II.C.2 Development of Hydrogen Selective Membranes/Modules as Reactors/Separators for Distributed Hydrogen Production

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Contract Number: DE-FG36-05GO15092

Subcontractor:
University of Southern California, Los Angeles, CA

Project Start Date: July 1, 2005
Project End Date: June 30, 2010

Project Objective

The water-gas shift (WGS) reaction becomes less efficient when the high CO conversion is required, such as for the distributed hydrogen production applications. Our project objective includes:

- Develop a highly efficient and low-temperature membrane-based WGS reaction process in a bench scale first, then tested in a pilot scale and finally demonstrated in a field test unit.
- Screen our existing membranes and then tailor them specifically for the proposed process and reactor.
- Determine hydrogen production cost and define the system integration requirement for commercialization.
- Reduce the capital and operating cost for distributed hydrogen production applications.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Reformer Capital Costs
(B) Reformer Manufacturing
(C) Operation and Maintenance (O&M)
(D) Feedstock Issues
(E) Greenhouse Gas Emissions
(F) Control and Safety

Technical Targets

Technical targets for dense metallic membranes for 2010 are listed below:

- Flux Rate - 250 scfh/sq foot at 20 psig pressure
- Membrane Material and all Module Costs - \$1,000/sq. foot of membrane
- Durability – 2,680 hours of testing has been completed
- Operating Capability - 400 psi
- Hydrogen Recovery - >80% (of total gas)
- Hydrogen Quality - 99.99%

Accomplishments

- **Balanced Performance vs. Cost for our H_2 Selective Membrane**. Through evaluation of a range of ceramic membrane substrates with various permeances, we have been successful in developing our H_2-selective membrane product to meet the low cost feature requested by our commercialization partner.
- **Corrected Leakage Issue of the 1st Generation Module and Ready for the Field Test.** Our first field test failed due to module leakage. The leakage of the 1st generation module has been corrected and the module is now ready for the field test scheduled in the second quarter.
- **Designed and Fabricated the 2nd Generation Module using Ceramic Membrane Bundles.** We have successfully developed the membrane bundle for our tubular H_2-selective membrane. This bundle approach can minimize module leak and reduce the module cost, and will be used for our field test in Phase II.
- **Conducted Membrane Reactor Test using our Full-Scale Membrane Tubes.** The WGS-membrane reactor process we developed from a bench-scale unit previously has been verified experimentally using a full-scale tubular membrane. Approximately 99% CO conversion, >83% H_2 recovery and >99.9% purity H_2 were achieved with this full-scale membrane reactor module.

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Introduction

Membrane separation has been traditionally considered to be a simple, low cost and compact process. Thus, the membrane process has been considered under this project as a WGS reactor/separator for enhancing the hydrogen production efficiency for distributed hydrogen production. In this project, we have focused on the development of the technology components required for integrating a membrane reactor process for distributed hydrogen production. During 2009-2010, we have completed the first field test using our full-scale Pd membrane bundle/module. In addition, we have generated the WGS membrane reactor database using our full-scale Pd membrane and a commercial catalyst for the design and construction of the full-scale membrane reactor module for Phase II study.

Approach

Our overall technical approach includes three steps as follows:

1. Bench-Scale Verification
   - Evaluate membrane reactor: use existing membrane and catalyst via math simulation.
     - Experimental verification: use upgraded membrane and existing catalyst via bench unit.
     - Validate membrane and membrane reactor performance and economics.
2. Pilot-Scale Testing
   - Prepare membranes, module, and housing for pilot testing.
   - Perform pilot-scale testing.
   - Perform economic analysis and technical evaluation.
   - Prepare field testing.
3. Field Demonstration
   - Fabricate membranes and membrane reactors and prepare catalysts.
   - Prepare site and install reactor.
   - Perform field test.
   - Conduct system integration study.
   - Finalize economic analysis and refine performance simulation.

