II.D.1 Composite Pd and Pd Alloy Porous Stainless Steel Membranes for Hydrogen Production and Process Intensification

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Contract Number: DE-FC26-07NT43058

Subcontractor:
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Project Start Date: May 7, 2007
Project End Date: May 6, 2010

Objectives

The primary project objectives are:

- Synthesis of composite palladium (Pd) and Pd/alloy porous Inconel membranes for water-gas shift (WGS) reactors with long-term thermal, chemical, and mechanical durability with special emphasis on the stability of hydrogen flux and selectivity.
- Demonstration of the effectiveness and long-term stability of the WGS membrane shift reactor for the production of fuel cell quality hydrogen.
- Research and development of advanced gas cleanup technologies for sulfur removal to reduce the sulfur compounds to <2 ppm.
- Development of a systematic framework towards process intensification to achieve higher efficiencies and enhanced performance at a lower cost.
- Rigorous analysis and characterization of the behavior of the resulting overall process system, as well as the design of reliable control and supervision/monitoring systems.
- Assessment of the economic viability of the proposed intensification strategy through a comprehensive calculation of the cost of energy output and its determinants (capital cost, operation cost, fuel cost, etc.), followed by comparative studies against other existing pertinent energy technologies.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Long-term selectivity and flux stability
- H_2 flux targets
- Mixed gas and WGS reaction studies
- Composite membrane reactor (CMR) modeling simulations
- Process intensification
- Adsorbent selection and testing

Technical Targets

A number of composite Pd and Pd/alloy porous Inconel membranes for WGS reactors have been and will be synthesized and their long-term thermal, chemical, and mechanical stability and hydrogen flux and selectivity have been determined. Technical targets and current membranes operational data are listed in Table 1.

Accomplishments

- Successfully synthesized a 4.2-µm thick, Pd/Inconel membrane and a 7.6-µm thick, Pd/Inconel membrane.
- Completed long-term hydrogen permeation and the selectivity stability testing of membranes (greater than 175 days or ~4,270 hours). Also completed extended tests of 3,550 hours over the temperature range of 400°C to 450°C. Showed that the helium (He) leak of a 7.6-µm thick, Pd/Inconel membrane was undetectable, indicating an essentially infinite H_2/He selectivity that remains stable.
- Demonstrated a hydrogen flux of ~166 standard cubic feet per hour (scfh)/ft^2, which is in close proximity to the U.S. Department of Energy's (DOE) 2010 target, based on a high-pressure (P_{high}=118 pounds per square inch absolute [psia], P_{low}=15 psia, ΔP=103 psia) hydrogen flux measurement at 450°C at the end of 3,550 hours. A small helium leak was detected after 3,550 hours that amounted to 0.016 scfh/ft^2, corresponding to an H_2/He selectivity

TABLE 1. Projected Technical Targets* and Test Data for a Number of Composite Pd and Pd Alloy Porous Membranes for Hydrogen Production

	DOE Targets§		Current WPI Membranes				
	2010	2015	#025R	#027	#029	#031	#032
Flux [scfh/ft²]	200	300	65.9	36.1	166	26.6	359
ΔP (psi) H_2 partial pressure (P_{Low}=15 psia)	100*	100*	15	15	100	15	100
Temperature [°C]	300-600	250-500	400	400	450	450	442
H_2/He Selectivity	n/a	n/a	~220	~120	∞	~4500	~450
Total Test Duration [hours]	n/a	n/a	1015	~1250	~4500	~2200	~523
Thickness [μm]	n/a	n/a	4.2 Pd	6.2 Pd/$Au_{5\ wt\%}$	7.6 Pd	7.0 Pd	3-5 Pd
WGS Activity	Yes	Yes	Not tested	Not tested	Not tested	Not tested	Not tested
CO Tolerance	Yes	Yes	Not tested	Not tested	Yes	Not tested	Not tested
S Tolerance [ppm]	20	>100	Not tested	Not tested	Not tested	Not tested	Not tested
H_2 Purity	99.5%	99.99%	99.0%	99.5%	≥99.999%	99.98%	99.8%
ΔP Operating Capability (Max. System Pressure, psi)	400	800-1000	15**	15**	225**	15**	100**

