II.C.9 High Performance Palladium-Based Membrane

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Chevron Technology Ventures, Houston, TX
Colorado School of Mines, Golden, CO
Oak Ridge National Laboratory, Oak Ridge, TN

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Objectives

- Optimize the formation of the Pd alloy membrane on AccuSep® porous metal tube substrates.
- Fabricate functional gas separation tubes and modules.
- Test performance and durability.
- Characterize and analyze membranes.
- Design commercial scale module.
- Compare projected system performance to DOE target goals.
- Analyze economics of membrane use in a gas separation system including capital and operating costs and energy requirements.

Technical Barriers

This project addresses the following technical barriers from the Separations and Other Cross-Cutting Hydrogen Production section (3.1.4.2.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(L) Durability
(M) Impurities
(N) Defects
(O) Selectivity
(P) Operating Temperature
(Q) Flux
(R) Testing and Analysis
(S) Cost
(T) Oxygen Separation Technology
(U) High-Purity Water Availability

Technical Targets

Comparison to DOE Membrane Performance Targets

Performance Criteria	Units	2010 Target	2015 Target	Progress
Flux at 20 psid and 400ºC	scfh/ft^2		300	220*
Hydrogen permeate quality	%		>99.99	99.98**
Membrane cost (including module cost)	\$/ft^2	\$1,000		\$1,500

* Flux at 20 psid ΔP H_2 partial pressure and 15 psia permeate side pressure and 400ºC
** Projected quality based on H_2/N_2 ideal selectivity

Accomplishments

- Achieved a flux of 220 scfh/ft^2 on a 2 micron thick Pd membrane, exceeding the 2010 target goal on the Mod-1 AccuSep® substrate. Test conditions were 20 psid of pure H_2 and 400ºC. It is recognized that this now needs to be achieved with a Pd alloy in a mixed gas reformate stream.
- H_2 permeate quality on this 2 micron membrane measured at the Colorado School of Mines (CSM) was 99.98%, also exceeding the 2010 target goal based on H_2/N_2 ideal selectivity.
- Completed construction of a synthetic reformate pilot plant at Chevron. System "shakedown" is now underway. Initial results reproduced the high fluxes observed at CSM.
- Conducted a cost analysis for membrane and module and achieved the 2005 cost goal.
- Quantified the contribution of diffusion barrier layer/substrate to the overall flux.
- Developed a modified diffusion barrier layer/AccuSep® substrate (Mod-1) that enabled achievement of high fluxes on Pd membranes coated on the substrates.
- Successfully applied a series of Pd membranes of various thickness on the modified diffusion barrier

layer/AccuSep® substrate (Mod-1) and developed a permeance vs. membrane thickness curve.

- Initiated alloying studies on the Pd-Cu system with preliminary results obtained on the sensitivity of H_2 permeance to alloy composition.
- Formalized detailed plans for the energy/economic cost analysis and initiated studies.

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 proton exchange membrane (PEM) fuel cell power generation. Our plan is to develop and demonstrate pilot-scale technology to purify hydrogen-rich feed gas, based on thin, sulfur-tolerant, Pd alloy membranes on durable, cost-effective, porous stainless steel tubular supports in a module using reformed natural gas ("reformate") streams.

Pressure swing adsorption (PSA) is the currently available, primary technology for hydrogen purification. However, there are numerous drawbacks associated with PSA, especially for hydrogen-fuel applications. A durable, high-performance, Pd alloy membrane offers the potential to overcome all of the PSA drawbacks, while producing hydrogen of equivalent or higher purity. Colorado School of Mines, a team partner, has extensive experience in Pd alloy membrane technology. Their focus has been to adapt this technology to Pall's diffusion barrier layer/AccuSep® porous stainless steel support. Pall developed an improved diffusion barrier layer on the AccuSep® substrate. This enabled CSM to apply thin Pd membranes on porous stainless steel AccuSep® tubes resulting in high H_2 fluxes. CSM is now focusing its effort on development of Pd alloy membranes on this substrate. Our team partner Chevron, designed, constructed and started up a pilot plant test unit having the capability to test the Pd alloy membrane modules in synthetic reformate gas streams. Chevron started work on economic and energy analysis comparisons of our membrane system to PSA systems and to the DOE target goals.

