II.A.9 High Performance Palladium-Based Membrane for Hydrogen Separation and Purification

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

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Project End Date: June 30, 2010

Objectives

- The project objective is the development, demonstration and economic analysis of a Pd-alloy membrane that enables the production of 99.99% pure H_2 from reformed natural gas at a cost of \$2-3/gasoline gallon equivalent (gge) by 2010.
- The objective for the past year was to identify and control the variables that influence the performance, economics and manufacturability of a suitable Pd-alloy membrane.
- Determine the cost impact of the membrane on the overall reforming system and methods of reducing H_2 production cost through integration of the membrane into the reforming process.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan April 27, 2007:

(A) Reformer Capital Costs
(B) Reformer Manufacturing
(C) Operation and Maintenance (O&M)
(E) Greenhouse Gas Emissions
(K) Durability
(L) Impurities
(M) Membrane Defects
(N) Hydrogen Selectivity
(O) Operating Temperature
(P) Flux
(Q) Testing and Analysis
(R) Cost

Technical Targets

Performance Criteria	2010 Target	2015 Target	Accomplished FY 2007	Accomplished FY 2008
Flux SCFH/ft^2 at 20 psi ΔP H_2 partial pressure and 15 psig permeate side pressure	250	300	270*	200**
Membrane Cost, \$/ft^2 (including all module costs)	\$1,000	<\$500	\$1,500	\$1,000
ΔP Operating Capability, system pressure, psi	400	400 - 600	350	400
Hydrogen Recovery (% of total gas)	>80	>90	78***	TBD
Hydrogen Permeate Quality	99.99%	>99.99%	99.999%****	99.999%****
Stability/ Durability	2 years	>5 years	TBD	TBD

* H_2 flux on membrane #102 measured at 20 psid ΔP H_2 partial pressure and 15 psia permeate side pressure at 400°C

**Fiscal Year 2007 flux was based on the best sample. FY 2008 flux was an average, consistently achieved across several samples.

*** Measured on a 95%H_2/2.5%CO_2/2.5%CH_4 mixed gas stream. Measurements to be made with other impurities starting in mid-2008 when the new test stands are operational.

**** Projected purity based on H_2/N_2 ideal selectivity.

TBD - to be determined

Accomplishments

- A significant accomplishment was achieved by substituting a 310SC stainless steel alloy for the original 316L alloy and scaling it up for manufacturing. This increased the operating capabilities to 400°C and 400 psi and resulted in a reduced cost.

- The diffusion barrier coating on the substrate was optimized and adapted to the 310SC stainless steel substrate. Scale-up to 12" long tubes was completed. Plans for commercial scale manufacturing in lengths up to 1 meter are in place.
- The process for welding the non-porous tube end fittings to the porous substrates was optimized and is now a commercial-scale manufacturing process.
- Multiple membrane samples were produced with repeatable results.
- Membranes were tested on a "research-scale" mixed gas test and encouraging results were obtained with respect to sulfur tolerance.
- Two larger mixed gas test stands were designed and are now being fabricated to perform sensitivity analyses to water-gas shift reaction impurities and long term durability testing, respectively.
- Developed an analytical method to ensure that the process flow conditions maximize use of membrane area.
- A preliminary evaluation of the module design, fabrication techniques and materials for a stand-alone membrane separator device showed that \$1,000 per ft^2 of area cost to end user is achievable. The cost was reduced by an increase in manufacturing yield for the substrate.
- Confirmed that Directed Technologies' membrane area calculations match Pall's model.
- Continued interaction with Directed Technologies, Inc. to modify the H2A model to account for use of a combined membrane reactor.
- Preliminary results showed the cost of the separation device (pressure swing adsorption or membrane) to be a relatively small percentage of the capital cost of the reforming system, so the membrane module cost is not the dominating factor but it can enable cost reduction through process intensification.
- Determined that membrane separation enables the design of a more efficient reforming system, reducing operating cost and lowering the cost per kg of H_2, and that membrane performance and process integration are key to achieving the overall H_2 production cost goals.

