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

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Fiscal Year (FY) 2011 Objectives

- Develop a highly efficient, low-temperature membrane-based bench-scale water-gas shift (WGS) reaction process, test it at pilot scale, and demonstrate the process in a field test unit.
- Screen existing membranes and modify the membranes for the proposed process and reactor.
- Determine hydrogen production costs and define system integration requirements for commercialization.
- Reduce capital and operating costs for distributed hydrogen production applications.

Technical Barriers

This project addresses the following technical barriers as presented in Section 3.1 Hydrogen Production Technical Plan, Fuel Cell Technologies Program, Multi-Year Research, Development and Demonstration Plan for 2005 to 2015 (updated October 2007):

(K) Durability
(L) Impurities (Hydrogen Quality)
(M) Membrane Defects
(N) Hydrogen Selectivity
(P) Flux
(R) Cost

Technical Targets

The WGS reaction is considered one of the least efficient unit operations for hydrogen production via steam reforming. This project focuses on developing a highly efficient, low-temperature, low-cost membrane-based WGS reaction process. 2010 Technical Target values for dense metallic membranes include:

- Flux Rate - 250 scfh/ft^2 at 20 psig pressure
- Membrane Material and All Module Costs - \$1,000/ft^2 of membrane
- Durability – 2,680 hours
- Operating Capability - 400 psi
- Hydrogen Recovery - >80% (of total gas)
- Hydrogen Quality - 99.99%

FY 2011 Accomplishments

- Verified palladium (Pd) membrane bundle performance and separation properties at pilot plant and end-user site.
- Confirmed Pd membrane bundles long term thermal cycling stability in nitrogen are similar to results for single membrane tubes (~20°C to 350°C).
- Developed a post treatment hydrogen product purity strategy that reduced 300, 70 and 10 ppm CO in hydrogen to 16, 1.2 and 0.3 ppm respectively.
- Identified a potential alloy for upgrading our Pd membrane product that will support improved stability during cooling in the presence of hydrogen.

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Introduction

Membrane separation traditionally has been considered a simple, low-cost and compact process. At the same time, the WGS reaction is one of the least efficient unit operations for hydrogen production via steam reforming. This project will focus on the development of technology components associated with a WGS reactor/separator membrane process to enhance the hydrogen production efficiency for distributed hydrogen production.

Pd membranes, one set of dense metallic membranes, are capable of delivering high purity hydrogen product with a high recovery ratio. Specifically, this project will fabricate tubular Pd membranes by depositing Pd thin film over a ceramic substrate and bundling the tubes into a reactor. During 2010-2011, a test quantity of Pd membrane bundles suitable for packaging into the membrane reactor were field tested. The project target of producing a hydrogen product stream with <<10 ppm CO was achieved. Also, an evaluation of a series of Pd-alloy foils established the fundamental basis for the development of a Pd-based membrane with cooling stability in the presence of hydrogen. Further confirmation through field testing will be pursued in FY 2011-2012.

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. Produced an 11-tube 24-Inch Length Second Generation Pd Membrane Bundle

Ceramic-based Pd membrane tubes were successfully developed and tested previously. In addition, a membrane bundling technique was developed for potting these tubes into a bundle for packaging into a membrane housing for commercial use. Over the last year, several Pd membrane tube bundles have been produced and evaluated, and these bundles will be packaged into the membrane reactor for field testing to demonstrate the proposed WGS membrane reactor in FY 2012. Table 1 shows the performance of the four bundles produced. One of these bundles (Pd-B-4) was evaluated for its mixed gas performance. Mixed gas testing was conducted at ca. 380˚C using an 80/20 vol% H_2/Ar blend. The H_2 permeance and H_2/Ar selectivity in the mixture were 7.1 and 1,220 $m^3/m^2/hr/bar$, respectively, and are consistent with the pure component result. Furthermore, the performance of these Pd membranes has been confirmed in field testing at our end-user facility using both synthetic and actual reformate.