§ DOE-National Energy Technology Laboratory Test Protocol v7 – 05/10/2008.
*Standard conditions are 150 psia hydrogen feed pressure and 50 psia hydrogen sweep pressure.
** Maximum pressure tested; however, the ΔP can be higher since previous WPI membranes were tested up to 600 psi under metal-steam reforming reaction conditions.

of ~6,000 after 4,200 hours of testing. The leak is possibly due to hydrogen embrittlement, caused by the large flow rates of hydrogen at elevated pressures resulting in the temperature of the permeating hydrogen stream to drop below 300°C due to the convective cooling effects.

- Prepared a 7.0-μm thick, pure-Pd/Inconel membrane via an identical synthesis procedure to validate the re-producibility of the long-term selectivity stability (~4,270 hours) results achieved with the 7.6-μm thick pure, Pd/Inconel membrane.
- Achieved 99% total carbon monoxide (CO) conversion and 89.9% H_2 recovery in a 12.5 μm thick, Pd-based CMR operated at ~350°C, ΔP=200 psi (P_{Low}=15 psia) H_2O/CO=1.44 and gas hourly space velocity ($GHSV_{stp}$)=150 h^{-1}. Under similar conditions, $X_{CO,PBR}$ and $X_{CO,Eqm}$ were 92.7% and 93.4%, respectively.

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Introduction

Hydrogen is viewed as the fuel source for the 21st century. Coal may be converted into hydrogen using gasification technology. Given the abundance, availability, and cost-competitiveness of coal in the United States, coal will likely play a major role in hydrogen production for the 21st century. The WGS reaction is typically used to increase hydrogen yield from coal gasification. The products from the WGS reaction (carbon dioxide [CO_2] and hydrogen) are separated at high (>95 percent) levels of purity using membranes. Combining the WGS reaction and hydrogen separation reduces capital costs and improves efficiency.

Since the separation of hydrogen in the WGS reaction requires high fluxes, as well as high separation selectivity and ability to operate at elevated temperatures, dense metal membranes, particularly Pd-based membranes are well suited for this type of applications.

The objective of this project is to reduce the number of unit operations required for hydrogen production through process intensification. In collaboration with Adsorption Research, Inc., WPI will produce an advanced synthesis gas (syngas) cleanup system and an asymmetric composite Pd-Pd/alloy membrane integrated downstream of the coal gasifier. The high-pressure CO_2 from the membrane shifter would be appropriate for recycling, sequestration, and/or conversion to industrially useful products. Compared with unsupported metal membranes, the development of an asymmetric composite membrane with a porous support and thin Pd or Pd-alloy dense layers would provide both higher trans-membrane flux and lower Pd loading.

Approach

This project will develop an integrated, cost-effective, hydrogen production and separation process using a unique hydrogen separation membrane for WGS reactors under process intensification conditions. A patented (WPI) membrane synthesis process has been used to synthesize thin layer Pd membranes. The process consists of pre-treatment of the porous metal support, in situ formation of an oxide layer to minimize the inter-metallic diffusion for long-term membrane stability, and surface activation and plating of Pd by electroless plating. Specific targets are for production of a Pd layer around 3-5 µm, as well as successful production of Pd/alloy layers of ~2 µm or less.

The synthesized membranes are characterized for their hydrogen permeation characteristics and potential membrane reactor performance. The characterization will include a determination of the hydrogen mass transfer characteristics associated with the membrane configuration and evaluation of the thermal and mechanical stability properties of the membrane through multiple thermal cycling. Characterizations will be conducted on Pd, Pd/gold (Au), and Pd/copper (Cu) membranes. The hydrogen permeation tests will examine effects of Pd alloy compositions and exposure of the membranes to gas mixtures containing sulfur.