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Introduction

Our project is focused on optimizing the overall composition of the Pd alloy, intermediate layers and tubular support, as well as the manufacturing methods required to produce a very thin, high-flux membrane for H_2 separation and purification on a robust, porous, inorganic substrate. The leading substrate candidate 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.

The primary objective of the HFCIT Multi-year RD&D plan is to produce and deliver H_2 that is economically competitive for applications in transportation and stationary proton exchange membrane fuel cell generation. Our project is focused on maximizing the performance and minimizing the cost of the membrane for that application.

Approach

The primary objective of this project is to achieve the DOE goal of producing H_2 at a cost of \$2-\$3/gge at a purity of 99.99%. Our project offers a new tool for process engineers to use for advanced system designs by development of a commercially viable Pd alloy membrane. Our 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 reformate. This is being accomplished by design of a composite membrane based on robust, tubular, porous metal media as a substrate. The substrate is being modified by the addition of a uniform, fine pore size diffusion barrier layer. The deposition methods are being modified to produce a thin, uniform, functional gas separation Pd-alloy membrane layer. Our approach 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. The alloy composition is one of the variables that can be modified to provide maximum stable H_2 flux over time in the mixed gas stream of interest. Physical properties will be analyzed though a range of tests to ensure long term durability under operating conditions. The DOE membrane performance targets are used as feasibility benchmarks. To confirm progress toward the goals, the membrane performance will be tested under operating conditions in a typical reformed natural gas stream. The H2A model, modified to incorporate a membrane reactor design, will be used to show economic viability.

Membranes with high operating temperatures that can be heat integrated with the process will be shown to have the benefit of reducing thermal losses and increasing the system efficiency. Membranes with high separation factors will be shown to reduce energy consumption from compression. 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 will be done to determine the cost benefit of an integrated membrane reactor that results from fewer pressure vessels and reduced catalyst volumes.

Results

Optimize the Formation of Membranes with Respect to Membrane Flux and Selectivity

Porous Metal Substrate Tubes

Porous metal media substrate tubes made from 310SC alloy stainless steel and rated for use at 400ºC and 400 psi were developed, scaled-up and adopted as the standard substrate, replacing the original 316L stainless steel that was limited to 400ºC and 150 psi. The alloy change resulted in increased operating temperature and pressure without increasing the cost.

Diffusion Barrier

A diffusion barrier is required to separate the Pd alloy layer from the metal substrate to prevent metallic reactions at elevated temperatures. The quality of the Pd alloy membranes is limited by the quality of the diffusion barrier surface. The diffusion barrier process has been optimized and the surface finish of the ZrO_2 can be controlled within a narrow range with a uniform pore size distribution. Optimization of this layer enables thinner membrane formation, lowers material cost per unit area of membrane and reduces the membrane area needed. The controlled manufacturing process increased the yield and reduced the cost per tube. Commercial scale-up of the process is underway with length capabilities increased from 4-inch to 12-inch tubes. Future scale-up to 1 meter long tubes is scheduled for the upcoming year to further reduce the module cost.

Alloy Composition

Research on the optimization of the alloy is continuing in parallel with the development and scale-up of the methods required to manufacture composite membranes. This includes Pd/Au alloy compositions having Au levels of 5, 10 and 15%. Initial data was collected on the performance in mixed gas streams with the objective to find the alloy that has the highest stable flux rate during long term exposure to reformed natural gas.

Membrane Formation Process

The typical Pd-alloy membrane formation process is illustrated in Figure 1.

Flux and Selectivity Testing in Pure Gas Streams

Pure gas testing has been used as a tool to expedite optimization of the membrane forming process and methods were developed to form thin, high flux, high separation factor membranes. The performance results on seven samples in pure gas stream are summarized in Table 1. The flux and purities achieved are quite consistent especially considering that the series contains membranes with different Au content and membrane thicknesses. The flux and selectivity curves on membrane #134 are shown in Figure 2.

