II.C.2 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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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 H_2 from reformed natural gas as well as reformed bio-derived liquid fuels (BILI) such as ethanol at a cost of $2-3/gge by 2010.
- The objectives for the past year were to identify and control the variables that influence the performance, economics and manufacturability of a suitable Pd-alloy membrane; and to demonstrate membrane performance in pure component as well as mixed gas studies.
- Another objective was to assess the cost impact of the membrane on the overall reforming system potentially reducing H_2 production cost by integration of the membrane in 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 Program Multi-Year Research, Development and Demonstration Plan:

(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

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
Hydrogen Recovery (% of total gas)	>80	>90	>60**
Hydrogen Permeate Quality	99.99%	>99.99%	99.999%***
Stability/Durability	2 years	>5 years	TBD

*Maximum observed flux. Average flux over more than 20 samples ~190 scfh/ft^2 Economic analysis indicates separation factor rather than flux to be stronger determinant of cost of hydrogen production
** Measured on a 50%H_2/21%H_2O/up to 3.5% CO/Balance CO_2 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 H_2/N_2 ideal selectivity.
SCFH – standard cubic feet per hour; TBD – to be determined

Accomplishments To-Date with Specific Barriers Addressed

- Increased operating capabilities to 400 psi at 550°C though use of 310SC SS tubular substrate.

- Optimized and scaled up the diffusion barrier coating process to 12” lengths with 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 (B, 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).
- Characterized membrane performance using synthesis gas mixtures (L, Q).
- Determined sulfur tolerance of the Pd-alloy membranes with promising results (K, L, N, P, Q).
- Fabricated, installed, and started up two larger mixed gas test stands to perform sensitivity analyses to water-gas shift (WGS) reaction impurities and long term durability testing, respectively (K, L, N, P, Q).
- Tested membranes at high pressure WGS reaction environment conditions for up to 120 hours. High mixed gas hydrogen flux rate (145 scfh/ft^2-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 against thermal cycling (50° – 400°C) (K, Q).
- 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 ft^2 of area to the end user is achievable (A, 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 (A, C, 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 (A, C, R).

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Introduction

This 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, cost effective membrane for H_2 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 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 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 BILI 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 H_2 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.

Results

Key milestones were achieved by focusing on the following activities:

1. **Diffusion Barrier (DB) Development** - Optimization of the DB layer enables thinner Pd membrane formation, lower material cost per unit area of membrane and reduces the membrane area needed. Process improvements included low profile weld techniques and controlled surface finish of the ZrO_2 with a narrow pore size range. The DB process was scaled up to 12” long tubes and a manufacturing facility is being set up capable of producing DB coated tubes up to 1 meter in length. Obvious cost reductions will occur due to amortization of set up labor over larger quantities and more mechanization of the process steps.
2. **Pd-Alloy Membrane Development and Testing** - Membrane synthesis process improvements included fabrication methods for PdRu and PdRuAu alloy compositions, lowering the temperature of air oxidation step to increase hydrogen flux

and selectivity without increasing leak rate, and development of a leak repair method to increase the selectivity of the membranes without adding significant thickness to the membranes. The membrane synthesis process is reproducible as evidenced by a large number of membrane samples produced with varying alloying gold content in a narrow thickness range (Figure 1). Laboratory-scale membrane testing focused on determining the effect of major components in the synthesis gas, especially steam and CO, as well as trace contaminant such as H_2S. As shown in Figure 2, the steam effect was negligible whereas CO exhibited minor but reversible influence on hydrogen flux reduction at 400°C. Performance of Pd and Pd-Au membranes was evaluated by adding H_2S to a WGS feed mixture at 400 and 450°C. As shown in Figure 3, Pd-Au membrane, even with only 1% Au, was more resistant to 5 ppm H_2S and the poisoning effect was less at the higher temperature of 450°C. At 25 ppm H_2S, although the hydrogen flux for the PdAu membrane decreased by over 50% the reduction was

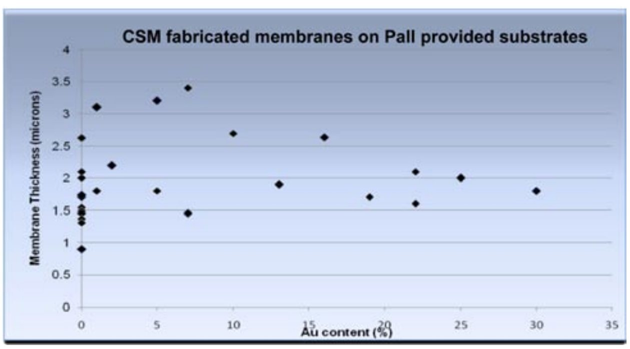

FIGURE 1. Reproducibility of Membrane Synthesis Process to Produce a Narrow Thickness Range

