

Executive Summary

Efficient Coal-to-Hydrogen System

Reporting Period: March 21, 2011 – September 30, 2012

Project End Date: September 30, 2012

Principal Investigator: Dr. Stephen N. Paglieri, TDA Research, Inc.

Collaborators: Prof. J. Douglas Way, Colorado School of Mines (CSM)

Beau Braunberger, Western Research Institute (WRI)

Dr. Michael Dolan, Commonwealth Scientific and

Industrial Research Organisation (CSIRO)

Contractor: TDA Research, Inc.

12345 W. 52nd Avenue

Wheat Ridge, CO 80033-1916

Contract Officer: Catherine J. Harris

Executive Summary

Efficient Coal-to-Hydrogen System

Stephen N. Paglieri
John D. Wright
Margarita Dubovik
Kerry A. Libberton
Vladimir Belits
Ewa Muteba

TDA Research, Inc.
12345 W. 52nd Avenue
Wheat Ridge, CO 80033-1916
(303) 422-7819
www.tdaresearch.com

J. Douglas Way,
Hani Abu El Hawa
Øyvind Hatlevik
Amanda E. Lewis

Colorado School of Mines (CSM)
Golden, Colorado
www.mines.edu

Beau Braunberger
Joshua Meranda

Western Research Institute (WRI)
Laramie, Wyoming
www.westernresearch.org

Michael D. Dolan
San Shwe Hla

Commonwealth Scientific and Industrial Research Organisation
Pullenvale, Queensland, Australia
www.csiro.au

Executive Summary

Coal is the most abundant domestically available fossil fuel in the U.S., and Wyoming has a large fraction of the U.S. coal reserves and derives a significant portion of its state revenue from its export. Therefore, it would be beneficial for the state economy to use this coal to generate higher value added products such as hydrogen, liquid fuels, and electricity for export to other states. The state of Wyoming has enough coal reserves to supply the U.S. for many decades, and more efficient and environmentally sustainable methods for generating power and making useful chemicals from coal are needed to ensure that Wyoming's coal resources can be used to their fullest extent.

One of the most efficient options for electrical power generation is to incorporate a high-temperature water-gas shift palladium (Pd) membrane reactor (HT-WGS PMR) into the Integrated Gasification Combined Cycle (IGCC) process, especially when pre-combustion CO₂ capture is required, as shown in Figure 1 [1-8]. As illustrated in Figure 2, a PMR can simultaneously generate and separate hydrogen for greater overall IGCC process efficiency by

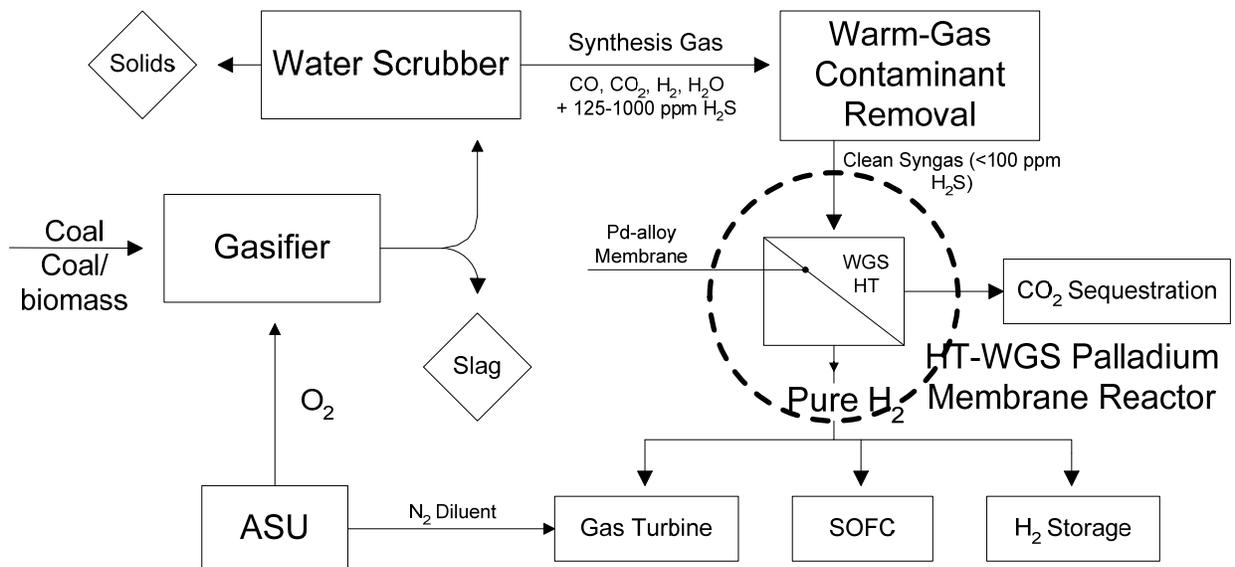


Figure 1. Process schematic for an IGCC system with an integrated palladium membrane reactor for the high-temperature water-gas shift reaction to improve the overall efficiency.