Results

1. Successfully Prepared an 11-tube 24" Length Full Pd Membrane Bundle as Our 2nd Generation Pd Membrane Module

a. Excellent pure gas permeation characteristics consistent with our single-tube membrane performance. The H_2 permeance of our Pd Bundle #2 is ca. 7.3 $m^3/m^2/hr/bar$. Single-tube permeances typically range from ca. 8 to 11 $m^3/m^2/hr/bar$.

b. Excellent pure gas selectivity. Pure component N_2 permeance is ca. 0.006 $m^3/m^2/hr/bar$, yielding selectivities on the order of 1,200 which is typical of our single-tube results.

c. Excellent mixed gas performance in a H_2/CO_2 blend. A blend of H_2/CO_2 (80/20 vol%) was also tested. Mixed gas H_2 permeance was ca. 7.5 $m^3/m^2/hr/bar$ and H_2/CO_2 selectivity was ~1,200, consistent with the single tube results.

d. Additional bundle in production. Pd Bundles #3 and #4 have been produced and are ready for testing.

2. Pilot and Field tests of the 1st Generation Pd Membrane Module

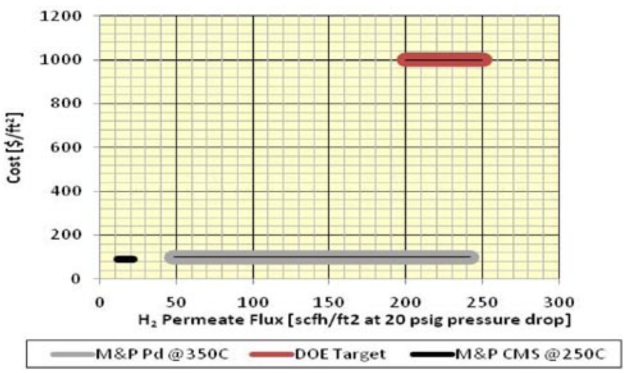
The 1st generation full-scale module was field tested last year; however, severe module leaks were encountered. During this year, we have redesigned the module seal to overcome this problem. Since leaking from the individual tubes after thermal cycling does not follow the sequence of thermal cycles for most tubes, we concluded that the tube seal was stable through multiple thermal cycles. Further, N_2 measurement of ~0.08 $m^3/m^2/hr/bar$ in average is equivalent to ~0.006 $m^3/m^2/hr/bar$ at 350°C based upon Knudsen diffusion, which is consistent with the measurement on the module basis. The selectivity of about 1,000 for H_2 over N_2 was obtained. The field test at our end user site using the actual reformate delivered performance consistent the laboratory using synthetic reformate.

3. Effect of Substrate on Permeance and Selectivity of Pd Membranes

A wide range of commercial and experimental ceramic membranes, with permeances ranging from 50 to 800 $m^3/m^2/hr/bar$ in N_2 at room temperature, were selected to study the Pd membrane performance and permeate quality. Hydrogen permeances of up to 25 $m^3/m^2/hr/bar$ at 350°C and H_2/N_2 selectivities ranging from 350 to >10,000 were obtained. Although the higher permeance substrates delivered higher H_2 permeances as a result of the reduced resistance, the selectivities, as expected, decreased because of the surface topography. As a result, an intermediate substrate has been selected for commercial product development, with hydrogen permeance of 15 to 25 $m^3/m^2/hr/bar$ and the selectivity of 1,000 to 3,000 at 350°C as presented in Figure 1.

4. Cost vs. Performance Evaluation with Regard to Our End-User Application

As shown in Figure 1, our cost vs. performance relationship is 2-10 times lower than the relationship target set by DOE for 2010. However, our end-user cost target is much more stringent than the DOE target.



