

II.C.1 High-Performance Palladium-Based Membrane for Hydrogen Separation and Purification

Ashok Damle
 Pall Corporation
 25 Harbor Park Drive
 Port Washington, NY 11050
 Phone (516) 801-9581
 E-mail: Ashok_Damle@Pall.com

DOE Technology Development Manager:
 Rick Farmer
 Phone: (202) 586-1623
 E-mail: Richard.Farmer@ee.doe.gov

DOE Project Officer: Katie Randolph
 Phone: (303) 275-4901
 E-mail: Katie.Randolph@go.doe.gov

Contract Number: DE-FG36-05GO15093

Subcontractors:

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

Project Start Date: July 1, 2005
 Project End Date: September 30, 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/gge by 2011.
- The objectives for the past year were to improve the membrane fabrication process to retain high flux and purity in water-gas shift (WGS) reaction environment and gas streams.
- An objective for last year was to extend the testing of Pd-Au alloy membranes to include H₂S-containing WGS streams.
- Another objective was to incorporate a potential end user on the program that will provide the system economic and energy analysis/assessment of the membrane technology and compare it to current state-of-the art hydrogen production processes.

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) Tolerance to Impurities
- (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 2009
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	400 psi
Hydrogen Recovery (% of total gas)	> 80	> 90	> 60**
Hydrogen Permeate Quality	99.99%	> 99.99%	99.999%***
Stability/Durability	2 years	> 5 years	to be determined

*Maximum observed flux. Average flux over more than 20 samples ~190 scfh/ft². Economic analysis indicates separation factor rather than flux to be stronger determinant of cost of hydrogen production.
 ** 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.

Accomplishments To-Date with Specific Barriers Addressed

- Increased operating capabilities to 400 psi at 550°C through use of 310SC stainless steel tubular substrate.
- Optimized and scaled up the diffusion barrier coating process to 12-inch lengths with the manufacturing capability of producing up to 1 m length substrate tubes. A commercial welding process has been developed for welding non-porous fittings to porous tube (N, R).
- Developed additional sequential steps in the membrane synthesis process (air oxidation

and layering sequences) to improve membrane performance as well as for repairing defects (M, N and P).

- Addressed durability through alloy and composite membrane structure (K).
- Characterized membrane performance using synthesis gas (WGS) mixtures (L, Q).
- Conducted tests with low concentration H₂S exposure (K, L, N, P, Q).
- Observed reversible H₂ flux decline with H₂S exposure (K, L, N, P, Q).
- Fabricated, installed, and started up two larger mixed gas test stands to perform sensitivity analyses to WGS reaction environment impurities and long term durability testing, respectively (K, L, N, P, Q).
- Demonstrated long-term (500 hr) stable performance in syngas environment (K).
- Tested membranes at high-pressure WGS reaction environment conditions for up to 120 hours. High mixed gas hydrogen flux rate (145 scfh/ft²-atm^{0.5}) and high hydrogen purity (<99.95%) were observed at an operating feed side pressure of >200 psig (K, L, N, P, Q).
- Demonstrated membrane performance stability with thermal cycling (50°–400°C) (K, Q).
- Evaluated effect of CO and H₂O on membrane performance (K, L).
- Determined acceptable H₂O:CO ratio for stable performance (K,L).
- Conducted a preliminary evaluation of the module design, fabrication techniques and materials for a stand-alone membrane separator device that showed that a cost of less than \$1,000 per ft² of area to the end user is achievable (R).
- Preliminary H₂A modeling analyses by Directed Technologies, Inc. (DTI) determined that the hydrogen flux rate of a membrane and its capital cost exhibited much smaller impact on the cost of hydrogen production when compared to the hydrogen recovery by the membrane (N, P, R).
- Membrane-based process can enable cost reduction through process intensification and cost analysis by DTI indicated that the hydrogen production cost target of \$3/kg is achievable. The capital equipment cost estimate is based on sale price to end user for membrane in a module (R).
- Demonstrated membrane performance meeting the goals of several milestones set for the Phase II completion and secured a go decision to move to Phase III.
- An end user will participate with Pall on the project to provide the system economic and energy analysis (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 H₂ separation and purification on a robust, porous, inorganic substrate. The substrate used is Pall's AccuSep[®] inorganic media which 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 H₂ 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 will be optimized for assuring high hydrogen flux and selectivity as well as long-term durability with tolerance to contaminants. The membrane performance will be determined under operating conditions in a typical reformed natural gas or bio-derived liquid fuels stream. The H₂A model, modified to incorporate a membrane reactor design, will be used to verify economic viability. Our plan is to confirm an increase in the overall energy efficiency of a H₂ reforming system through the use of membrane technology for process intensification. Economic modeling will be conducted to determine the cost benefit of an integrated membrane reactor that results from fewer pressure vessels and reduced catalyst volumes. An end-user will be conducting system economic and energy analyses and comparing the results to pressure swing adsorption (PSA) and amine-based systems.