eliminating the downstream hydrogen separation and cleanup steps [9-20]. After scrubbing the hot gasified coal to remove particulates and some of the impurities, sulfur and other contaminants can be removed down to low to moderate ppm levels using a sorbent-based

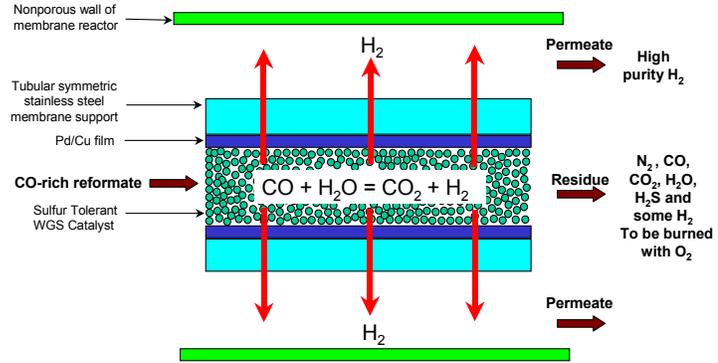


Figure 2. Schematic of a WGS membrane reactor (on our membranes, the palladium alloy membrane film was located on the outside of the tubular support).

warm-gas (250-400 °C) contaminant control system (e.g., ZnO-based for desulfurization) [21-23]. This hot, pressurized gas can then be fed to a one-step reactor/purifier to efficiently produce >99.995% pure hydrogen that can be burned in a turbine, used cleanly in a fuel cell, or sold as a commodity. The membrane reactor also produces a concentrated and pressurized carbon dioxide stream that can significantly reduce the cost associated with carbon capture and sequestration.

In this project, TDA Research collaborated with the Western Research Institute (WRI) in Laramie, Wyoming, the Colorado School of Mines (CSM) in Golden, Colorado and the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Pullenvale, Australia, to fabricate and test hydrogen separating membranes that could be used in a HT-WGS PMR. CSM's supported thin film (<10 μm) hydrogen separating membranes of new palladium alloys were synthesized on Pall Corporation's porous membrane supports (ZrOD AccuSep[®]) using electroless plating techniques. CSIRO provided samples of a candidate HT-WGS catalysts for characterization and also developed a catalytic reactor model to simulate the HT-WGS reaction at the conditions of interest in a PMR.

Long-term thermal stability and chemical tolerance are therefore essential for the hydrogen separating palladium membranes. Thermal stability is important because higher temperatures increase the process efficiency, and chemical stability is important because in addition to H_2 , CO , CO_2 and CH_4 , coal syngas contains multiple contaminants that can impact membrane performance, including sulfur (H_2S and COS), ammonia (NH_3), phosphorous (PH_3), halides ($NaCl$ and KCl), arsenic (AsH_3), and cyanide (CN), as well as traces of metals such as mercury (Hg).

Membranes and catalysts therefore need to be developed that can tolerate these impurities because ppm levels of

them can still pass through the sorbent-based hot- and warm-gas cleanup systems that are being developed. Even after warm-gas desulfurization, low ppm levels (~20 ppm) of H_2S are expected to be present in the coal syngas feed, so catalysts and membranes must be H_2S tolerant. Long-term tests were carried out on the membranes in this project to determine the hydrogen flux and chemical stability (as evidenced by increases in the leak rate of inert gases or impurities) of these membranes in pure hydrogen, synthetic WGS mixtures, and real coal syngas containing up to 100 ppm H_2S .

