II.D.4 Composite Pd and Alloy Porous Stainless Steel Membranes for Hydrogen Production and Process Intensification

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Fiscal Year (FY) 2011 Objectives

- Synthesis of composite Pd and Pd/alloy porous metal (316L, Inconel, Hastelloy) membranes for water-gas shift (WGS) reactors with long-term thermal, chemical, and mechanical stability with special emphasis on the stability of H_2 flux and selectivity.
- Demonstration of the effectiveness and long-term stability of the WGS membrane shift reactor for the production of fuel cell quality H_2.
- Research and development of advanced gas clean-up technologies for sulfur removal to reduce the sulfur compounds to <2 ppm (ARI).
- 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 Pd-based membrane reactors integrated into integrated gasification combined cycle (IGCC) plants 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 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:

(K) Durability associated with the determination of optimum temperature for the WGS reaction.

(L) Impurities associated with adsorbent selection and pressure swing adsorption (PSA) system build-up, testing completed with syngas + H_2O, H_2S and carbon oxysulfide (COS).

(M) Membrane defects associated with the study of membrane surface upon WGS reaction.

(N) Hydrogen selectivity, leak growth will be mitigated by working at 400-450°C.

(P) Flux and reproducibility of high H_2 flux targets already achieved. Setting of Pd thickness and support characteristics to meet 2015 DOE targets.

(R) Cost, two-dimensional (2D) model for catalytic membrane reactor (CMR) simulations, safety and economic analysis.

Technical Targets

A number of composite Pd and Pd/alloy porous metal (316L, Inconel, Hastelloy) membranes for WGS reactors have been synthesized and 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. The typical microstructure of composite Pd membranes listed in Table 1 is shown in Figure 1.

This project is conducting fundamental studies on composite Pd membranes permeance and selectivity stability in WGS reaction conditions. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2011 hydrogen storage targets:

- Durability (K): we are targeting a 1,000 hour WGS reaction long-term experiment with a stable H_2 permeance and H_2/He selectivity.
- Impurities (L): membranes were tested up to 20 ppm H_2S in pure H_2.
- Membrane defects (M): All membrane surfaces were studied after testing to investigate surface changes in syngas atmospheres.
- Hydrogen selectivity (N): a selectivity (H_2/N_2) of 10,000 at 180 psig was targeted.

TABLE 1. Characteristics and Results of Tested Pd Membranes at WPI

	DOE Targets		Current WPI membranes					
	2010	2015	#029	#031	#33	#038	#039	#RK04
Thickness (μm)	n/a	n/a	7.6	7	8.7	6	7.3	13
Flux (scfh/ft^2)	200	300	166	26.6	72.5	196	171	114
ΔP (psi) H_2 Partial Pressure (P_{low} = 14.7 psi)	100	100	100	15	100	100	100	100
Temp. (°C)	300-600	250-500	450	450	450	450	450	450
H_2/He Ideal Selectivity	n/a	n/a	∞	4,500	9,725	330	335	1,000
Test duration (hrs.)	n/a	n/a	4,500	2,200	800	170	165	1,250
WGS activity	Yes	Yes	Not tested	Not tested	Not tested	Not tested	Not tested	Not tested
CO Tolerance	Yes	Yes	Yes	Not tested	Not tested	Not tested	Not tested	Not tested
S Tolerance	20	>100	Not tested	Not tested	Not tested	Not tested	Not tested	Not tested
H_2 Purity At 180 psig	99.5	99.99	>99.999	>99.98	>99.99	>99	>99	>99.9
ΔP Operating Capability (Max System Pressure, psi)	400	800-1,000	225	15	100	30	100	100

