

II.C.3 High Performance Palladium-Based Membrane for Hydrogen Separation and Purification

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- Colorado School of Mines, Golden, CO
- Oak Ridge National Laboratory, Oak Ridge, TN

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Fiscal Year (FY) 2011 Objectives

The overall project objective is the development, demonstration and economic analysis of a Pd-alloy membrane that enables the production of 99.99% pure H₂ from reformed natural gas as well as reformed bio-derived liquid fuels such as ethanol at a cost of \$2-3/gasoline gallon equivalent by 2011. The specific objectives for the past year were:

- Conduct long-term durability testing of Pd-alloy membranes in syngas/water-gas shift (WGS) reaction environments meeting Phase III performance goals.
- Determine the optimal Pd-alloy membrane composition and thickness to assure stable performance with respect to product hydrogen flux and purity in WGS reaction environments.
- Scale up the substrate and membrane synthesis processes to 12" elements.
- Design and fabricate multi-tube modules minimizing concentration polarization effects at high hydrogen recoveries.
- Work with an end user to compare cost/performance of a membrane-based system to pressure swing adsorption (PSA) and solvent-based systems for large-scale hydrogen production with CO₂ capture.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan and the technical targets indicated in Table 1:

- (K) Durability
- (L) Impurities (Hydrogen Quality)
- (M) Membrane Defects
- (N) Hydrogen Selectivity
- (O) Operating Temperature
- (P) Flux
- (Q) Testing and Analysis
- (R) Cost

TABLE 1. Applicable Technical Targets for Dense Metallic Membranes and Current Project Status

Performance Criteria	2010 Target	2015 Target	Pall Status 2011
Flux SCFH/ft ² @20 psi ΔP H ₂ partial pressure and 15 psig permeate side pressure	250	300	270*
Membrane Cost, \$/ft ² (including all module costs)	\$1,000	<\$500	<\$1,000
ΔP Operating Capability, system pressure, psi	400	400-600	>600 PSI
Hydrogen Recovery (% of total gas)	>80	>90	>80**
Hydrogen Permeate Quality	99.99%	>99.99%	99.999%***
Stability/Durability	2 years	>5 years	To be determined

*Maximum observed. Averaged over more than 20 samples ~190 scfh/ft².

** Measured on a 50%H₂/21%H₂O/up to 3.5% CO/balance CO₂ mixed gas stream. Hydrogen flux and recovery measurements are planned with other impurities starting in mid-2009. The experimentally observed recovery is determined by chosen operating conditions and is not necessarily a limit of the membrane performance.

*** Projected purity based on H₂/N₂ ideal selectivity.

FY 2011 Accomplishments To Date with Specific Barriers Addressed

- Determined optimal Pd-alloy membrane composition as Pd₉₀Au₁₀ to assure stable performance with respect to product hydrogen flux and purity in WGS reaction environments (K, L, N, P, Q).
- Increased membrane operating capabilities to 400 psi at 550°C through use of 310SC stainless steel tubular substrate.

- Optimized and scaled up the membrane and diffusion barrier coating process to 12-inch lengths. The substrate tube manufacturing capability is up to 1 m length (N, R).
- Developed a commercial welding process for non-porous fittings to porous tubes (N, R).
- Met Phase III performance goal demonstrating up to 500 hours of durability testing on Pd-alloy membranes in syngas/WGS reaction environments meeting Phase III performance goals (K, L, N, P, Q).
- Observed high mixed gas hydrogen flux rate ($145 \text{ scfh/ft}^2\text{-atm}^{0.5}$) and high hydrogen purity ($<99.95\%$) for up to 120 hours at an operating feed side pressure of $>200 \text{ psig}$ (K, L, N, P, Q).
- Observed a reversible H_2 flux decline with H_2S exposure during testing with low concentration H_2S exposure (K, L, N, P, Q).
- Demonstrated membrane performance stability with thermal cycling ($50\text{--}400^\circ\text{C}$) (K, Q).
- Showed an achievable end-user cost of less than $\$1,000$ per ft^2 of area for a stand-alone membrane separator device (R).
- Minimized concentration polarization effects while maintaining high hydrogen recoveries for a 12-tube, 12-inch long, multi-tube module (P, R).
- Directed Technologies, Inc. calculated that a membrane-based process can enable cost reduction through process intensification and that the hydrogen production cost target of $\$/\text{kg}$ is achievable. The capital equipment cost estimate is based on sale price to the end user for membrane in a module (R).