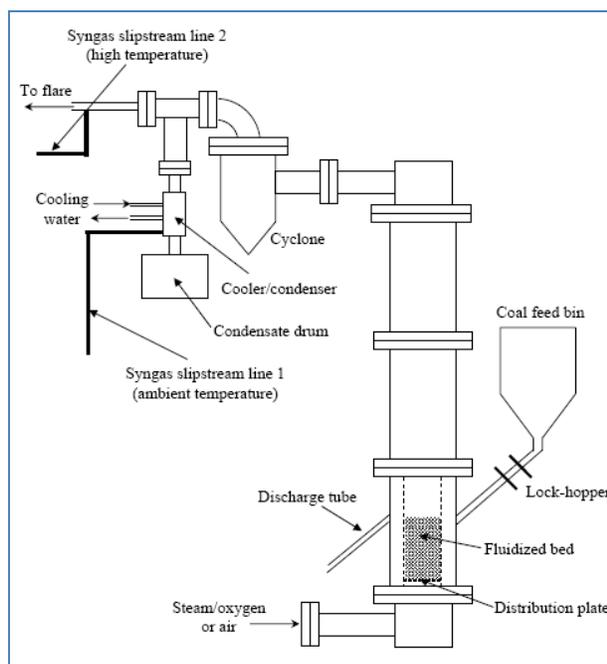


Figure 3. Top: WRI's pilot-scale fluidized-bed coal gasifier. Bottom: schematic of the gasifier.

The project culminated in a week-long testing campaign on Western Research Institute's (WRI, Laramie, Wyoming) coal gasifier to determine the impact of real coal syngas (containing up to 100 ppm H₂S) on overall membrane performance (both during and after testing), including hydrogen flux inhibition and long-term stability and hydrogen purity. Tests in clean (purified) and sour (contained up to 100 ppm H₂S) coal syngas were carried using WRI's pilot-scale fluidized-bed gasifier at its Advanced Technology Center in Laramie, Wyoming. Near the completion of the project, our membrane testing rig was transported to WRI and connected to



Figure 4. Bench-scale membrane testing apparatus at TDA Research (top photo). The system was connected to the slipstream from WRI's pilot-scale fluidized-bed coal gasifier for coal syngas tests (bottom photo).

the gasifier slipstream with stainless steel tubing, as pictured in Figure 3. A schematic of the stainless steel module used to test the membranes is shown in Figure 6 while Figure 4 shows the membrane testing rig in the laboratory at TDA and connected to the gasifier at WRI.

As shown in Figure 5, tests at WRI showed that a Pd-27Pt (wt.%) membrane could separate pure hydrogen from real coal syngas (after it underwent warm-gas cleanup to remove the bulk of the H₂S to 100 ppm); this was the only membrane stable in real sulfur containing coal gases. In clean conditions there were more acceptable choices; all of the palladium alloy membranes exhibited excellent thermal stability in pure and clean

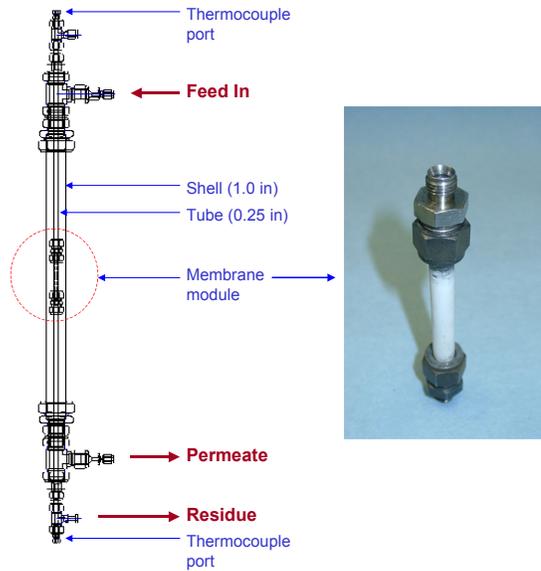


Figure 6. Single membrane test module. Inset shows 10 mm SS compression fittings attached to the membrane.

