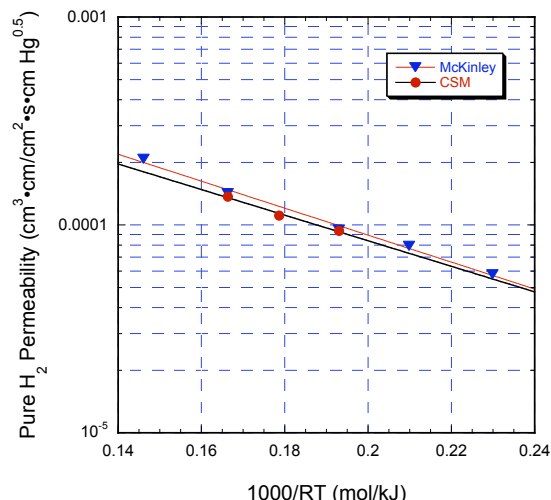


Figure 12. The influence of temperature on the pure H₂ permeability for Pd foil membranes. McKinley refers to U. S. Patent 3,439,474.

Table 1. DOE Hydrogen Membrane Performance Goals and Current Status of CSM Pd/Cu Alloy Membrane Technology

Performance Criteria	2007 Target	2010 Target	2015 Target	CSM Status
Flux ^a	100	200	300	508 (PdAu)
Operating Temperature (°C)	400 – 700	300 – 600	250 – 500	350 - 450
Sulfur Tolerance	Yes	Yes	Yes	Yes
WGS Activity	Yes	Yes	Yes	Yes (PdCu)
Cost (\$/ft ²)	150	100	<100	TBD
Operating Pressure Capability (psi)	100	400	800 – 1000	300
CO Tolerance	Yes	Yes	Yes	Yes ^b
Hydrogen Purity	95%	99.5%	99.99%	99.93% ^c
Stability/Durability (years)	3	7	>10	3 months pure H ₂ , 2 weeks PdAu

a) SCFH/ft² calculated @ 100 psi ΔP H₂ @ 50 psia perm side pressure from data in Figure 10.

b) Tested with 2 mol% CO, see Figure 8

c) From mixture test with WGS feed mixture, see Figure 9. CO concentration less than 5 ppmv.

Conclusions

In this grant from the DOE University Coal Research program, we made excellent progress toward our goal of contributing to the development of high productivity, sulfur tolerant composite metal membranes for hydrogen production and membrane reactors. Composite Pd and Pd alloy metal membranes with thin metal films (1-7 μm) were prepared on porous stainless steel and ceramic supports that meet or exceed the DOE 2010 and 2015 pure hydrogen flux targets at differential pressure of only 20 psi. A 2 μm pure Pd membrane on a Pall AccuSep® substrate achieved an ideal H₂/N₂ separation factor of over 6000, with a pure hydrogen flux of 210 SCFH/ft² at only 20 psig feed pressure. Similar performance was achieved with a Pd₈₀Au₂₀ composite membrane on a similar stainless steel substrate. Extrapolating the pure hydrogen flux of this membrane to the DOE Fossil Energy target conditions of 150 psia feed pressure and 50 psia

permeate pressure gives a value 508 SCFH/ft², greatly exceeding the 2015 target. At these thicknesses, it is the support cost that will dominate the cost of a large scale module. In a direct comparison of FCC phase PdCu and PdAu alloys on identical supports, we showed that a Pd₈₅Au₁₅ (mass %) alloy membrane is not inhibited by CO, CO₂, or steam present in a water-gas shift feed mixture at 400 °C, has better resistance to sulfur than a Pd₉₄Cu₆ membrane, and has over twice the hydrogen permeance.

Technology Transfer Activity

Journal Articles Published/Accepted/In Press

- 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.*, **43**(15), 4188-4198(2004).
- Roa, F., Way, J. D., DeVoss, S., and G. Alptekin, Effect of CO₂, CO, H₂S on a Pd-Cu Ceramic Composite Membrane Made by Electroless Plating, Proceedings of the International Conference on Inorganic Membranes (ICIM 8), Cincinnati, OH, July 18-22, 2004.
- Roa, F. and J. D. Way, “The Effect of Air Exposure on Palladium-Copper Composite Membranes,” *Applied Surface Science*, **240**(1-4), 85-104(2005).
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- Thoen, P. M., Roa, F., and J. D. Way, “High Flux Palladium-Copper Composite Membranes for Hydrogen Separations,” *Desalination*, **193**, 224-229(2006).
- Gade, S. K., Keeling, M., Steele, D., Thoen, P. M. and J. D. Way, Sulfur Resistant Palladium-Gold Composite Membranes for Hydrogen Separations, Proceedings of the International Conference on Inorganic Membranes (ICIM 9), Lillehammer, Norway, June 26 – 29, 2006.
- Gade, S. K., Keeling, M., Steele, D., Thoen, P. M. and J. D. Way, High Flux Pd and Pd Alloy Membranes Deposited on Stainless Steel Supports by Electroless Plating, Proceedings of the International Conference on Inorganic Membranes (ICIM 9), Lillehammer, Norway, June 26 – 29, 2006.

Journal Articles in Preparation

- Gade, S. K., Thoen, P. M., Lusk, M. J., and J. D. Way, “Palladium-Gold Composite Membranes for Hydrogen Separations, in preparation.

Presentations at Technical Meetings and/or Seminars (*Invited Talks)

- Palladium-Copper Composite Membranes for Hydrogen Separation, Paper #HFC.33 presented at the World Renewable Energy Conference (WREC), Denver, CO, 8/04.
- Palladium-Copper Composite Membranes for Hydrogen Separation, Paper presented at the DOE University Coal Research Contractor’s Meeting, Pittsburgh, PA, 6/05.
- Palladium-Copper Composite Membranes for Hydrogen Separation, paper presented at the International Conference on Membranes (ICOM), Seoul, Korea, 8/05.

- *Palladium-Copper Composite Membranes for Hydrogen Separation, Paper presented at the Joint China-Japan-USA Chemical Engineering Conference, Beijing, China, 10/05.
- Palladium-Alloy Composite Membranes for Hydrogen Separation, Paper presented at the DOE University Coal Research Contractor's Meeting, Pittsburgh, PA, 6/06.
- High Flux Pd and Pd Alloy Membranes Deposited on Stainless Steel Supports by Electroless Plating, International Conference on Inorganic Membranes (ICIM 9), Lillehammer, Norway, June 26 – 29, 2006.
- Sulfur Resistant Palladium-Gold Composite Membranes for Hydrogen Separations, International Conference on Inorganic Membranes (ICIM 9), Lillehammer, Norway, June 26 – 29, 2006.
- *Self-supported and Composite Palladium Alloy Membranes for Hydrogen Separation, Gordon Research Conference on Membranes: Materials and Processes, New London, NH, August 6 - 10, 2006.

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