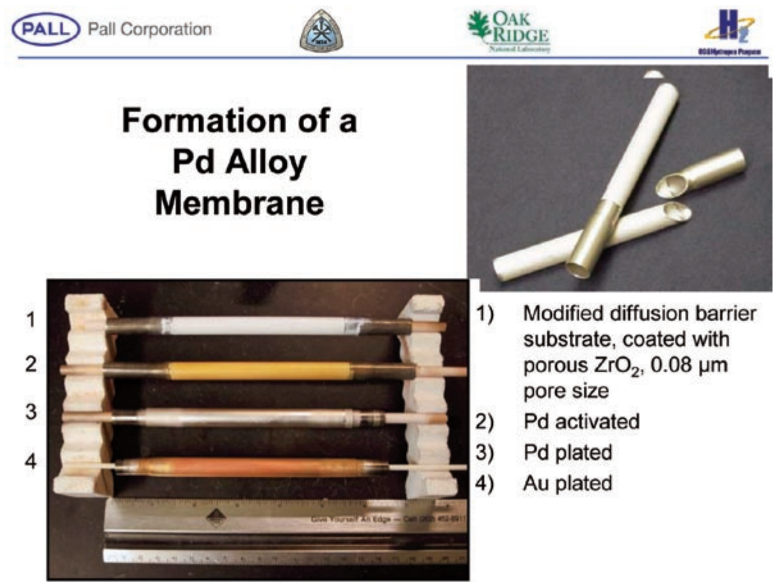

FIGURE 1. Formation of a Pd-alloy membrane

TABLE 1. Pd/Au Alloy Performance Summary in Pure Gas Streams

Membrane #	H_2 Flux	N_2 Flux	Separation Factor	Estimated H_2 Purity
	scfh/ft^2	scfh/ft^2		%
97	160	0.010	150,000	99.994
98	140	0.005	28,100	99.996
102	270	0.003	90,000	99.999
115	200	0.001	20,000	99.995
131	230	0.006	36,700	99.997
132	180	0.001	180,000	99.999
134	220	0.006	36,700	99.997
Average	**200**	**0.046**	**77,357**	**99.997**

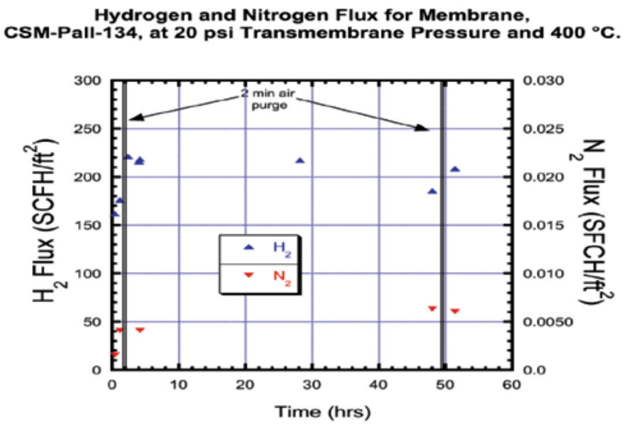

FIGURE 2. Flux curves for membrane #134 in H_2 and N_2.

Flux and Selectivity Testing in Mixed Gas Streams

Pd and Pd alloy membranes were tested in a H_2, CO_2, H_2O, CO mixed gas stream on a research-scale test stand. The performance data is shown in Figure 3. Conditions were identified where the steam to carbon ratio prevents coking and appropriate start-up/shut-down conditions were established.

Two mixed gas test stands are being fabricated with an estimated completion by October 2008. One stand is for alloy development and characterization, the other stand is for long term durability testing. Membranes differing in alloy composition and fabrication method will be tested at temperatures and pressures consistent with syngas composition streams.