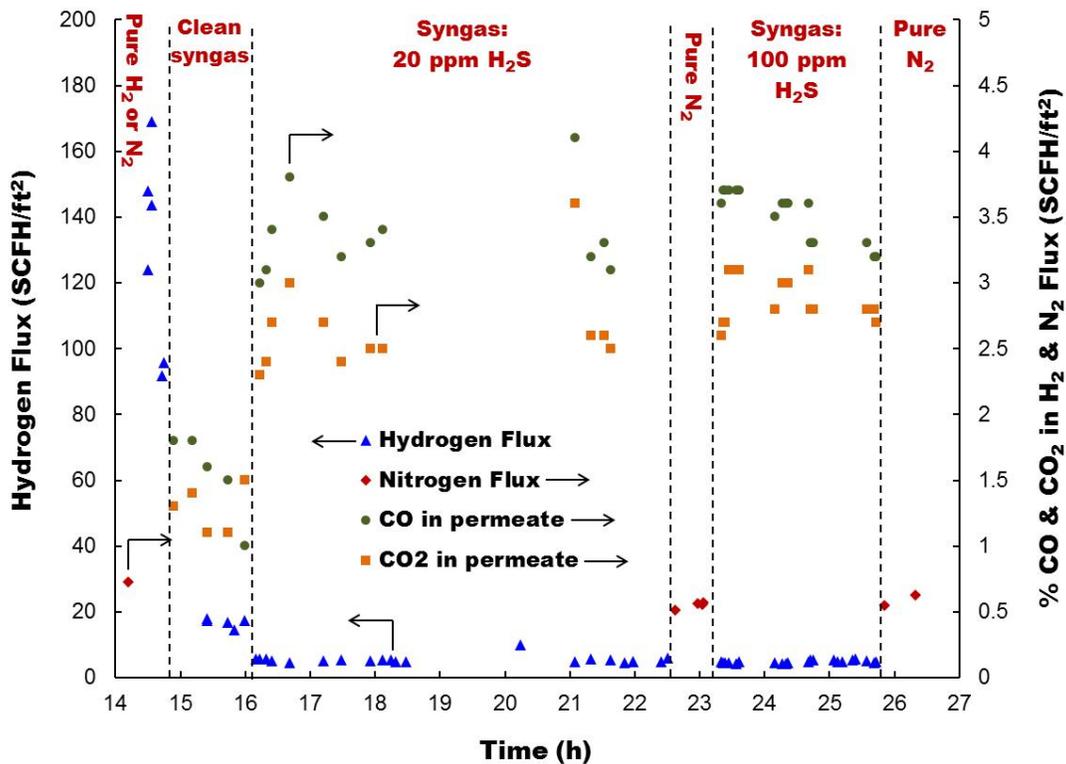


Figure 5. Fluxes (H₂ and N₂) and impurity contents (CO and CO₂) in the hydrogen permeate for a 4.4 μm thick Pd-27Pt membrane during pure gas tests and tests in coal syngas that contained 0 ppm (clean), 20 ppm, or 100 ppm H₂S at 450 °C and 200 psig (0 psig permeate pressure). The impurity concentrations remained constant and the nitrogen flux (leak rate) actually decreased slightly by the end of the test.

400-450 °C, as evidenced by stable hydrogen flux after an initial annealing period of several hundred hours, during which the hydrogen flux increased. However, at temperatures ≥ 500 °C, the nitrogen or helium flux (leak rate) increased to higher levels (except for the Pd-27Pt membrane, which was stable up to 600 °C), suggesting that an improved membrane annealing protocol needs to be developed to promote both alloy formation and mechanical stability.

In the case of PdRu binary alloy membranes with low Ru compositions (~ 1 wt.%), CSM has observed that the hydrogen permeance of these membranes was similar to pure palladium, but the PdRu membranes had almost twice the hardness of similar pure palladium films [24]. The implication of increased hardness, with a corresponding increase in tensile strength, is that membranes can be fabricated that are much thinner than pure palladium membranes, yet they have better selectivity and higher flux [24].

In this project, we hoped to combine the sulfur tolerant properties of the PdAu alloy with the high-temperature strength of the PdRu alloy to obtain a membrane that performed well in long-term mixed-gas tests. Membranes were synthesized by either sequential plating; that is plating alternating layers of palladium and another alloying element such as gold or platinum, or co-deposition through simultaneous deposition of both metals from the same bath. In either case, high-temperature annealing was required to promote the formation of a homogenous alloy [25, 26]. The surface activation and electroless plating sequence is illustrated in Figure 7. Ternary alloy Pd-1Ru-



Figure 7. Supported thin film Pd-alloy membrane preparation sequence. A 6"-long, porous AccuSep ZrO_2 -coated stainless steel substrate as-received from Pall Corporation (top), activated with Pd acetate and then reduced for electroless plating (2nd and 3rd from top), coated with a thin film of Pd (2nd from bottom) and then coated with Au on top of the Pd film (bottom). The active membrane surface area is ~ 2.3 in² (15 cm²).

Table 1. Fabrication parameters for the membranes tested during this study.

