II.C.1 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

Project Start Date: July 1, 2005
Projected End Date: December 31, 2012

Fiscal Year (FY) 2012 Objectives

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

- Develop a highly efficient and low temperature membrane-based WGS reaction process in a bench scale first, test it at a pilot scale, and finally demonstrate it 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 requirements for commercialization.
- Reduce the capital and operating costs for distributed hydrogen production applications.

Technical Barriers

Although various hydrogen selective membranes have been developed and reported in the literature, their use as a membrane reactor for hydrogen production has not been demonstrated commercially. Major technical barriers include:

- Testing/Analysis: few commercial scale membrane- and membrane reactor-based processes in operation
- Permeate Flux/Selectivity: cost vs. performance target to meet our end user requirements; in particular for cost sensitive applications
- Stability: lack of long-term membrane and membrane reactor performance data under our target field conditions

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 have been completed
- Operating Capability – 400 psi
- Hydrogen Recovery – >80% (of total gas)
- Hydrogen Quality – 99.99%

FY 2012 Accomplishments

- Completed the foil evaluation to choose a promising palladium alloy for asymmetric membrane development. Commercially available palladium-copper (Pd-Cu), palladium-silver (Pd-Ag) and palladium-gold (Pd-Au) foils along with the Pd foil (as control) were evaluated for their stability of cooling in hydrogen. The Pd-Cu foil shows structural stability through multiple cooling cycles in H_2 (i.e., >60 cycles), not Pd –Ag and Pd-Au.
- Developed palladium-copper alloy membranes that meet the cost vs. performance target set by DOE. Pd-Cu thin film (~5 µm) was successfully deposited on our commercial ceramic substrate with a H_2 permeance of 10-15 m^3/m^2/hr/bar at 350°C (i.e., 50-75 scfh @ 20 psig) and the selectivity of H_2/N_2 of 200 to >1,000, meeting the DOE 2015 cost vs. performance target.
- Verified the cooling stability in the presence of hydrogen. More than 10 PdCu membranes are currently undergoing cooling stability testing, i.e., cooling from 350°C to room temperature in the presence of H_2. Several of them have experienced >85 cycles with no signs of performance degradation.
- Designed and constructed membrane bundles which can accommodate (i) heat transfer requirement and (ii) flexibility in catalyst volume to membrane surface area ratio. Our unique membrane bundling configuration permits a membrane reactor that can be integrated with internal cooling coils without significant modifications

to the membrane housing and module for the exothermic WGS reaction. In addition, the bundling configuration allows flexibility in catalyst volume to surface area ratio.

- Assembling a test system for the field test. We currently are assembling the test unit/system around the membrane reactor to perform the field test in the 3rd and 4th quarter of 2012. The reformer and the membrane subunit have been fully tested to meet syngas productivity and separation and purification requirements (i.e., 16 liter/min syngas and <10 ppm CO).
- Continuing the long term thermal stability test of the Pd and Pd-Cu membranes. Thermal stability testing of our Pd membrane bundle is continuing as part of the test requirement to verify that the DOE performance specification is met. Stability for >9,000-10,000 hours at 350°C has been demonstrated for Pd and >600 hrs for PdCu membranes.

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 2010-2011, we completed the development and produced a test quantity of Pd membrane bundles for packaging into the membrane reactor to be field tested in 2011-2012. The project target of producing a hydrogen product stream with <<10 ppm CO has been achieved. Finally, we have identified a pathway to develop a Pd-based hydrogen membrane with cooling stability in the presence of hydrogen through evaluation of a series of Pd-alloy foils, which 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 & 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. Preparation of Palladium-Copper Alloy Membranes with Improved Material Stability: Although the Pd membranes we developed demonstrated excellent functional performance and thermal stability at the target application temperature, i.e., 350°C, its cooling stability in a hydrogen rich environment is poor. This result is consistent with those reported in the literature (discussed in Sec. 2). Our screening study conducted in 2010-2011 showed that Pd alloy with 40% Cu was superior to the foils made with Pd-Ag, Pd-Au, and pure Pd. During this year, we have focused on the deposition of the Pd-Cu thin film on porous ceramic substrate. Pd-Cu thin film (~5 µm) was successfully deposited on our commercial ceramic substrate with an H_2 permeance of 10-15 $m^3/m^2/hr/bar$ at 350°C (i.e., 50-75 scfh @ 20 psig) and the selectivity of H_2/N_2 of 200 to >1,000, meeting the DOE 2015 cost vs. performance target. Table 1 presents a summary of the Pd/Cu alloy membranes prepared during this year.