2. Tested Thermal and Thermal Cycling Stability of Our Pd Membrane Tube Bundles

This year membrane tube bundles were subjected to thermal and thermal cycling stability testing similar to testing performed last year on Pd membrane tubes for >2,500 hours (see Figure 1). About 140 thermal cycles between 25 and 350°C have been performed. The Pd membrane bundle maintains its excellent H_2/N_2 selectivity of ~4,000. Separately the thermal stability of the membrane bundle was tested for ~400 hours. The bundle maintains its hydrogen permeance of ~15 $m^3/m^2/hr/bar$ and selectivity of 10,000 – 15,000 at 350°C. This thermal stability test will be continuing into the next year. In summary, the thermal and thermal cycling stability of the Pd membrane tube bundles are excellent, similar to the tubes tested previously, and the improved performance is, in part, the result of the potting technique developed for the proposed applications.

3. Demonstrated H_2 Post-Treatment CO Reduction in the WGS-Membrane Reactor

Our previous bench-top WGS membrane reactor experimental study demonstrated the ability of our membrane to reduce CO contamination of hydrogen to 50 ppm or below, depending in part upon the degree of hydrogen recovery, and the transmembrane pressure drop. During this year, we have developed a post-treatment technique that is to be integrated into our membrane reactor to further reduce the CO level. Our experimental study demonstrated the reduction of CO from 50-300 ppm to ~0.3 to 16 ppm respectively, as illustrated in Figure 2. In

TABLE 1. Pure Component Permeance and Selectivity of the Pd Bundles Prepared and Tested during 2010-2011

Bundle ID (-)	Tube Count (#)	Temperature (°C)	Pressure (psig)	H_2 ($m^3/m^2/hr/bar$)	H_2/N_2 (-)	Comments
#1	11	336	2.6	6.1	1,100	Broken
#2	14	337	2	9.8	1,600	
#3	14	338	2	7.9	780	
#4	14	337	2	6.2	1,800	