Designator	Fabrication method	Layers	Thickness (μm)	Composition by mass change (wt.%)
Pd-7Au	sequential	Pd/Au	9.5	7% Au
Pd-1Ru-11Au	sequential	PdRu/Au/PdRu	3.0	11% Au & 1% Ru
Pd-1Ru-10Au	sequential	PdRu/Au/PdRu/Au	5.3	10% Au & 1% Ru
Pd-1Pt	co-bath	PdPt	4.5	unknown
Pd-27Pt	sequential	Pd/Pt/Pd	4.4	27% Pt

10Au and Pd-1Ru-11Au membranes were therefore fabricated for the first time by electroless deposition. Electroless plating methods for simultaneously co-depositing PdRu alloys were used in combination with sequential gold electroless plating to create $<6 \mu\text{m}$ thick PdRuAu films on porous ZrO_2/PSS substrates (ZrOD AccuSep membranes, Pall Corp.) [24, 25].

By subsequently annealing these multilayered thin films, $3.0 \mu\text{m}$ thick Pd-1Ru-11Au and $5.3 \mu\text{m}$ thick Pd-1Ru-10Au ternary alloy membranes were formed. Electroless co-deposition and sequential deposition methods were also used to fabricate $9.5 \mu\text{m}$ thick Pd-7Au, $4.5 \mu\text{m}$ thick Pd-1Pt, and $4.4 \mu\text{m}$ thick Pd-27Pt binary alloy membranes for evaluation. The compositions and thicknesses of the membranes used in this study are listed in Table 1. These membranes were tested for $>4,500$ h (cumulative) at $400\text{-}600 \text{ }^\circ\text{C}$ in pure hydrogen and helium, and for >500 h in simulated water-gas shift mixtures (DOE1 and DOE2a conditions: 50% hydrogen, 19% H_2O , 1% CO and 30% CO_2 , without or with 20 ppm H_2S) at $400\text{-}450 \text{ }^\circ\text{C}$. A high hydrogen flux of 715 SCFH/ft^2 was measured through the Pd-1Pt membrane with a pure hydrogen feed at 100 psia and $550 \text{ }^\circ\text{C}$.

All of the membranes were very thermally and chemically stable and produced high purity hydrogen (99.98% to 99.995%) in clean conditions (no H_2S), as demonstrated during >4500 h of cumulative laboratory testing in pure gases (H_2 , N_2 , and He), synthetic WGS gas mixtures (DOE1: H_2 , H_2O , CO, and CO_2), and purified coal syngas with added steam at 400 and $450 \text{ }^\circ\text{C}$. However, the hydrogen flux through the Pd-1Ru-10Au membrane was significantly inhibited by 20 ppm H_2S in the synthetic WGS mixture (DOE2a) and the membrane was not structurally