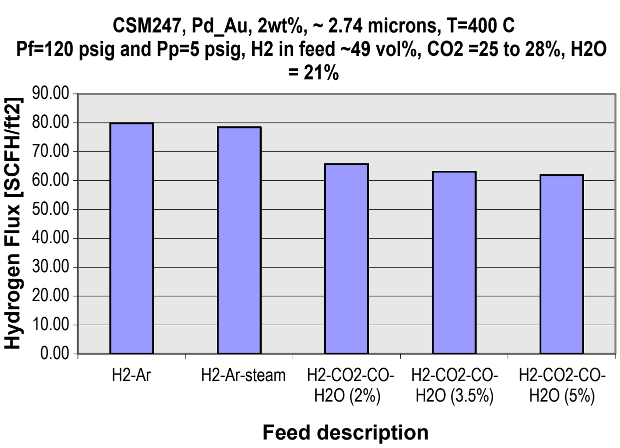

FIGURE 2. Effect of Steam and Carbon Monoxide on Membrane Hydrogen Flux Rate

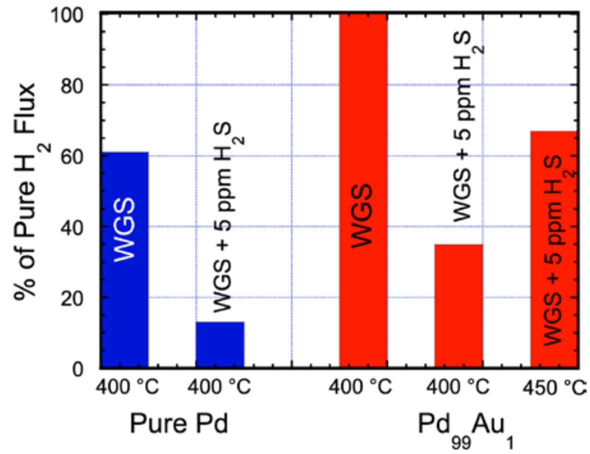

FIGURE 3. Effect of H_2S on Pd-Alloy Membranes

found reversible. Pd membranes were also tested for performance stability against thermal cycling over 50 thermal cycles of 50°C to 400°C and were found to retain both high flux and selectivity.

Two larger scale mixed gas test stands were fabricated, installed, and have been started up to perform sensitivity analyses to WGS reaction impurities as well as to conduct long term durability testing, respectively. The long-term durability tests in synthesis gas environment have just begun.

3. **High-Pressure WGS Mixture Testing** - Two Pd-alloy membranes were tested in a pilot-scale high pressure environment typical of synthesis gas after the WGS reaction. (This testing was conducted at TDA Research facilities.) The data summarized in Table 2 and Figure 4 show that high hydrogen flux was observed for both membranes, up to 245 SCFH/ft^2. The feed gas contained: 50% H_2, 1% CO, 30% CO_2, 19% H_2O at 400°C, with a differential pressure across the membrane of 170 psi. The average hydrogen permeate purity was 99.96% for membrane #199. Difficulties in controlling the feed pressure caused the observed oscillations in the flux and hydrogen purity at the end of this test and limited the test duration to 75 hours.

TABLE 2. Membrane Performance in WGS Conditions

CSM Membrane Sample #	201	199
Performance		
Pure Gas (SCFH/ft^2 atm$^{0.6}$)	303	331
Mixed Gas (SCFH/ft^2 atm$^{0.5}$)	219	149
Flux - Mixed Gas (SCFH/ft^2)	245	216
H_2 Recovery (%)	67	60
Punty (%)	99.5	99.96
Test time (hrs)	120	75

Although these tests indicated hydrogen recoveries of 60 and 67%, 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. Maximum achievable hydrogen recovery is dictated by process operating conditions rather than membrane performance characteristics. Controlled laboratory mixed synthesis gas testing demonstrated hydrogen recoveries greater than 80% by appropriate selection of permeate and feed side pressures.