Membrane Cost for 5 kW Genset

Targets	H_2 Flux*	Cost [$/5 kW]
DOE Target	250	2,000
M&P current	121	416

* in scfh/ft^2 at 20 psig

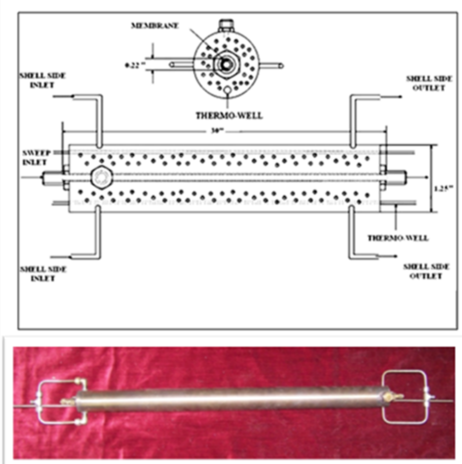
COST ALLOCATIONS FOR A 5 KW FUEL CELL-BASED GENSET

Based upon a conventional diesel fuel forming (provided by our end user participant)

Component	Typical Equipment	Cost [$]	$/kW
Purifier	Pd membrane*	400	80

M&P Substrate	Substrate N_2 Permeance [m³/m²/hr/bar]	Pd Permeance [m³/m²/hr/bar]	Selectivity [H_2/N_2]
Current Standard	50 to 70	10 to 25	350 to >10,000

FIGURE 1. Cost analysis of our Pd membranes for stationary power generators and the cost target set by our end-user participant.



Physical Characteristics and Operating Parameters	
Pd Membrane:	30"L, 0.57cm OD
Temperature:	300°C
Catalyst:	30g of Cu/ZnO
Feed:	
H_2:CO:CO_2:CH_4:H_2O	5.22:1:0.48:0.22:2.8
Pressure:	30 to 50 psig
Sweep Ratio:	0 to 0.3

Membrane Performance Characteristics:
Single Component Gas Permeances at 300°C

Gas	Permeance [m3/m2/h/bar]	Sepn Factor
H_2	16.82	1
CO	0.01	2,369
CO_2	0.01	2,951
Ar	0.01	2,474
N_2	0.01	2,548

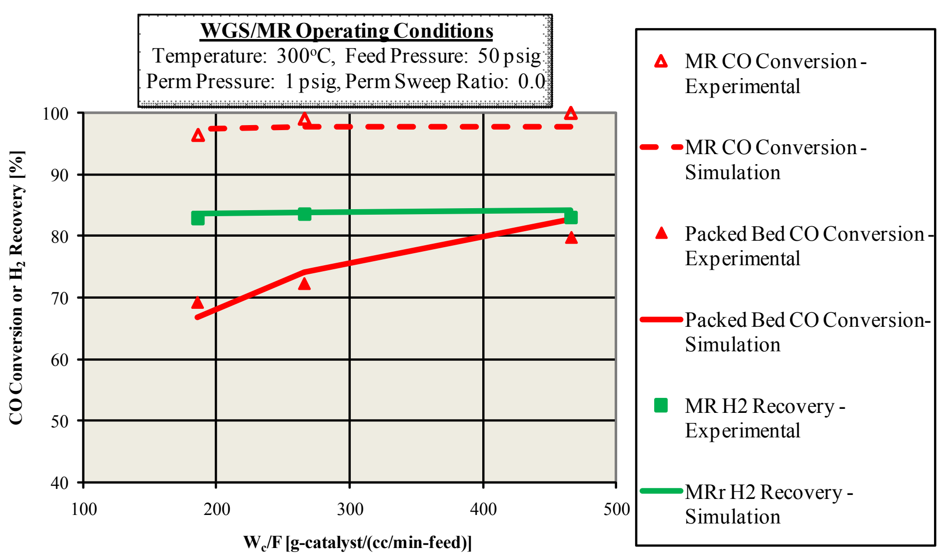


FIGURE 2. Experimental results from the membrane reactor operation at 50 psig with no sweep using a full-scale H_2 selective membrane

Based upon the input from our end user, for a 5 kW genset, about $400 at 121 scfh H_2 at 20 psig pressure drop is required, which is about 2.5 times lower cost than the DOE target on a comparable throughput basis. The cost vs. performance analysis of our products meets this stringent target set by our customer.

