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

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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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(N) Hydrogen Selectivity
(P) Flux
(N) Hydrogen Selectivity
(K) Durability

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 Pd, Pd/Cu and Pd/Au membranes on 316L porous stainless steel and porous Inconel supports and demonstrated high permeances and selectivities which exceeded the DOE 2010 targets.
- Completed characterizations and stability testing of the Pd, Pd/Au and Pd/Cu membranes in the temperature range of 350-525°C.
- Successfully implemented a one-dimensional simulation to predict the optimal operating conditions for isothermal and adiabatic WGS-composite membrane reactors (CMRs) for process intensification. The model was accurate in predicting the experimental CO conversion values.
- Demonstrated the cost effectiveness of the isothermal CMRs over the non-isothermal CMRs with an unsteady-state WGS-CMR process control model.
- Achieved experimentally a 98% CO conversion and 87 and 85% H_2 recovery at 400 and 450°C, respectively in a Pd-based WGS–CMR operated at: $\Delta P = 212$ psi (P_{Low}=14.7 psia), $H_2O/CO = 2.6$ and gas hourly space velocity (GHSV) = 1,000 h^{-1}. The

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/ft^2]	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 membrane steam reformer reaction conditions.

long-term stability of the CO conversion and H_2 recovery were demonstrated for 80 h.

- Demonstrated the tolerance of Pd/Au and Pd/Cu membranes to H_2S over the temperature range of 350-500°C and atmospheres of 0.2–50 ppm H_2S/H_2 mixtures.
- Demonstrated for pressure swing absorption (PSA) that for five component gas mixtures with 1,000 ppm H_2S, the H_2S absorbent 5A achieved He recoveries of 99% and the product stream contained less than 0.05 ppm H_2S if a recycle of the blowdown gas was used.

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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 application.

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. (ARI), Worcester Polytechnic Institute (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.

Approaches

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 valuation 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.

Results

Several high permeance Pd, Pd/Au and Pd/Cu membranes were tested in pure H_2 and He atmospheres for permeation and selectivity characterization. Figure 2 shows the Sieverts' Law regressions performed at 450°C for the Pd membranes #038 and #039.

- Figure 2 shows that both #038 and #039 followed Sieverts' Law and exceeded the DOE 2010 target with fluxes of 250 and 225 scfh/ft^2 respectively, at a ΔP of 100 psi (P_{low} = 14.7 psia). The selectivities were 250 and 240 respectively, yielding a H_2 purity of 99.6 and 99.58%, also meeting the 2010 DOE target. Furthermore, the Pd and Pd/alloy membranes also exceeded DOE 2010 flux and hydrogen purity targets.