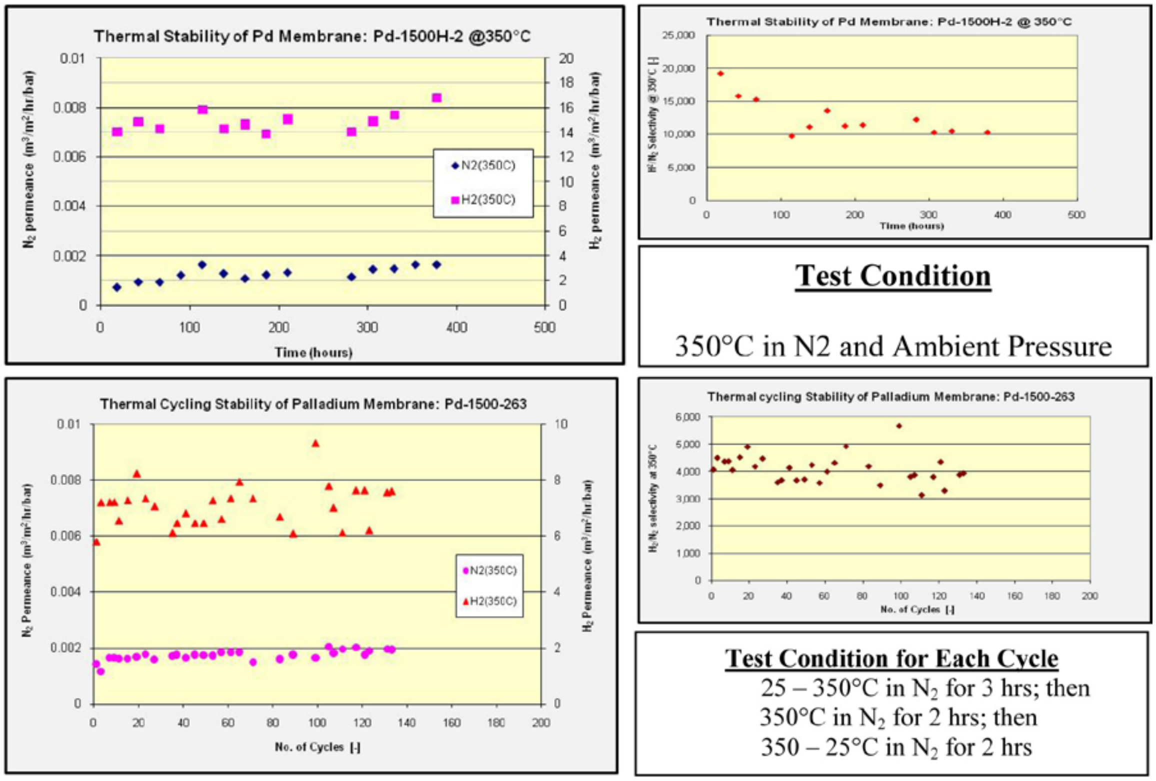

FIGURE 1. Evaluation of Thermal and Thermal Cycling Stability of the Pd Membrane Tube Bundles

the upcoming year, we will perform WGS membrane reactor runs integrated with this post treatment to demonstrate the reduction of CO in the final product to <<10 ppm.

4. Cooled Pd Membranes in the Presence of Hydrogen

The application selected by our end-user requires the ability to cool the membrane in the presence of residual

CO Contaminant in the Hydrogen Stream Produced from WGS-MR

As shown in our previous membrane reactor study, our palladium membrane has been able to deliver a hydrogen product stream with ~50 ppm CO using our standard Pd membrane as a reactor.

Our Proposed Solution to Reduce CO Contaminant Level

A post treatment strategy has been developed and experimentally demonstrated on the technical feasibility in reducing CO contaminant to an extremely low level, such as <10-1 ppm as shown below

Concentration of CO in Feed [ppm]	Residual CO in Product [ppm]	W/F [g catalyst/(mol CO/hr)]
300	16	4,148
70	1.1	17,778
50	0.3	24,889

Activities Planned in 2011

- demonstrate this post treatment strategy in conjunction with our WGS-MR.
- further incorporate this post treatment into our WGS-MR as an integrated membrane reactor.

FIGURE 2. Post-Treatment for Reduction of CO Contaminant Level in Hydrogen Produced from our WGS-Membrane Reactor

hydrogen following shut-down of the hydrogen generator. Although this is a very desirable feature for the commercial use of the Pd membrane, very few literature studies have addressed this issue. The pure Pd membrane such as those we have produced thus far failed to maintain their membrane materials stability through cooling from 350 to 25°C in the presence of hydrogen. This year we conducted a laboratory evaluation study using commercially available Pd alloy flat discs to determine the alloy formula required to sustain the cooling cycle. The results of our evaluation for the Pd-Ag (23%) and Pd-Cu (40%) alloys are presented in Figures 3 and 4. No damage through the cooling test for both alloys was observed under visual and scanning electron microscope examination. However, the H_2/N_2 selectivity