Approach

The specific objectives of our project are to achieve the DOE membrane flux rate goal, the membrane durability goal, the H_2 quality and recovery goals, the delta pressure goals, the cost goal and the system economic and energy goals for H_2 purification.

To achieve the membrane flux requirement and durability requirements, Pall placed a significant amount of effort on development of a diffusion barrier layer to isolate the Pd-based membrane from the porous stainless steel AccuSep® substrate. This layer needs to be sufficiently dense to prevent metallic diffusion at elevated temperatures. It also needs to provide a smooth surface to enable formation of a thin membrane coating, but it needs to be porous enough not to offer major resistance to the H_2 flux. Adjustments were made to the project schedule based on the availability of funding. In the first year of our project, a diffusion barrier was developed that met these criteria and in conjunction with a Pd membrane, yielded a high flux that is reported in the following section. Effort on membrane development and optimization is currently focused on the Pd alloy system with annealing, performance and analytical results proceeding along the adjusted project schedule. Pd alloy membranes have been shown to exhibit very high selectivity and high flux in a steam environment that is useful to prevent coking. Pd alloy systems offer the potential advantages of lower cost, greater resistance to H_2S and other potentially corrosive constituents of reformate streams, improved mechanical properties and higher thermal cycle stability over pure Pd membranes. Performance and durability testing of the Pd-based membranes is being conducted at both CSM and at Chevron. An iterative process is being used to maximize the membrane performance. Membrane and module designs are being developed at Pall to meet the delta pressure and cost goals. Chevron will use their modeling programs along with actual cost and performance data to verify achievement of the DOE system economic analysis and cost effectiveness goals and will compare the analysis to actual PSA cost and performance.

Results

Initial H_2 flux rates measured on the baseline diffusion barrier layer/AccuSep® substrates fabricated were very low. As an example, a 20 micron thick Pd membrane on a "baseline" diffusion barrier layer/AccuSep® substrate yielded 5 scfh/ft^2 at 20 psid and 400ºC. A major effort was expended at Pall on development of a modified diffusion barrier layer/AccuSep® substrate (Mod-1). As a result of this development work, high flux rates of 220 scfh/ft^2, exceeding the 2010 target goal, were eventually achieved on the Mod-1 diffusion barrier layer/AccuSep® substrate at 20 psid and 400ºC. The ideal H_2/N_2 selectivity of the membrane was >6,000. These results are shown in Figure 1. This goal now needs to be achieved using a Pd alloy in a mixed gas reformate stream. The high quality of the surface of the Mod-1 diffusion barrier layer/AccuSep® substrate enabled the formation of Pd membranes as thin as 2 microns to be applied to the substrate. CSM measured the effect of membrane thickness on H_2 flux through pure Pd membranes as shown in Figure 2. With this accomplishment, CSM has initiated work on Pd/Cu alloy membranes that possess superior mechanical properties over pure Pd membranes, the pure Pd membranes being plagued by a hydride phase transition that can cause severe damage to the membrane. CSM initiated studies on the effect of annealing time on a 5 micron thick Pd_{67}/Cu_{33} (mass %) alloy as shown in Figure 3. Since H_2 permeability is highly sensitive to the Pd/Cu ratio in the range of 40 to 70% Pd, CSM is making small changes to the Pd/Cu ratio to quantify the sensitivity of H_2 flux to alloy composition in order to maximize H_2 flux. The diffusion barrier layer is continuing to be further optimized with respect to chemical inertness by Pall to minimize any potential chemical reactions between the Pd-based membrane layer and the AccuSep® stainless steel substrate in order to maximize durability. The diffusion barrier is also being optimized with respect to smoothness to enable reproducible processing of thin membrane layers.

A synthetic reformate pilot plant test was constructed at Chevron Richmond. Ten-inch long AccuSep® tubes with both Pd and Pd/Cu membranes were made for testing in the pure gas laboratory test set at CSM and in the synthetic reformate gas pilot plant test set at Chevron Richmond. Phase analyses were initiated on the Pd/Cu alloy membranes at CSM using x-ray diffraction, scanning electron microscopy and energy dispersive analysis as a baseline prior to testing. CSM and ORNL will analyze the membranes after testing in the synthetic reformate stream to determine any changes in phases present that may affect durability. H_2 flux, H_2/N_2 separation factor, and H_2 quality and recovery tests were initiated on a Pd-membrane on the synthetic reformate pilot plant at Chevron. Chevron's initial high H_2 flux results with a pure H_2 feed stream at 20 psid at 400°C are shown in Figure 4.

