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

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Subcontractors:
- Colorado School of Mines, Golden, CO
- Chevron Energy Technology Company, Richmond, CA
- Oak Ridge National Laboratory, Oak Ridge, TN

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Project End Date: June 30, 2010

Objectives

- Establish the technical and economic viability for use of a Pd alloy composite membrane in a distributed H_2 production system as per DOE targets.
- Develop a Pd alloy membrane on AccuSep® porous metal tube substrates:
  - Optimize the formation of the membrane/substrate.
  - Fabricate functional gas separation tubes and modules.
  - Test performance and durability.
  - Characterize and analyze membranes.
  - Compare results against Dense Metallic Membrane targets established in the RD&D plan.
- Design a commercial scale membrane module.
- Conduct an economic analysis:
  - Analyze economics of membrane use in a gas separation system including capital and operating costs and energy requirements.
  - Compare projected system performance to DOE target goals.
  - Compare to the pressure swing absorption (PSA) 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 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	Units	2010Target	Progress
Cost of distributed H_2	$/gge	2.50	Note 1
H_2 quality	% of total gas	99.99	99.999*
Flux at 20 psid and 400ºC	scfh/ft^2	250	270**
H_2 recovery 95%H_2/5%N_2 95%H_2/5%Ar 95%H_2/2.5%CO_2/2.5%CH_4	%	>80	 76*** 77*** 78***
Module cost (including membrane)	$/ft^2	$1,000	$1,500
Durability	hr	26,280	Note 2
Operating capability	psi	400	Note 3

* Projected H_2 quality based on H_2/N_2 ideal selectivity on membrane #102 measured at 20 psid ΔP H_2 partial pressure and 15 psia permeate side pressure at 400°C.
** H_2 flux on membrane #102 measured at 20 psid ΔP H_2 partial pressure and 15 psia permeate side pressure at 400°C.
*** Mixed gas tests on membrane #102 measured at 20 psid and 400°C.

Note 1. The cost of distributed H_2 target will be demonstrated by incorporating the performance data obtained on the membranes in computer models to calculate the overall cost of this process. The computer models are operational.

Note 2. The durability goal is being addressed by procurement of a test furnace for long-term membrane testing at operating pressure and temperature conditions under mixed gas streams. Membrane #102 was tested at 400°C and 20 psid ΔP for 546 hours and six thermal cycles.

Note 3. A project was initiated to determine collapse pressures at operating temperature to create a design that meets the pressure capability and cost goals.

Accomplishments

- Achieved a flux of 270 scfh/ft^2 on a 2 micron thick Pd/Au alloy membrane using pure H_2 and N_2 gas streams, exceeding the 2010 target goal. Tests were at 20 psid and 400ºC.
- H_2 permeate quality on this membrane was 99.999%, also exceeding the 2010 target goal based on H_2/N_2 ideal selectivity.
- Achieved a H_2 recovery on this membrane of 78% on a 95%H_2/2.5%CO_2/2.5%CH_4 mixture, 77% on a 95%H_2/5%Ar mixture and 76% on a 95%H_2/5%N_2 mixture at 20 psid and 400°C.
- Validated the results for this membrane by independent testing at the three team locations.
- Further improved the diffusion barrier layer/AccuSep® substrate from a surface finish of 25-35 micro-inches to 8-12 micro-inches that enabled achievement of consistently high fluxes on Pd alloy membranes coated on the substrates.
- Improved the porous-to-dense transition stainless steel tube welding process from having zero leakage at 20 psi to having zero leakage at 40 psi.
- Continued development of the membrane module design by initiating a project to yield material collapse test data and by calculating membrane surface area requirements based on membrane performance tests.
- Membrane, energy and economic computer models were developed.
- Initiated comparisons of an in-house economic computer model to H2A model.

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Introduction

The project goal is to make significant contributions to the Hydrogen Fuel Initiative (HFI) by enabling hydrogen production that is economically competitive with conventional fuels and energy sources for application in transportation and stationary polymer electrolyte membrane (PEM) fuel cell power generation. Our plan is to develop and demonstrate pilot-scale technology to produce high purity hydrogen from reformed natural gas streams using thin, sulfur-tolerant, Pd alloy membranes on durable, cost-effective, porous stainless steel tubular supports contained in a module.

Our team has developed a smooth, high-quality, zirconia-coated, porous, stainless steel tubular substrate that has enabled the formation of high-flux Pd alloy membranes as thin as 1 micron. A new Pd/Au alloy membrane yielded high H_2 flux and quality performance test results. Mixed gas measurements were made on a Pd/Au alloy membrane and H_2 recovery measurements were obtained. Progress was made in design of a membrane module based on constraints specified for the process and the cost goal. Computer models also were developed to evaluate progress toward achieving the economic goals of the project.