n/a – not applicable

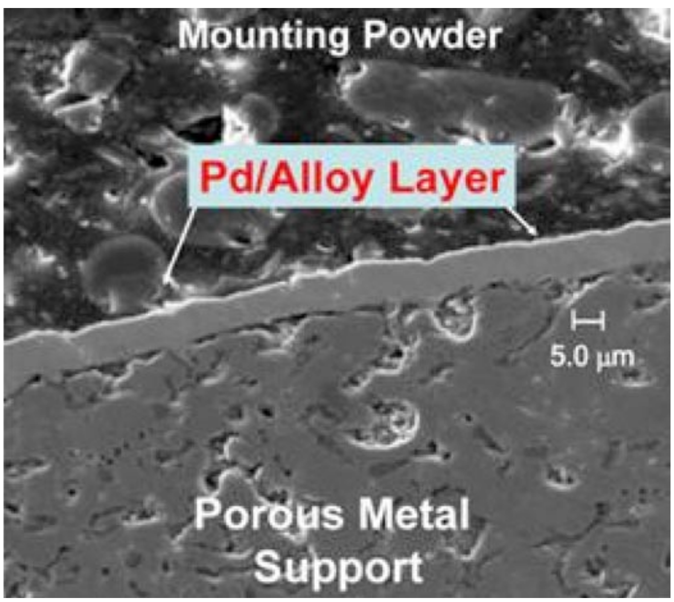

FIGURE 1. Composite Pd/Porous Metal Support Microstructure

- Flux (P): H_2 permeances ranging from 29.2 to 43.8 scfh/ft^2 psi$^{0.5}$ were targeted to achieve DOE 2010-2015 targets.
- Cost (R): 1,000 \$/ft^2 to meet DOE's target.

FY 2011 Accomplishments

- Shown and re-produced selectivity H_2/He stability at 400-450°C over thousands of hours.
- Consistently achieved composite Pd membranes with thicknesses ranging between 4-12 μm porous metal supports indicating the reproducibility of our fabrication method.
- Pd/316L-PSS membranes have been synthesized and tested under WGS and H_2/H_2O mixed gas conditions at 400°C for 65 and 225 hours, respectively. The membrane leak growth was less than 11% over those testing periods.
- An integration option of the WGS-composite membrane reactor into IGCC plants was proposed and the performance of the industrial-scale WGS-composite membrane reactor's performance was assessed via a more accurate 2D model to achieve 98% CO conversion and 95% H_2 recovery.
- In the net present value (NPV)-based comparative assessment analysis, the positive NPV of \$40M for IGCC-membrane reactor (MR) with carbon capture with a net power output of 550 MW showed the advantage of the membrane reactor technology over more traditional options such as supercritical pulverized coal (SC-PC), IGCC baseline, IGCC-PBR (IGCC with traditional packed bed reactor) with CO_2 capture in the presence of CO_2 taxes.
- The uncertainty analysis performed with the Monte-Carlo techniques to access the risk associated with the Pd-based membrane reactor technology indicated that regulatory action on CO_2 emissions would induce an appealing NPV profile for the IGCC-MR technology option.
- Accomplished PSA studies in collaboration with ARI.

Introduction

Combining the coal-derived syngas WGS reaction in a Pd-based membrane reactor leads to high purity hydrogen (>99.999%), high pressure CO_2 ready to be sequestered and energy and capital costs savings. The integration of the membrane technology into coal-fired power plants is an attractive option particularly due to benefits associated with both H_2 and CO_2 separation. MR technology should be economically competitive with the SC-PC, IGCC baseline and IGCC-PBR. Thus, the NPV-based economical analysis was performed on the basis of co-production of hydrogen and power from coal using Pd-based composite membrane reactors with sequestration. Moreover, the inherent uncertainty of the inputs of the NPV model has to be recognized and explicitly taken into account in investment decision-making.

However, coal gasification feedstocks raised challenges such as hydrogen permeance stability under H_2S, COS and heavy metal pollutants [1,2]. Selectivity stability was the second largest challenge since thin electrolessly deposited membranes developed leaks at temperatures ranging from 400 to 450°C [3]. The objective of this project was to develop a membrane module for the production of hydrogen using WGS reaction working at temperatures close to 450°C and under real gasification conditions.