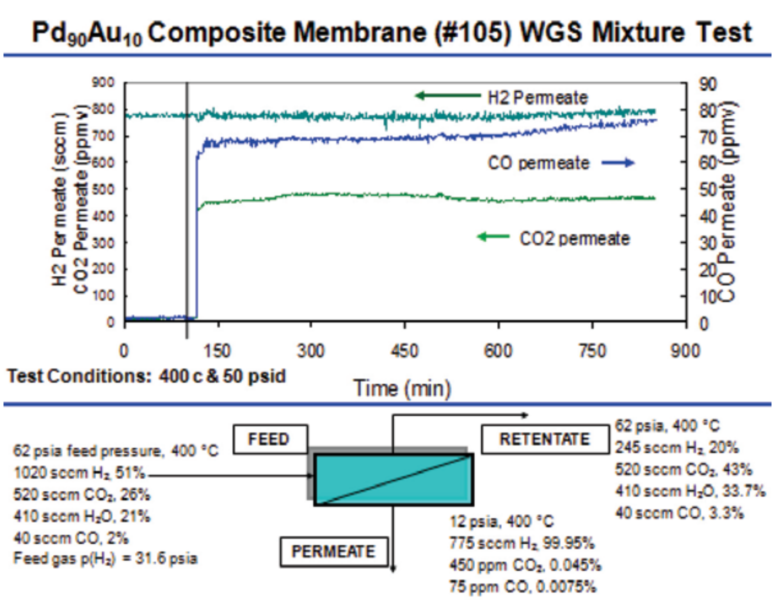

FIGURE 3. Research scale mixed gas tests on a Pd-Au alloy membrane.

Membrane Module Cost

Cost Reduction Through Module Design

An analytical method was developed to ensure that process flow conditions maximize the use of the total available membrane area. Preliminary evaluation of module design, fabrication techniques and materials for a stand-alone membrane separator device show that $1,000 per ft^2 of area cost to the end user target is achievable

Cost Reduction Through Manufacturing Scale-Up

The scale-up and transfer to manufacturing of the 310SC stainless steel substrate will increase yield and minimize labor resulting in reduced cost. The scale-up of the modified diffusion barrier will enable thinner membrane formation. This will increase flux and reduce the amount of membrane area required and will reduce the material cost of Pd and Au per unit area of membrane.

Seal

The process for producing smooth weld transition from porous media to nonporous fitting is now a standardized manufacturing operation. This seal design is illustrated in Figure 4.

Membrane Durability Goal

The mixed gas test stand for testing membrane durability is expected to be operational in October 2008.

Hydrogen Recovery and Quality Goals

Modeling indicates that a H_2 recovery of >80% can be achieved in part by optimizing flow rate and increasing the pressure of the feed stream. A recovery of over 80% is possible for a reformate stream containing 50% H_2 at 200 psia or higher with a permeate pressure of 30 psia. Additional H_2 recovery testing will be initiated on membranes after the test stands are completed in October 2008 to verify the conclusion drawn from the modeling.

Delta P Operating Capability Goals

The continuing high-temperature mechanical testing initiated at the Oak Ridge National Laboratory High Temperature Materials Laboratory (ORNL-HTML) will yield actual data on

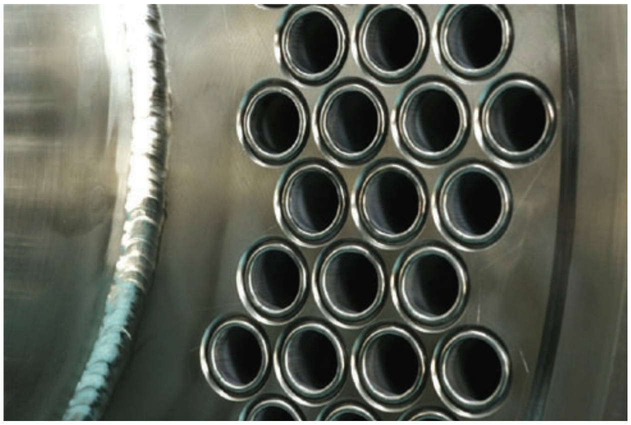

FIGURE 4. AccuSep® tubes welded to tube sheet header using scaled-up process.

the mechanical strength of the AccuSep® tubular substrate at temperature.