A benchmark was established for the cost of the Pd alloy membrane in a module. Evaluation was based on conceptual scale-up of the composite membrane using current techniques and fabrication of a module suitable for use with H_2 under specified conditions. The calculated selling price for a single tube test module is $1,500/ft². Design work is on-going to minimize the cost associated with manufacture of the pressure vessel

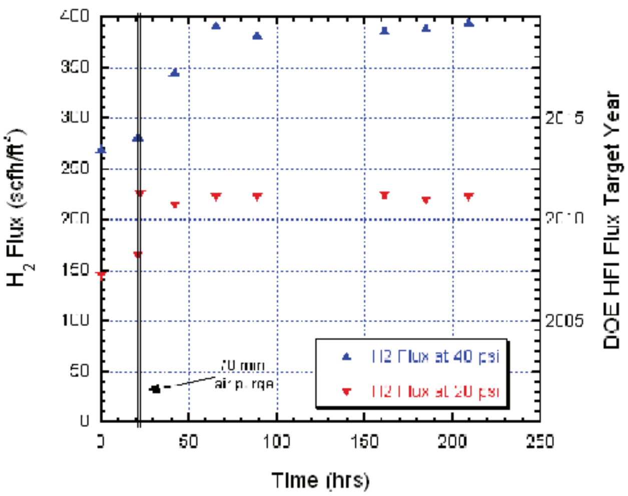

FIGURE 1. H_2 flux Versus Time as a Function of Pressure at 400°C of a 2 Micron Thick Pd Membrane on a Mod-1 Diffusion Barrier Layer/ AccuSep® Substrate

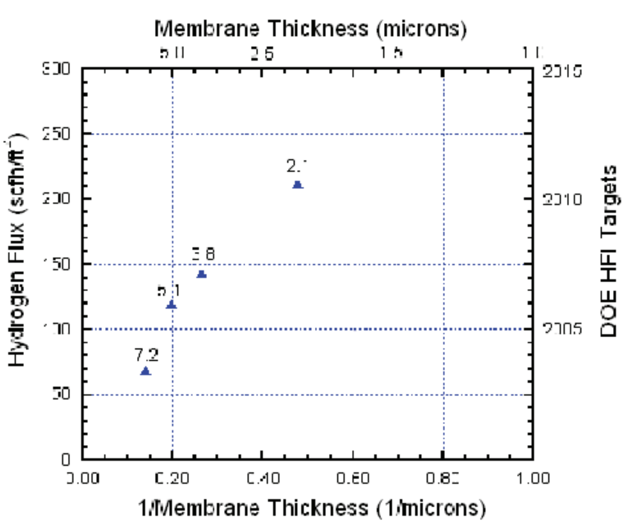

FIGURE 2. H_2 Flux Versus Reciprocal Membrane Thickness at 400°C and 20 psid

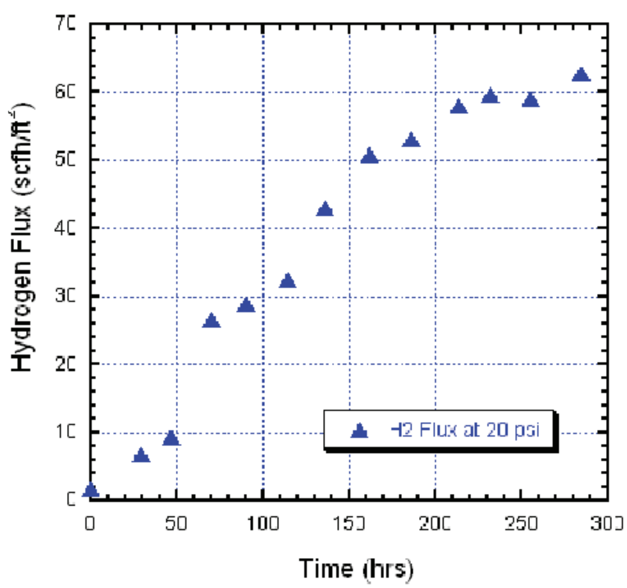

FIGURE 3. H_2 Flux Versus Time at 400°C and 20 psid of a 5 Micron Thick PdCu Membrane on a Mod-1 Diffusion Barrier Layer/AccuSep® Substrate