TABLE 1. Summary of the Pd/Cu Alloy Membranes Prepared

	Permeance [$M^3/m^2/hr/bar$] @350°C					
Sample ID	H_2	N_2	Selectivity	n^{th} Cooling Cycle	Cu [wt%]	Thickness [µm]
PdCu-500-51	11.9	0.044	271	65	44.5	5.0
PdCu-500-52	10.3	0.075	138	65	45.3	4.7
PdCu-500-53	9.1	0.007	1,379	Fail	45.4	5.4
PdCu-500-54	11.4	0.008	1,354	Fail	43.3	3.8
PdCu-500-57	10.9	0.010	1,136	16	42.8	3.0
PdCu-500-58	11.5	0.053	219	16	44.3	5.1
PdCu-500-60	7.9	0.032	248	26	40.3	5.0
PdCu-500-62	6.2	0.010	616	6	41.5	
PdCu-500-63	10.6	0.015	695	3	43.2	
PdCu-500-64	15.4	0.038	403	3	45.0	

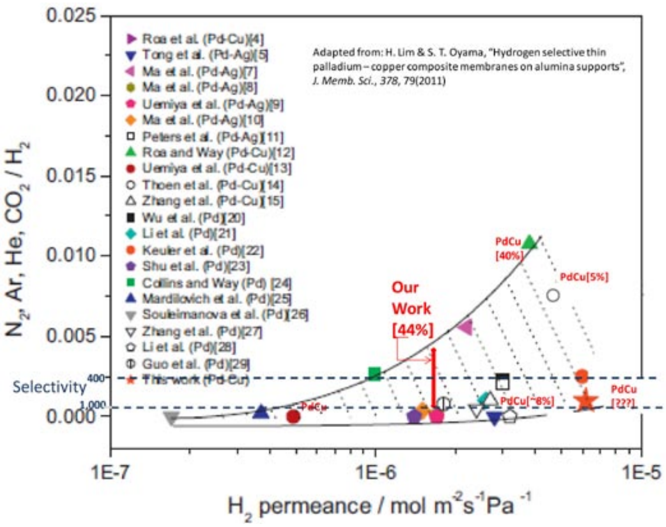

FIGURE 1. Hydrogen Permeances and Selectivity for PdCu Asymmetric Ceramic Membranes: Ours vs. Literature Study

Evidently our deposition technique allows us to deposit a rather consistent layer thickness (i.e., 3-5 um) and Cu content (~44 wt%). In comparison with the performance of the supported Pd/Cu membranes published in the literature shown in Figure 1, our Pd/Cu membrane demonstrates excellent balance in the performance vs. selectivity.

2. Long-Term Thermal Stability and Thermal Cycling in the Presence of H_2: Thermal cycling in the presence of H_2 is an important feature required of a commercially viable Pd membrane based upon our discussion with our end user. In this regard, work has been on-going over the past one year on the development of a Pd-alloy membrane that can tolerate thermal cycling in the presence of hydrogen. Figure 2 shows the N_2 permeance stability (leak rate) of the Pd alloy membrane. In all, 85 thermal cycles were conducted with little change in the H_2 permeance and only modest fluctuation in the N_2 permeance. In comparison, no other supported Pd membranes have demonstrated stability with an extended number of cooling cycles in an H_2-charged environment