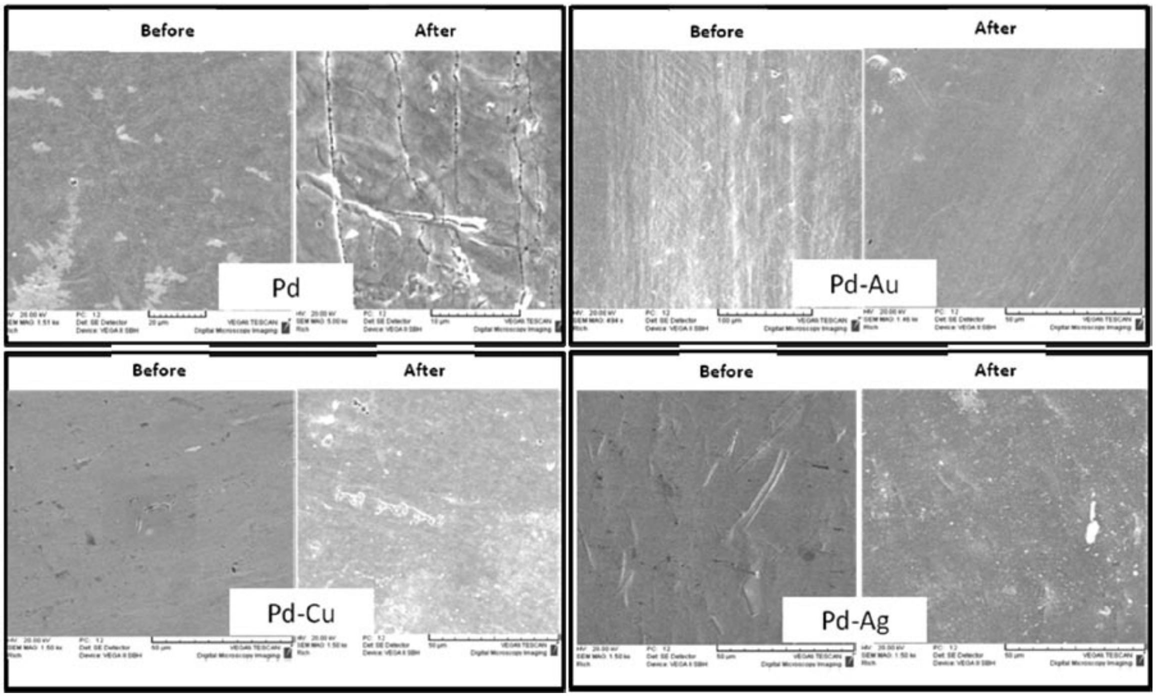

FIGURE 3. Evaluation of Pd Alloy Flat Discs for their Cooling Stability in the Presence of Hydrogen Required by Our Target Applications