Approach

Composite Pd membrane preparation consisted of the pretreatment of the porous stainless steel support i.e. deposition of an intermetallic diffusion barrier and a grading layer, surface activation and Pd deposition by the electroless plating method [4-5]. Pd thicknesses of 4-12 microns were targeted in order to reach DOE's flux target without compromising H_2/He leak stability at 450-500°C. WPI worked in collaboration with ARI to develop a PSA process to decrease contaminants level in syngas feed. In a parallel fashion Pd-Au alloy membranes and special protective coatings are being developed at WPI to mitigate H_2S and other coal contaminants. A complete WGS-CMR, seen in Figure 2, was also built at WPI to test 1-inch outer diameter, 10-inch long composite Pd membranes with synthetic syngas shown in Figure 3.

A comprehensive economic analysis was performed to identify the industrial-scale membrane reactor module cost, capital and operating and maintenance costs of the whole IGCC plant with the Pd-based membrane reactor technology. The NPV model was included into the economical analysis to compare the profitability of power plants with a net power output of 550 MWe both with and without future CO_2 taxes. In addition, the consequences and impact on project value of uncertain futures was calculated with the Monte Carlo simulation effectively. Detailed Monte Carlo simulations integrated into the detailed NPV model were performed in order to explicitly take into account the main uncertainty drivers associated with the NPV of the whole IGCC-MR, namely, the plant capacity factor, initial CO_2 tax, CO_2 tax growth rate, nominal discount rate, inflation rate, electricity selling price, Pd price, support price and membrane life.

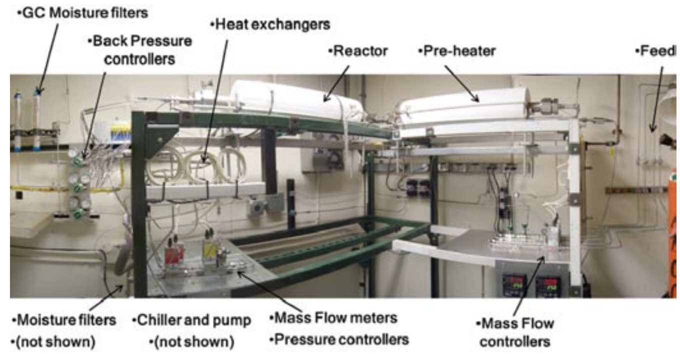

FIGURE 2. WGS-CMR for the Test of 1-Inch Outer Diameter, 10-Inch Long Composite Pd-Alloy/Porous Metal Membranes

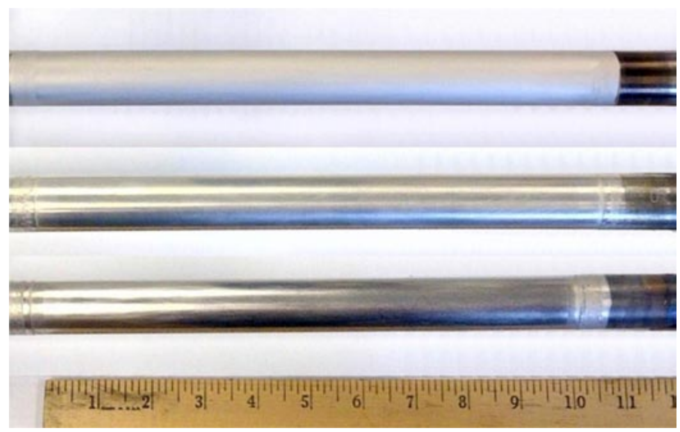

FIGURE 3. 1-Inch Outer Diameter, 10-Inch Long Pd/Porous 316L Composite Membranes

Results

- Achieved excellent long-term H_2/He selectivity stability, of essentially infinite value, over over a total testing period of ~3,550 hours (>147 days) at 300-450°C and at a ΔP of 15-100 psi (P_{Low}=15 psia).
- At 450°C, achieved re-producible, long-term H_2/He selectivity stability with several membranes with H_2 purity ≥99.99% over a testing period of 30 to 90 days.
- Achieved flux of ~359 scfh/ft^2, which exceeded DOE's 2010 and 2015 H_2 flux targets (T=442°C and ΔP of 100 psi [with P_{Low}=15 psia]). Such high fluxes were also achieved on high surface area composite Pd membranes 1-inch outer diameter, 10-inch long shown in Figure 3.
- Conducted an additional ~3,000 hours of mixed gas permeation experiments (61.7% H_2, 37.1% CO_2 & 1.2% carbon monoxide [CO] w/ and w/o 19% steam).