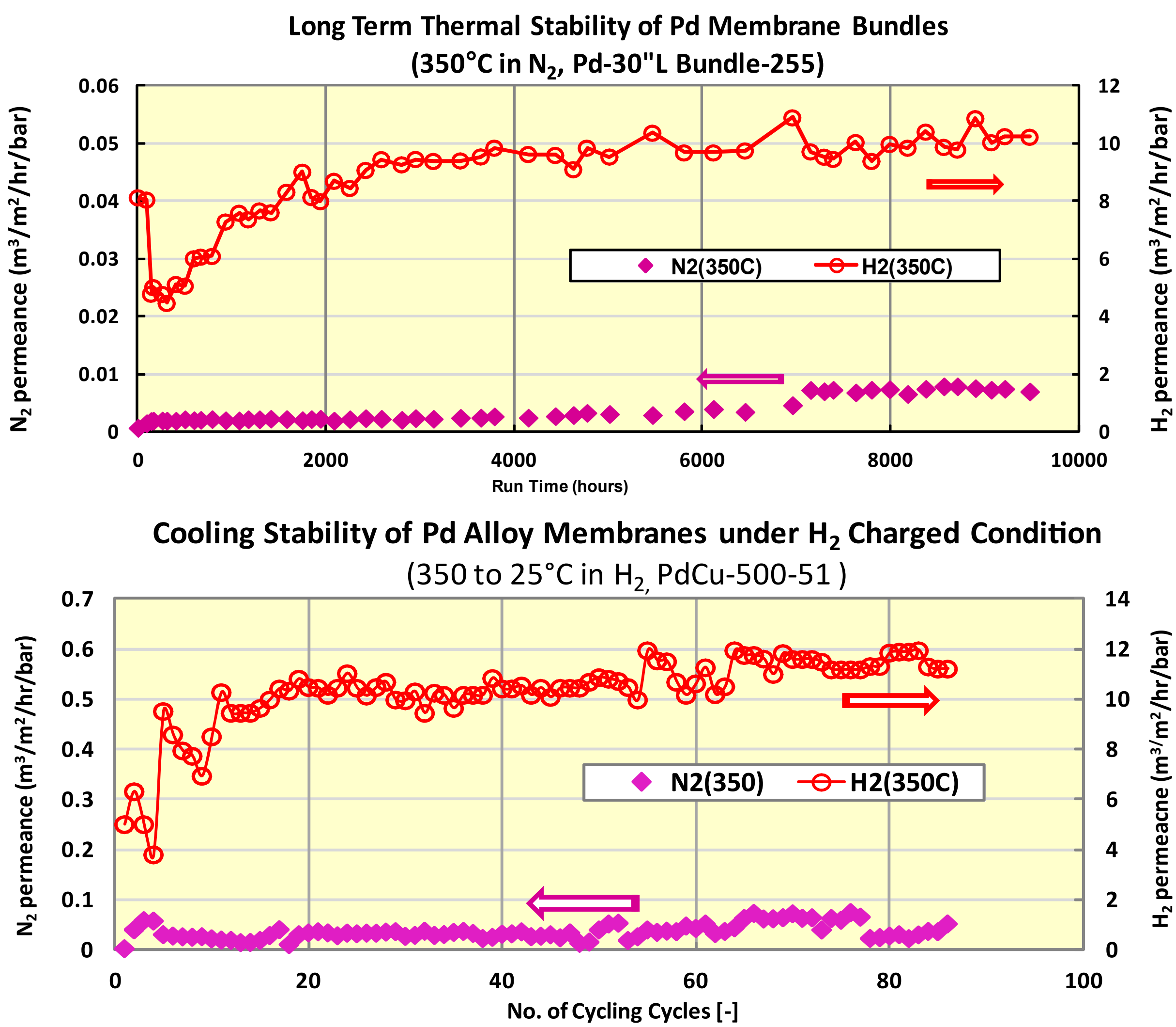

FIGURE 2. Palladium Membrane Stability: Long-Term Thermal Treatment and Cooling under Hydrogen Charged Atmosphere