4. **Cost and Economic Analysis** - Techniques for fabricating a multi-tube module were reviewed and preliminary evaluation of module design, fabrication techniques and materials show that less than \$1,000 per ft^2 of area membrane module cost is achievable in high volume (>1,000 units) production. High temperature Pd-alloy membranes may be integrated in a conventional natural gas steam reforming process or in reforming of BILI fuels such as ethanol. Cost analysis was conducted in collaboration with DTI using their H2A model modified to include a membrane reactor process for ethanol reforming. Membrane reactor costs are determined by the membrane performance (flux rate) as well as operating parameters (hydrogen recovery). The results show that the capital cost of the membrane unit is a small fraction of the capital cost of the reforming system, and therefore has a very minor influence on the cost of hydrogen produced. Hydrogen recovery on the other hand determines the yield of hydrogen per unit amount of feed stock (ethanol) and therefore significantly influences the operating costs of hydrogen production. This analysis indicated that separation factor rather than the hydrogen flux rate is a stronger determinant of the hydrogen production cost. Slightly thicker membranes with a tradeoff for greater selectivity and durability over membrane flux may thus be preferable. The economic analysis indicated that the membrane-based hydrogen production process can potentially reduce the cost of hydrogen to below \$3/kg meeting DOE's target.

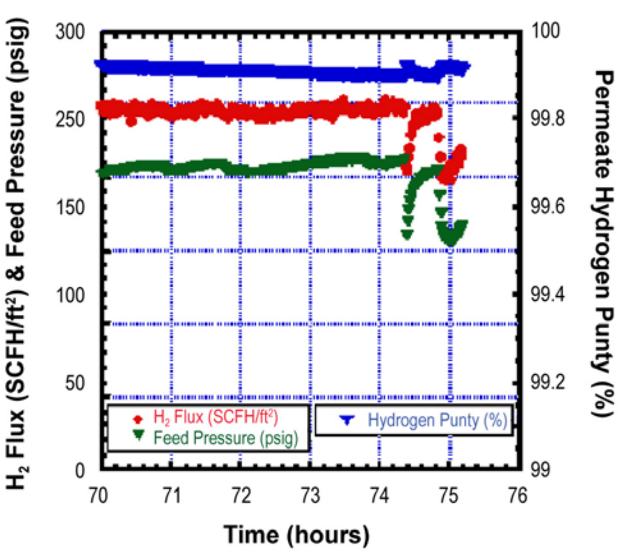

FIGURE 4. Membrane Performance in High Pressure Post-WGS Synthesis Gas Environment

Conclusions

- The DB substrate process is being finalized and a manufacturing facility is being established.
- Improvements were made in membrane synthesis process and membranes were evaluated for their performance in synthesis gas environment in 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. Membrane synthesis process is capable of producing membranes in the appropriate thickness range.
- Estimation of module costs indicated that less than \$1,000 per ft^2 of module area cost is achievable and the membrane-based hydrogen production process can potentially reduce the cost of hydrogen to below \$3/kg meeting DOE's target.

Future Plans

- Membrane synthesis process will be finalized and scaled up for manufacturability.
- 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 H_2S) and hydrogen recovery. The membrane performance data collected from these tests will be used 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.

FY 2009 Publications/Presentations

1. Acquaviva, J., “High-Performance, Durable, Palladium Alloy Membrane for Hydrogen Separation and Purification”, Presented at the DOE Annual Merit Review Meeting, May 19, 2009.

2. Singh, R. and Hopkins, S., “Gas Separation Membrane”, Poster Session, AIChE 2008 Annual Meeting, Philadelphia, PA. Nov. 2008.

3. Damle, A.S. and J. Acquaviva, “Steam Methane Reforming in a Membrane Reactor for Hydrogen Production,” Presented at the AIChE Annual Meeting, Philadelphia, PA, November 2008.

4. Way, J.D., “Palladium and Palladium Alloy Membranes for Hydrogen Separation and Production: History, Fabrication Strategies, and Current Performance,” Invited Plenary Lecture, 10th International Conference on Inorganic Membranes (ICIM 10), Tokyo, Japan, August 2008.

5. Gade, S.K., Payzant, E.A., Park, H.J., Thoen, P.M. and J.D. Way, “The effects of fabrication and annealing on the structure and hydrogen permeation of Pd–Au binary alloy membranes,” J. Membrane Science, 340(1-2), 227–233 (2009).