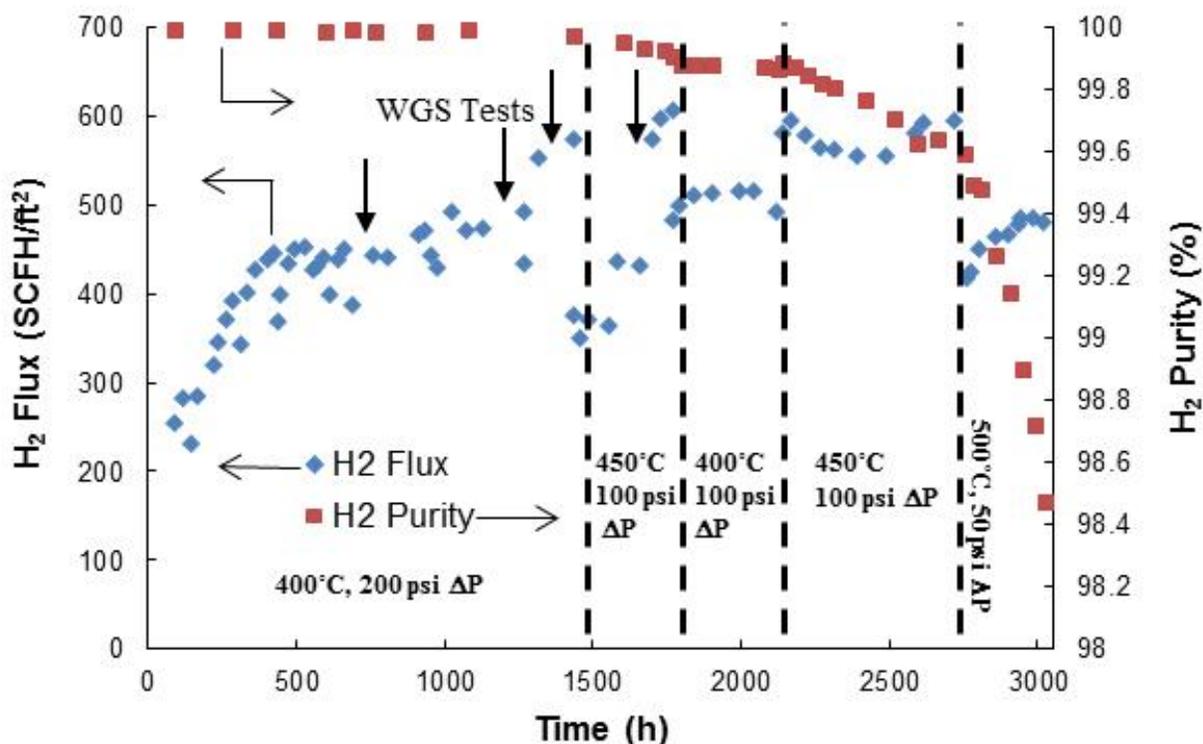


Figure 8. Hydrogen flux and purity (based on the pure hydrogen and helium fluxes) for a 3.0 μm thick Pd-1Ru-11Au (wt.%) membrane at 400-500 $^{\circ}\text{C}$ and 200 psig. The hydrogen purity decreased at an accelerated (but linear) rate with each 50 $^{\circ}\text{C}$ increase in temperature. The arrows indicate where >120 h tests were carried out in a synthetic WGS gas mixture at 400 or 450 $^{\circ}\text{C}$ (DOE1 conditions).

stable in the presence of H_2S , as evidenced by the increase in impurities (e.g., CO and CO_2) in the permeate hydrogen during this sour WGS test. However, the Pd-1Ru-10Au membrane tested in the WGS mixture that contained H_2S did not have a final gold layer deposited onto its surface and energy dispersive X-ray spectroscopy (EDS) showed that the composition was not completely homogenous throughout its cross-section; both of these factors probably contributed to the poor resistance of the Pd-1Ru-10Au membrane to H_2S .

The H_2 flux and selectivity data for >3000 hours of testing on a 3.0 μm thick Pd-1Ru-11Au membrane are shown in Figure 8. The hydrogen purity was essentially constant at 400 $^{\circ}\text{C}$. An initial hydrogen purity of 99.995% ($J_{\text{H}_2}/J_{\text{He}}$) was obtained; helium was used at a feed pressure of 200 psig because the nitrogen leak rate could not be detected with our soap film flow meter. In

fact, very high H₂/He pure gas flux ratios (<500 ppm helium in hydrogen based on the pure gas values) were measured for >1500 hours of testing, corresponding to a hydrogen purity of 99.95%. The helium flux did increase slowly throughout the test at 400 °C, but after 1400 h the hydrogen purity was still 99.97%, as shown in Figure 8.

Table 2. Rates of decline in the hydrogen purity for a Pd-1Ru-11Au membrane showing excellent thermal stability at 400 °C, but increasing rates decline in hydrogen purity at 450 & 500 °C.

Temperature (°C)	Rate of H ₂ Purity Decline (ppm/h)
400°C	0.19
400°C (during DOE1)	0.51
450°C	4.7
450°C (during DOE1)	2.7
500°C	42.8

Once the synthetic WGS gas mixture

tests on the Pd-1Ru-11Au membrane were completed at 400 °C, subsequent pure and mixed-gas tests were conducted to assess the long-term thermal and chemical stability of the membrane at higher temperatures. The rates of decline in the hydrogen purity for the Pd-1Ru-11Au membrane at different temperatures are given in Table 2. At 400 °C the rate of helium leak increase due to pinhole development was very slow (0.19 ppm/h of purity loss), but the rate increased by about a factor of 10 for each 50 °C increase in temperature. The leak rate of helium through the membrane increased linearly at each temperature.