as ours, in particular for the Pd membranes with ceramic substrate. In addition to thermal cycling stability, it is also important to establish the long-term membrane performance stability at high temperature. During this year, we continued our long-term performance stability testing of the palladium membrane, Pd-30” Bundle-255, at 350ºC in the presence of H_2 and N_2. Figure 2 shows the performance of the single tube bundle after ca. 10,000 hours of service. As can be seen, after the slight increase in the N_2 permeance of the -255 membrane at ca. 8,000 hours, the N_2 permeance stabilized. Overall, the Pd-based membranes we have been developing show very good long term stability in the presence of H_2 and N_2 at the expected minimum operating temperature of 350°C.

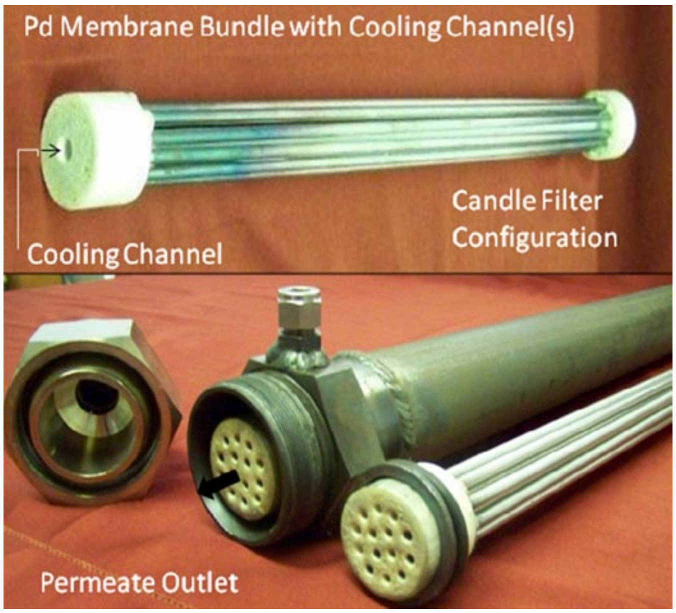

FIGURE 3. Fabrication of a Membrane Reactor for Pd Ceramic Composite Membrane with Integral Cooling Coil for the Target Exothermic WGS Reaction

3. Development and Construction of Membrane Reactors with Internal Cooling Features: Membrane bundles which can accommodate (i) heat transfer requirement and (ii) flexibility in catalyst volume to membrane surface area ratio are essential for a commercially viable membrane reactor, targeting exothermic WGS shift reaction. Our unique membrane bundling configuration as shown in Figure 3 permits a membrane reactor that can be integrated with internal cooling coils without significant modifications to the membrane housing and module. In addition, the bundling configuration allows flexibility in catalyst volume to surface area ratio. These bundles will be used for our field test to demonstrate its commercial viability.

4. Design, Construction, and Installation of a Hydrogen Production System for Field Test: Once the membrane reactor was constructed, we began the design, construction, and installation of the peripheral subsystem components for the field test. The reformer and the membrane subunit have been fully tested to meet syngas productivity and separation and purification requirements (i.e., 16 liter/min syngas and <10 ppm CO). As presented in Figure 4, the Pd membrane installed in the system is able to enrich the membrane from 62% to >99.9% purity. CO less than 10 ppm was obtained. With the post treatment, the CO contaminant level is expected to be << 10 ppm as reported in the previous annual report. The entire testing system is expected to be