Figure 1 shows the test set-up for measurements of membrane properties and permeation rates.

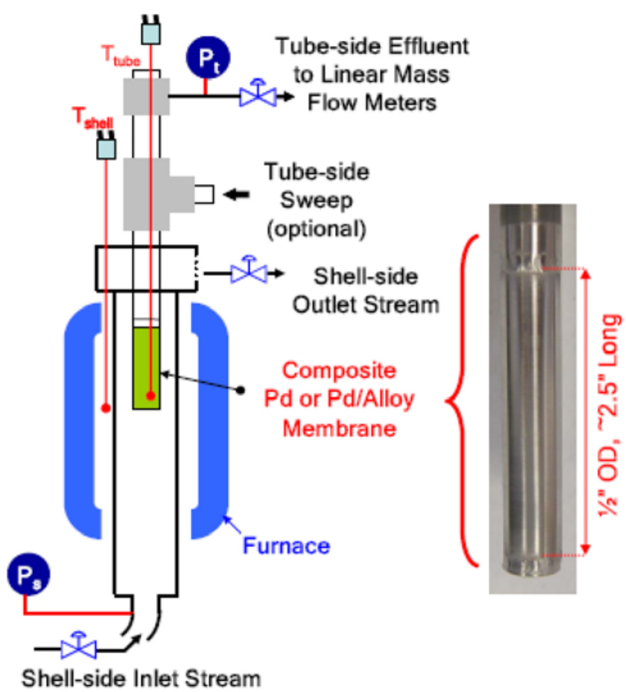

FIGURE 1. Set-Up for Membrane Properties and Permeation Tests

Results

Hydrogen characterization of composite Pd/Inconel membranes was determined under various conditions. Figure 2 displays long-term H_2/He selectivity and flux over a total testing period of ~3,550 hours (>147 days) at temperatures up to 450°C (membrane #029).

- High pressure flux measurements of the membrane #029 (7.6 µm thick pure-Pd/Inconel) at ~400 and 450°C and at a ΔP of ~100 psi (P_{High}=115 psia and P_{Low}=15 psia) led to a H_2 flux of ~150 and ~166 scfh/ft^2, respectively.
- The excellent H_2/He selectivity stability of membrane #029 over the temperature range of 300 to 450°C, was successfully reproduced with the membrane #031 (7 µm thick pure-Pd/Inconel).
- At ~450°C and at a ΔP of 15 psi (P_{High} = 30 psia), the H_2 flux and the final H_2/He selectivity were ~26.6 scfh/ft^2 and ~4,500, respectively, after a total testing period of ~2,200 hours (>90 days).