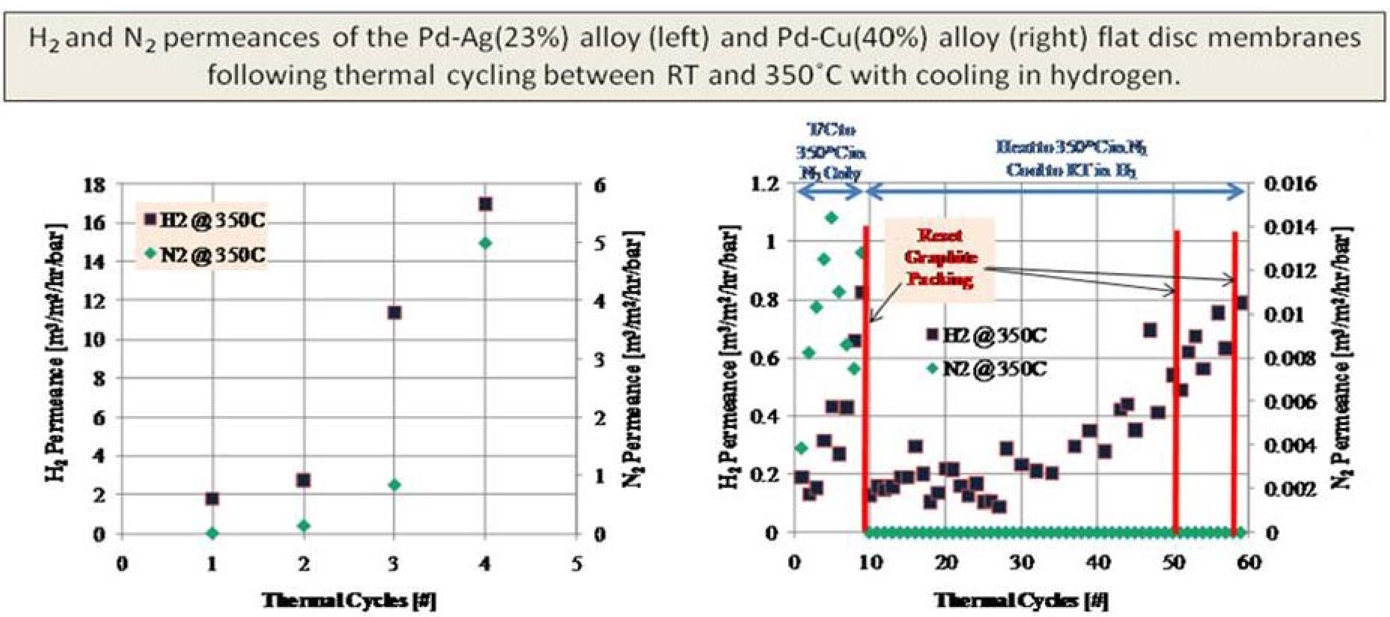

FIGURE 4. Evaluation of Pd-Ag vs. Pd-Cu for the Cooling Stability in the Presence of Hydrogen

for the Pd-Ag alloy deteriorates severely after 3-4 cycles while the Pd-Cu remains intact (i.e., N_2 permeance ≤0.01 $m^3/m^2/hr/bar$) for up to 60 cycles. In addition when the Pd-Au alloy was used in the Pd membrane considerable damage was exhibited throughout the test. In summary, we believe the Pd-Cu (40%) offers a fundamental basis for us to prepare a supported Pd membrane which can sustain the cooling in the presence of hydrogen. We will pursue fabrication of the Pd-Cu alloy membrane on our ceramic support in FY 2012.

Conclusions and Future Direction

- A newly developed potting technique has enabled packaging low-cost Pd membrane tubes into commercially viable bundles.
- Both pilot and field tests confirmed the separation efficiency of the Pd membrane bundles is similar to the performance of single membrane tubes.
- Bench-top feasibility tests indicate that the new post treatment strategy should reduce CO contamination to well below 10 ppm.
- A full-scale membrane reactor packed with our Pd membrane bundles and equipped with internal cooling coils has been designed and is currently under fabrication for the field test to be conducted in 2011.
- Commercially available Pd alloy foils of Pd-Ag (23%) and Pd-Cu (40%) remain intact through multiple cooling cycles, suggesting that Pd-Cu alloy could produce cooling stability for the reactor in the presence of hydrogen. This cooling stability is a desirable feature for our target application.

Our FY 2012 activities will be focused on the following areas:

- Complete fabrication and field test the full-scale membrane reactor packed with the Pd membrane bundles and equipped with cooling coils.
- Integrate the post-treatment strategy into the membrane reactor to deliver hydrogen product with <<10 ppm CO.
- Conduct a field test with the use of the membrane reactor at the participating end-user site.
- Develop the third generation Pd membrane with the cooling stability in the presence of hydrogen.

FY 2011 Publications and Presentations

1. Abdollahi, M., Yu, J., Liu, P.K.T., Ciora, R., Sahimi, M., and Tsotsis, T.T., "Process Intensification in Hydrogen Production from Syngas," *Ind. Eng. Chem. Res*., 49, 10986, 2010.

2. Tsotsis, T.T., Sahimi, M., Fayyaz-Najafi, B., Harale, A., Park, B.G., Liu, P.K.T., "Hybrid Adsorptive Membrane Reactor," *U.S. Patent* 7,897,122, March 1, 2011.

3. Abdollahi, M., Yu, J., Liu, P.K.T., Ciora, R., Sahimi, M., and Tsotsis, T.T., "Ultra Pure Hydrogen Production from Reformate Mixtures using a Palladium Membrane Reactor System," submitted to *J. Membrane Sci.*