Results

1. Membrane Development and Testing

Optimization and characterization continued on the membrane formation process with emphasis being placed on developing a technique with a sequence of multiple thin layers and treatments to maximize performance over extended time periods in WGS streams. Some mechanical issues have been observed

with regard to bonding between the membrane layers. Positive results were obtained with membrane #286 fabricated using the multi-layer process as shown in Figure 1. The hydrogen flux remained constant at 70 scfh/ft² and the hydrogen permeate purity varied between 99.98 and 99.99% with methane as the only detected impurity until ~175 hours of test time. Membrane #286 is 8.4 micron thick and has the following alloy composition Pd₈₃Au₁₇. Additionally, there was no observed downward trend in the permeate hydrogen purity over the duration of the test that included shutdown cycles.

Scale up of the membrane process to deposit 10-inch long Pd-Au alloy membrane on a 12-inch long diffusion barrier coated AccuSep substrate tube has been initiated.

2. Membrane Durability in Pure Gas Streams

In order to test the ΔP capability of the membrane, ORNL determined the maximum operating pressure of the Pd-alloy membrane at room temperature. The membrane tube didn't collapse even with external pressure of up to 4,000 psia.

The membrane housing is rated for 1,596 psi at 537°C exceeding the 400 psi and 400°C DOE target goal.

3. Membrane Durability in WGS Streams

Effect of WGS Environment on the Hydrogen Flux of Pd and Pd-Alloy Membranes

A primary goal of this project is to determine the performance trends as a function of Au level and membrane thickness in WGS streams. One test series was completed. As shown in Figure 2, Pd-Au alloy membranes exhibited a 10% flux reduction, whereas a

pure Pd membrane exhibited a 30% flux reduction in a WGS atmosphere. The pure Pd membrane showed a sharp decrease in H₂ purity indicating leaks. Additional tests are in progress.

Effect of WGS Environment on Stability of Membrane Hydrogen Flux with Time

A Pd-Au alloy membrane was tested in WGS environment to determine the stability of H₂ flux with time up to 500 hours. As shown in Figure 3, flux remained constant at 65 scfh/ft² for 460 hours after an initial decline (consistent with the acclimatization of the membrane to the syngas composition) from 73 scfh/ft² in the first 40 hours. H₂ flux remained constant at 65 scfh/ft² through 500 hrs H₂. The H₂ recovery was 56% and the purity was 99.8%.