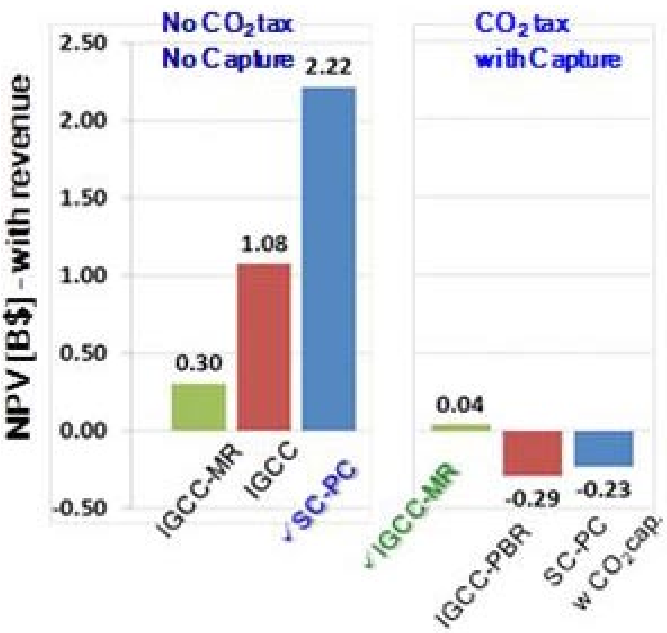

FIGURE 4. Single-Point NPV with Revenue Results of the Power Plants in Case of no CO_2 Tax (Without Capture) and with CO_2 Tax (With Capture)

- Reduced the number of synthesis steps for the large-scale membrane preparation for potential commercialization of WPI's composite Pd-based membrane production technologies.
- Achieved 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 (P_{Low}=15 psia) H_2O/CO=1.44 and gas hourly space velocity ($GHSV_{stp}$)=150 h^{-1}, exceeding equilibrium conversion of 93.4% and traditional packed bed conversion of 92.7% [5].
- Successfully completed steady-state methane steam reforming (MSR) and WGS reaction modeling studies and process intensification analysis.
- Successfully completed unsteady-state WGS reaction modeling studies and implemented process control strategies.
- Successfully completed a 2D model for WGS tube and shell membrane reactors.
- Successfully used the 2D model to calculate CO conversion and H_2 recovery for different configurations of MR integration into IGCC plants.
- Completed capital, operating and maintenance costs of a IGCC-MR plant.
- Completed NPV analysis of IGCC, IGCC-PBR, IGCC-MR and SC-PC plants.
- Completed isotherm measurements for the selected adsorbents (ARI).
- Completed the PSA system construction and PSA testing at 200°C and a feed pressure of 200 psia (with P_{low}=1 atm.), (ARI).
- A WGS experiment was conducted with a 10.3 µm Pd/316L-PSS membrane over 65 hours at 400°C, 200 psig, and with a feed rate of 2,100 h^{-1} syngas feed (23% CO, 45% H_2O, 22% H_2, 10% CO_2). A stable CO conversion of 96% was achieved with an H_2 recovery in excess of 80%. The H_2 recovery declined by 10% over the course of the reaction due to coke formation on the membrane surface.
- The single estimate/projection NPV results showed that the IGCC-MR was an economically attractive technology option generating a positive NPV in a scenario with a $25/ton CO_2 tax starting in 2015 as shown in Figure 4. The negative NPV values of IGCC-PBR and SC-PC with CO_2 capture plants would possibly preclude these options from investment consideration in the presence of regulatory action on carbon emissions.
- The expected total capital investment (average) for membrane reactor module consisting of 10 micron thick Pd-based membrane tubes was estimated at 1,285 $/ft^2 which was slightly higher than the 2015 DOE target of 1,000 $/ft^2 with a maximum and minimum of 2,267 and 310 $/ft^2 (lower than the 2015 target), respectively.
- A comparatively more attractive NPV/cost distribution profile obtained in the IGCC-MR case assessed against the ones in the IGCC-PBR and SC-PC cases in the presence of regulatory action on CO_2 emissions made the Pd-based membrane reactor technology option integrated into an IGCC power plant a promising investment choice.