5. CO Conversion and H_2 Separation via Our Full-Scale Palladium Membrane Reactor

Although numerous bench top membrane reactor studies have been performed, no experimental work has been performed using a full-scale Pd membrane. During this year, we successfully demonstrated the membrane reactor using a 30"L Pd membrane as summarized in Figure 2 as a transition step for us to move this technology to the field. Using the synthetic reformate as feed, the low-temperature WGS reaction was performed at 300°C using a commercial catalyst at 30 and 50 psi under the conditions of with and without permeate purge. High CO conversion and high purity hydrogen product at a high hydrogen recovery ratio was obtained. Specifically, ~83% H_2 recovery ratio and 99% CO conversion at >99.9% H_2 purity were obtained from this experimental study.

Conclusions and Future Direction

- The low-cost Pd membranes supported on our ceramic substrate were developed, which can meet the very stringent cost target set by our commercialization partner.
- We have improved the 1st generation module and successfully verified its stability (i.e., acceptable leak through thermal cycling, Figure 3) and performance, which was successfully field tested at our end user side for hydrogen separation from reformate.
- The 2nd generation module, i.e., Pd membrane bundle, which is more economical and less prone to leaks, has been developed and successfully tested (Figure 4). This module will be used for field test in Phase II.
- Greater than 99% CO conversion and >99.9% purity hydrogen at >83% hydrogen recovery ratio was demonstrated experimentally using a reactor packed in our full-scale Pd membrane with a commercial catalyst. We are now ready to move to the field test of the membrane reactor to be undertaken in Phase II.

Our Phase II activities will focus on:

- Prepare 2nd generation membrane/modules for use as a full-scale WGS-membrane reactor.
- Design and construct the full-scale membrane reactor for field test at the selected end-user site.
- Conduct field test at the participated end-user site.

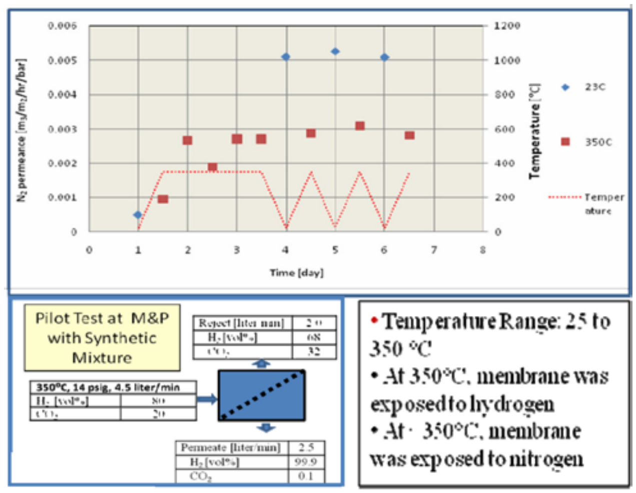


FIGURE 3. Thermal cycle stability through the multiple thermal cycling tests and the performance evaluation of the 2nd generation membrane.

FIGURE 4. Photo of the standard 2nd generation Pd (i.e., candle filter) bundle showing the open and closed ends.

FY 2010 Publications and Presentations

1. Elyassi, B., Sahimi, M., and Tsotsis, T.T., "Inorganic Membranes," *Encyclopedia of Chemical Processing*, Taylor

& Francis Group, LLC, Sunggyu (K.B.) Lee, Editor, 1:1, 1-16, 2009.

2. Abdollahi, M., Yu, J., Liu, P.K.T., Ciora, R., Sahimi, M., and Tsotsis, T.T., "Process Intensification in Hydrogen Production from Syngas," Submitted for Publication, *Ind. Eng. Chem. Res*.