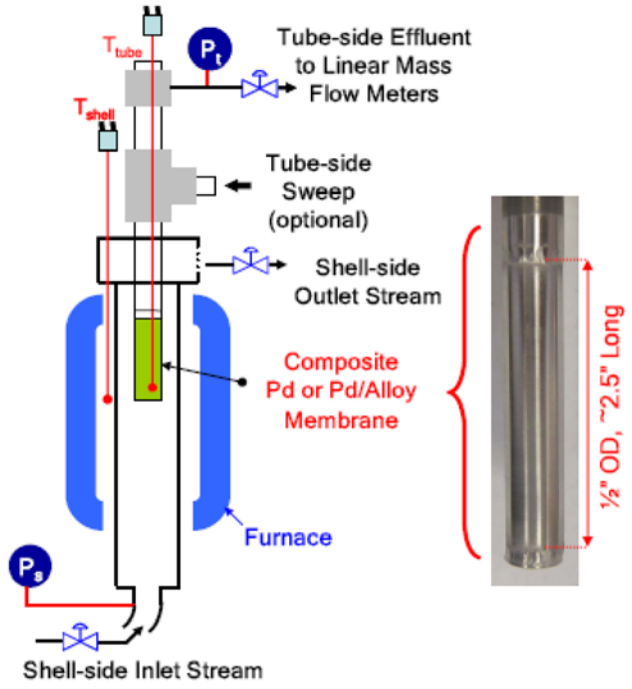

FIGURE 1. Set-Up for Membrane Properties and Permeation Tests

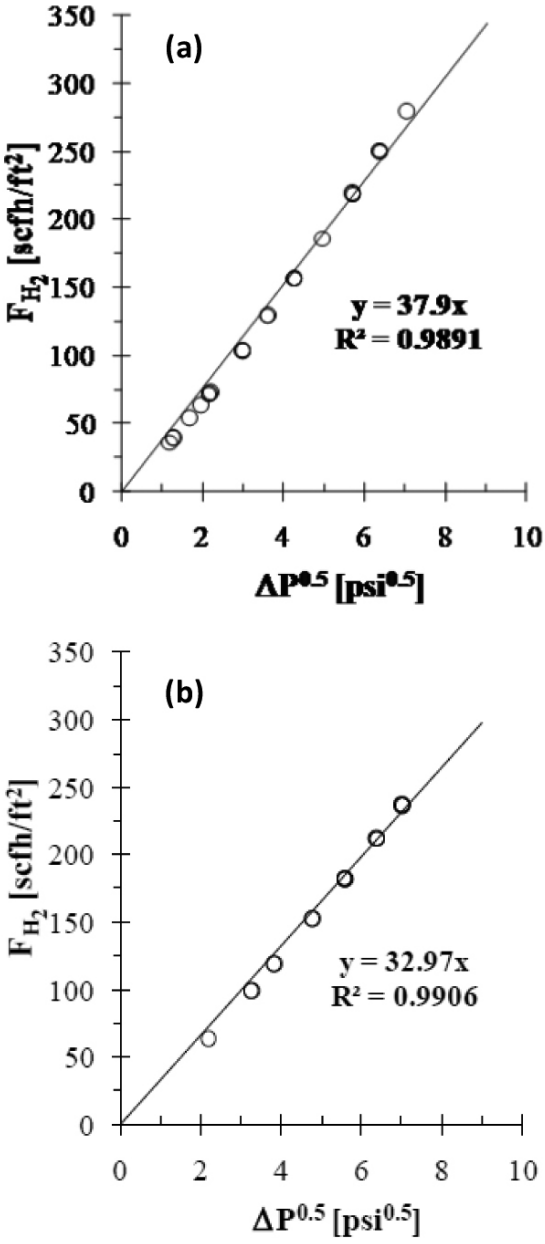

FIGURE 2. High Pressure Sieverts' Law Regressions at 450°C for Membranes (a) #038 and (b) #039.

- WGS-CMR experiments using syngas feed (41.6% CO, 40.3% H_2 and 18.1% CO_2 [dry basis]) achieved CO conversions of 97.9% (15% above equilibrium) at 400ºC with a ΔP of 212 psi (P_{low} = 14.7 psia) and GHSV values of 1,100 h^{-1}. Conversions of 98.2% (5.2% above equilibrium) were achieved at 450ºC with a GHSV of 2,900 h^{-1}. A simple mathematical model predicted the experimental conversion data reasonably well.
- H_2 recoveries of 87% were achieved at 400°C and a GHSV of 1,000 h^{-1}. However, the simulation exceeded the experimental H_2 recovery data by as much as 20% at high GHSV values due to not accounting for radial mass transfer resistance in the simple model.
- The long-term WGS-CMR experiment showed that the system reached steady-state within one hour and remained stable for 80 h. While the membrane permeance remained constant, the selectivity declined from 4,000 to 400 over the duration of the experiment.
- A comprehensive approach to process intensification has been developed that integrates process modeling and performance monitoring for safety and control to optimize performance levels, favorable process economics, efficiency and safe operation resulting from smaller units, identification of advantageous operating conditions, catalyst use and energy input. A 10 µm Pd tubular membrane was used in the calculations (0.5" outside diameter x 2.5" long).
- The model predicted that isothermal operation at 450°C resulted in a maximum CO conversion and H_2 recovery of 97 and 91% respectively, while operating at and above 60% permeability of the Pd foil. Adiabatic operation yielded slightly higher conversions than the isothermal operation at 98–99% for GHSV values below 4,000 h^{-1} at a permeability of 60% of the Pd foil. However, adiabatic operation caused hot spots to form exceeding 565°C, which would be detrimental to the stability of both the membrane permeance and selectivity.
- The model further predicted that the flux ratio of H_2 to the other components (CO, CO_2, H_2O) had little effect on the CO conversion for both isothermal and adiabatic CMRs. However, to prevent the conversion from decreasing by 3% or more, the separation factors of the isothermal and adiabatic CMRs would need to be at or above 15,000 and 7,500, respectively. Reducing the catalyst weight from 15 to 0.3 g resulted in no decrease in the conversion for both adiabatic and isothermal CMRs, allowing for a more efficient use of catalyst.
- Exposing Pd and Pd alloy membranes to H_2S resulted in an increasing permeance decline with increasing H_2S feed concentration. However, at 15 ppm the Pd membrane formed a bulk Pd_4S which destroyed the membrane. The Pd/Cu and Pd/Au membranes both reached a steady-state values of permenace, retained their selective properties and did not form bulk sulfides within the H_2 selective layer even up to 50 ppm H_2S/H_2 mixtures. At concentrations <5 ppm H_2S, the Pd/Cu membrane performed better than the Pd/Au membrane which performed better than the Pd membrane.
- Higher temperatures were required to recover the permeance loss during poisoning due to the exothermic nature of H_2S adsorption on metals. Roughly 80% of the permeance of the Pd/Cu membrane could be recovered at 500°C after poisoning. At 500°C, the recovery in H_2 was nearly 100% for Pd/Au membranes.
- Based on the isotherms and diffusivity tests for the gas phase components, the two best adsorbent candidates for H_2S were 5A and Hisiv 3000. 5A was deemed the better choice due to the higher adsorption capacity and H_2 recovery and lower cost.
- For five component mixtures with 200 ppm H_2S, He recoveries up to 98.76% could be achieved with no H_2S detected in the product stream if a recycle of the blowdown gas was used. Increasing the H_2S concentration to 1,000 ppm resulted in several hundred ppb H_2S detected in the product stream with He recoveries up to 99.10%. Further increasing the H_2S concentration to 4,800 and 9,500 ppm reduced the He recoveries to roughly 91 and 88% respectively, and increased the H_2S in the product stream to a few ppm.