The Pd-27Pt membrane was not permanently affected by tests in either clean (e.g., no H₂S) or sour (20 or 100 ppm H₂S) coal syngas at WRI. However, the hydrogen flux through this Pd-27Pt membrane and other Pd-1Pt, and Pd-7Au membranes was inhibited by both the clean and sour syngas, and defects formed in the Pd-1Pt and Pd-7Au membranes. When either of these two membranes were exposed to either synthetic WGS gas mixtures or real coal syngas which contained 20 or 100 ppm H₂S, the purity of the hydrogen permeate decreased over a period of hours in the order (from least to most stable): Pd-1Pt > Pd-1Ru-10Au > Pd-7Au. The only exception was the Pd-27Pt membrane, for which stable performance was observed with no

permanent decrease in the hydrogen flux and purity, even after testing in real coal syngas that contained 100 ppm H₂S for 2.5 h. The Pd-7Au membrane also fared reasonably well; the total concentration of impurities in the hydrogen permeate was still <500 ppm during a subsequent test in DOE1 conditions, which corresponds to a hydrogen purity of >99.95%.

SEM/EDS, XRD, and ICP-AES/MS were used to characterize membrane morphology, microstructure, and chemical composition to learn more about alloy formation during the annealing process. The cross section of the Pd-1Ru-11Au membrane after testing is shown in Figure 9. The EDS and ICP results generally confirmed the compositions (with the exception of the PdRuAu alloys) of the membranes estimated by the mass changes in between the electroless plating steps during synthesis, but some compositional gradients existed in some of the films due to incomplete annealing, even after testing for thousands of hours at temperatures of 400-500 °C. Specifically, the surfaces of the PdRuAu membranes were either slightly enriched or depleted in gold.

Catalytic reactor modeling was carried out at CSIRO

to simulate the HT-WGS reaction. The model was validated by comparison to experimental results and provided temperature and composition profiles for use in membrane reactor design. We also developed a way to pelletize CSIRO's non-precious-metal HT-WGS catalyst to make it into a form suitable for use in a membrane reactor.

Some of the membranes developed in this project exceeded the performance of previous supported thin film palladium alloy membranes reported in the literature, particularly with respect to increased H₂S tolerance. However, further work in several specific areas is still required to

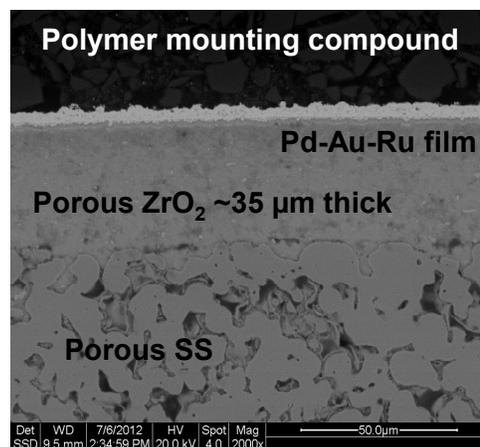


Figure 9. SEM image of a membrane cross-section showing a PdRuAu alloy film and the underlying ZrOD AccuSep support with a layer of porous zirconia on PSS.

meet the demands of industrial use, including:

- improve both chemical and thermal stability by optimizing membrane composition and microstructure
- decrease manufacturing costs and scale up to produce larger surface area membranes and modules
- demonstrate long-term membrane reactor performance in purified real coal syngas

Hydrogen separating membranes are an important component of an efficient coal-to-hydrogen process that incorporates CO₂ capture; a potential large-scale value-added market for Wyoming coal. Long-term membrane tests at TDA Research, CSM and WRI in pure gases, simulated WGS gas mixtures, and real coal syngas that contained up to 100 ppm H₂S demonstrated that supported thin film palladium alloy membranes have the potential to efficiently recover pure hydrogen from coal syngas, which could result in significant cost savings and conservation of resources when used in a HT-WGS membrane reactor. With a continued effort to optimize their chemical and thermal stability, hydrogen flux, and the fabrication method, supported thin film palladium-alloy membranes may provide a more efficient, cost effective and environmentally sustainable way to generate pure hydrogen from coal syngas.

References

1. Jansen, D., et al., *Hydrogen membrane reactors for CO₂ capture*. Energy Procedia, 2009. **1**(1): p. 253-260.
2. Sridhar, S., et al., *Materials Challenges for Advanced Combustion and Gasification Fossil Energy Systems*. Metall. Mater. Trans. A, 2011. **42**(4): p. 871-877.
3. Dolan, M.D., R. Donelson, and N.C. Dave, *Performance and economics of a Pd-based planar WGS membrane reactor for coal gasification*. Int. J. Hydrogen Energy, 2010. **35**(20): p. 10994-11003.
4. Bracht, M., et al., *Water gas shift membrane reactor for CO₂ control in IGCC systems: techno-economic feasibility study*. Energy Convers. Manage., 1997. **38**: p. S159-64.
5. Criscuoli, A., et al., *An economic feasibility study for water gas shift membrane reactor*. J. Membr. Sci., 2001. **181**: p. 21-7.
6. Dijkstra, J.W., et al., *Techno-economic evaluation of membrane technology for pre-combustion decarbonisation: Water-gas shift versus reforming*. Energy Procedia, 2011.