Introduction

This project is focused on optimizing the overall composition of the Pd alloy, intermediate layers and tubular support, as well as on the manufacturing methods required to produce a very thin, high-flux, cost-effective membrane for H_2 separation and purification on a robust, porous, inorganic substrate. The substrate¹ is readily scalable to high volume production as it is manufactured in long lengths. Robust high area modules can be made by welding multiple tubes into a pressure vessel, eliminating low temperature seal materials.

Approach

The approach is to further develop and optimize the performance of Pd alloy membranes that have been shown to have both high flux rate and high separation factor for H_2 from reformat. This is being accomplished by design of a composite membrane based on robust, tubular, porous metal media as a substrate. The substrate is modified by the addition of a uniform, fine pore size diffusion barrier

layer. The deposition methods are modified to produce a thin, uniform, functional gas separation Pd-alloy membrane layer. The project plan includes commercial scale up of the high quality porous metal substrate and diffusion barrier layer that enables the development of a technically and economically viable composite membrane. Membrane alloy composition and thickness is optimized for assuring high hydrogen flux and selectivity as well as long-term durability with tolerance to contaminants. The membrane performance is determined under typical operating conditions for a reformed natural gas or bio-derived liquid fuels stream. The H₂A model, modified to incorporate a membrane reactor design, is used to verify economic viability. Our plan is to confirm an increase in the overall energy efficiency of a H_2 reforming system through the use of membrane technology for process intensification. Economic modeling is conducted to determine the cost benefit of an integrated membrane reactor that results from fewer pressure vessels and reduced catalyst volumes. An end user is conducting system economic and energy analyses and comparing the results to PSA and amine-based systems.

Results

Membrane Development

The process for depositing ceramic on the porous metal tubes was modified to increase the diffusion barrier substrate surface roughness and eliminate potential film stresses and membrane film delaminations observed in some of the earlier composite Pd-alloy membrane samples. Synthesis of membrane with varying thickness in 3 to 9 micron range and Pd-Au alloy composition in 0-30% Au range were prepared for determining optimal membrane composition and thickness for long-term stable membrane performance.

The substrate as well as Pd-alloy composite membrane synthesis processes were successfully scaled up to prepare elements of 12" overall length with 10" active membrane length. The scaled up membranes were tested to confirm their hydrogen separation performance as observed in shorter (2" active length) membranes. Several 12" overall length ceramic porous metal AccuSep[®] substrates were prepared and composite Pd-alloy membranes are being prepared for assembling them in a multi-tube module and testing in WGS environment. For the 12-tube module assembly, eight Pd-alloy membranes are complete while five more are currently being fabricated.

Membrane Durability Testing in WGS Streams and Membrane Optimization

Extensive testing of Pd-alloy membranes in pure gas streams and in methanol/natural gas reformat environments was conducted for parametric evaluation of their performance. For example, effect of concentration polarization and CO concentration was observed in another test with a $\text{Pd}_{95}\text{Au}_5$ membrane of $8 \mu\text{m}$ thickness with three

¹ Pall's AccuSep[®] inorganic media

different feed gas mixtures consisting of H₂/Ar, H₂/Ar/steam and WGS mixture (50% H₂, 25%CO₂, 20% H₂O, 5%CO – WGS-5) at 400°C and 132 psi feed pressure with a feed flow rate of 2,000 mL/min. The permeate pressure was 17 psia. The results shown in Figure 1 indicated a H₂ flux reduction due to the concentration polarization effect of ~20%, with an additional flux reduction of 20% due to CO.

The standard WGS composition was determined to be insufficient to cause a decline in flux or H₂ purity of most of the membranes for determination of the optimum alloy composition or thickness. For example, a 2.2 micron thick Pd₈₇Au₁₃ alloy membrane on Pall Accusep® support was tested in WGS with high CO content and steam to CO ratio of 1:1 (50% H₂, 10% CO₂, 20% CO and 20% steam – WGS-20). Temperature was varied between 400°C and 450°C. This composition also was determined to be insufficient to cause a decline in flux or purity and stable permeance and purity performance over ~400 hours is shown in Figure 2.