Conclusions and Future Directions

The membranes developed and tested during this period exceeded both the DOE 2010 flux and selectivity targets. The membrane stability during long-term WGS reactions and atmospheres containing small quantities of H_2S has been demonstrated. High CO conversions (98%) and H_2 recoveries (87%) have been achieved in the Pd-based WGS-CMRs and simulations incorporating process control, capable of predicting the experimental CO conversion values, have predicted the optimal conditions for isothermal and non-isothermal WGS-CMR operation for process intensification. The adsorbent 5A was deemed to be the best choice for PSA and yielded He recoveries as high as 99% for five component gas mixtures which included 1,000 ppm H_2S.

Future work will:

- Continue long-term WGS reaction studies with and without H_2S for Pd, Pd/Au and Pd/Cu membranes.
- Complete 2010 technical target screening and qualification tests.

- Improve flux and selectivity of Pd, Pd/Au and Pd/Cu membranes.
- Initiate economical analysis for the proposed process intensification framework.
- Add carbon oxysulfide to the feed mixture for PSA testing.

FY 2010 Publications/Presentations

1. Augustine, A.S., Ayturk, M.E. and Ma, Y.H. "*Composite Pd membrane reactor for H_2 production with syngas feed*." Presented at NAMS 2010/ICIM 11, Washington, D.C., July 17–22, 2010.

2. Chen, C.H. and Ma, Y.H. "*Effect of H_2S concentration on H_2 permeance of a composite Pd/Au H_2 separation membrane prepared by galvanic displacement*." Presented at the ACS 239th National Meeting and Exposition, San Francisco, CA, USA, March 21–25, 2010.

3. Chen, C.H. and Ma, Y.H. "*The effect of Au content in composite Pd/Au membranes prepared by galvanic displacement on H_2 permeation and H_2S resistance*." To be presented at the AIChE Annual Meeting 2010, Salt Lake City, UT, USA, November 7–12, 2010.

4. Chen, C.H. and Ma, Y.H. "*The effect of H_2S on the performance of Pd and Pd/Au composite membranes*." In Press, Journal of Membrane Science.

5. Koc, R., Kazantzis, N.K. and Ma, Y.H. "*A process dynamic modeling framework for performance assessment of Pd-based membrane reactors*." Presented at NAMS 2010/ICIM 11, Washington, D.C., July 17–22, 2010.

6. Koc, R., Kazantzis, N.K. and Ma, Y.H. "*A process modeling framework for performance assessment of Pd-based water-gas-shift membrane reactors*." To be presented at the AIChE Annual Meeting 2010, Salt Lake City, UT, USA, November 7–12, 2010.

7. Koc, R., Kazantzis, N.K. and Ma, Y.H. "*A theoretical study to integrate the Pd-based water gas shift membrane reactors into the IGCC plants*." To be presented at the ACS 240th National Meeting and Exposition, Boston, MA, USA, August 22–26, 2010.

8. Ma, Y.H. and Pomerantz, N. "*Pd-based membrane reactor for simultaneous H_2 production, CO_2 sequestration and process intensification*." Presented at the 2010 International Membrane Conference of Taiwan (IMCT), Chung-Li, Taiwan, May 28, 2010.

9. Pomerantz, N. and Ma, Y.H. "*A novel method for high H_2 permeance Pd/Cu alloy membranes in the sulfur tolerant fcc phase*." Submitted, Journal of Membrane Science.

10. Pomerantz, N. and Ma, Y.H. "*Effect of H_2S on the performance and long-term stability of Pd/Cu membranes*." Industrial & Engineering Chemistry Research. 48(8) (2009) 4030 - 4039.

11. Pomerantz, N. and Ma, Y.H. "*Effect of mass transfer on Cu plating rate and deposition morphology for Pd/Cu alloy membranes for H_2 separation*." Presented at the ACS 239th National Meeting and Exposition, San Francisco, CA, USA, March 21–25, 2010.

12. Pomerantz, N., Meyer III, H., Chen, C. and Ma, Y.H. "*Sulfur poisoning studies of high permeance Pd/Cu alloy membranes for H_2 separation from coal gas*." Presented at NAMS 2010/ICIM 11, Washington, D.C., July 17 – 22, 2010.

13. Pomerantz, N., Meyer III, H., Payzant, E.A., and Ma, Y.H. "*Fabrication, characterization and testing of high permeance Pd/Cu alloy membranes for H_2 separation from coal gas*." Presented at NAMS 2010/ICIM 11, Washington, D.C., July 17–22, 2010.

14. Pomerantz, N., Payzant, E.A. and Ma, Y.H. "*Isothermal solid-state transformation kinetics applied to Pd/Cu alloy membrane fabrication*." In press, AIChE Journal.