Approach

The primary objective of our project is to achieve the DOE goal of producing H_2 at a cost of $2-3/gge and at a purity of 99.99% by 2010. Achieving the other target goals of membrane flux rate, membrane durability, H_2 recovery and ΔP will assist achieving the primary cost and purity goals. To achieve the target flux and quality goals, the Pd alloy composition and process are being optimized. To maximize the H_2 recovery, it was determined that the mixed gas test conditions need to be adjusted to ensure that the total available surface area of the membrane is being utilized. Our approach to the module cost goal is to design a membrane module based on the surface area calculated from a membrane computer model using our performance test data. Information also will be obtained on collapse pressures measured at operating temperatures to design the membrane module to meet the cost and ΔP goals. Progress on the durability goal will be achieved by long-term testing of membranes on a furnace dedicated to this test. Energy and economic computer models will predict progress toward the H_2 cost goal and to compare the membrane process performance to the DOE target goals and to competing technology.

Results

The formation of high quality, thin Pd alloy membranes is highly dependent upon the quality of the membrane support or substrate. Significant emphasis was placed on improving the quality of the porous, zirconia-coated, porous stainless steel AccuSep® tubular substrate. By modifying the fabrication process, the surface finish of the barrier layer was improved from 25-35 micro-inches to 8-12 micro-inches. This improvement in the quality of the substrate resulted in our ability to achieve consistently high fluxes. It was determined that the 8-12 micro-inch finish was optimal for our membrane. Substrates with finer surface finishes resulted in membranes with inadequate adhesion, most likely due to elimination of any mechanical interlocking of the two phases.

A non-porous, stainless steel tube is used to connect the porous stainless steel substrate to a tube sheet header. A welding process was developed to seal the dense tube to the porous substrate. The process was improved from where leakage at the weld initiated at pressures of 20 psi to where leakage initiates at 40 psi. Welded stainless steel tubes are shown in Figure 1.

A flux of 270 scfh/ft^2 was achieved on Pd/Au alloy membrane #102 using pure H_2 and N_2 gas streams, exceeding the 2010 target goal as shown in Figure 2. Test conditions were 20 psid of pure H_2 and 400ºC. The membrane was 2 microns thick. The H_2 permeate quality on this membrane was 99.999% as can be determined from the data in Figure 2. This also exceeded the 2010 target goal based on H_2/N_2 ideal selectivity. The H_2 recovery curve on membrane #102 is shown in Figure 3. A H_2 recovery of 78% was measured on a 95%H_2/2.5%CO_2/2.5%CH_4 mixed gas stream, 77% on a 95%H_2/5%Ar mixed gas stream and 76% on a 95%H_2/5%N_2 mixed gas stream at 20 psid and 400°C. It was determined that the H_2 recovery values obtained may not have been maximized with test conditions used. The technical team reached a consensus conclusion that the membrane was in a "starved" condition in which the total area of the membrane was not being utilized. Test conditions will be modified and repeated.

A scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDAX) was carried out on membrane #102 after a few hundred hours at 400°C and after several thermal cycles and some limited mixed gas testing. The alloy composition was determined to be $Pd_{95}Au_5$. The original composition was not able to be determined since our current method for composition analysis is based on the destructive test using SEM/EDAX. On future membranes, techniques will be developed to determine the composition before and after testing to determine if any changes occurred. A project was initiated to conduct an analytical study on the kinetics of intermetallic diffusion during the alloy formation process. Another task on this project is to determine the phase composition of the alloys as a function of temperature, time and environment. Changes in the micro/nanostructure as a function of the alloy formation process will also be investigated.

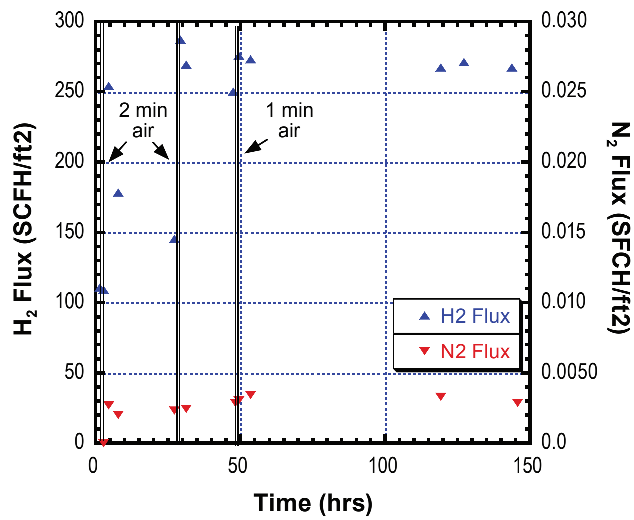

FIGURE 2. H_2 Flux and Quality of Pd/Au Alloy Membrane #102 at 20 psid and 400°C

FIGURE 1. AccuSep® Substrate Tubes with Welded Dense Stainless Steel End Fittings