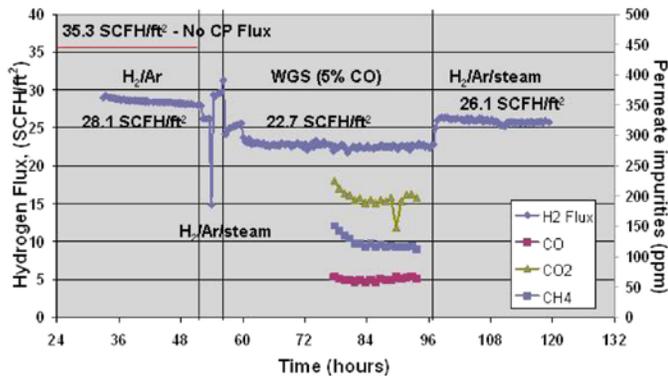


FIGURE 1. Hydrogen Flux Reduction due to Concentration Polarization and CO

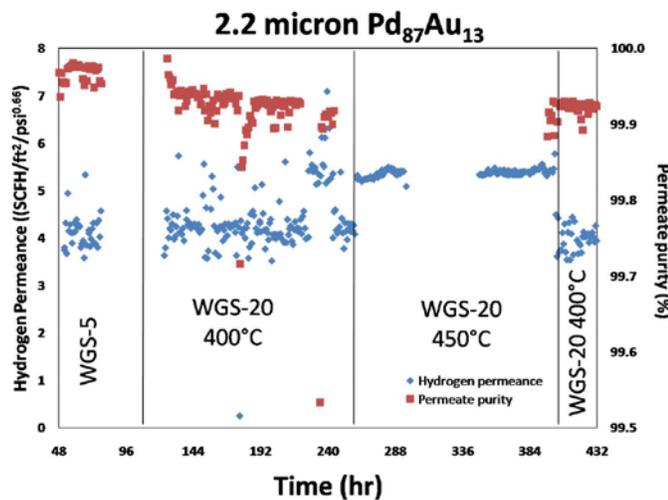


FIGURE 2. Stable Membrane Performance in WGS-5 and WGS-20 Syngas Conditions

To facilitate rapid durability evaluation of several alloy compositions an accelerated life test based on an aggressive variant of the WGS composition was tested and determined to be sufficient to cause a decline in the H₂ purity and H₂ recovery in the 100 hour range. The accelerated test conditions use a WGS gas mixture without any steam (50% H₂, 30% Ar, 20% CO – WGS-20D). As shown in Figure 3, a linear decrease in permeate purity was obtained in approx 100 hours for the same membrane referenced in Figure 2. Evaluation of two sets of three membranes with varying alloy composition were tested with results given in Table 2. One membrane of each composition was tested at each location. From the performance in WGS20D the Pd₉₀Au₁₀ alloy was selected for next durability tests.

TABLE 2. Performance evaluation of membranes of varying alloy compositions in accelerated test conditions for a minimum of 100 hours.

Thickness (micron)	Au content (wt%)	Purity Decline (ppm/day)
3.0	0	42
4.1	0	74
4.0	9	0
3.9	11	6
3.6	20	356
3.6	24	652

Module Development

A major advantage of using the porous metal AccuSep® is the ability to weld individual membrane elements in a metal tube sheet similar to the conventional shell and tube architecture. However, a multi-tube module must be designed to minimize the concentration polarization effect typically observed at high hydrogen recoveries. Different concepts of multi-tube membrane module design were

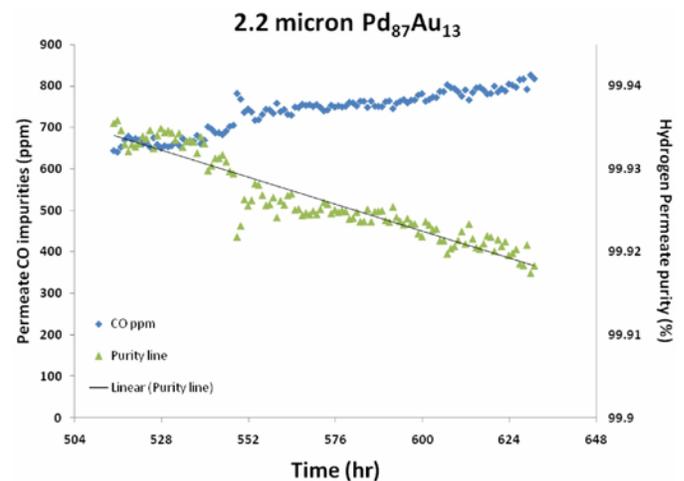


FIGURE 3. Membrane Degradation in WGS-20D Syngas Conditions

evaluated to overcome concentration polarization effects². Multi-tube modules were fabricated and tested to confirm hydrogen flux and recovery as predicted by the model shown in Figure 4. A test facility with a feed gas flow capacity of 200 liters/minutes needed for testing the performance of the 12-tube module is being assembled.