Characterize and Analyze Membranes

ORNL-HTML used high-temperature X-ray diffraction (XRD) to analyze the lattice structure of the Pd-Au alloy as a function of time and temperature. This provided insight into the dynamics of the alloying process. As a result, focus is being placed on the membrane formation process as well as the membrane composition to maximize the flux and the resistance to impurities in the Pd-Au alloy system. This is a significant conclusion as the critical interrelationship between the alloy composition and manufacturing method has now been established.

ORNL-HTML carried out tensile strength and strain at failure for Pd-alloy foils over the composition range of 0-38 mass % Au to determine the high pressure operating capability for the functional membrane layer.

System Economic and Energy Analysis Goals

Membrane Model

Based on performance test data in pure gas streams, membrane surface areas were calculated to yield 1,500 kg/day H_2 as shown in Table 2. Directed Technologies, Inc. provided us with a membrane surface area model and their membrane area calculations match Pall's model.

H2A Economic Model

Preliminary H2A analysis (with Directed Technologies, Inc.) showed the cost of the separation device (pressure swing adsorption or membrane) to be a small percentage (6%) of the capital cost of the reforming system, so membrane capital cost is not the dominating factor. The most significant factor is that membrane separation enables design of a more efficient reforming system where the operating cost is reduced, lowering the cost per kg of H_2. Work is continuing with Directed Technologies, Inc. on their newly developed combined membrane reactor design version of the H2A model to confirm these results.

TABLE 2. Membrane Surface Area Requirements

Membrane #	H_2 Permeance SCFH/ft^2.atm$^{0.5}$	H_2 Recovery to obtain 1,500 kg H_2/day	Calculated Membrane Area DT Spreadsheet (ft^2)
CSM-Pall #115	674	77.2	28.5
CSM-Pall #102	468	77.2	41.1
CSM-Pall #134	365	77.2	52.6

Conclusions

- The flux and purities achieved on several membrane samples are quite consistent and repeatable with an average flux of 200 scfh/ft^2 and a separation factor of 99.997%.
- Variables that influence the performance, economics and manufacturability of a Pd-alloy membrane were identified and the 310SC stainless steel substrate, the diffusion barrier and the end seal welding processes were scaled-up.
- Membranes were tested on a research-scale H_2, CO_2, H_2O, CO mixed gas stream and the preliminary results for limited test periods were encouraging with respect to flux stability.
- Preliminary evaluation of module design, fabrication techniques and materials for a stand-alone membrane separator device show that $1,000 per ft^2 of area cost to end-user is achievable.
- Preliminary results show the cost of the separation device (pressure swing adsorption) or membrane) is a small percent (6%) of capital cost of the reforming system, so membrane module capital cost is not the dominating factor. An integrated membrane separation system is projected to enable the design of a more efficient reforming system, reducing operating cost and lowering the cost per kg of H_2.

Future Plans

- Additional Pd-Au alloy compositions will be evaluated and high-temperature XRD will be conducted in the cross-sectional mode to determine the alloy composition and structure. XRD data will be correlated with performance and durability in mixed gas streams.

- Collapse pressures at operating temperature will be determined to create a design that meets the pressure capability and cost goals.
- The two test stands will be completed and mixed gas testing of the membranes will commence. The alloy with the best cost/performance data after mixed gas testing will be selected for system economic and energy modeling analysis.
- The cost of distributed H_2 target will be demonstrated by incorporating the performance data obtained on the membrane in the membrane reactor H2A computer model to calculate the overall cost of this process. Sensitivity analyses will be conducted using this H2A model to optimize the benefit from process integration.
- Long term testing will be initiated to establish membrane durability against DOE targets.

FY 2008 Publications/Presentations

1. Acquaviva, J., et al, "Performance Claims Define the Product – Commercialization of a Palladium Alloy Membrane for Hydrogen Production", NHA 2008 Conference, April 13-16, 2008, Washington, D.C.

2. A presentation on the project status was given at the DOE Annual Merit Review Meeting (June 10, 2008).