Conclusions and Future Directions

- Membrane preparation led consistently to thin 4-12 µm membranes. Some membranes experienced relatively low flux when considering their thicknesses indicating the presence of mass transfer resistance in the porous metal support.
- Consistent H_2/He selectivities over thousands of hours were obtained at 400-450°C.
- The membrane stability during long-term WGS reaction and H_2/H_2O mixed gas conditions has been demonstrated, and the synthesis methodology necessary for producing those membranes has been developed.
- Total capital investment for the membrane reactor module was calculated to be around 1,285 $/ft^2 very close to the DOE target (1,000 $/ft^2).
- NPV analysis suggested that if CO_2 taxes were implemented, IGCC-MR with carbon capture would be a quite attractive technology option. The most significant risk source was technological (reflected on lower capacity factor values) due to the lack of IGCC-membrane reactor operating experience, adversely impacting project value.
- Monte-Carlo techniques were used to study the effect of uncertainties namely, capacity factor, initial CO_2 tax, CO_2 tax growth rate on project economic value,

suggesting that regulatory action on CO_2 emissions, would induce an appealing NPV-profile for the IGCC-MR technology option.

Future Work (to be conducted under new award #FE0004895)

- A long-term WGS experiment will be conducted with a Pd-316L/PSS membrane for up to 1,000 hours at 400°C, 200 psig, and with a feed rate of 2,700 h^{-1} syngas feed (19% CO, 55% H_2O, 18% H_2, 8% CO_2).
- Pd-Au and Pd-Ru membranes will be synthesized for testing under WGS conditions for up to 200 hours with up to 20 ppm H_2S present in the feed.
- Flexibility analysis will be included into the NPV-based economical model for the integration of the membrane reactor technology into IGCC plants to increase the value of the project (increased NPV) and also to decrease the risk associated with the membrane reactor technology.
- Prepare thin and stable composite pure Pd membranes on 1-inch outer diameter PSS 316 and test them under real gasification conditions at National Center for Carbon Capture, Wilsonville, Alabama.
- Conduct DOE Test 2A (simulated effluent of WGS reactor) on MembraGuard®-coated Pd membrane to further confirm the stability of MembraGuard®-coated membrane under WGS reaction conditions.
- Composite Pd membranes will be prepared on new supports with higher initial He permeability in order to decrease mass transfer resistance within the support.

FY 2011 Publications/Presentations

1. Koc R,; Kazantzis N.K. and Ma, Y.H. "Membrane Reactor Technology Integrated Into IGCC Power Plants: An Economic Evaluation in the Presence of Uncertainty", Presented at the 2011 North American Membrane Society Annual Meeting. Las Vegas, NV, June 4–8, 2011

2. Augustine A.; Mardilovich I.; Ma Y.H. and Kazantzis N.K. "Long-term testing of H_2 permeable, PSS supported Pd-membranes under mixed gas and water-gas shift reaction conditions". Presented at the 2011 North American Membrane Society Annual Meeting. Las Vegas, NV, June 4–8, 2011.

3. Augustine, A.S., Ma, Y.H., Kazantzis, N.K. "*High pressure palladium membrane reactor for the high temperature water-gas shift reaction.*" International Journal of Hydrogen Energy. 36(2011), 5350-5360.

4. Pomerantz, N. and Ma, Y.H., "Isothermal Solid-State Transformation Kinetics Applied to Pd/Cu Alloy Membrane Fabrication", AIChE J, 56, 3062 – 3073 (2010).

5. Chen, Chao-Huang and Ma, Yi Hua, "The Effect of H2S on the Performance of Pd and Pd/Au Composite Membrane", 362(1-2), 535-544(2010).