At a high feed pressure of 170 psig and 6 l/min WGS feed flow rate in a 2" single membrane tube module, the

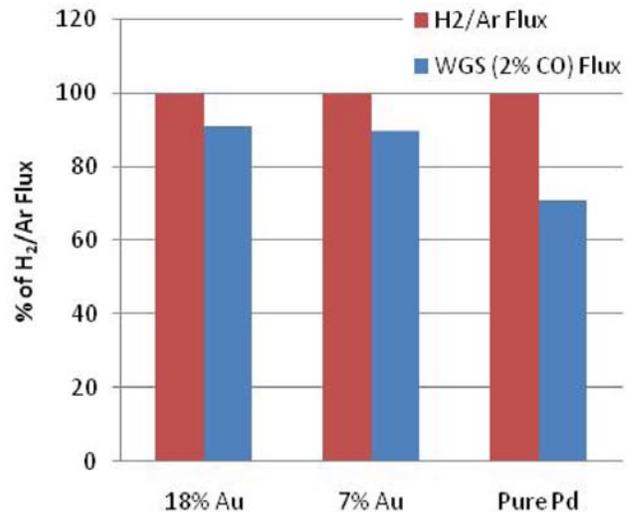


FIGURE 2. Effect of WGS Environment on the Hydrogen Flux of Pd and Pd-Au Alloy Membrane

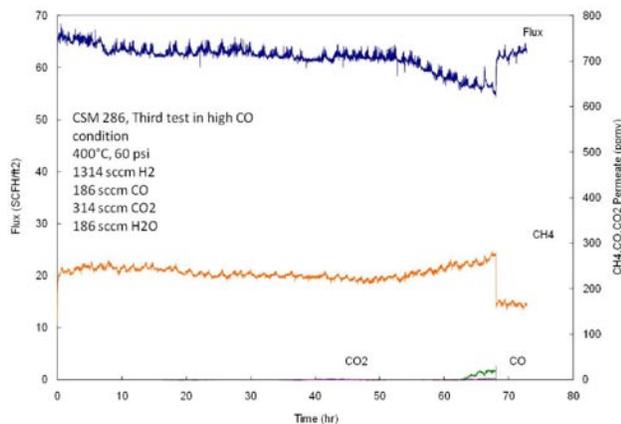


FIGURE 1. Permeation Data for the Last 70 Hours of the 175-Hour Test after Two Shutdown Procedures

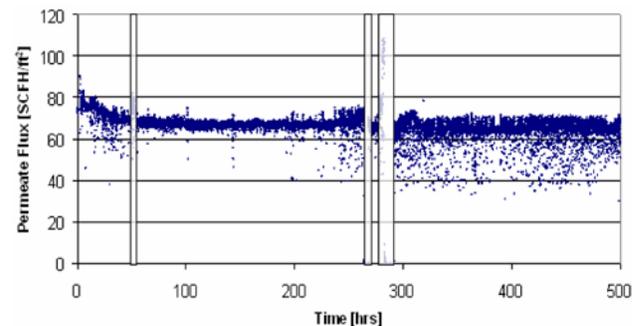


FIGURE 3. Stability of Membrane Hydrogen Flux with Time in WGS Streams

H₂ flux was 285 scfh/ft² for >100 hours tested and the H₂ purity was 99.997% with a H₂ recovery of 78%.

Effect of WGS Environment on Membrane Performance as a Function of Feed Flow Rate

H₂ flux increased by 20% as the feed flow rate was increased from 2 to 6 l/min. This was attributed to a reduction in the concentration polarization effect. Hydrogen purity remained high.

Effect of WGS on the Performance of Pd-Au Alloy Membranes as a Function of Steam/CO Ratio

The membrane performed well at steam/CO ratios above 1.5.

Effect of Various Concentrations of H₂S in WGS on Membrane Hydrogen Flux

As shown in the Figure 4, the H₂ flux decreased with increasing H₂S content, however, the flux was almost fully recovered when the H₂S was removed from the feed stream. The membrane was a Pd₉₀Au₁₀ alloy, 2.8 microns thick with a 2-inch active length. The WGS composition was 51% H₂, 26% CO₂, 2% CO, 21% H₂O plus up to 25 ppm H₂S. The feed flow rate was 2 l/min, feed pressure was 50 psig and the temperature was 450°C.