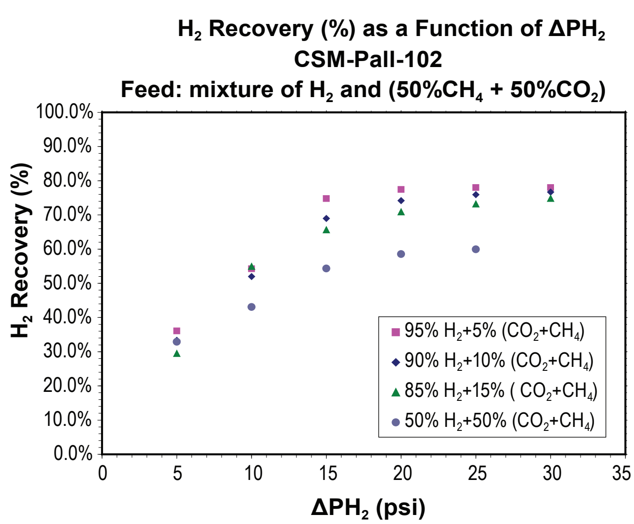

FIGURE 3. H_2 Recovery as a Function of ΔP_{H2} in H_2, CO_2 and CH_4 Mixed Gas Streams

Additionally, the phase stability of the alloy films will be examined under appropriate atmosphere and temperature combinations.

Design work was initiated on a commercial membrane module. A schematic of this concept is illustrated in Figure 4. A key factor in the design is to minimize the wall thickness of the membrane element as well as the housing to meet the 2010 process operating capability (400 psid) and module cost ($1,000 per ft^2) target goals. High-temperature tensile tests were initiated at Oak Ridge National Laboratory using the expected operating conditions on the AccuSep® tubular substrates to confirm the calculated strength. This will permit us to accurately specify the minimum wall thickness required. Mechanical properties on Pd alloy membranes at expected operating conditions will also be conducted. The membrane surface area required for the module was determined using the membrane computer model and performance data obtained with the non-optimal H_2 recovery values. These tests will be repeated using modified test conditions to maximize the performance of the membrane and a new surface area will be calculated for the module design.

Progress was made on our system economic and energy analysis task. An in-house membrane model was developed that calculates the surface area requirement from membrane performance test results. An energy model was developed to calculate the parasitic energy. An in-house system economic model will calculate H_2 production costs, net present value and internal rate of return for the membrane system based on our module cost and performance data. It will be compared to H_2 production cost using a PSA system and to the DOE target goals. All three models are currently operational. The parameters of our internal energy and economic models will be aligned with the parameters and assumptions of the H2A model so that the results can be compared.

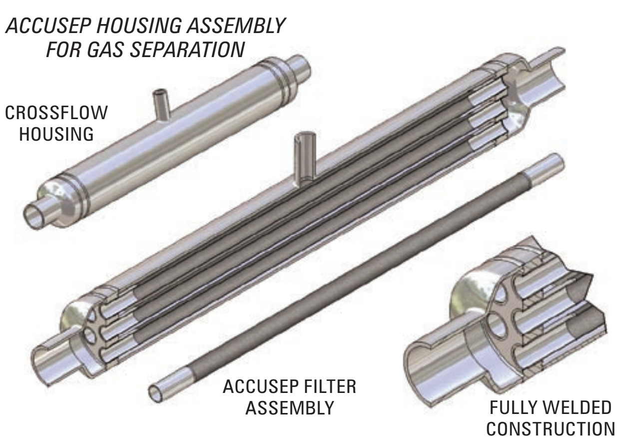

FIGURE 4. Proposed Design of Membrane Module

Conclusions and Future Directions

- In the second year of our project, it was shown that a new alloy system (Pd/Au) yielded H_2 flux and quality measurements with pure gases that exceeded the 2010 target goals.
- H_2 recovery values as high as 78% were achieved in a 95%H_2/2.5%CO_2/2.5%CH_4 mixed gas stream. The mixed gas test procedure will be modified to maximize utilization of the entire surface area of the membrane in order to maximize the H_2 recovery.
- Improvements were made to the diffusion barrier layer that increased the consistency of Pd alloy formation and increased the separation factor and flux rate.
- The process for welding the end fitting seals to the membrane was improved resulting in an increase in the integrity of the seals.
- Modifications are continuing to being made to the Pd/Au ratio to maximize the performance of this alloy system. Studies are continuing on the Pd/Cu alloy system to maximize performance of that system before down-selecting to one alloy system.
- Using new mixed gas test conditions, membrane performance test results will be measured. These test results will be used in the membrane model to calculate the surface area required. This surface area will be used to design the membrane module and to calculate the cost of the module.
- A durability furnace will be set up and long-term tests will be conducted on membranes to determine their lifetime and replacement operating costs for the economic model analysis.
- The parameters of our internal energy and economic models will be aligned with the parameters and assumptions of the H2A model so that the results can be compared.

FY 2007 Publications/Presentations

1. A presentation on the project status was given at the DOE Annual Merit Review Meeting (May 15, 2007).

2. Way, J.D., "Palladium-Gold Composite Membranes for Hydrogen Separations", 233rd ACS National Meeting, March 25-29, 2007, Chicago, IL.

3. Way, J. D., "Composite Palladium Alloy Membranes for Hydrogen Separation," presented at the Membranes: Materials and Processes Gordon Research Conference, New London, NH, August 2006.