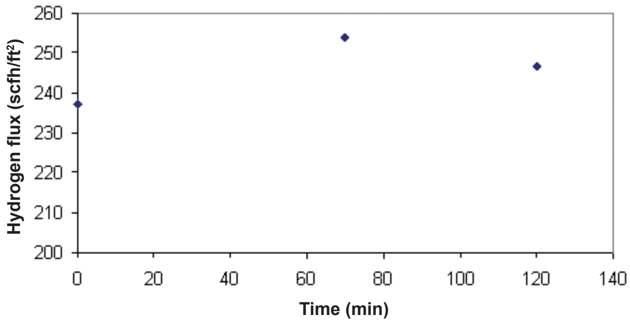

FIGURE 4. H_2 Flux Versus Time at 400ºC and 20 psid of a Pd Membrane on a Mod-1 Diffusion Barrier Layer/AccuSep® Substrate

and module hardware for a commercial scale multi-tube unit. Optimization of the membrane manufacturing will be done later in the project once composition of the membrane and processing steps are determined.

Detailed plans have been formalized for the System and Energy Analysis task. Chevron is currently adapting and modifying their existing economic analysis model. The computer model will incorporate the data from the Pd-membrane module and simulations will be performed on various permeate side total pressures and steam sweep vs. no sweep gas scenarios. From these results, the required membrane surface area will be determined. Economic analyses (net present value, internal rate of return and hydrogen production costs) will be determined in the two following general cases. First, the hydrogen production cost will be determined using the DOE 2010 target flux value of 200 scfh/ft^2 and the 2010 target cost goal of \$1,000/ft^2. Second, the hydrogen production cost will be determined based on measured flux and membrane cost. Chevron will assume life cycles of 3, 5 and 10 years and will investigate the effect of life cycle on hydrogen production cost in the previously mentioned economic model. These results will be compared with hydrogen production cost produced by the PSA method. Membrane simulation results will indicate the energy requirement for hydrogen purification and compression by the membrane. The hydrogen production cost determined from the economic analysis will be compared to the 2010 target goal. Chevron also is developing an economic model to analyze methods to minimize parasitic power. The effect of steam sweep and the effect of flow direction (co-current vs. counter current) to improve driving force and reduce hydrogen production cost will be investigated. Feedback will be provided to the mechanical design team at Pall to optimize internal configuration of the membrane in the module.

Conclusions and Future Directions

- In the first year of our project, under a budget adjusted schedule, it was shown that membranes can be formed at a thickness and defect level that will achieve targeted goals. This was accomplished with pure Pd membranes and pure H_2 gas streams.
- Using the pure Pd and pure H_2, the DOE 2010 membrane flux target goal was exceeded by applying a 2 micron thick Pd membrane on a diffusion barrier layer/AccuSep® porous stainless steel tube.
- The DOE 2010 H_2 quality goal was exceeded with this Pd membrane and pure H_2.
- Chevron's synthetic reformate pilot plant was built and system "shakedown" is under way. Initial results reproduced the high flux values observed at CSM.
- Fundamental understanding of the factors affecting flow resistance in the substrate and membrane interface was achieved.
- Process technology developed to control the composition and morphology of the diffusion barrier layer was critical to achieving thin Pd based membranes and minimal substrate resistance to hydrogen flow. This technology has enabled a pathway forward to achieve the membrane flux, hydrogen quality and recovery and durability goals.
- Alloying experiments with Pd/Cu were initiated.
- The 2005 module cost goal has been achieved and further reductions are being evaluated. The results are to be integrated on an on-going basis into the economic and energy analysis models.
- Economic and energy analysis models have been developed and analyses have been initiated to compare the performance of the Pd alloy membranes to PSA technology and the DOE target goals.

FY 2006 Publications/Presentations

1. A presentation on the project status was given at the DOE Annual Merit Review Meeting (May 16, 2006).

2. Thoen, P. M. (speaker), Gade, S. K., Keeling, M., Steele, D., and J. D. Way, "High Flux Pd Membranes Deposited on Stainless Steel Supports by Electroless Plating," paper presented at the 9th International Conference on Inorganic Membranes, June 26–29, 2006, Lillehammer, Norway.