4. System Economic and Energy Analysis

Agreement was reached with an end-user to work with Pall on this project. The end-user will carry out system economic and energy analyses at no cost to the project but with certain restrictions on confidentiality. The end-user will provide the results of a confidential report that they will prepare on a cost comparison between Pall's membrane system, an amine-based solvent system and a PSA system. They will compare the cost of producing H₂ and the cost of carbon capture for all three processes. The cost for the membrane system capital equipment will be based on performance

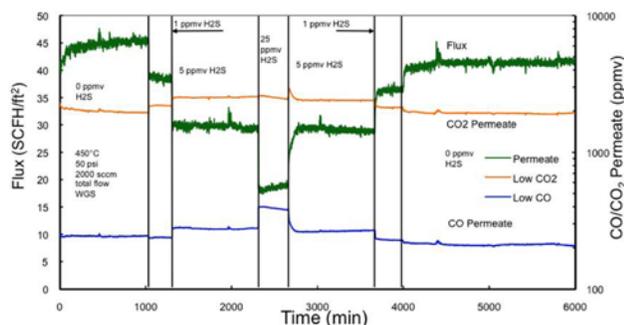


FIGURE 4. Effect of Various Concentrations of H₂S on Membrane Hydrogen Flux

and cost figures provided by Pall Corporation to the end-user, based on our test performance results in WGS atmospheres.

Conclusions

- Improvements were made in membrane synthesis process and membranes were evaluated for their performance in a synthesis gas environment in the presence of contaminants.
- High hydrogen purity was demonstrated in high pressure WGS environments.
- The membrane cost and economic analysis indicated hydrogen recovery to be more influential than hydrogen flux with a slightly favorable tradeoff for a little thicker membrane. The membrane synthesis process is capable of producing membranes in the appropriate thickness range.
- An end-user has agreed to work with Pall Corporation to provide information on the system economic and energy analysis task.

Future plans

- Improvements in the membrane synthesis process will be verified and scaled up for manufacturability.
- The optimum alloy composition and membrane thickness with respect to performance and durability in WGS streams will be determined.
- Mixed gas testing of the membranes will be conducted using the two test stands to determine long term membrane performance at various operating conditions of feed pressure, permeate pressure, gas composition, contaminant composition (especially H₂S) and hydrogen recovery. The membrane performance data collected from these tests will be used for system economic and energy modeling analysis.
- System analysis and energy analyses will be conducted by an end user. It will include the cost of producing H₂ and the cost of carbon capture for Pall's membrane system, an amine-based solvent system and a PSA system.

FY 2010 Publications/Presentations

1. Gade, S.K. Coulter, K.E. and J.D. Way, "Effects of fabrication technique upon material properties and permeation characteristics of palladium-gold alloy membranes for hydrogen separations, submitted to the *Gold Bulletin*, 3/10.
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. Gade, S.K., Keeling, M.K., Davidson, A.P. Hatlevik, Ø., and J.D. Way, "Palladium-ruthenium membranes for hydrogen separation fabricated by electroless co-deposition," *International Journal of Hydrogen Energy*, 34, 6484 – 6491(2009).
4. Properties of Palladium-Gold Alloys for Hydrogen Separation and Purification," paper 620a, AIChE Annual Meeting, Nashville, TN, November, 2009.
5. Hopkins, S., C. Love, J. Acquaviva, O. Hatlevik, J.D. Way, and A. Damle, "Commercialization of Pd Membrane for H₂ Production," presented at the Fuel Cell Seminar, Palm Springs, CA, November 2009.
6. Hopkins, S., D. Henkel, M. Keeling, C. Love, K. Rekczi, K. Stark, H. Zhao and A. Damle, "Development of Pd-alloy Composite Membranes for Hydrogen Separation, presented at the AIChE Annual Meeting, Nashville, TN, November, 2009.
7. Damle, A., "Commercialization of Pd-Alloy membrane for H₂ Production," presented at the 2010 National Hydrogen Association Meeting, Long Beach, CA, March 2010.