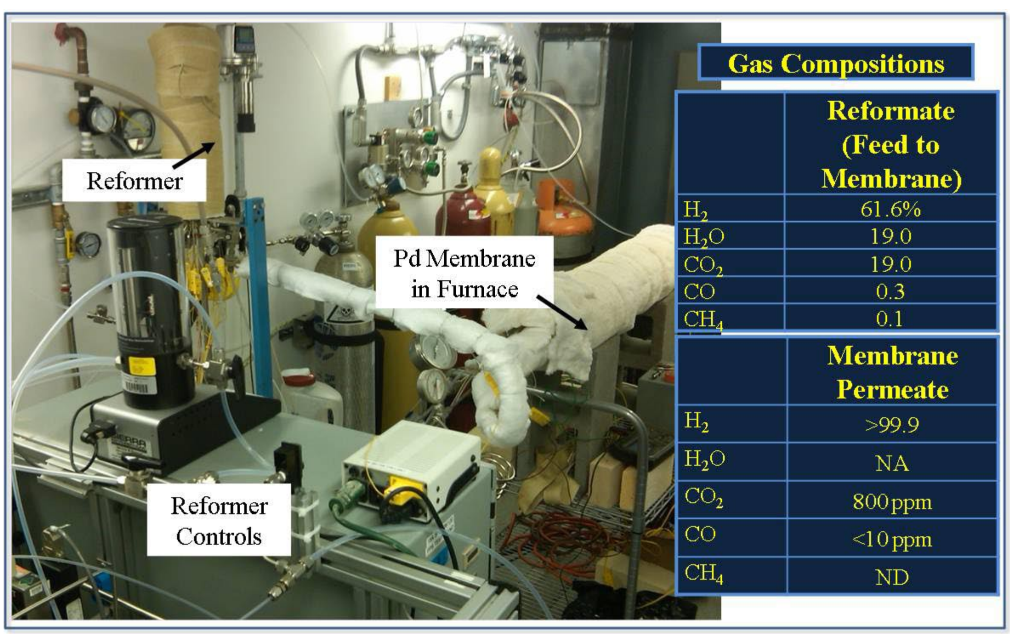

FIGURE 4. Reformer and Hydrogen Selective Membranes Installed and Fully Tested for the Field Test Unit

completely installed by the end June and ready for field test beginning July.

Conclusions and Future Directions

- Performance stability during thermal cycling in the presence of hydrogen is essential for the Pd membrane to be viable for portable power generation applications. Through a screening study with the commercially available Pd alloy foils, PdCu was identified as a promising alloy candidate. PdCu shows no sign of degradation for >60 cycles while PdAg shows degradation from the 2^{nd} cycle in our screening study.
- During this year, we have successfully deposited the PdCu alloy thin film (~5 µm) on our commercial ceramic substrate as an asymmetric Pd alloy membrane in terms of performance, and thermal and cooling stability.
- The Pd alloy membrane thus developed meets the cost performance target set by DOE for 2015, i.e., 0.6 scfh @ Δp=20 psi/unit $ membrane cost. In general, the permeance is 10-15 m^3/m^2/hr/bar with the selectivity of ≥~1,000 at 350°C.
- The Pd alloy membranes developed demonstrated performance stability during cooling from 350°C to room temperature in H_2 for >85 cycles as of today.
- A full-scale membrane reactor packed with our PdCu membrane bundle and equipped with an internal cooling device has been designed and is currently under fabrication. The reformer and the membrane subunits have been fully tested. The entire system is scheduled to be ready for field test by the 2^{nd} quarter 2012.

Our FY 2012-13 activities will be focused on the areas below:

1. Complete the field test system assembly which is equipped with a full-scale PdCu membrane bundle and integrated with internal cooling coils by the 2^{nd} quarter 2012.
2. Conduct a field test for 1 month (i.e., ~700 hrs) in the 3^{rd} quarter 2012. The target performance is 99.999% purity and >83% recovery of H_2.
3. Upgrade the permeance of the 3^{rd} generation Pd alloy membrane we have developed by the end of 2012 to the level similar to our existing 2^{nd} generation Pd membrane, i.e., H_2 permeance increase from 15 to 25 m^3/m^2/hr/bar.

FY 2012 Publications

1. M. Abdollahia, J. Yua, P. K.T. Liu, R. Ciora, M. Sahimia, and T.T Tsotsis, “Ultra-pure hydrogen production from reformate mixtures using a palladium membrane reactor system”, *Journal of Membrane Science,* 390–391,32 (2012) .