6. Pomerantz, N., Ma, Y.H., "Novel Method for Producing High H2 Permeability Pd Membranes with a Thin Layer of the Sulfur Tolerant Pd/Cu fcc Phase", J Memb Sci., 370, 97-108 (2011).

7. Koc, Reyyan, .Kazantzis, Nikolaos K and Ma, Yi Hua, "A Process Dynamic Modeling and Control Framework for Performance Characterization and Enhancement of Pd-Based Membrane Reactors Used in Hydrogen Production", International J of Hydrogen Energy", Vol. 36, Issue 8, 4934-4951, (2011).

8. Ma, Yi Hua, "Composite Pd and Pd Alloy Porous Stainless Steel Membranes for Hydrogen Production and Process Intensification", US DOE FY11 Advanced Fuels Peer Review", October 18–22, 2010, Morgantown, WV.

9. Koc, Reyyan, Kazantzis, Nikolaos K. and Ma, Yi H., "A Process Dynamic Modeling Framework for Performance Assessment of Pd-Based Membrane Reactors", Oral presentation, Session: Process Modeling, NAMS/ICIM, July 17–22 2010, Washington, D.C., USA.

10. Koc, Reyyan, Kazantzis, Nikolaos K, and Ma, Yi H., "Theoretical study for the integration of the Pd-based water gas shift membrane reactors into the IGCC plants", Poster presentation, 240th ACS National Meeting, Division of Environmental Chemistry, August 22–26, 2010, Boston, MA, USA.

11. Koc, Reyyan, Kazantzis, Nikolaos K. and Ma, Yi H., "Process Safety Aspects in Water-Gas-Shift (WGS) Catalytic Membrane Reactors Used for Pure Hydrogen Production", Mary Kay O'Connor Process Safety Center International Symposium, October 26–28, 2010, College Station, TX, USA.

12. Koc, Reyyan, Kazantzis, Nikolaos K and Ma, Yi Hua, "Process safety aspects in water-gas-shift (WGS) membrane reactors used for pure hydrogen production"

13. Koc, Reyyan, Kazantzis, Nikolaos K and Ma, Yi Hua, "The Integration of Pd/alloy-Based Water-Gas Shift Membrane Reactors into Coal Gasification Plants: A Performance Assessment Study", Presented at the 2011 International Congress on Membranes and Membrane Processes, Amsterdam, Holland, July 23–29, 2011.

14. Koc, Reyyan, Kazantzis, Nikolaos K and Ma, Yi Hua, "A Dusty Gas-Based Modeling Framework to Characterize the Selectivity of Pd/Alloy-Based Membrane Reactors Under Water-Gas Shift Conditions in the Presence of Defects", Presented at the 2011 International Congress on Membranes and Membrane Processes, Amsterdam, Holland, July 23–29, 2011.

References

1. Chen, C.H. and Ma, Y.H. "the effect of H2S on the performance of Pd and Pd/Au composite membranes". Journal of membrane science, 362(1-2), 535-544 (2010).

2. Pomerantz, N. and Ma, Y.H. "Effect of H_2S on the Performance and Long-Term Stability of Pd/Cu Membranes". Ind. Eng. Chem. Res., 2009, 48 (8), pp 4030–4039.

3. Guazzone, F.; Ma, Y.H. "Leak Growth Mechanisms in Composite Pd Membranes Prepared by the Electroless Deposition Method." AIChE Journal, 54(2), 2008, 487-494.

4. Guazzone, F. "Engineering of substrate surface for the synthesis of ultra-thin composite Pd and Pd-Cu membranes for H_2 Separation", PhD Thesis (2005).

5. Ma et al. US patent 7 727 596 (2010), US patent 7 255 726 (2007), US patent 7 175 694 (2007), US patent 6 152 987 (2007), US patent 6 152 987 (2000).

6. Augustine, A.S.; Ma, Y.H.; Kazantzis, N.K. "High pressure palladium membrane reactor for the high temperature water-gas shift reaction." International Journal of Hydrogen Energy, 36(2011), 5350-5360.