System Economic and Energy Analysis

The end user conducted a techno-economic study to compare Pd-membrane-based process to competing PSA and solvent scrubbing-based processes for large-scale hydrogen production (~36,000 kg/hr) from natural gas with CO₂ capture. This analysis assumed an autothermal oxygen-blown reforming of natural gas to provide hydrogen-rich reformat gas for further processing by the three option processes considered. A two-stage cascade of WGS reactor/membrane separator was found to be able to provide the desired 90% H₂ recovery with 90% H₂ purity. Utilization of an inert nitrogen sweep gas stream in the second stage was necessary to achieve the target 90% recovery from the reformat gas mixture generated by autothermal reforming of natural gas. The amount of sweep gas that could be used was dictated by the requirement of achieving the 90% target hydrogen purity. Pall Corporation provided estimates of total membrane area needed to produce 36,000 kg/hr of hydrogen. The total costs of the membrane system were estimated assuming utilization of 2,000-tube modules. This analysis included the costs of sequestration-ready CO₂ capture in addition to that would be needed for just the hydrogen production. As a result additional equipment was needed to be incorporated increasing the costs of processes based on hydrogen separation, i.e. PSA and membrane-based processes, significantly increasing the costs of those processes when compared to the amine scrubbing option. This report is being reviewed to modify the analysis to conform to the

²The resultant module designed to reduce concentration polarization was developed using Pall Corporation's internal funds in a separate project.

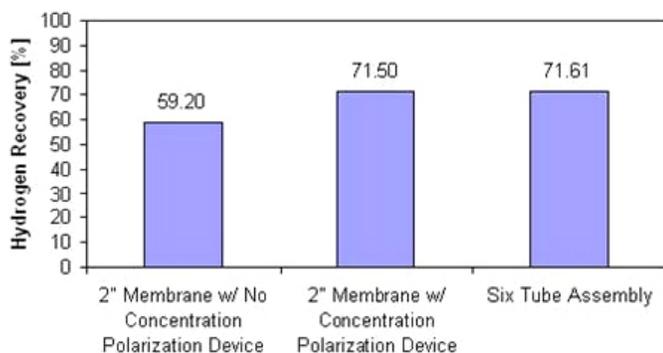


FIGURE 4. Multi-Tube Module Design with Minimization of Concentration Polarization

goals of hydrogen production in our DOE contract. A separate report is being prepared for DOE's review.

Conclusions

- Eliminated delaminations and improved membrane quality by optimizing the substrate/diffusion barrier substrate process.
- The PdAu alloy membranes were stable in a standard WGS stream environment.
- Developed more aggressive gas stream compositions to accelerate a decline in membrane performance in a reasonable time.
- Verified long-term durability of the optimal Pd₉₀Au₁₀ alloy composition.

Future Plans

- Complete membrane optimization tests to determine both the optimum membrane composition and thickness to assure long-term durability in WGS reaction environments.
- Demonstrate additional long-term durability to meet Phase III goals using membranes with optimum composition and thickness.
- Complete fabrication of 12-inch overall length PdAu membranes for the multi-tube module assembly and test a module with at least six tubes.
- Demonstrate multi-tube module performance is close to single-tube performance.
- Complete the techno-economic analysis of the membrane-based hydrogen production process.

FY 2011 Publications/Presentations

1. Ø. Hatlevik, M.K. Keeling, K. Rekcis, J.D. Way, "High carbon monoxide test conditions for accelerated qualitative evaluation of palladium gold alloy membranes for use in CO₂ capture from water-gas-shift mixtures," presented at the North American Membrane Society annual meeting, Las Vegas, NV, June 2011.
2. Hatlevik, Ø., Gade, S.K., Keeling, M.K., Thoen, P.M. and J.D. Way, "Palladium and Palladium Alloy Membranes for Hydrogen Separation and Production: History, Fabrication Strategies, and Current Performance," *Separation and Purification Technology*, 73, 59-64(2010).
3. A. Damle, "Commercialization of Pd Membrane for H₂ Production," presented at the Fuel Cell Seminar, San Antonio, TX, October, 2010.