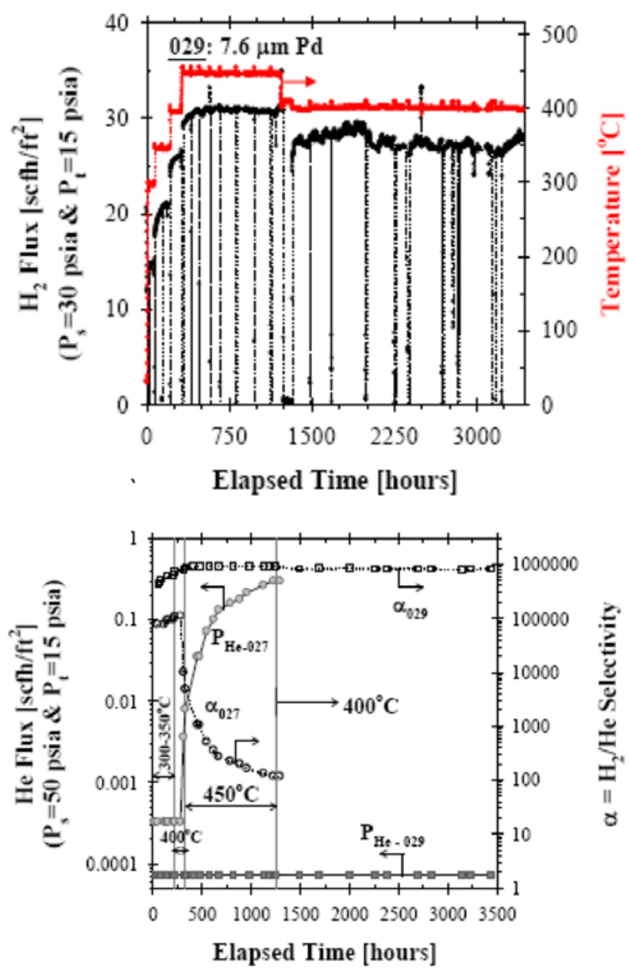

FIGURE 2. H_2/He Selectivity and Flux over a Testing Period of ~3,550 Hours and Under Different Pressure and Temperature Conditions

- At 442°C and at a ΔP of 100 psi (P_{High}=115 psia), the H_2 flux of the 3-5 µm thick Pd/Inconel membrane #032 was as high as ~359 scfh/ft^2 at the end of ~285 hours of testing with H_2/He selectivity of ~450, which exceeded the DOE's 2010 and 2015 H_2 flux targets.

Conclusions and Future Directions

Membranes developed and tested through this project show excellent long-term H_2/He selectivity and stability over a testing period of about 3,550 hours. A 99% total CO conversion and 89.9% H_2 recovery in a 12.5 µm thick Pd-based CMR operated at 350°C, ΔP=200 psi (PLow=15 psia) have been achieved.

Future work will:

- Continue WGS reaction and mixed gas testing studies.
- Complete 2010 technical target screening and qualification tests.
- Synthesize thin separation layers to achieve higher H_2 flux using support with minimum mass transfer resistance.
- Continue Pd/Au alloying studies to improve H_2 flux.
- Further refine and improve the CMR model (i.e., 2-dimensional non-isothermal finite element modeling via the Comsol Multiphysics).
- Conduct long-term sulfur poisoning and recovery experiments.
- Continue process intensification and performance assessment analyses coupled with process control strategies.
- Complete building and testing of a pressure swing adsorption system.
- Continue synthesis of new Pd and Pd/Au membranes to improve the H_2 flux.
- Test Pd/Au membranes for long-term H_2/He selectivity stability at 450°C and sulfur tolerance within the temperature range of 300 to 450°C.
- Initiate economical analysis for the proposed process intensification framework.

FY 2009 Publications/Presentations

1. Ayturk, M.E., Kazantzis, N.K. and Ma, Y.H, *"Modeling and Performance Assessment of Pd- and Pd/Au-based catalytic Membrane Reactors for Hydrogen Production,"* Energy and environmental Science, 2, 430 – 438 (2009).

2. Ayturk, M.E. and Ma, Y.H,. "Defect-Free Composite Pd Membranes with High Temperature Long-Term Stability," in preparation.

3. Ma, Y.H., Ayturk, M.E., Agustine, A.S., and Kazantzis, N., *"Palladium Membrane Reactor for Water Gas Shift Reaction,"* Submitted to the Catalysis Today.

4. Ma, Y.H., Ayturk, M.E., Agustine, A.S., and Kazantzis, N., *"Palladium Membrane Reactor for Water Gas Shift Reaction,"* Presented at the 9th International Conference on catalysis in Membrane Reactors (ICCMR9), June 28 – July 2, 2009, Lyon, France.

5. Ma, Y.H., Kazantzis, N., Ayturk, M.E., Pomerantz, N. and Chen, C.-H., *"Synthesis and Long-Term Characterization of Sulfur Tolerant Pd/Cu and Pd/Au Alloy Membranes for Hydrogen production via catalytic Membrane Reactor Applications."* Proceedings of the 10th Intl. Conf. on Inorganic Membranes (ICM10), Tokyo, Japan, 2008.