- 4(0): p. 723-730.
7. Beavis, R., *The EU FP6 CACHET project - Final results*. Energy Procedia, 2011. **4**: p. 1074-1081.
 8. Amelio, M., et al., *Integrated gasification gas combined cycle plant with membrane reactors: Technological and economical analysis*. Energy Convers. Manage., 2007. **48**(10): p. 2680-2693.
 9. Buxbaum, R.E., *Membrane Reactor Advantages for Methanol Reforming and Similar Reactions*. Sep. Sci. Tech., 1999. **34**(10): p. 2113-23.
 10. Shu, J., et al., *Catalytic Palladium-based Membrane Reactors: A Review*. Can. J. Chem. Eng., 1991. **69**(5): p. 1036-60.
 11. De Lorenzo, L., et al., *Carbon-free hydrogen and electricity from coal: options for syngas cooling in systems using a H₂ separation membrane reactor*. J. Eng. Gas Turbines Power, 2008. **130**(3): p. 031401-1.
 12. Gryaznov, V.M., M.M. Ermilova, and N.V. Orekhova, *Membrane--catalyst systems for selectivity improvement in dehydrogenation and hydrogenation reactions*. Catal. Today, 2001. **67**: p. 185-188.
 13. De Falco, M., *Ethanol membrane reformer and PEMFC system for automotive application*. Fuel, 2011. **90**(2): p. 739-747.
 14. Damle, A.S., *Hydrogen production by reforming of liquid hydrocarbons in a membrane reactor for portable power generation-Experimental studies*. J. Power Sources, 2009. **186**(1): p. 167-177.
 15. Shirasaki, Y., et al., *Development of membrane reformer system for highly efficient hydrogen production from natural gas*. Int. J. Hydrogen Energy, 2009. **34**(10): p. 4482-4487.
 16. Mahecha-Botero, A., et al., *In-situ CO₂ capture in a pilot-scale fluidized-bed membrane reformer for ultra-pure hydrogen production*. Int. J. Hydrogen Energy, 2011. **36**(6): p. 4038-4055.
 17. Matsumura, Y. and J. Tong, *Methane Steam Reforming in H₂-permeable Membrane Reactor for Pure Hydrogen Production*. Top. Catal., 2008. **51**(1-4): p. 123-132.
 18. Birdsell, S.A. and R.S. Willms, *Tritium recovery from tritiated water with a two-stage Pd membrane reactor*. Fusion Eng. Des., 1998. **39-40**: p. 1041-8.
 19. Mueller-Langer, F., et al., *Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term*. Int. J. Hydrogen Energy, 2007. **32**(16): p. 3797-3810.
 20. Itoh, N., *A Membrane Reactor Using Palladium*. AIChE J., 1987. **33**(9): p. 1576-1578.
 21. Dolan, M.D., et al., *Glass-Based Processing of Mixed-Oxide Desulfurization Sorbents*. Ind. Eng. Chem. Res., 2009. **48**(23): p. 10498-10503.
 22. Gribble Jr., D.A., S.A. Rolfe, and M.V. Mundschau, *Perovskite sorbents for warm-gas removal of sulfur*, in *Twenty-Sixth Annu. Int. Pittsburgh Coal Conf.* 2009: Pittsburgh, PA.
 23. Jung, S.Y., et al., *The simultaneous removal of hydrogen sulfide and ammonia over zinc-based dry sorbent supported on alumina*. Sep. Purif. Technol., 2008. **63**(2): p. 297-302.
 24. Gade, S.K., et al., *Palladium–ruthenium membranes for hydrogen separation fabricated by electroless co-deposition*. Int. J. Hydrogen Energy, 2009. **34**: p. 6484-6491.
 25. Hatlevik, Ø., et al., *Palladium and palladium alloy membranes for hydrogen separation and production: History, fabrication strategies, and current performance*. Sep. Purif. Technol., 2010. **73**(1): p. 59-64.
 26. Mundschau, M.V., et al., *Dense inorganic membranes for production of H₂ from methane and coal with carbon dioxide sequestration*. Catal. Today, 2006. **118**(1-2): p. 12-23.